International Conference on Advanced Materials

ICAM'97

European Materials Research Society
Spring Meeting

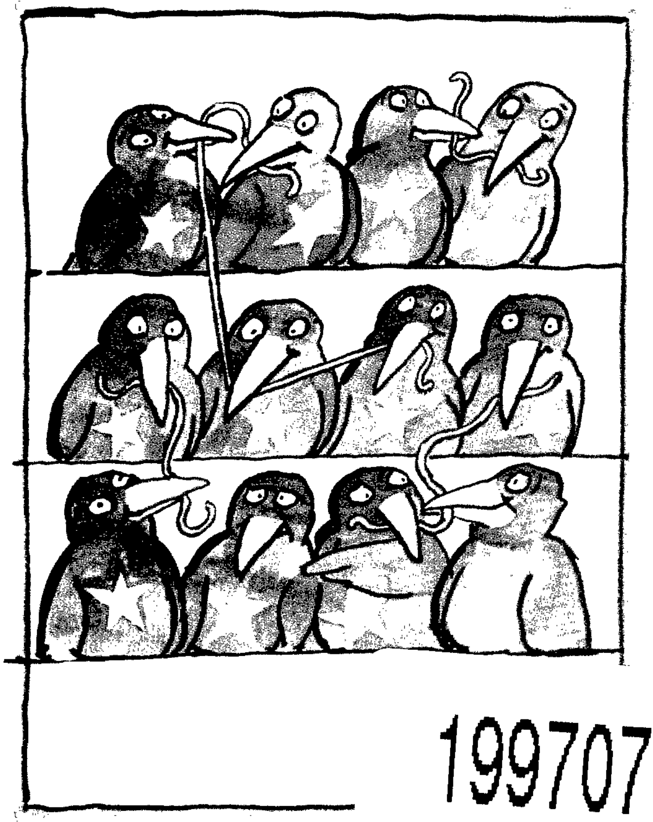
E-MRS'97

(In collaboration with the European Physical Society, Solid State Division - EPS)

Congress Center
- Palais de la Musique et des Congrès -
Strasbourg (France)

June 16 - 20, 1997

BOOK
of
ABSTRACTS



E-MRS

ICAM-97

ICAM/E-MRS'97 SPRING MEETING

ICAM-97

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June 18-19, 1997
Congress Center
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ICAM/E-MRS'97 SPRING MEETING

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BOOK of ABSTRACTS

PLENARY SESSION

Monday June 16, 1997 **Morning**
Lundi 16 juin 1997 Matin

9:00-9:30 **OPENING SESSION**

- ALLOCUTION of **I.W. Boyd**
  E-MRS President
- ALLOCUTION of **P. Glasow**
  ICAM/E-MRS'97 Conference Chairman
- ALLOCUTION of **G.M. Crean**
  ICAM/E-MRS'97 Conference Chairman

PLENARY SESSION

PS-1. 9:30-10:00 MATERIALS DEVELOPMENT AND ENGINEERING IN LOW-TEMPERATURE FUEL CELLS FOR ELECTROTRACTION, **H. Wendt**, Inst. f. Chem.Technologie, Technical University Darmstadt, Petersenstr.20, 64287 Darmstadt, Germany

After a long period of fundamental research, fuel cells became technically mature and are entering now commercialization with phosphoric acid fuel cells (PAFCs). Today the Proton Exchange Membrane Cell (PEMFC) - a low temperature cell operated at close to 100 °C - is believed to be a candidate for automobile electrotraction of zero emission vehicles.

For PEMFCs nanostructured electrocatalysts for direct anodic oxidation of methanol and the development of innovative proton conducting membranes operating at enhanced temperature (up to 200 °C) are the most important issues. Nanostructured catalysts are made by preparing nano-emulsions of catalytic metals and depositing the metallic nanoparticles on high-surface, active carbon. The very thin and porous electrodes are prepared by a spray-sinter procedure, which could be easily converted into a mass-production procedure. The development of alternative high temperature membrane materials has not yet succeeded in a real advance, because the particular microscopic phase-segregation of Nafion membranes which causes its high protonic conductivity, is not easy to imitate with other polymers.

Furthermore developing mass production procedures of cells and cell components is of highest priority.

PS-2. 10:00-10:30 SILK POLYMERS - BIOSYNTHESIS, PROPERTIES AND APPLICATIONS, **D.L. Kaplan**, Tufts University, Biotechnology Center, Department of Chemical Engineering, 4 Colby Street, Medford, Massachusetts 02155, USA

Fibrous proteins perform essential material functions in biology. They provide scaffolding for tissues, matrices for shell formation, anchoring systems for many organisms, and many other roles. These protein polymers are characterized by a regular secondary structure and a repetitive primary sequence. Protein-based materials provide useful systems from which to elucidate structure-function relationships in materials science because of the repetitive structure and the ability to genetically tailor the polymers. The fidelity and control of primary sequence and the ability to genetically engineer proteins with precision, offer unprecedented options to explore these relationships. Aside from synthesis issues, many of these fibrous proteins are processed in novel ways, starting as aqueous-soluble building blocks and ending as insoluble matrices or assemblies. These conversions are of interest for new opportunities in solventless processing at ambient conditions based on insights from these biological mechanisms. Organization of these materials at different length scales through self-assembly is an additional feature worthy of study. This talk will review some of these features related to recent advances being made in the field of fibrous proteins. Spider silks will be the focus although a number of other protein systems will also be described.

10:30-11:00 **BREAK**

PS-3. 11:00-11:30 THE DESIGN OF «COMPUTER EXPERIMENTS», **V. Heine**, Cavendish Laboratory, Madingley Road, Cambridge CB30HE, UK

The purpose of physical science is to gain understanding of the physical world. But what do we understand by the word 'understanding'? Computer experiments are akin to laboratory experiments: indeed most of them one would do in the laboratory if one could. But the computer allows one a unique power to control the variables in a system, giving a whole new freedom in designing computer experiments to elucidate understanding. Examples will be given of the current state of the art, particularly regarding simulations based on ab initio quantum calculation of electronic structure of the system at every step.

PS-4. 11:30-12:00 UNIVERSITY R&D FOR INDUSTRIAL DEVELOPMENT?, **G. Wrixon**, National Microelectronics Research Centre (NMRC), Prospect Row, Cork, Ireland

PS-5. 12:00-12:30 MATERIALS RESEARCH: THE KEY TO EUROPEAN COMPETITIVENESS IN THE NEXT CENTURY, **A. Garcia-Arroyo**, Director of DGXII, Commission of the European Communities, Rue de la Loi, 200, 1049 Brussels, Belgium

12:30 **LUNCH**

ICAM/E-MRS'97 SPRING MEETING

CONFERENCE PROGRAMME

SYMPOSIUM A	Fullerenes and Carbon Based Materials
SYMPOSIUM B	Epitaxial Thin Film Growth and Nanostructures *Joint with EPS-Solid State Division*
SYMPOSIUM C	Recent Developments in Electron Microscopy and X-Ray Diffraction of Thin Film Structures
SYMPOSIUM D	Computational Modeling of Issues in Materials Science
SYMPOSIUM E	Materials Aspects for Electric Vehicles including Batteries and Fuel Cells
SYMPOSIUM F	Second International Symposium on Advanced Materials
SYMPOSIUM G	Biomaterials: Perspectives for Research & Industry at the Century Change
SYMPOSIUM H	Biodegradable Polymers & Macromolecules
SYMPOSIUM I	Interrelation of Science, Economics & Policy in Materials Research & Processing
SYMPOSIUM J	Light-Weight Materials for Transportation
SYMPOSIUM K	Coatings and Surface Modifications for Surface Protection and Tribological Applications
SYMPOSIUM L	III-V Nitrides Semiconductors and Ceramics from Material Growth to Device Applications
SYMPOSIUM M	Materials, Physics and Devices for Molecular Electronics and Photonics

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM A

Fullerenes and Carbon Based Materials

Symposium Organizers

H. KUZMANY, Institut für Materialphysik, Universität Wien, Wien, Austria

H.W. KROTO, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK

P. DELHAES, Centre de Recherche Paul-Pascal, CNRS, Pessac, France

R.P.H. CHANG, Northwestern University, Evanston, IL, USA

C.N.R. RAO, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

The assistance provided by the
SGL Carbon AG
is acknowledged with gratitude.

A-II.5 18:00-18:15

PHASE TRANSFORMATION OF HYDROGEN FREE AMORPHOUS CARBON FILMS UNDER ION BEAM BOMBARDMENT, Ch. B. Lioutas, N. Vouroutzis, S. Logothetidis, S. Boultadakis. Aristotle University of Thessaloniki, Department of Physics, 54006, Thessaloniki, Greece.

The features of hydrogen free tetrahedral amorphous Carbon films (ta-C) prepared by RF magnetron sputtering in room temperature, under different preparation conditions (power on the target, partial argon pressure, substrate-target distance, target biasing), were examined by transmission electron microscopy (TEM). Planar view TEM observations on specimens prepared by chemical polishing, shown characteristic amorphous rings indicating a significant difference from the graphite and crystalline diamond structure. Electron Diffraction patterns from specimens bombarded with low energy Ar ion beam show characteristic polycrystalline rings that identified with a very good accuracy to the diamond reflections. The observed phase transformation takes place without any heating treatment in room temperature conditions. The crystallite grains size, measured from dark field imaging using <111> diamond reflection, found to be up to 40 nm, not clearly dependent on preparation conditions. Moreover SiC crystallites were detected in several specimens treated under similar bombardment conditions.

A-II.6 18:15-18:30

ULTRATHIN SUPPORTED GRAPHITE OXIDE AND CARBON FILMS, N.Kovtyukhova, A. Chuiko, Institute of Surface Chemistry, 31 Pr.Nauky, 252022 Kiev, Ukraine, E. Buzaneva, National T.Shevchonko University, 64 Vladimirskaya Str., 252033 Kiev, Ukraine, A. Senkevich, A. Shpak, Institute of Metal Physics, 36 Vernadsky Str., 252142 Kiev, Ukraine

Modern wet colloid-chemical synthetic method is considered as a new approach to supported nanostructured graphite oxide (GO) and carbon films. The films are prepared by self-assembly from aqueous colloids of chemically exfoliated GO onto substrates of different nature. The multilayer films are grown one monolayer at a time on surfaces by the consequent adsorption of two-dimensional anionic GO sheets and inorganic/organic polycations on solid/liquid interface. The procedure works on both planar and high surface area substrates. It is found by XRD, XPS and LSM analysis that the chemical nature of substrate surface determines the structure and particles orientation of the monolayer.The monolayer thickness depends on GO colloid concentration. Thermal treatment of the GO films at 200 C leads to GO decomposition and the formtion of supported carbon films.

Creation of the ultrathin supported films that can be utilized as matrices in which to incorporate a range of ions (Cu, Ni, Co, Ag) provides a viable approach to the construction of advanced materials.

Tuesday June 17, 1997 **Morning**
Mardi 17 juin 1997 Matin

Session III - Carbon, Part 3
Chairperson: R. Schlögl, Fritz-Haber-Institut der MPG, Berlin, Germany

A-III.1 - invited - 9:00-9:30

ELECTROCHEMICAL PREPARATION OF CARBYNE-LIKE MATERIALS, **L. Kavan**, J. Heyrovsky, Institute of Physical Chemistry, Dolejskova 3, 18223 Prague, Czech Republic

«Carbyne» is a hypothetical carbon allotrope containing linear chains of sp-carbon atoms. Electrochemical cathodic carbonization of perfluorinated hydrocarbons with alkali metal (M = Li, Na, K) amalgams gives a solid composite of n-doped elemental carbon and the equivalent amount of MF. Raman spectra of C-MF show an unusually strong band at 2000-2100 cm^{-1} which was assigned to the $C \equiv C$ stretching mode of polyyne. An optimum synthesis of carbyne-like materials represents the electrochemical reduction of stretch-oriented poly(tetrafluoroethylene) with K- or Na- amalgams. Electrochemical polyyne is partly stabilized against interchain crosslinking towards graphene by interspersed MF. A polyyne-to-graphene conversion occurs by ageing in a long time scale (years). It can be monitored by well-defined changes of electronic and optical properties of C-MF. Carbyne decomposes spontaneously if the alkali metal fluoride is extracted from the composite, both in aqueous and aprotic media.

A-III.2 9:30-9:45

ELECTRONIC AND STRUCTURAL PROPERTIES OF FRACTAL CARBON NANO-STRUCTURES, H.E.Roman, A. Lorenzoni, R.A. Broglia and G. Benedek, Istituto di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy.

We study the electronic structure of nanoaggregates of Carbon atoms arranged in a self-similar fashion. The hypotetical structure we consider is a two dimensional one, and is built up of exagons, forming a sort of self-similar David 'star', which we call the Davidene. The two dimensional disposition of chemical bonds between two Carbon atoms is similar to that in graphite. We employ an accurate tight-binding model, based on a set of sp^3 two-center hopping parameters, to obtain the structure of valence electrons for the ground state geometries of aggregates of increasing size L. From these results we obtain the scaling behavior of the energy 'gap' (Homo-Lumo gap) as a function of the length scale L. A detailed analysis of the energy spectrum shows that it becomes similar to a Cantor set for large L and possesses multifractal properties. The question of the spatial extension of eigenstates is also discussed. In addition to the electronic structure, we study the structure factor of the aggregates and discuss the relevance of the present calculations to adsorption experiments.

A-III.3 9:45-10:00

SPONGY CARBON NANOBEADS-A NEW MATERIAL, M. Sharon(1), K. Mukhopadhyay(1), K. Yase(2), S. Iijima(3), Y. Ando(4) and X. Zhao(4); (1)Department of Chemistry, Indian Institute of Technology, Poway, Bombay 400 076, India; (2)National Institute of Materials and Chemical Research, Department of Polymer Physics, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan; (3)NEC Corporation, Fundamental Research Lab, 34 Myukigaoka, Tsukuba, Ibaraki 305, Japan; (4)Department of Physics, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468, Japan

Spherical carbon nanobeads (solids and hollow) of two sizes of around 500 nm (large) and 250 nm (small) have been synthesized by pyrolysing vapour of camphor at 1000°C in Ar atmosphere, using ferrocene, as catalyst, for the first time.

The EEL spectrum suggests the carbon beads to be non-graphitic and these are covered by a graphitic shell of 80-100 nm as revealed by TEM micrographs. The large beads, more than 10 are interconnected, and outer shell covering the train of carbon beads takes the shape of fibrous graphitic carbon which perhaps gives the spongy elastic character to the material. The average surface area of nanobeads determined by BET studies is calculated to be 16 m^2g^{-1}. It is suggested that this material may be useful anode for secondary lithium ion battery.

A-III.4 10:00-10:15

NETWORK FORMATION AND THE CONDENSATION OF ATOMIC CARBON VAPOR UNDER QUENCHING, S.A. Shagynian, N.N.Semenov Institute of Chemical Physics, Moscow, Russia.

It is possible to point out two processes that play decisive role in fullerene formation: condensation and chemical reactions of network formation that occur in the expanding flow of atomic carbon vapor under quenching. A model of the influence of expanding flow on the vapor condensation has been suggested by us previously. In framework of the model it is possible to consider here influence of the chemical clusterization on the condensation in the immovable vapor.

The influence of network formation on vapor condensation under quenching has been studied using Stockmayer's model of random polycondensation. This model allows to approximate the cluster systems of all sizes appearing after quenching of atomic carbon vapor. The distribution of clusters on sizes corresponds to quenching temperature. The model is applicable to the process, when the chemical reaction proceeds much faster than the phase condensation of vapor. Then Sanchez-Lacombe model has been used to take into account both the mixing processes of clusters of different type and the phase condensation in the system. There have been found the equation of state of the clustered system, with the unusual boundary of stability of the space homogeneous states.

A-III.5 10:15-10:30

ELECTRON MICROSCOPY STUDIES OF FCC CARBON, S.M. Zharkov, J.N. Titarenko, G.N. Churilov Institute of Physics, Russian Acad. of Sci., 660036, Krasnoyarsk, Russia

The products of plasma-chemical reactor have been investigated using transmission electron microscopy. Particles have been found out, they had dimensions from 10 nm to 1000 nm. The electron-diffraction pattern of particles is a face-central-cubic characteristics of the electron-diffraction pattern agree with those of the fcc carbon which has lattice constant a=3.57 A [1].

In our case, the fcc carbon is formed in the form of particles of different shapes (round, ellipsoidal, cut). The cut particles have 6, 8, 10 faces. Within many particles one can see complex structures. The inner structures are varied, in addition.

[1] L.S.Palatnic et al., Zh. Eksp. Teor. Fiz. 87, 914 (1984).

10:30-11:00 **BREAK**

Session IV - Fullerene, Part 1
Chairperson: G. Van Tendeloo, University of Antwerp, Antwerpen, Belgium

A-IV.1 - invited - 11:00-11:30

ION MOBILITY STUDIES OF CARBON CLUSTERS FULLERENES AND METAL-COATED FULLERENES, P. Dugourd, R; Hudgins, J. Fys and **M. F. Jarrold**, Northwestern University, Department of Chemistry, Evanston IL 60208-3113, USA

High resolution ion mobility measurements have recently revealed the presence of a number of previously unresolved structural isomers for carbon clusters, these include a variety of ring isomers and fullerenes with holes in the cage. The results of these studies wlll be described along with new results on clusters generated by coating fullerenes with metal atoms. In the case of niobium, a single niobium stays on the outside of the cage, but two or more niobium atoms promote the formation of an endohedral metallofullerene.

A-IV.2 11:30-11:45

MOLECULAR ORIENTATIONAL ANGLES IN THE LOW-TEMPERATURE PHASE OF C_{60} DERIVED FROM ELASTIC DIFFUSE NEUTRON SCATTERING, O. Blaschko, G. Krexner, Ch. Maier, R. Karawatzki, Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, 1090 Wien, Austria

The low-temperature phase of C_{60} is currently described by an orientational two-state model in which double bonds of a given molecule roughly lie opposite to either pentagon or hexagon faces of its nearest neighbours. The disorder resulting from the random occupation of these energetically nearly equivalent states gives rise to elastic diffuse scattering whose distribution in reciprocal space depends sensitively on the molecular orientational angles. We present a neutron scattering investigation which by clear separation of elastic and inelastic intensity contributions leads to an improved understanding of static disorder. The orientational angles derived from our data are close to 102° and 42° for the pentagon and the hexagon variant, respectively.

The significance of this finding can be summarized as follows: The original angles were interpreted as an attempt to reconcile molecular symmetry with crystalline long-range order. By way of contrast, the new angles optimize the local arrangement of double bonds with respect to adjacent pentagon and hexagon faces. Our results indicate that the structural state of C_{60} at low temperatures is governed by short- range interactions to an extent which as yet has not been recognized in either theoretical or experimental work.

A-IV.3 11:45-12:00

THE GROWTH MECHANISMS AND MORPHOLOGY OF C_{60} FILMS ON DIFFERENT SUBSTRATES, A. Richter, Department of Physics and Technology, Technische Fachhochschule Wildau, Bahnhofstr. 1, 15745 Wildau, Germany; R. Smith, Department of Mathematical Sciences, Loughborough University, Leicestershire LE3 3TU, UK

Fullerite C_{60} films have been grown by thermal evaporation on mica, glass, sodium cloride and hard diamond-like carbon over a temperature range from 20°C to 250°C at different deposition rates. A number of films with contrasting morphologies for different thicknesses is investigated with scanning force microscopy, x-ray diffraction and Raman scattering. The unusual growth characteristics of molecular C_{60} on different substrates are discussed within simple models and compared. Epitaxial, polycrystalline and textured films have been grown.The roughness of the substrate surface and internal stress in interlayers also influence the morphology of the C_{60} films. The films can aggregate through either an island growth mode or a layer-by-layer growth depending on the substrate material and deposition temperature. The effect of additional ion bombardment in the energy range 300-1000 eV during film growth is studied. The damage induced to the lattice causes C_{60}'s to be linked together in the form of polymerised chains. Beside that new film structure individual carbon atoms and C_{60} molecules are displaced from the film surface so that also amorphous carbon is detected.

A-IV.4 12:00-12:15

INDUCED ABSORPTION IN THE FULLERENE C_{60}, J. Schell, D. Ohlmann, B. Hönerlage, IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France, J. Serughetti, C. Bovier, Département de Physique des Matériaux, Université de Lyon I, 43, blv. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

We measured induced absorption on free standing Xero-gel samples impregnated by C_{60}. To prepare these samples, the Xero-gel matrix is immersed in a solvent containing the Fullerene in solution. The solvent is then slowly evaporated at room temperature, the C_{60} remaining in the pores of the matrix.

To study the induced absorption of the sample, we measured the transmission of laser pulses as a function of their energy. For this means, we used the second harmonic of a pulsed NdYAG laser (532 nm) with a pulse duration of 30 ps. With increasing pulse energy, the transmission of the sample diminishes considerably. We also studied the dynamics of this effect, using a pump-test configuration with variable delays between pump and test pulses. The strong 532 nm beam provided the pump pulses while we tested at the same wavelength or at longer wavelengths using a dye continuum.

A-IV.5 12:15-12:30

C_{60} ADSORPTION ON Ni(110): A COMBINED STM AND PHOTO-EMISSION STUDY,

P. Rudolf, K. Hevesi, O. Comite, R. Sporken and R. Caudano, Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, 5000 Namur, Belgium; A. Fardelli, N. Zema and M. Pedio, Instituto Struttura della Materia, C.N.R., Via E. Fermi 38, 00044 Frascati, Italy

Molecular beam epitaxy growth of well-ordered ultra thin C_{60} films has attracted much interest over the last few years because such surfaces can be used as templates for the deposition of single-crystalline thick films. The C_{60} adsorption geometry depends on the lattice match between substrate and adsorbate overlayer, on the substrate's reactivity and its tendency towards reconstruction. In this contribution the C_{60} adlayer structure was directly imaged for submonolayer coverages on Ni(110), using Scanning Tunneling Microscopy. For adsorption at substrate temperatures above 600 K (necessary to give rise to long range order [1]), we found that at very low coverages the preferred adsorption sites are the step edges. Increasing the coverage, once the step decoration is completed, two dimensional C_{60} islands grow out on the upper terrace of the Ni steps. In agreement with LEED studies[l] we identified three distinct phases with different symmetry: a rectangular phase and two quasi-hexagonal phases, and a coverage dependance of the abundance of each phase which indicates that the quasi- hexagonal phases are favoured at higher coverages. However, the STM images clearly show that all three phases coexist at all coverages and that there is no clear temperature dependance for one of the two quasi-hexagonal phases as previously deduced [1]. X-ray and UV photoemission data indicate strong hybridization between the metal and the fullerene adlayer. Both chemisorption and charge transfer show up in the core level and valence band spectra.

[1] M.R.C. Hunt. S. Modesli P. Rudolf and R. E. Palmer. Phys. Rev. B51. 10039 (1995).

12:30-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Session V - Diamond like Carbon, Poly, Part 1
Chairperson: A.R. Krauss, Argonne National Laboratory, Argonne, IL, USA

A-V.1 - invited - 14:00-14:30

APPLICATIONS OF DIAMOND-LIKE CARBON THIN FILMS, **A.H. Lettington**, JJ Thomson Physical Laboratory, The University of Reading, Whiteknights, PO Box 220, Reading RG6 6AF, UK

This paper reviews the current state of published work relating to the use of diamond-like carbon (DLC) coatings in a range of optical, mechanical, electronic and biomedical applications. DLC does not have a unique composition but consists of a mixture of amorphous and crystalline phases. Its properties vary considerably with deposition conditions but it can be deposited cheaply over large areas on a variety of substrates.

DLC films can be exceedingly hard. Values in excess of 3000 kg.mm^{-2} have been reported for its knoop hardness. In addition, the materials usually have a low coefficient of fruition and are chemically durable. This makes them excellent candidates for a variety of wear-resistant applications. The films are generally absorbing in the visible but have good transmission in the infrared region of the spectra and are used for a number of infrared application. There have been a number of electronic applications of DLC reported in the literature. These range from photoemissive to electron photolithography of semiconductor surfaces. Preliminary tests with DLC have shown an encouraging degree of biocompatibility and trials are underway on coated prostheses.

A-V.2 14:30-14:45

PHYSICAL PROPERTIES OF PRESSURE POLYMERIZED C_{60}, B. Sundqvist, A. Soldatov, P-A. Persson and P. Jacobsson, Dept. of Experimental Physics, Umea University, 90187 Umea, Sweden.

When C_{60} is submitted to high pressures at temperatures above ambient, intermolecular bonds are formed. The resulting polymeric materials are insoluble, denser, and harder than the initial material. The exact structures formed depend on the reaction conditions and a large number of phases have been observed. We discuss here the structures and properties of the material produced when C_{60} is reacted under relatively low pressures in the range 1-2 GPa, either completely hydrostatic (in He, N_2, or silicone oil) or containing large pressure gradients. Under special conditions, even polymeric single crystals can be formed. We discuss both structural details and the phase diagram and reaction time of C_{60} in this range, as well as spectroscopic properties and thermal transport properties.

A-V.3 14:45-15:00

STRUCTURAL ANALYSIS OF PHOTOTRANSFORMED C_{60} BY VIBRATIONAL SPECTROSCOPY, B. Burger and H. Kuzmany, Institut für Materialphysik der Universität Wien, 1090 Wien, Austria; T.M. Nguyen and H. Sitter, Institut für Experimentalphysik der Universität Linz, 4040 Linz, Austria, M. Walter K. Martin and K. Müllen, MPI für Polymerforschung, 55128 Mainz, Germany

C_{60} is known from previous studies to form two different structures upon illumination at different temperatures. We present Raman-, IR- and mass spectroscopic experiments on these two different materials. The mass spectra are found to depend strongly on the energy used for the desorption. The differences in the mass spectra are surprising. A single line at 720 daltons is observed for pure C_{60}. In the spectrum of the dimer like material short oligomers can be detected as it is expected. On the other hand in the mass spectrum of the material transformed at room temperature, which is expected to consist of higher oligomers, nearly no signal from masses which are multiples to C_{60} can be seen. In both cases the line of pure C_{60} dominates the mass spectrum, even after washing the transformed samples in 1,2,4-Trichlorobezene to remove all residual C_{60}.

The results can be explained by the fact that the desorption energy is still high enough to break up the bonds which are formed upon illumination.

A-V.4 15:00-15:15

STRUCTURE AND VIBRATIONAL SIGNATURES OF HOMO- AND HETERONUCLEAR BRIDGED FULLERENE STRUCTURES, D. Porezag, R. Gutierrez, G. Jungnickel, Th. Frauenheim. Technische Universität, Institut für Physik, 09107 Chemnitz, Germany; G. Seifert, Technische Universität, Institut für Theoretische Physik, 01069 Dresden, Germany

We have applied a density-functional based nonorthogonal tight-binding (DF-TB) method to study the structure, energetics, and vibrational properties of different $[C_{60}]_n$-oligomers (n=2, 3, and 4) as well as the oxygen-bridged analogues, $C_{120}O$, $C_{120}O_2$, $C_{180}O_3$. The applicability of the scheme for finding the ground state of these systems was carefully checked against more sophisticated methods including an all-electron, self-consistent (SCF) scheme based on the local-density-approximation (LDA), and the recently developed generalized-gradient approximation (GGA). We present theoretically calculated vibrational spectra, including Raman- and IR-intensities, which yield nice agreement with recent experimental studies. We find that dimers made of C_{60} show a pronounced peak in the Raman spectrum at 89 cm^{-1}, which is very close to a low energy mode found experimentally for a C_{60} fcc-crystal illuminated at 380 K. Moreover, the overall agreement between experiment and theory is helpful in discriminating between different structural models. Clearly, dimers are identified to be most responsible for the experimental observation at high temperatures. Another material transformed at 300 K shows completely different Raman signals, that almost perfectly match the theoretical signatures of the open triangular trimer. Finally, comparing the calculated IR-spectra of various oxygen-bridged configurations with recent experiments we again obtain nice agreement in the observed spectral pattern, the number of bands and their relative intensities, and confirmed by this the C_{2v} structure with two C_{60} molecules connected by a planar furane ring for $C_{120}O$.

A-V.5 15:15-15:30 NANOLITHOGRAPHY WITH FULLERENES FILMS, S.A.Gusev, E.B.Kluenkov, L.A.Mazo, A.S.Molodnyakov, L.V.Sukhodoev, Institute for Physics of Microstructures, GSP-105, Nizhny Novgorod, 603600, Russia

C_{60} fullerenes film shows considerable promise as a material for nanolithography because of small size of molecules and owing to high sensitivity to photon irradiation or electrons. In the present paper we demonstrate the capabilities of fulleride as a negative resist for electron beam lithography.

Amorphous films deposited by sublimation of fullerenes powders in a vacuum on different substrates. The films thickness was varied from 20 nm to 150 nm. We used the ZRM20 electron beam writing system at 20 kV acceleration voltage and the JEM 2000EXII electron microscope operating at 200 kV for nanopatterns delineation and characterization. Electron beam irradiation of C60 films reduces the solubility of fullerenes in organic solvents: if the dose exceeds 0.1 C/cm^2, the material in exposed region of the film is virtually insoluble in the toluene. Several sets of dot partterns with a diameter of 25-30 nm and different aspect ratio had been fabricated by this manner and used as the etching masks to make nanostructures in semiconductors and metal layers. The minimum distance of ~5÷6 nm between walls of patterns had been measured, that is demonstrated high resolution capability of fullerenes as a negative resist for electron lithography. This research has been supported by the Grant N° 96-02-16990 of Russian Scientific Fund.

A-V.6 - invited - 15:30-16:00 SYNTHESIS; STRUCTURE AND PROPERTIES OF SUPERHARD AND ULTRAHARD MATERIALS FROM FULLERITE C_{60}, V.D. Blank, S.G. Buga, G. A. Dubitsky, N.R. Serebryanaya, M.Yu. Popov, V.M. Prokhorov, C.A. Sulyanov, B.N. Mavrin, A.N. Ivlev, B.N. Denisov, Research Center for Superhard Materials, Troitsk, Moscow Reg., 142092 Russia

Extended investigations of the structure and properties of carbon states metastable at standard conditions synthesized from pure C_{60} at pressures higher than 8 GPa and temperatures in the range 600-2100 K are the topical task at the recent time. It is caused by the revealed high hardness of obtained material. Using the high pressure up to 13 GPa in a Thoroid type chamber we have obtained bulk samples, weighting up to 80 mg, of different C_{60} states based on polymerized molecules and their fragments. In the pressure range 9.5 - 13 GPa and the temperature range 600 - 1000 K the phase transitions into dense bulk polimerized FCC structure of C_{60} with the elementary cell parameter between 13.6 - 12.1 A were revealed, as well as into distorted BCC structures, namely: the pseudo-tetragonal with parameters a = 9.53 A, b = 8.87 A, c = 8.34 A, Z = 2; the orthorombic with parameters a = 10.93 A, b = 8.98 A, c = 7.62 A, Z = 2; and also into monoclinic crystal structure with parameters a = 10.27 a, b = 7.80 A, c = 9.49 A, ß = 92.4°, Z = 2. The density of hard FCC phases equals to 2.05 to 2.6 g/cm^3, the density of distorted BCC phases is 2.95 to 3.3 g/cm^3. Besides of crystal states, three types of amorphous ones were synthesized.

The obtained materials have the specific resistance in a wide range from 1 Ω•cm to 1 MΩ•cm, and belong to semiconductive and semimetal type. All obtained states are stable on annealing at temperature up to 1000°C.

16:00-16:30 **BREAK**

Session VI - Diamond like Carbon, Poly, Part 2
Chairperson: A.H. Lettington, University of Reading, Reading, UK

A-VI.1 16:30-16:45 SUPERHARD AND ULTRAHARD FULLERITE C_{60} PHASES AND DIAMOND HARDNESS,V. D. Blank(1,2), M. Yu. Popov(1,2), N. Lvova(2), (1)Research Center for Superhard Materials, Troitsk, Moscow Reg., 142092 Russia, (2)Institute of Spectroscopy, Ac. Sci., Troitsk, Moscow Reg., 142092 Russia, K. Gogolinsky, HTE company, Zelenograd, Moscow K-681, 103681, Russia, V. Reshetov, Moscow Physical Engineering Institute, Moscow, 115409, Russia

New data concerning the hardness of superhard and ultrahard carbon 3D polymerized phases synthesized from fullerite C_{60} in the pressure-temperature range 8-30 GPa and 300-2100 K (Blank et al., Phys. Lett. A, 220 (1996), 149) and natural diamond are presented.

The hardness test of material characterized by hardness close to or exceed that of diamond have been a problem, because of the hardness of indenter close to that of the specimen. To solve this problem, the ultrahard fullerite was used as indenter material and a new procedure for the hardness test of superhard materials and diamond was developed. The method of sclerometry and an indenter calibration by reference to a primary standard were applied for the hardness measurements using the atomic force microscope («NanoScan» measurement system).

A hardness comparison of ultrahard 3D polymerized fullerite with diamond was performed using two types of indenters: made from ultrahard fullerite and diamond. A crack-free indentation and indentation plasticity was observed when the ultrahard fullerite indenter was used for the diamond hardness test. The measured hardness is 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111) respectively. The diamond indenter can not produce an indentation on the ultrahard fullerite specimen. The 3D polymerized phases of C_{60} reveal extremely high hardness values: 75 - 200 GPa depending on the syntheses conditions.

A-VI.2 - invited - 16:45-17:15

DIAMOND FILM GROWTH FROM FULLERENE PRECURSORS, **A.R. Krauss**, D.M. Gruen, D. Zhou, T. McCauley, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne IL 60439, USA

A process has been developed for the growth of phase-pure nanocrystalline diamond thin films using fullerene precursors in a microwave plasma consisting primarily of Ar and C60 vapor. Growth occurs in the near-absence of atomic hydrogen, and the mechanism differs significantly from that of previously employed CVD methods, being based on the direct incorporation of the carbon dimer (C2) as the diamond growth species, rather than the conventional CH_3*-atomic hydrogen growth mechanism. For very small grain sizes, diamond, rather than graphite is the stable form of carbon, and the initial growth therefore consists of phase-pure diamond. However, small grains are rapidly etched by atomic hydrogen, and in the conventional growth process, which relies on the use of large amounts of atomic hydrogen, the growth of larger, grains is kinetically preferred over formation of new diamond nuclei. Use of the carbon dimer growth species resulting from C60 fragmentation makes it possible to achieve continuous renucleation of the diamond phase, and promotes formation of ilms with very small average grain size (~15 nm). These films are exceptionally smooth (30-45 nm rms roughness) and form continuous, conformal, pinhole-free coarings at thicknesses of a few tens of nanometers. Such films lead themselves to a variety of applications involving friction and wear properties, protection against chemical attack and cold cathode electron emission devices.

Work supported by the U.S. Department of Energy, BES-Materials Science, under contract W-31-109-ENG-38.

A-VI.3 17:15-17:30

THE NUCLEATION AND GROWTH OF DIAMOND IN CARBON ONIONS, F. Banhart, Y. Lyutovich, P. Redlich, and P.M. Ajayan, Max-Planck-Institut für Metallforschung, 70569 Stuttgart, Germany

Spherical carbon onions consist of nested fullerene-like shells. They form under intense electron irradiation of carbon nanoparticles in an electron microscope. At specimen temperatures above 600°C, in-situ annealing of radiation damage in the graphitic shells enables us to obtain onions with perfectly coherent shells of high tensile strength. These onions show a considerable self-compression, seen as a decreasing spacing between the shells, from 0.34 nm at the surface down to 0.22 nm in the centre. Under prolonged irradiation, the cores of the onions transform to cubic diamond crystals. Once nucleated, these crystals grow under irradiation until almost the whole onion has transformed to diamond. The nucleation of diamond occurs under high-pressure conditions which prevail in the centres of the irradiated onions. By contrast, growth proceeds at decreasing, possibly even at zero pressure. This experiment enables us, for the first time, to monitor the transformation of graphite-like material into diamond in-situ on an atomic scale. Results from in-situ high-resolution imaging, EELS, and electron diffraction will be presented. Thermodynamical models describing this phase transformation in a dissipative system will be discussed.

A-VI.4 17:30-17:45

HFCVD DIAMOND NUCLEATION AND GROWTH ON DLC CARBON FILMS OBTAINED BY LASER ABLATION, J. Müller(1), E. Fogarassy(2) and F. Le Normand(1), (1)IPCMS-GSI, 23 rue du Loess, 67037 Strasbourg, France; (2)CNRS/PHASE, 23 rue du Loess, 67037 Strasbourg, France

One requirement to grow Hot Filament Chemical Vapour Deposition (HFCVD) heteroepitaxial diamond is to start from a carbon buffer layer. Therefore diamond nucleation and growth were studied on Diamond Like Carbon (DLC) films. The DLC films were prepared by laser ablation with different depths (5-20 nm) and different temperatures (300-573K) on Si(100). The nature of the DLC films were studied by electron spectroscopies including X-ray photoemission, Auger electron and electron loss spectroscopies directly connected to the growth chamber. It is shown that, whatever the depth and the deposition temperature of the DLC carbon layer, this carbon layer is removed in the gase phase or react with silicon to form a silicon carbide layer onto which diamond nucleates and grows. The instability of the DLC layer is ascribed to the occurrence of hydrogen radicals highly reactive with the graphitic carbon formed at the high temperature of the diamond growth (1073K). These results underline the need to get in the future a carbon layer of high stability to the CVD growing conditions of diamond (high temperature, presence of hydrogen radicals).

A-VI.5 17:45-18:00

ENHANCEMENT OF DIAMOND NUCLEATION BY APPLYING SUBSTRATE BIAS IN ECR PLASMA CVD, H. Jeon, Chongmu Lee, Department of Metallurgical Engineering, Inha University 253 Yonghyeon-dong, Inchon, 402-751, Korea; A. Hatta, T.Ito, T. Sasaki and A. Hiraki, Department of Electrical Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

Oriented diamond films were grown uniformly on Si(100) substrates by low pressure ECR microwave plasma CVD. The substrates were positively dc biased relative to the electrically grounded chamber to get several eV ion energies. In the ECR microwave plasma CVD the CH-He gas mixture was used as source gas to obtain a radical density as high as that in the conventional microwave CVD. Radical densities higher than those with the CH_4-H_2 gas mixture were obtained using the CH_4-He gas mixture. Results show that diamond nucleation densities as high as $10^9 cm^{-2}$ can be attained uniformly on a four-inch Si wafer using the low pressure ECR microwave plasma CVD method. The dependence of the diamond nucleation density on gas concentrations, rf-power, substrate bias voltage, and deposition time was also investigated.

A-VI.6 18:00-18:15

INFLUENCE OF BORON INCORPORATIN ON THE GROWTH RATE AND PHASE STABILITY OF DIAMOND FILMS, J. Mambou, E. Gheeraert and A. Deneuville, LEPES CNRS, BP 166, 38042 Grenoble Cedex 9, France

Boron is widely used to achieve passive as well as active devices with mono as well as polycrystalline films. We show here, that boron incorporation has also tremendous effect at relatively low incorporation level (< $3x10^{-4}$ at) on the growth rate and phase stability of diamond films. The films are deposited by MPCVD from Hydrogen/Methane/Diborane mixtures on Si and Ib diamond substrates. The boron concentration is calculated from its Infrared absorption.

For polycrystalline films, the growth rate decreases first slowly (10%) up to $5.3x10^{19}$ B-cm^{-3}, then much more rapidly (50%) to 8.1x10 B-cm^{-3}. From Raman, the edge corresponds to the begining of loss of the crystalline selection rules with the increasing appearance of a forbidden one-phonon band around 1230 cm^{-1}. At $8.1x10^{19}$ B-cm^{-3} only an amorphous phase remains.

For monocrystalline films, the growth rate is nearly constant up to $4.8x10^{19}$ B-cm^{-3}, then decreases drastically (90%) to $9.7x10^{20}$ B-cm^{-3}. From Raman, the edge presents the same correlation than previously, but this induces rapidly in these films a poorer crystallinity ($4.8x10^{19}$ B-cm^{-3}), then microcrystalline graphitic phases ($1.9x10^{20}$ B-cm^{-3}).

The analogies and differences between the boron behaviour in poly and monocrystalline films will be discussed in relationship with the different boron incorporation rate according to the growing sector in polycrystalline films.

A-VI.7 18:15-18:30

ELECTRONIC PROPERTIES OF TETRAHEDRAL AMORPHOUS CARBON (ta-C) FILMS CONTAINING NANOTUBE REGIONS, G.A.J. Amaratunga, M. Chhowalla, G. Lim, A. Mumidradasa, S. Pringle, M. Baxendale, I. Alexandrou, C.J. Kiely and B. Keyse, University of Liverpool, L69 GT, UK

Tetrahedral amorphous carbon(ta-C), sometimes loosely termed «amorphous diamond», is an amorphous form of carbon in which the sp3 bonded carbon content can be as high as 90%. We have recently shown that the cathodic vacuum arc method used for ta-C deposition can be adapted to create a new type of all carbon nanocomposite film in with a mixed ta-C/nanoparticle carbon(NC) structure[l]. The carbon nanoparticles are in the form of well formed and fragmented nanotubes and onions which introduce extended sp2 bonded carbon regions with π electronic states.

The electronic properties of these ta-C/NC films are reported in this work. The residual sp2 bonding in ta-C, which is energetically favoured to be in paired sites in preference to an sp3 dangling bond, introduce π electronic states within the wide band-gap which results due to the sp3 diamond-like bonding. The ultimate electronic and optical band-gaps of ta-C (2.0 - 2.9 eV) are therefore determined by these π states. The π states are only weakly delocalised and therefore give ta-C poor electronic transport properties. The extended sp2 regions introduced in the form of carbon nanoparticles into the ta-C film act to aid the delocalisation of the π electronic states in the ta-C matrix. This clearly seen in the conductivity vs temperature data as thermally activated transport process with a well defined energy of activation. The conductivity of the ta-C/NC films when doped with N is also significantly higher than that of a comparable ta-C film. Details of the transport process in ta-C/NC films have been studied using the thermopower method. The thermopower derived free carrier concentration and the conductivity data are used to estimate the mobility. Preliminary results indicate that the ta-C/NC composite structure leads to an improvement in the electronic properties of semiconducting low temperature deposited thin film carbon.

[l] G. A. J. Amaratunga, M. Chhowalla, C. J. Keily, 1. Alexandrou, R. Ahranov and R. Devenish, Nauture, 383, p321, 1996.

Wednesday June 18, 1997 — Morning
Mercredi 18 juin 1997 — Matin

Session VII - Fullerene, Part 2
Chairperson: L. Forro, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

A-VII.1 - invited - 9:00-9:30

ELECTRONIC STRUCTURE STUDIES OF INTERCALATED, HETERO AND ENDOHEDRAL FULLERENES, **J. Fink**, M.S. Golden, M. Knupfer, T. Pichler, S. Haffner, R. Friedlein, P. Kuran, U. Kirbach and L. Dunsch, IFW Dresden, Postfach 270016, 01171 Dresden, Germany

We present a review on electronic structure studies of intercalated, hetero and endohedral fullerenes by photoemission and electron energy-loss spectroscopy in transmission.
In particular, recent results on the dimers of the heterofullerene $C_{59}N$, on alkali metal doped $C_{59}N$, the endohedral fullerene $Tm@C_{82}$, and on alkalimetal doped $Tm@C_{82}$ are reported.

A-VII.2 9:30-9:45

THE ELECTRONIC STRUCTURE AND THE OPTICAL PROPERTIES OF $Tm@C_{82}$ PROBED BY HIGH ENERGY SPECROSCOPY, T. Pichler, M.S. Golden, M. Knupfer, J.Fink, U. Kirbach, P. Kuran and L. Dunsch, Institut für Festkörper- und Werkstofforschung Dresden, 01171 Dresden, Germany

We present recent results on the electronic structure and the optical properties of endohedrally doped, isomer separated $Tm@C_{82}$ measured using electron energy-loss spectroscopy (EELS) in transmission and photoemission spectroscopy (PES). We compare the electronic structure of $Tm@C_{82}$ with that of other metallofullerenes, especially regarding the valency of the rare earth dopant, the optical properties of the endohedral compound (from EELS at low momentum transfer) and the occupied and unoccupied electronic structure (from PES and EELS). From PES recorded using monochromatic AlK_{α} radiation we obtain not only direct evidence for the endohedral nature of the compound but also conclusive proof of the $4f^{13}$ configuration of the Tm ion, which means that, in this case, the Tm ion is divalent, in contrast to the well known case of $La^{3+}@C_{82}^{3-}$. From the loss function we determined the optical gap of the three isomers of $Tm@C_{82}$ in the solid state and derived the optical conductivity performing a Kramers-Kronig analysis.
We thank the B M BF (13N 6676) and the E U (T M R) for financial support.

A-VII.3 9:45-10:00

VIBRATIONAL SPECTRA OF $Tm@C_{82}$ AND $Gd@C_{82}$, M. Krause, P. Kuran, U. Kirbach, L. Dunsch, Institut für Festkörper- und Werkstofforschung Dresden, Helmholtzstr. 20, 01171 Dresden, Germany

In order to clarify the electronic and structural properties of endohedral metallofullerenes we have studied the infrared and Raman spectra of three isomers of $Tm@C_{82}$ and of a soluble and an insoluble form of $Gd@C_{82}$. The infrared and Raman spectra of the 5 samples showed a similar spectral pattern. The majority of the infrared and Raman bands of the three $Tm@C_{82}$ isomers agreed within 10 cm^{-1} and only few isomer sensitive bands were found. The insoluble form of $Gd@C_{82}$ was characterized by a supercomposition of very broad and sharp infrared bands and a loss of fine structure in the Raman spectrum in contrast to the soluble $Gd@C_{82}$ sample. However, the majority of the vibrational frequencies of the two $Gd@C_{82}$ forms had comparable values indicating a similar principal electronic structure. Strong frequency differences on the other hand were established between the three $Tm@C_{82}$ isomers and the two $Gd@C_{82}$ samples.

A-VII.4 10:00-10:15

CHARGE TRANSFER IN INTERCALATED FULLERENES, P.V. Huong, Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux 1, 351 cours Libération, 33405 Talence, France, J.Z. Liu, Dept. Physics, Univ. of California, Davis CA 95616, USA

The superconductivity obtained by intercalation of simple elements in the solid system of fullerenes opens up a new path in the research on the mechanism of their conduction.
Several fullerenes intercalated with elements like Yterbium and with simple molecules like interhalogens have been prepared and examined by various techniques in particuliar by Raman micro-spectoscopy.
Correlations have been established between phonons frequencies and microstructure of these materials.
The phonons frequency shifts by intercalation allow to deduce that if in the complex (C_{60},Yb), the charge transfer undergoes from Yterbium to the fulllerene; in that of (C_{60},IBr) it is exactly the reverse, i.e. the partial elctron transfer is made from the fullerene to the halogen.
References:
1. P.V.HUONG, Solid State Comm. 88, 23,1993
2. P.V. HUONG, P.M. AJAYAN, R. CAVAGNAT, O. STEPHAN, Physical Reviews B 51, 10048, 1995

A-VII.5 10:15-10:30

SUPERCONDUCTING STATE OF ALKALINE-EARTH C_{60} FULLERIDES, B. Gogia, K. Tanigaki, NEC Corporation, Tsukuba 305, Japan; K. Kordatos, K. Prassides, Sussex University, UK and H. Suematsu, University of Tokyo, Tokyo, Japan

Doping of C_{60} with alkali metals results in simple ionic, charge transfer fulleride-compounds, A_xC_{60}'s which show metallic behaviour near x = 3 and then exhibit superconducting behaviour at low temperatures. The highest Tc(33K) observed in A_3C_{60} has been only surpassed by cuprate high Tc superconductors. On the other hand, intercalation of C_{60} with alkaline earth metals (Sr, Ca, Ba) results in more complex and hybrid electronic structure. Superconductivity has also been reported in this class of materials in fcc Ca_5C_{60} and bcc $(Ba,Sr)_6C_{60}$ with Tc in the range of 4 to 8K. In the later superconducting compounds the Fermi level is in the next higher t_{1g} band in comparison to alkali metal doped fullerides where it is in t_{1u} derived band. Whether bcc AE_6C_{60} structure (where AE = Ba or Sr) has really any correlation with occurance of superconductivity, is still a question which requires further detailed investigation. We have attempted to prepare superconducting phases with high quality for $(Ba, Sr)_xC_{60}$ fullerides. In this paper, we present our results depicting the nature of superconducting phase based on the data acquired using X-Ray diffractometry, SQUID and NMR.

10:30-11:00 **BREAK**

Session VIII - Fullerene, Part 3
Chairperson: M.F. Jarrold, Northwestern University, Evanston IL,USA

A-VIII.1 - invited - 11:00-11:30

STUDY OF BONDED FULLERENE NETWORKS; **L. Forro**, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Following the discovery of high temperature superconductivity in doped fullerenes, the latest excitement in fullerene chemistry and solid state physics is coming from structures based on intermolecular bonding of the C_{60} spheres to form C_{60} dimers, one-dimensional polymers, two-dimensional structures, high pressure polymeriezed phases 1-4, etc. In this presentation the structural, electronic and magnetic properties of these systems will be reviewed.

1. 0. Chauvet, G. Oszlanyi, L. Forro, P.W. Stephens, M. Tegze, Rev. Lett., 72 (1994) 2721.
2. P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. oszlanyi and L. Forro, Nature 370 636 (1994)
3. S. Pekker, A. janossy, L. Mihaly, O. Chauvet, M. Carrard, L. Forro, Science, 265, 1077 (1994)
4. G. Oszlanyi, G. Bortel, G. Faigel, L. Granasy, S. Pekker, G. Bendele, P.W. Stephens and L. Forro, Phys. Rev. B54, 12228 (1996).

A-VIII.2 - invited - 11:30-12:00

NMR INVESTIGATION OF ALKALI FULLERIDES AND AZAFULLERIDES, F. Rachdi(1), L. Hajji(1), H. Dollt(1), M. Ribet(1), T. Yildirim(2), J.E. Fischer(2), C. Goze(3), M. Mehring(3), A. Hirsch(4), B. Nuber(4), (1)G.D.PC. Université Montpellier 2, 34095 Montpellier, France; (2)L.R.S.M. University of Pennsylvania, Philadelphia PA 19104, USA; (3)2. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart 80, Germany; (4)Institut für Organische Chemie, 91054 Erlangen, Germany

We report on ^{13}C and ^{23}Na NMR measurements on Na_2C_{60} and Na_6C_{60} compounds. The ^{13}C NMR spectrum of Na_2C_{60} sample presents a narrow isotropic line at 172 ppm. The Na_6C_{60} resonance appears at 176ppm and is 20 ppm more shifted down field than the resonances of A_6C_{60} compounds with heavier alkalis, reflecting a strong polarization of the transferred electrons to the C_{60} molecules. The ^{23}Na NMR spectrum of A_2C_{60} shows one line at 73 ppm and the one of A_6C_{60} presents two lines at 73 ppm and 147 ppm. The intensities ratio of the latter lines is about 2:1. According to previously reported X-ray data we attribute the line at 147 ppm to the Na tetramers in the octahedral sites and the line at 73 ppm to the Na cations in the tetrahedral ones which are singly occupied. We also present ^{13}C MAS NMR measurements on the $(C_{59}N)_2$ dimer. The room temperature NMR spectrum obtained by spinning the sample at 10KHz shows a weak line at 90 ppm and a group of lines around 140 ppm. The simulation of the obtained spectra allows us to attribute the line at 90 ppm to the sp^3 carbons forming the expected interball single bond and the other lines to the sp^2 carbons of the dimer molecules. The distortion of the $C_{59}N$ molecules due to the introduction of the nitrogen atom into the C_{60} cage and the ^{13}C-^{14}N dipolar coupling must be at the origin of the observed group of resonances.

A-VIII.3 12:00-12:15

STABILITY OF THE CHARGED C_{60} OLIGOMERS WITH VARIOUS LENGTH, J. Kuerti and P. Rajczy, Department of Atomic Physics, R.Eotvos University, Puskin u. 5-7, 1088 Budapest, Hungary

It is well known by now that the covalent bonding between C_{60} molecules in various oligomers and polymers occurs typically through the [2+2] cycloaddition, where the resulting four-membered ring between the C_{60} moieties has D_{2h} symmetry. This structure is verified for the linear chain polymers in A_1C_{60} (A=K,Rb) by X-Ray measurements. X-Ray experiments also showed, however, that $C_{60})_2^{2-}$ dimers prefer to be formed with only a single bond between the two C_{60} molecules, in the quenched phase of A_1C_{60}. The two balls are in trans-position with C_{2h} symmetry. Increasing the length of the $(C_{60})_n^{n-}$ linear oligomer, a cross-over should occur from the single-bonded structure (S_C_{2h}) to the four-membered ring structure (D_D_{2h}). We carried out semiempirical calculations to investigate this question. Already the $(C_{60})_4^{4-}$ - tetramer turned out to favor the D_D_{2h} structure energetically. Even more, the S_C_{2h} tetramer was unstable and dissociated into dimers.

A-VIII.4 12:15-12:30

PROPERTIES OF ENDOHEDRAL N@C_{60}, B. Pietzak, M. Waiblinger, T. Almeida Murphy, A. Weidinger, Hahn-Meitner Institut Berlin, Glienickerstr. 100, 14109 Berlin,Germany; M. Höhne, Institut für Kristallzüchtung, Rudower Chaussee 6; 12489 Berlin, Germany and E. Dietl, A. Hirsch, Universität Erlangen-Nürnberg, Institut für Organische Chemie, Henkestr. 42, 91054 Erlangen, Germany

Endohedral N@C_{60} (atomic nitrogen inside C_{60}) is produced by ion implantation in C_{60}. N@C_{60} is soluble in organic solvents and stable in air. A special feature is that it gives a very clear, hyperfine splitted EPR signal with sharp lines even in the solid. In solution, the homogenous line width is at least a factor of 10 narrower than any EPR line observed so far. This makes it an ideal probe for monitoring chemical reactions of C_{60} via changes of the EPR signal. As example, the formation of the monoadduct of diethyl malonate on C_{60} will be discussed. In general, N@C_{60} can be used as a probe or tracer for monitoring reactions or the transport of C_{60}.
N@C_{60} is an ideal trap for atomic nitrogen. Nitrogen is in the center of C_{60} and keeps its atomic structure. Opening of the C_{60} shell (e.g. by heating) leads to a release of atomic or radical nitrogen. In this contribution, studies on the vibration of N in C_{60} will also be presented.

12:30-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-Midi

Session IX - Nanot., Part 1
Chairperson: A. Loiseau, ONERA, Châtillon, France

A-IX.1 - invited - 14:00-14:30

CARBON NANOTUBES & BEYOND, **T.W. Ebbesen,** ISIS, Louis Pasteur University, 67000 Strasbourg, France and NEC Research Institute, 4 Independence Way, Princeton, NJ 08540, USA

The state of the art with regards to nanotubes will be briefly reviewed. Several examples of their physical properties will be presented. Possibilities of making materials other than nanotubes from graphitic sheets will be discussed and some novel structures will be reported.

A-IX.2 14:30-14:45

HIGH RESOLUTION ELECTRON MICROSCOPY OF BENDS IN MULTIWALLED CARBON NANOTUBES, D.N. Weldon, W.J. Blau, Physics Department, Trinity College Dublin, Dublin 2, Ireland and G. Miehe, FG Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany

Transmission electron microscopy shows that a fraction of multiwalled nanotubes produced in a Carbon arc generator is actually curved. Theoretical modelling predicts that such curvature is accomplished by the inclusion of heptagon / pentagon pairs into the structure. The experimental result, however, reveal no evidence for structures with either seven or five fold symmetry. Bending is achieved merely by folding or fracture of the lattice planes. An explanation of this observation can be given from molecular mechanics geometry optimisation calculations which show that the inclusion of sp^3 hybrids in the graphitic sheets can lead to similar bends.

A-IX.3 14:45-15:00

CARBON NANOTUBES AND NANOFIBERS PRODUCTION BY CATALYTIC PYROLYSIS OF BENZENE, A.M. Benito, E. Munoz, M.T. Martinez, Instituto de Carboquimica, CSIC, Luciano Gracia 5, 50015 Zaragoza, Spain and Y. Maniette, Serveis Cientifico-Tecnics, Universitat de Barcelona, Lluis Solé i Sabaris s/n, 08028 Barcelona, Spain

Catallytically grown carbon nanotubes and nanofibers are novel materials that can be produced by decomposition of carbon-containing gases over different transition metal surfaces.

Pyrolysis of bencene at ca. 600-900°C over powdered Ni generated different types of carbonaceous materials, ranging from amorphous carbon and graphitic nanofibers to fullerene nanostructures, possesing a variety of morphologies.

Effect of temperature and time parameters on the carbon nanofibers and nanotubes growth was analysed in the present work.

A-IX.4 15:00-15:15

FULLERENES AND NANOTUBES WITH NON-POSITIVE GAUSSIAN CURVATURE, H. Terrones, Instituto de Fisica, UNAM, Apartado Postal 20-364, C.P. 01000 Mexico, D.F. Mexico and M. Terrones, School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, UK

It is well known that classical fullerenes should have 12 pentagonal rings of carbon and any number of hexagonal rings (except one). All these fullerenes, which have been matter of extensive study, present the same topology (genus) as the sphere. However, by incresing the topology (genus greater than 1) it is possible to generate closed graphitic arrangements with no dangling bonds possessing hexagons and heptagons only. Therefore, these new closed structures do not present the positive Gaussian curvature introduced by the pentagonal rings. We have constructed computer models of different cubic (Oh symmetry) with genus 5 and icosahedral(Ih symmetry) with genus 11 fullerene-like structures (holey-balls). We also have applied this idea to carbon nanotubes (holey-tubes) with genus up to 21. The geometry and stability of these new complex arrangements which can be considered as finite zeolites are analyzed.

A-IX.5 15:15-15:30

HOW DOES A NANOTUBE GET OVER A SHARP STEP AT THE SURFACE ON WHICH IT IS ADSORBED? Ph. Lambin, Département de Physique, Facultés Universitaires N.D-P., 5000 Namur, Belgium and L.P. Biro, KFKI-Research Institute for Materials Science, 1525 Budapest, Hungary

Carbon nanotubes prepared by catalytic thermal decomposition of hydrocarbon molecules on transition metal nanoparticules were investigated by scanning tunneling microscopy (STM). One of the STM images showed a nanotube with a diameter around 1.5 nm climbing a sharp step 1 nm high on the (HOPG) graphite substrate on which samples were deposited. The deformation and the stresses in this nanotube were evaluated from continuous-medium elasticity, using atomic 12-6 C-C pair potentials to describe the interaction between the tube and the stepped surface. A good agreement was found between the computed shape of the deformed nanotube and that revealed by STM. This indicates that the value of the Young modulus of carbon nanotubes measured recently,l and that was used in the calculations, still applies to a tubule having a diameter as small as ~l nm. The calculations also revealed that the stresses only slowly increased with increasing step height and, for that reason, a nanotube adsorbed on a surface can get over sharp steps a few nm high without breaking. This result attests to the high flexibility of the carbon nanotubes, as often reported in recent literature.

1 M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson, Nature 381 (1996) 678.

A-IX.6 15:30-15:45 FORMATION OF FILLED CARBON NANOTUBES AND NANOPARTICLES USING POLYCYCLIC AROMATIC HYDROCARBON MOLECULES, A.A. Setlur, J.Y. Dai, J.M. Lauerhaas, and R.P.H. Chang, Northwestern University, Evanston, IL 60208 USA

Nanotubes filled with pure Cu and Ge have been formed by arcing metal/graphite composite anodes in a hydrogen atmosphere. These nanotubes are found in the soot deposited on the chamber walls instead of on the redeposited rod on the cathode. Since Cu and Ge do not form stable carbide phases, catalyze carbon fiber growth, or have significant carbon solubility, a new mechanism is needed to explain the formation of these nanowires. We propose that polycyclic aromatic hydrocarbon (PAH) molecules, produced by the hydrogen arc are the precursors to the graphitic layers encapsulating the Cu or Ge nanowire. Direct evidence for this mechanism is given by evaporating pyrene ($C16H10$) and Cu or Ge together to form filled nanotubes. When arcing a composite anode in hydrogen using ferromagnetic elements, such as Fe, Ni, or Co, encapsulated nanoparticles are formed instead of nanowires. Encapsulated nanoparticles are also obtained when evaporating pyrene and cobalt, leading to a similar mechanism using PAH molecules for the formation of these materials. Differences between nanoparticle and nanowire formation will be reported.

A-IX.7 15:45-16:00 THE INVESTIGATION OF GROWTH AND MORPHOLOGY OF NANOTUBE CARBON FILMS, Z.Ya. Kosakovskaya, Institute Radio Engineering & Electronics RAS, Mokhovaya str. 11, Moskow 103907, Russia

The experimental and theoretical investigations of the growth of carbon films at early stages (nucleation, coalescence) which were synthesized on various substrates by electron-beam evaporation of graphite in vacuum, were conducted. The kinetic model of carbon films growth on singular and vicinal surfaces, taking into account Shvebel barriers has been worked out. It has been shown that at the conditions of full condensation (the formation of two-dimensional nucleai of graphite or diamond-like phase) the growth mechanism is determined by one non-scaled parameter D/J, where D- normalized diffusion coefficient, J- normalized adatom arrival rate. At $D/J > 10^8$ the layer by layer epitaxial growth of graphite takes place. When $D/J \leq 10^{-4}$ we have the case of random Poisson precipitation process with high level of roughness. In this case, the film consist of diamond-like phase. Further diminishing of $D/J << 10^{-4}$ leads to the formation of oversaturated vapour phase near the substrate surface and thus the conditions for nanotube nucleai formation are created. It is known, that the thermal situation on surface of substrate during growth of films to a considerable extent influences upon value D. The experimental studies of the film surface tempereture change during growth and its correlation with the final structure have been made. It was shown that vapour phase like-time depends upon thermal constants of the substrate and they determine the final nanotubes structure.

16:00-16:30 **BREAK**

Poster Session I - Carbons, Fullerenes

16:30-18:00 See programme of this poster session p. A-25 to A-30.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session X - Nanot., Part 2
Chairperson: T.W. Ebbesen, ISIS, Louis Pasteur University, Strasbourg, France

A-X.1 - invited - 9:00-9:30

CARBON SINGLE WALL NANOTUBES: ELABORATION AND PROPERTIES; **P. Bernier**, W. Maser, C. Journet, GDPC-University of Montpellier II, 34095 Montpellier Cedex 5, France, A. Loiseau, ONERA, Chatillon, France, M. Lamy de la Chapelle, S. Lefrant, IMN, University of Nantes, France, and R. Lee, J. Fischer, LRSM, University of Pennsylvania, Philadelphia, USA

Co-evaporation of carbon, in the presence of helium with some other element as a catalyst yields interesting new molecules of the fullerene family which have tubular morphologies with a cross-section at the nanoscale but lengths at the macroscale. In particular, using Ni or Co based mixtures as catalyst with the electric arc technique, one obtains single wall carbon nanotubes in large quantities, with an average diameter of 1.4 nm and which assemble themselves in highly crystalline bundles containing a few tens elements. The diameter dispersion has been studied in detail using Raman spectroscopy which shows impressively resolved structures of the observed modes. A majority of (10,10) armchair tubes is observed but some other configurations are also present with slightly different diameters. These nanotubes have been observed, characterized and studied using high resolution microscopy techniques. X-rays and electron diffractions have been used to characterize the crystalline nature of individual bundles.

A-X.2 - invited - 9:30-10:00

SCANNING TUNNELING MICROSCOPY (STM) IMAGING OF CARBON NANOTUBES **L.P. Biro** and J. Gyulai, KFKI-Research Institute for Materials Science, 1525 Budapest, P.O.B. 49, Hungary, Ph. Lambin, J. B.Nagy, S. Lazarescu, A. Fonseca, P.A. Thiry, and A.A. Lucas, Institute for Studies in Interface Sciences, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles 61, 5000 Namur, Belgium

Scanning tunneling microscopy (STM), or atomic force microscopy (AFM), are versatile methods for the investigation of carbon nanotubes. However, the interpretation of the images of 3D objects of nm size is not always possible in a straightforward way. Convolution effects of the probe tip affect both STM and AFM. If objects, like coiled carbon nanotubes are investigated by STM, further complications may arise from contributions of electrical resistivity. STM measurements and detailed image analysis of individual carbon nanotubes and «rafts» of grown-together nanotubes produced by the catalytic decomposition of acetylene are reported. Two families of nanotubes of 1 nm in diameter and of 10 nm in diameter are found. One some of the nanotubes atomic resolution images were taken. A similar lattice as in the case of graphite was found. STM images of coiled carbon nanotubes are reported for the first time.

A-X.3 10:00-10:15

SCANNING TUNNELING MICROSCOPY OF CARBON NANOTUBES, U. Hubler, P. Jess, H.P. Lang, H.-J. Güntherodt, Institute of Physics, University of Basel, Klingelbergstr. 82, 4056 Basel, Switzerland, L. Forro, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

To obtain a macroscopic amount of purified multi-wall carbon nanotubes, sootlike deposit from the cathode of an arc discharge apparatus was ultrasonically dispersed in spectroscopic grade ethanol and centrifuged to remove larger particles. The suspension was subsequently drawn through a 0.2 µm pore ceramic filter to produce a thin film of nanotubes. This film can be further aligned by brushing it with a teflon rod resulting in a change of optical properties. Two types of samples were investigated by scanning tunneling microscopy (STM): Nanotubes applied from the suspension onto various substrates, such as highly oriented pyrolytic graphite (HOPG), and deposits on the filter before and after brushing. While in the first case STM images show sparse nanotubes on the substrate, a dense film of randomly oriented nanotubes is observed on the ceramic filter. By brushing, a preferential direction is applied to this layer and STM images show an almost parallel arrangement of nanotubes. On nanometer scale, an atomic lattice is observed.

A-X.4 10:15-10:30

ELECTRON ENERGY LOSS ANALYSIS OF PLASMON EXCITATION OF NANOTUBES AND ONION-LIKE FULLERENES, L. Henrard, P. Rudolf, K. Hevesi, F. Malengreau, L.M. Yu, Ph. Lambin and A.A. Lucas, ISIS Physics Department, Rue de Bruxelles 61, 5000 Namur, Belgium and W. Basca, C. Coluzza, W.A. De Heer, Institut de Physique Expérimentale, EPFL, Lausanne, Switzerland and Th. Cabioch, J.P. Rivière, Université de Poitiers, France

EELS was performed in reflection geometry on mechanically aligned tubular fullerenes and on onion-like hyperfullerenes. For low primary energy (E_p=30 eV), the $\sigma+\pi$ collective plasmon was found centered at 12 eV in both cylindrical and spherical carbon structures. At higher primary energy (E_p=100-150 eV), the broad resonance was shifted at 22 eV for onion-like fullerene and at 23 eV for tubular aligned cluster. XPS C1s shake-up analysis showed the bulk plasmon of tubular structure centered at 30 eV.

In theoretical calculations based on a continuum dielectric approximation and on a discrete dipole approach, we studied surface plasmon of multishell fullerenes, the fullerene-substrate and fullerene-fullerene interactions. These computational results allowed us to identify the 12 eV resonance as the excitation of dipolar interface mode. Contribution of quadrupolar and multipolar excitations and of bulk plasmon were also considered in the analysis of experimental spectra.

10:30-11:00 **BREAK**

Session XI - Nanot., Part 3
Chairperson: Ph. Lambin, Facultés Universitaires N.D-P., Namur, Belgium

A-XI.1 11:00-11:15

ELECTRON SPIN RESONANCE OF OXIDATION PURIFIED CARBON NANOTUBES PRODUCED IN DIFFERENT HELIUM PRESSURE, H. Zhang(1,2), D. Wang(1), Y.He(2), N. Ke(3), S.P. Wong(3) and S. Peng(1); (1)Department of Physics, Zhongshan University, Guangshou, China, (2)Guangdong Industrial University, Guangzhou, China, (3)Department of Electronic Engg., Chinese Univ; of Hong Kong, Hong Kong

Based on the thermal analysis of the cathod deposit produced by the carbon arc-discharge method, we have reported [1] that the ratio of nanotubes to nanoparticles in deposits increases with increasing the formation helium pressure(ranging from 80-700 torr). As a further investigation, we report here the study of electron spin resonance(ESR) of oxidation purified carbon nanotubes produced in different helium pressure ranging from 150 to 800 torr.

The ESR results are as follows:

(1) The g value of purified nanotubes decreases from 2.0123 at 150 torr to 2.0105 at 800 torr with increasing He pressure.

(2) Both the spin density and the peak-to-peak linewidth increase with increasing He pressure.

(3) The ratio of peak heights A/B of the ESR first derivative curve increases with increasing He pressure from 0.8 to 1.6 towards that of graphite (about 3.0 [2]).

The above results show that the electronic properties of nanotubes are more and more metallic with increasing He pressure.

[1] H.Zhang, D.Wang, B.Chen, S.Peng, S.P.Wong, MRS Fall Meeting (1996, Boston)
[2] G.Wagoner, Phys. Rev. 118, 647 (1960).

A-XI.2 11:15-11:30

STRUCTURE ANALYSES OF CARBONACEOUS DEPOSIT FORMED BY PULSED Nd:YAG LASER DEPOSITION WITH A TARGET OF C:Ni:Co FOR INFERRING SINGLE WALL CARBON NANOTUBE GROWTH MECHANISM, M. Yudasaka(1), Y. Zhang(1), T. Ichihashi(1), S. Yoshimura(2), and S. Iijima(1), (1)NEC Corporation, Miyukigaoka 34, Tsukuba, Ibaraki 305, Japan, (2)ERATO, JST, c/o Matsushita R.I. Tokyo, Inc., Tama-ku, Kawasaki 214, Japan

Smally et al. has found that single wall carbon nanotube (SWCNT) can be formed with a high yield by irradiating pulsed Nd:YAG laser light on a target composed of carbon, Ni and Co. Since the laser power must be high (1-1.4 joule/pulse cm^2) and the temperature must be kept at about 1200°C for the SWCNT formation, it is difficult to clarify the formation mechanism by using conventional methods.

By analyzing the components and structures of carbonaceous deposits obtained by the Nd:YAG pulsed laser deposition (PLD) at room temperature under vacuum, it was found that the deposit was a mixture of randomly connected carbon (rc-C) and clusters of Ni and Co. The size of the Ni and Co clusters was less than several nm. The deposits obtained by PLD at room temperature in Ar gas with an atmospheric pressure was composed of sp^2 rich carbon. It is inferred that, first, the sp^2 carbon of graphite changed to rc-C carbon by the laser light and, then, rc-C carbon collided with each other and/or with Ar atoms and became sp^2 rich carbon. Ni and Co acted as catalysts for graphitization only at elevated temperatures and contributed to form SWCNT at temperatures around 1200°C.

A-XI.3 - invited - 11:30-12:00

BORON NITRIDE NANOTUBES, **A. Loiseau**(1), F. Willaime(2), N. Demoncy(1,3), G. Hug(4), K.Suenaga(5), C. Colliex(5), H. Pascard(3); (1)LPS(OM), Onera, Châtillon, France; (2)SRMP, Cea Saclay, Gif-sur-Yvette, France; (3)LSI, Cea-Cnrs, Ecole Polytechnique, Palaiseau, France; (4)LEM, Cnrs-Onera, Châtillon, France; (5)LPS, Université Paris Sud, Orsay, France

Boron-nitride nanotubes have been successfully synthesized by arc-discharge between HfB$_2$ electrodes in a nitrogen atmosphere.

The Electron Microscopy (HREM) observations reveal a high cristallinity of the tubes and reduced numbers of layers, including single- and double-layer tubes. The helicities have been determined from diffraction patterns. Electron-energy-loss spectroscopy (EELS) yields a B:N ratio of approximately one. Line scans recorded across the tubes show a perfect chemical homogeneity. The fine structures of B and N K-edges attest for an sp^2 type of bonding as in h-BN.The observation of the tips shows interesting features: the typical morphology consists of layers perpendicular to the tube axis. A tip model, preserving BN units in the honeycomb network, accounts for these observations. This model contains three 120° disclinations leading to a triangular facet for the cap. Atomistic calculations have been performed using the Tersoff potential to generate their equilibrium structures. Finally HREM images were simulated for Russian-dolls of these tips and compared with experiments, giving additional support to this model. Soot containing B, N and C was also produced by using a graphite rod for the cathode. Tubes and encapsulated metal-particles are formed. Their EELS characterization provides interesting information on their formation in the arc process for a mixed plasma.

A-XI.4 12:00-12:15

STM CHARACTERISATION OF BORON NITROGEN CARBON NANOTUBES, S. Curran(1), D.L.Carroll(2,3), P.Ajayan(4), P. Redlich(3), and S.Roth(1); (1)Max Planck Institut für Festkörperforschung, Heisenberg Str.1, Stuttgart 70569, Germany; (2)Department of Physics and Astronomy, 118 Kinard Laboratories, Clemson University, Clemson SC, 29634 USA; (3)Max Planck Institut für Metallforschung, Seestr. 92, Stuttgart 70174, Germany; (4)Department fo Materials Science, Rensselaer Polytechnic Institute, Troy New York, USA

Incorporating both Boron and Nitrogen in Carbon nanotubes dramatically alters their electronic nature analogous to that of doping traditional semiconductors. Using scanning tunneling microscopy and tunneling spectroscopy, the electronic properties of these Boron Nitrogen Carbon nanotubes have been compared with those of undoped nanotubes. The doping induces a peak in the density of states within the energy gap, which can be readily identified as donor and acceptor levels analogous to 3-D semiconducting systems. Additional features in the density of states perticularly related to the 2-D nature of the nanotube will be discussed as well.

A-XI.5 12:15-12:30

NANOTUBE BN-C HETEROSTRUCTURES: ELECTRON PROPERTIES,

L.A. Chernozatonskii, Institute of Biochemical Physics, 117334 Moscow, Russia, E.G.Gal'pern, I.V. Stankevich, Institute of Organoelement Compounds, 117813 Moscow, Russia

New quasi I-D objects - nanotubes constructed of BN and C fragments - are considered and their electron spectra are computed by methods of crystal orbitals.

It is shown that there is a broad variation of main and mini-zone gaps by changing in (n,0) zigzag and (n,n) armchair tube superlattices with $BN_{1n}C_{2kn}$ (l, k = 1, ...) unit cells when BN and/or C fragment lengths are changed.

«Dot» and interface states are studied when a C-ring fragment is situated on the BN tube top, in the middle of BN tube or between two BN fragments in a C tube. A broad variation of electron spectra is presented in this case also.

Our results are used to modelling of some nanoelectronic elements, and possible manufacturing technologies of considered structures.

This work was supported in part by grants No 079 ISTC and RFFI No 96-02-18445.

12:30-14:00 **LUNCH**

Thursday June 19, 1997 **Afternoon**
Jeudi 19 juin 1997 Après-Midi

Session XII - Carbonitr
Chairperson: G. Seifert, Technische Universität, Dresden, Germany

A-XII.1 14:00-14:15

CARBON NITRIDE THIN FILMS PREPARED BY REACTIVE RF MAGNETRON SPUTTERING, S. Logothetidis, H. Lefakis, M. Gioti and G. Stergioudis, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

Nitrogenated amorphous carbon thin films (CN_x) were prepared by reactive rf magnetron sputtering from a graphite target, in a nitrogen containing plasma (up to 4.4 at. %) and on Si substrates. All main controllable deposition conditions, (such as base and deposition pressure, power at target, target-substrate distance, substrate bias voltage), were kept constant throughout the series of experiments and the only variable parameter was the nitrogen flux (0-2 sccm). In-situ Spectroscopic Ellipsometry (SE) in the energy region 1.5-5.5 eV in combination with Bruggeman's Effective Medium Theory analysis was used per iterative deposition layer to monitor the film thickness and diamond character. Ex-situ SE, and X-ray Reflectometry were also used, upon completion of film deposition, on select samples. The sp^3/sp^2 ratio as a function of film thickness and nitrogen concentration in the plasma was determined. The plasma nitrogen concentration seems to directly affect the film deposition rate and diamond character by favoring sp^3 bond formation. The presence of C:N chemical bonding was identified by the new Fourier Transform IR ellipsometry technique. Raman measurements revealed the presence of the characteristic D (disordered) and G (graphite) bands which seem to be favored by the plasma nitrogen content.

A-XII.2 14:15-14:30

LIKELY NITROGEN DOPING IN NOVEL PURELY sp^2-BONDED FORMS OF CARBON, G. Jungnickel, P. K. Sitch, Th. Frauenheim, Technische Universität, Institut für Physik, 09107 Chemnitz, Germany; M. I. Heggie, B. R. Eggen, School of Chemistry, University of Sussex, Falmer Brighton, UK; C. D. Latham, C. Cousins, Dept. of Physics, University of Exeter, EX4 4QL Exeter, UK

Hypothetical crystalline forms of carbon have been studied using the recently developed density-functional based tight-binding method. Within this method the electronic band structure energy for a crystal is calculated non-selfconsistently using the two-center approach for representing the Hamiltonian matrix. The total energy calculations make use of the Γ-point approximation employed for sufficiently large supercells. The scheme has been carefully checked against self-consistent field results using plane wave basis sets for the hypothetical metallic phases BCT4 and H6 as well as against results obtained with a multicenter linear combination of atomic orbitals method for the Polybenzene structure. The DF-TB method was found to accurately reproduce the data of the more sophisticated methods and has been successfully applied to study the stability of other three-dimensionally connected networks made of either sp^2- or sp^3-like carbon atoms. We have determined the ground state geometries of these novel forms of carbon and have analyzed their structural and electronic properties. We discuss elastic constants, the bulk modulus and structure factors as well as electronic densities of states. We find structures with helical subunits that are as stable as fullerene C_{60} but do have quite large electronic gaps of about 2 eV. The unique feature of these crystals is that they would allow for n-type doping by nitrogen. This is in sharp contrast to recent doping studies in diamond where doping is impossible due to the existence of a mid gap state and in tetrahedrally bonded amorphous carbon ta-C where doping is inefficient due to the presence of π-bonded subclusters. The location of the donor levels is confirmed by self-consistent field calculations using small cluster models of the helical units. By comparing the doping results, we deduce necessary conditions for successful n-type doping in carbon based materials.

A-XII.3 14:30-14:45

BORON-NITROGEN ANALOGUES OF THE FULLERENES: ELECTRONIC AND STRUCTURAL PROPERTIES, G. Seifert(1), P.W. Fowler(2), D. Mitchell(2), D. Porezag(3) and Th. Frauenheim(3), (1)Technische Universität, Institut für Theoretische Physik, 01069 Dresden, Germany, (2)Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK, (3)Technische Universität, Institut für Physik, 09107 Chemnitz, Germany

On the basis of a systematic density-functional-tight-binding study of boron-nitrogen polyhedra $(BN)_x$ composed entirely of four- and six-membered rings, it is predicted that octahedron-like structures $B_{12}N_{12}$, $B_{16}N_{16}$ and $B_{28}N_{28}$ are 'magic' (i.e. anomalously stable) clusters. The infrared (IR) spectrum of $B_{12}N_{12}$ is predicted. The similarities and differences between these 'inorganic fullerenes' and the carbon-based equivalents are outlined. High stability of the $(BN)_x$ clusters is found to correlate with a large HOMO-LUMO gap.

A-XII.4 14:45-15:00

CHARACTERIZATION OF CARBON NITRIDE THIN FILMS PREPARED BY REACTIVE MAGNETRON SPUTTERING, A.Fernandez, J.C.Sanchez-Lopez, G.Lassaletta, Instituto de Ciencia de Materiales de Sevilla, Centro de Investigaciones Cientificas Isla de la Cartuja, Avda. Americo Vespucio s/n, 41092-Sevilla, Spain

Carbon nitride (CN_x) thin films have been obtained by reactive magnetron sputtering in a pure N_2 discharge. The films have been characterized by electron-energy-loss spectroscopy (EELS), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS) and UV-vis absorption spectroscopy. A maximum value of N/C=0.5 has been achieved. Evidences are presented of the formation of a polymer like CN_x amorphous phase which contain C≡N, C=N and C-N bonds. Two new peaks at 286.5 and 287.7 eV energy loss in the C K-edge EELS spectra have been assigned to C=N and C≡N bonds with carbon in the sp^2 and sp hybridization states respectively. Infrared spectroscopy indicates that a cyanogen-like impurity is present in the films and can be removed by thermal annealing. Contribution of C-N and C=N bonds have been also determined by infrared and XPS spectroscopies.

A-XII.5 15:00-15:15

PROPERTIES AND PREPARATION CONDITIONS OF CN_x THIN FILMS PREPARED BY LASER CVD F. Falk, K. Schuster, Institut für Physikalische Hochtechnologie, Helmholtzweg 4, 07743 Jena, Germany

Results on qualitative and quantitative analyses of CN_x thin films derived from EDX, XPS, RBS, effusion and FT-IR techniques are presented. The films were produced by excimer laser CVD at a wavelength of 193 nm from the precursor systems ammonia/carbon tetrachloride as well as cyanogen azide NCN_3. Tauc plots derived from optical ab- sorption spectra yield band gaps between 1.65 and 2.59 eV. Comparing these results with the deposition conditions proves the dependence of the band gap on the total pressure in the reaction chamber. With increasing pressure up to a limit of 8 mbar the band gap increases and at the same time the NH-absorption intensity in IR-spectra decreases. In tendency the band gap of C-N-films prepared from cyanogen azide is higher than this of films resulting from NH_3/CCl_4

A-XII.6 15:15-15:30

PULSED LASER DEPOSITION OF CARBON NITRIDE THIN FILMS FROM GRAPHITE TARGETS Y. Suda and T. Nakazono, Department of Electrical Engineering, Sasebo National College of Technologv, 1-1 Okishin-machi, Sasebo, Nagasaki 857-11, Japan; K. Ebihara, Department of Electrical and Computer Engineering, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860, Japan; K. Baba, Technology Center of Nagasaki, 2-1303-8 Ikeda, Omura, Nagasaki 856, Japan; S. Aoki, Kumamoto Institute of Technology, Ikeda, Kumamoto 860, Japan

Carbon films with up to 31 at.% of nitrogen have been prepared on Si (100) substrates by a pulsed Nd:YAG laser deposition. The laser beam is incident on the high-purity graphite targets. The films are grown using a laser repetition rate of 10 Hz at energy density 3.8 J/cm^2. The nitrogen gas pressure in the chamber is 10 Pa. Morphology features of the films have been obtained by employing the technique of scanning electron microscopy. Auger electron spectroscopy has been used to obtain compositional information about the films. IR absorption spectra show two characteristic bands; a broad band composed of graphite G-band and disordered D-band of carbon, and the other associated with C≡N triple bonds. Raman spectra have also been used to characterize the films.

A-XII.7 15:30-15:45

COLD REMOTE NITROGEN PLASMA EFFECTS ON PULSED LASER DEPOSITED CN_x FILMS CHARACTERISTICS C. Jama, O. Desgaux and P. Goudmand, Laboratoire de Physicochimie de l'Energétique et des Plasmas, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France

Carbon nitride CN_x films are deposited by pulsed CO_2 laser ablation of molecular carbon fragments from a graphite target under different deposition media. The films characteristics obtained under a non excited nitrogen flow (NENF) or under a cold remote plasma nitrogen (CRNP) are compared. FTIR spectra of the NENF-films show absorption bands characteristic of C=N and C≡N environments. For CRNP-films a very efficient nitrogen fixation is observed. FTIR spectra show C-N bands in a tetrahedral environment and a complete disappearance of the C≡N band. These results are confirmed by Raman and X-ray photoelectron spectroscopies.
Optical emission spectroscopy demonstrates that the $C^{n+}_{(n=1,2,3)}$ concentration in the gas phase decreases when CRNP is used. This result is correlated to the formation in the film of the C-N tetrahedral environment. The effect of nitrogen atoms concentration in the gas phase on the film characteristics is also discussed.

A-XII.8 15:45-16:00

MICRO - RAMAN AND MICROHARDNESS STUDY OF NITROGEN IMPLANTED DIAMON-LIKE CARBON FILMS, V.V. Artamonov, N.I. Klyui, B.N. Romanyuk, M.Ya.Valakh, O.Vasilik, Institute of Semoconductor Physics, 45 pr. Nauki.252028, Kiev, Ukraine; V.A.Semenovich, Institute of Superhard Materials, 2 Avtozavodskaya str., 254074, Kiev, Ukraine and A. Perez-Rodrigues, J.R. Morante, Universitat de Barcelona, Avda. Diagonal 645-47, 08028 Barcelona, Spain

Diamond-like carbon (DLC) films grown by PE-CVO technique have been implanted with nitrogen ions at room temperature, with an energy of 150 keV and dose $1 \cdot 10^{17}$ cm^{-2}. The optical analysis of the samples has revealed the presence of structural inhomogeneities (with sizes of about 100 nm), in the implanted region.
The different regions in the films (implanted and not implanted) have been analyzed by Raman scattering and Microhardness measurements. The results obtained show that the films hardness in the inhomogeneous region exceeded more than 5 times the hardness of implanted homogeneous film. The effect mentioned takes place due to ion-beam induced compaction of DLC film and phase - structural transformation in inhomogeneous region. This conclusion has been confirmed by micro-Raman results. The mechanism of the effect observed taking into account the existence of local mechanical strains in DLC film has been proposed.

16:00-16:30 **BREAK**

Poster Session II - Nanotubes, Parent, etc

16:30-18:00 See programme of this poster session p. A-31 to A-36.

Friday June 20, 1997 — Morning

Vendredi 20 juin 1997 — Matin

Session XIII - Parent & Chemistry, Part 1

Chairperson: S. Logothetidis, Aristotle University of Thessaloniki, Thessaloniki, Greece

A-XIII.1 - invited - 9:00-9:30

THE UNUSUAL STRUCTURE, PHASE TRANSITIONS, AND DYNAMICS OF SOLID CUBANE, **T. Yildirim**, University of Maryland, College Park, MD 20742, and NIST, Gaithersburg, MD 20899, USA; P. M. Gehring, D.A. Neumann, NIST, Gaithersburg, MD 20899, USA, P. E. Eaton, T. Emrick, University of Chicago, Chicago, IL 60637, USA.

The cubic structure of the cubane molecule, C_8H_8, gives rise to many unusual properties in the solid state. X-ray powder diffraction measurements of solid cubane reveal a huge thermal expansion, followed by a strong first-order phase transition at 394 K from an orientationally-ordered phase (R3: a = 5.40 Å, a = 72.7°) to a non-cubic orientationally-disordered phase (R3 or R3 m: a = 5.45 Å, α = 103.3°). The resulting volume expansion is 5.4%. Model calculations remarkably predict the correct non-cubic high and low-temperature phases. The orientational potential in the disordered phase resembles a rounded square well over a large angular range. Cubane thus represents a nearly perfect textbook example of a system with large-amplitude collective motions.

A-XIII.2 9:30-9:45

FULLERENE $B_{30}N_{30}$ FROM BORAZINE $B_3N_3H_6$, V.P. Sanygin(1), G.S. Yurjev(2), M.L. Kosinova(2), A.Ya. Mikhailova(1), (1)RAS Kurnakov Insitute of General and Inorganic Chemistry, 31 Leninsky pr., 117907 Moscow, Russia; (2)RAS SB Institute of Inorganic Chemistry, 3 Lavrentiev pr., 630090 Novosibirsk, Russia

C_{60} fullerene and based on it molecular crystals atomization energies have been calculated by using carbon thermodynamics and structure data. The value of Δ_fH (C_{60}g, 298 K)=2565 kJ/mol calculated by such manner is in agree with the quantum mechanic calculation results and Δ_fH (C_{60} cr, 298 K)=2290 kJ/mol is in agree C_{60} molecular crystals calorimetry investigation results. Thermodynamic parameters of $B_{30}N_{30}$ fullerene as well as C_{60} case have been calculated on the thermodynamic parameters of h-BN and c-BN. The calculations were based on chemical energy of B-N, B-B and N-N bonds of the s-icosaehedron $B_{30}N_{30}$. According to thermodynamic calculations data $B_{30}N_{30}$ fullerene is stable under standard conditions: $\Delta_fH°$ ($B_{30}N_{30}$, g, 298K)=(-1350)-(-4380) kJ/mol. The structure of the layers of boron nitride obtained by low temperature plasma enhanced chemical vapour deposition of borazine as precursor has been investigated by X-ray diffraction method. The diffraction pattern consists of the superposition of the next patterns: from non-crystalline turbostrate am-3N, from polycrystalline h-BN, c-BN and from unknown structure. The diffraction pattern of unknown structure consists of two reflections with $d(hlk)_1$=14.8 Å and $d(hlk)_2$=7.6 Å and are suggested to be (001) and (002) reflections of distorted face-centred cubic package, for example, C4/mm (L1o) consisted of fullerene $B_{30}N_{30}$ with R_1=5.1 and R_2=5.6 Å.

A-XIII.3 9:45-10:00

FRICTION AND WEAR OF INORGANIC FULLERENE-LIKE MATERIALS, L. Rapoport, Center for Technological Education, PO Box 305, 58102 Holon, Israel and Y. Feldman, S.R. Cohen, R. Tenne, Weizmann Institute, 76100 Rehovot, Israel

Metal dichalcogenide MX_2 (m=Mo, W, etc.; X=S, Se) compounds with structures closely related to the carbon fullerenes and nanotubes, generally termed inorganic fullerene-like materials (IF) have been developed. It was hypothesized that the absence of dangling bonds on the surface of IF particles would lower their adhesion thus improving their tribological properties. The validity of this hypothesis was tested by comparison with the common lubricant 2H-MoS_2. IF-WS_2 and 2H-MoS_2 were deposited as dense films onto separate glass slides and covered with a top glass. These friction pairs (glass/SL/glass sandwich) showed friction coefficients of 0.16 and 0.32 for and 2H-MoS_2 respectively. In another experiment LiF single crystals have been studied in the ball-flat sclerometer with solid lubricant layers deposited from 5% solid lubricant in mineral oil. Wear tracks were more damaged and for 2h-MoS_2 lubricant. Ball-on-flat test showed that the width of wear track and the friction coefficient were smallest in the case of IF-WS_2 powder. Thus, all experiments prove high antifriction and wear properties of IF-WS_2.

A-XIII.4 10:00-10:15

MoS_2 AND WS_2 MICROTUBES AND MICRORIBBONS M. Remskar, Z. Skraba, J. Stefan Institute, 1001, Ljubljana, Slovenia and M. Regula, C. Ballif, R. Sanjinés and F. Lévy, Institute of Applied Physics, Ecole Polytechnique Féderale de Lausanne, 1015 Lausanne, Switzerland

MoS_2 and WS_2 layered crystals can grow during the chemical transport reaction as hollow microtubes [1], which show similar crystal structure as much smaller inorganic nanotubes [2]. These microtubes are cylindrically shaped single crystals with diameters up to 20 µm and with length up to several mm. They grow in the spiral growth mode from the vapour phase together with usual plate-like crystals. Thin weakly bonded sheets of plate-like crystals can directly roll up in the form of tube or they can bend and produce in their microfolds a turbulent gas flow of transported molecules which promotes tube-like growth mode. During the growth the hollow microtubes can collapse to form flattened ribbons and continue to grow as twisted nnicroribbons. We present comparative electron microscopy and diffraction studies of MoS_2 and WS_2 microtubes and microribbons. Their polytypic structure and some structural defects are analyzed and structural models are proposed.

[1] M.Remskar, Z.Skraba, F.Cléton, R.Sanjinés, F.Lévy: Appl.Phys.Lett. 69, 351 (1996);

[2] R.Tenne, L.Margulis, M.Genut, G.Hodes: Nature 360, 444 (1992).

A-XIII.5 10:15-10:30 CRYSTALLINITY PROMOTION IN WS_2 THIN FILMS, M. Regula, C. Ballif, M. Remskar, and F. Lévy, Institute of Applied Physics, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Layered transition metal dichalcogenides (TMDC) like MoS_2, WS_2 or WSe_2 have attracted continuous interest due to their applications as solid lubricant, catalyst and in the field of photovoltaics. More recently carbon-like tubular and polyhedral structures have been discovered in sulfide phases. Nevertheless, some aspects of the crystallization mechanism are not yet well understood, like the intriguing promoting effect of nickel on the crystallization of TMDC [1]. We present a systematic study on this promoting effect of various alkali and transition metals on the crystallinity of WS_2 thin films. It is shown, that best crystallization at relatively low annealing temperatures T_a=650-750 °C is achieved by adding sodium sulfide or nickel to the film, while the strongest textured films are obtained with cobalt. An improvement of crystallization is equally achieved with iron, manganese, or cesium. The promoting element can be added as a thin layer on the substrate or on the top of the WS_2 film. It can also be co-deposited with the WS_2 film. Since the originally proposed rheotaxy [l] or intercalation [2] models can not satisfactorily explain these results, the possibility of a catalytic growth mechanism is discussed.

[l] G. Salitra, G. Hodes, E. Klein, and R. Tenne: Thin Solid Films 245,180 (1994).
[2] R. J. H. Voorhoeve and J. C. M. Stuiver, J. of Catal. 23, 243 (1971).

10:30-11:00 **BREAK**

Session XIV - Parent & Chemistry, Part 2
Chairperson: T. Yildirim, University of Pennsylvania, Philadelphia, PA, USA

A-XIV.1 11:00-11:15 SYNTHESIS OF EPITAXIAL ß-SiC BY C_{60}, CARBONIZATION OF SILICON ON SAPPHIRE, J. Müller, K. Volz, B. Rauschenbach and B. Stritzker, Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany

Silicon Carbide is a wide band semiconductor for high temperature, high power and high frequency applications. Different techniques are investigated at present to prepare SiC films suitable for electronics. For device applications it is favourable to grow the SiC on an insulator. It is known that C_{60} deposition onto silicon substrates at temperatures around 800°C results in the formation of SiC. In this study C_{60} molecules were deposited onto commercial SOS wafers with (100)-silicon on r-plane (1102)-sapphire. The thickness of the epitaxial silicon layer is 350nm. After the C_{60} deposition on the SOS substrates at 810°C the composition, topography and structure of the resulting layers has been analyzed using RBS, AFM, XRD and cross-sectional TEM.
RBS measurements combined with RUMP/SIM indicate that a 200 nm stoichiometric SiC-layer has been formed. X-ray pole-figure measurements confirm that the main part of the resulting ß-SiC grows epitaxially with the underlaying silicon. AFM measurements show that the surface of the SiC-layer is very smooth ($\Delta h=\pm 30$nm) and that the layer consists of small grains (d=40nm).

A-XIV.2 11:15-11:30 OLIGOPHENYLENES AS BUILDING BLOCKS FOR WELL DEFINED GRAPHITE SUBUNITS - FROM C_{54} TO ORDERED GRAPHITE MONOLAYERS, K. Müllen, M. Müller and C. Kübel, Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Large polybenzenoide hydrocarbons are of academic and industrial interest due to their high thermal stability, their UV absorption and their partially high fluorescence quantum yield. An ideal access towards such polycyclic systems with well defined molecular mass and structure is based on soluble oligophenylene precursors, which are finally subjected to cyclodehydrogenation by oxidation. The easy synthesis of several oligophenylenes enables the construction of a series of large aromatic compounds with different symmetry.
Self assembled, space filling molecular layers of $C_{54}H_{22}$ can be obtained on suitable substrates by fractionated sublimation. The characterization of these layers is achieved by electron diffraction experiments and scanning tunneling microscopy.

A-XIV.3 - invited - 11:30-12:30 C_{60} BUCKMINSTERFULLERENE: NOT JUST A PRETTY MOLECULE, **H. Kroto**, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 0QJ, UK

In 1985 C_{60} Buckminsterfullerene (the third allotropic form of carbon) was discovered serendipitously during experiments designed to unravel the carbon chemistry in Red Giant Stars. It has now come down to Eearth giving rise to the Fullerenes, a family of pure carbon cage molecules with fascinating properties which promise exciting new developments in 21st Centry Materials Science and Technology.
The molecule has a beautiful and elegant symmetry, as well as other attributes, which appeal to our Renaissance sensibilities. The structure forms the basic pattern of the geodesic domes devised by Buckminster Fuller - the strongest, lightest and largest space-spanning structures yet devised. The earliest attributable images of this shape are to be found in the works of the 15th century artists Piero della Francesca and Leonardo da Vinci. Furthermore the pattern is the same as that of the modern football - with 12 pentagons and 20 hexagons.
The molecule has also attracted the attention of non-scientists and it is highly gratifying that children in particular are fascinated by the molecule. C_{60} has made a positive contribution to the aura of science and discovery at a time when the public and governmental appreciation of the massive contribution of Science to our social and economic well-being is either totally overlooked or completely misunderstood.
It is difficult to comprehend that though man has known of graphite and diamond (the other two well characterised forms of carbon) since time immemorial, now at the end of the 20th century a third form has been discovered. Furthermore it has been under our noses all the time as - amazingly - the molecule forms in a sooting flame. So almost everyone has made the molecule, including our primaeval ancestors, indeed the molecule appears to have been made and overlooked over decades of research into combustion processes.
There is food for thought in the fact that a fascinating, new round world of carbon chemistry and materials science was discovered as a consequence of a curiosity about the role of carbon in space and stars - rather than the directed study of carbon's material properties. It thus stands as a timely warning of the serious limitations inherent in over-reliance on applied research strategies.

12:30-14:00 **LUNCH**

Friday June 20, 1997 **Afternoon**
Vendredi 20 juin 1997 Après-midi

Session XV - Parent & Chemistr., Part 3

Chairperson: V.P. Sanygin, RAS Kurnakov Insitute of General and Inorganic Chemistry, Moscow, Russia

A-XV.1 14:00-14:15 MAGNETIC ORDERING AT 20K AND BELOW, A. Mrzel, D. Mihailovic, P.Cevc, A. Omerzu, Institute «Jozef Stefan», Jamova 39, 1000 Ljubljana, Slovenia

Fullerene monoderivatives were synthesized and doped with tetrakis(dimethylamino)ethylene (TDAE) and cobaltocene (Cp_2Co) to charge transfer complexes with the aim of finding novel magnetic materials based on fullerenes. Familiar derivatives were chosen in order to help toward better understanding of magnetic properties of those materials as well as TDAE-C_{60}. In this work we present X band measurements of these new materials. We found a new magnetic transition at 20K for cobaltocene doped derivative of C_{60} 3-aminophenylmethano-[60]fullerene. This material curently has the record high Tc for a molecular organic feromagnet.

A-XV.2 14:15-14:30 PREPARATION AND CHARACTERISATIONOF PHENYLATED FULLERENE DERIVATIVE $C_{60}(ph)_6$, N. Sivaraman and P.R. Vasudeva Rao, Chemical Group, IGCAR, Kalpakkam - 603 102, India

We observed the formation of hexa phenylated derivative, $C_{60}(ph)_6$ on Friedel-Crafts reaction of hexa chlorinated fullerene derivative, $C_{60}Cl_6$ with benzene in the presence of catalysts such as aluminium chloride and ferric chloride which was not reported earlier. The compound was characterised by FAB Mass spectrometry, IR and by HPLC techniques.

The stability of phenylated and halogenated derivatives to UV radiation were investigated. The halogenated derivative was found to be readily degraded by UV-radiation.The product formed, when the irradiation was carried out in the presence of air, was found to be insoluble in solvents such as heptane but readily soluble in polar solvents such as acetone. The degradation product of phenylated derivative was also studied.

The thermal stability of the phenylated and halogenated fullerene derivatives was investigated by thermo gravimetric analysis and the results are discussed in the paper.

A-XV.3 14:30-14:45 THIN FILM OF SPHERICAL CARBON ONIONS ONTO SILVER, T. Cabioc'h, J.C. Girard, J.P. Rivière, Université de Poitiers, Laboratoire de Métallurgie Physique, UMR 6630, SP2MI, Bd3, Téléport 2, BP. 179, 86960 Futuroscope Cedex, France

We recently demonstrated that high dose carbon ion implantation into copper substrates heated at high temperature ($\geq$ 600°C) was an original technique to synthetize giant carbon onions (50-300 nm in diameter) heterogeneously distributed onto the copper surface. In order to better understand the influence of the different experimental parameters we perform the same kind of experiment, but into silver in which, as in copper, carbon has a very low solubility.

TEM, HRTEM and AFM observations then revealed that a very high density of carbon onions has been formed for an implanted dose of $3.10^{17}cm^{-2}$. These spherical carbon clusters, 10-20 nm in size, distributed homogeneously on the surface are linked together by an external graphene layer and formed a thin film. Further experiments in the temperature range 500-600°C confirm the reproducibility of the synthesis of a high density of carbon onions on polycrystalline silver substrates as well as on silver thin film deposited onto different substrates.

We propose that carbon precipitation into the silver volume leads to the formation of onions, the latter appearing on the surface due to the silver preferential sputtering.

A-XV.4 14:45-15:00 RAMAN IDENTIFICATION OF ONION-LIKE CARBON, E. D. Obraztsova, General Physics Institute RAS, 38 Vavilov street, 117942 Moscow, Russia, M.Fujii, S. Hayashi, Faculty of Engineering, Kobe University, Rokko, Nada, Kobe 657, Japan, V.L.Kuznetsov, Yu.V.Butenko, A.L.Chuvilin, Boreskov Inst. of Catalysis, 630090 Novosibirsk, Russia

Different modifications of a multishell fullerene-like carbon have been synthesized recently: nanotubes, nanocones, nanofolders, nanospheres. The geometrical shape and number of graphitic shells constituting the materials become essential for their characterization. The influence of the shell curvature to the Raman spectrum shape allows to use this technique to distinguish between such carbon materials. In this work we studied the spherical closed carbon shells - so called «onion-like carbon» (OLC). It has been produced from the ultradispersive diamond powder by thermal treatment (T=l 100-2100 K). The «fingerprint» of the OLC Raman spectra was a narrow (15 cm^{-1}) band shifted toward low frequencies (comparing with that of a planar graphite) up to 10-12 cm^{-1}. Taking the virgin powders with the different average grain size (3-5 nm) we were able to control the average number of shells (4-7) in the final onions. The correlation has been established between the position of the specific Raman peak and the sphere number and curvature. The onion structural parameters have been obtained by HRTEM.

A-XV.5 15:00-15:15

FULLEREN-LIKE SILICON CLUSTERS: LASER SYNTHESIS AND FEATURES, S.A.Batishche, A.A. Kuz'muk, N.A Malevich, Institute of Physics of Academy of Sciences of Republic of Belarus, F.Scoryna Ave. 70, 220072, Minsk, Republic of Belarus

The principal possibility of creating multi-atom fullerene-like silicon clusters, first of all of the Si_{60} or $Si60H_{60}$ types, in highly ionised laser spark plasma initiated in compressed silan SiH_4 was investigated. In experimental study a mixture of SiH_4 and noble gas under total pressure of 1-20 atmosphere was sealed into a reactor chamber with optical windows. A laser beam of YAG:Nd laser with the pulse energy up to 1.5 J at λ=1064 nm, 0.5 J at λ=532 nm and 0.1 J at λ=266 nm, pulse duration ~16 ns, repetition rate 1-5 Hz and divergence ~0.3 mrad was focused through the optical window into the centre of the chamber and, as a result, in silan an intense laser spark was formed. Due to the high temperature, pressure, and intensive radiation in the region of laser spark silan was decomposed to ionised Silicon and Hydrogen atoms which have a high reactive capability, and various complicated compounds (among which multi-atom fullerene-like silicon clusters may exist) have appeared in the chamber. Brown thin porous films on quartz substrates as well as water and ethanol solutions of these compounds were created. Absorption and fluorescence spectra of the samples as well as their mass-spectra were investigated. Some of the compounds have a maximum of fluorescence in the region of 370-380 nm and 420-430 nm. The possible structures are discussed.

A-XV.6 15:15-15:30

PHYSICO-CHEMICAL BEHAVIOR IN SOLUTION OF STAR-SHAPED POLYSTYRENE WITH A C_{60} CORE, V. Weber, M. Duval, Y. Ederlé and C. Mathis, Institut Charles Sadron (CNRS-ULP), 6 rue Bousingault, 67083 Strasbourg Cedex, France

Fairly pure hexa-adducts of molar mass ranging from 2.10^4 to over 10^6 could be prepared by reacting PS-Li with C_{60} in toluene. These stars compared to «classical» star-shaped polymers, present the particularity to associate a low polymolecularity of the arms (I < 1.1) and a good control of the functionality (6) with a very well defined core of an exceptionally small size. Such, these compounds can be considered as «models» for the behavior of star-molecules in dilute and semi-dilute solutions as compared to that of linear polymers of same mass. The PS stars were studied in «good» and «theta» solvents by static and quasi-elastic light scattering as well as viscometric technics. The variation of the radius of gyration and the hydrodynamic and viscometric dimensions were determined as a function of the mass of the star, and compared to theoretical predictions using specific models.

A-XV.7 15:30-15:45

FULLERENE HYDRIDE $C_{60}H_{36}$: MAGNETIC PROPERTIES AND ELECTRONIC STRUCTURE, A.S. Lobach, Y.M. Shul'ga, Institute of Chemical Physics RAS; Y.G.Morozov, Institute of Structural Macrokinetics RAS, 142432 Chernogolovka, Moscow Region and A.I. Rebrov, Topchiev Institute of Petrochemical Synthesis RAS, Leninsky pr. 29, 117912 Moscow, Russia

Fullerene hydrides are new materials whose physical and chemical properties are not investigated. We present the study of $C_{60}H_{36}$ by solid state ^1H and ^{13}C NMR, X-ray PS and EELS. The ^1H NMR spectrum appears as a wide signal with two sharp peaks with the chemical shifts at 6.55 and 3.04 ppm and one wide peak with the chemical shift at 1.3 ppm. The ^{13}C NMR spectrum exhibits 3 solved signals attributed to three types of sp^3 hybridized carbons (31.1, 37.2, 44.1 ppm) and 3 signals attributed to three types of Sp^2 hybridized carbons (124.9, 134.7, 137.3 ppm). The ratio of the integral intensities of sp^3 and Sp^2 peaks of carbons is equal to 36:24 that corresponds to the composition of $C_{60}H_{36}$ reaction product. The comparison of the experimental spectrum with the simulated ones for different $C_{60}H_{36}$ isomers allows a conclusion that the spectrum of the $C_{60}H_{36}T$ symmetric isomer which has 4 isolated benzenoid rings located in the tetragonal positions on the surface of a closed molecular skeleton, most closely corresponds to the experimental one.

The hydride $C_{60}H_{36}$ is studied by EELS and the loss functions for C_{60} and $C_{60}H_{36}$ are compared. The loss functions have the similar shape, however the peak maximum stipulated by the oscillations of all valence electrons ($\sigma+\pi$)-plasmon, is less for the hydride (21.5 eV) than for the solid C60 (26.1 eV). This implies that the density of valence electrons participating in this process, decreases from C_{60} to $C_{60}H_{36}$ Besides, X-ray PS Cls and magnetic properties of $C_{60}H_{36}$ hydride are described for the first time.

A-XV.8 15:45-16:00

THE INVESTIGATION OF THE ELECTRONIC STRUCTURE OF THE FULLERENE COMPOUNDS BY MEANS OF QUANTUM CHEMISTRY AND X-RAY EMISSION SPECTROSCOPY METHODS, A.V. Okotrub, L.G. Bulusheva, E.S. Fomin, Yu.V. Shevtsov, L.N. Mazalov, Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia

The electronic structure of fullerene compounds with metals and halogens has been studied by means of quantum chemistry and X-ray emission spectroscopy methods. The CKα - spectra of the K_xC_{60} (x=3,6) and Pd_xC_{60} (x=1,2,3) were obtained. For the Pd_xC_{60} samples, the CKα-spectra regular intensity decrease, which corresponds to the r-molecular orbital and takes place in the short-wave region of the spectrum, is observed as the intercalation degree increases. Then the intercalation of fullerite by potassium atoms lead to increase of intensity in short-wave part of the spectra.

The investigation of the electron structure of the fullerene compounds with halogens (F, Cl, Br) and NO_2 was carried out on the base of semi-empirical quantum-chemical calculations using PM3 - approach and experimental X-ray emission and X-ray electron spectra. The isomers of $C_{60}F_{24}$ of the various size of carbon π-system were constructed. The theoretical CKα- and FKα- spectra of $C_{60}F_{24}$ isomers were calculated. The CKα-spectra of bromofullerenes $C_{60}Br_6$, $C_{60}Br_8$ were compared with the spectrum of the pure fullerene C_{60} sample.

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SYMPOSIUM A
POSTER SESSIONS

Wednesday June 18, 1997 **Afternoon**
Mercredi 18 juin 1997 Après-midi

Poster Session I
16:30-18:00

A-I/P1 EFFECTS OF ION IMPACT INTO FULLERENE D. Fink, M. Müller, and R. Klett, Hahn-Meitner-Institute GmbH, Glienicker Str. 100, 14109 Berlin, Germany and F. Zawislak, P. Grande and M. Behar, Instituto de Fisica, Universidade Federal do Rio Grande do Sul, 95000 Porto Alegre, RS, Brasil and V. Hnatowicz and J. Vacik, Nuclear Physics Institute, Rez near Prague, 25068 Czech Republic

Carbon atoms of fullerene molecules have a very high binding energy which is released upon the fullerene destruction by ion impact. This leads to two peculiar effects - extremely high sputter yields and considerable densification of the remaining material. It appears that the large free volume formed after sputter ejection of fullerene fragments from the region of impact collapses by relaxation of the neighboring pristine matter.

A-I/P2 MICROSTRUCTURE INVESTIGATION OF MAGNETRON SPUTTERED AMORPHOUS CARBON FILMS, A.A.Onoprienko, L.R. Shaginyan, Institute for Problems of Materials Science, 3 Krzhyzhanovsky str., 252142 Kiev, Ukraine and V.V. Artamonov, M.Ya. Valakh, Institute of Semiconductor Physics, 45 Prospect Nauky str., 252028 Kiev, Ukraine

Amorphous carbon (a-C) films were obtained by magnetron sputtering of graphite target in argon discharge. Films were deposited at various substrate temperatures and discharge power values. Films structure was studied by electron diffraction and Raman scattering. Carbon films resistivity was evaluated by measuring at room temperature the film resistance in two directions: parallel and perpendicular to the substrate surface.

It was shown that a-C films have prominent resistivity anisotropy which essentially depends on deposition parameters. This effect is discussed in connection with Raman spectra obtained. The features of spectra give evidence of defect graphite-like structure of all films investigated. The microstructure model is proposed which accounts for the diamond-like properties of a-C films.

A-I/P3 AUGER-SPECTROSCOPIC INVESTIGATION OF a-C:H FILMS ON SUBSTRATES BEING WITH MICRORELIEF, A.V.Vasin, L.A. Matveeva, T.Y. Gorbach, Institute for Semiconductor Physics, av. Nauki 45, 252028 Kiev, Ukraine.

The analysis of high-resolution Auger electron spectra shape was used to investigate carbon bonding in a-C:H films deposited on unheated silicon substrates being with different microrelief patterns. The a-C:H films were deposited from rf- discharg (13.56MHz) activated gaseous mixture H_2(60%) and CH_4(40%). Microrelief on Si(111) surface was obtained by its chemical etching in different chemical environment. There were used some substrates with different microrelief pattern and scale. The polished flat substrate was a standard.

It was shown that the surface microrelief have an appreciable effect on carbon Auger spectra shape. The surface peculiarities could stimulate sp^3 or sp^2 hybridisation depending on microrelief type. Especially such influence take place in case of thinner films. With increasing films thickness up to 240 nm sp^2/sp^3 ratio increases in all specimens including standard specimens.

A-I/P4 LASER PHOTOLYSIS OF LIQUID BENZENE AND HEXAFLUOROBENZENE: GRAPHITIC AND POLYMERIC CARBON FORMATION AT AMBIENT TEMPERATURE, M. Urbanova and J. Pola, Institute of Chemical Process Fundamentals, 165 02 Prague, Czech Republic; Z. Bastl, J. Heyrovsky Institute of Physical Chemistry, 182 23 Prague, Czech Republic; Z. Plzak and J. Subrt, Institute of Inorganic Chemistry, 250 68 Rez, Czech Republic; V. Vorlicek, Institute of Physics, 180 40 Prague, Czech Republic

ArF laser photolysis of liquid benzene yields hydrogen, C_1-C_2 hydrocarbons, various polyaromatic hydrocarbons (PAH) and carbon. ArF laser photolysis of liquid hexafluorbenzene affords a number of polyfluorinated PAH and carbon agglomerates. The preponderance of biphenyl among PAH from benzene and that of decafluorobiphenyl among PAH from hexafluorobenzene reveals the importance of the phenyl and pentafluorophenyl radical combination in the initial steps of photolysis. Mechanism of both photolyses will be discussed and compared.

XPS and Raman spectroscopies show that carbon produced in both processes consists of graphitic and polymeric constituents.

The remarkable feature is that the carbon formation in both cases occurs at ambient temperature of the irradiated liquids; photolytic graphitization modes must therefore be different from those involved in thermally-induced graphitization which takes place at temperatures above 2500°C.

A-I/P5 LASER-INDUCED CHEMICAL VAPOUR DEPOSITION OF CARBON-RICH GLASSY PHASES FROM 3-BUTYN-2-0NE, V. Drinek, M. Urbanova and J. Pola, Institute of Chemical Process Fundamentals, 165 02 Prague, Czech Republic; Z.Bastl, J. Heyrovsky Institute of Physical Chemistry, 182 23 Prague, Czech Republic; V. Vorlicek, Institute of Physics, 180 40 Prague, Czech Republic; J. Subrt, Institute of Inorganic Chemistry, 250 68 Rez, Czech Republic

TEA CO_2 laser induced decomposition of 3-butyn-2-one in the gas phase affords various C_1-C_4 hydrocarbons and CO together with thin films of glassy carbon. The volatile hydrocarbons are minor products and this makes the decomposition an efficient method for producing the carbon films. The structure of the gaseous and solid products implies that the decomposition of 3-butyn-2-one is governed by the cleavage of the C-C(O) bonds and by polymerization/dehydrogenation reactions of CH_3, HC_2 and C_2 transients.

FTIR and Raman spectroscopies show that the carbon films can be described as disorded carbon with very low content of C-H bonds. XP and UV spectroscopies reveal some fraction of C in 2p πstate, but no significant π-conjugation.

The IR laser photolysis is proved as a suitable technique for chemical vapour deposition of carbon-rich glassy phases on substrates kept at relatively low temperatures.

A-I/P6 XPS STUDY OF PLASMA TREATED CARBON LAYERS ON POROUS SILICON, G.Beshkov, Institute of Solid State Physics, BAS, 72 Tzarigradsko shausee blvd. 1784 Sofia; V. Krastev, Ts. Marinova, Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences (BAS), Acad. G. Bonchev st. bl 11, 1113 Sofia, Bulgaria; N.Velchev, Plovdiv University, Electronics Department, 24 Tzar Assen st., 4000 Plovdiv, Bulgaria

A 6000Å carbon layer is deposited by sputtering on porous Silicon. As prepared samples are treated at 2 Torr and 300 V in N-plasma. Using XPS it is established that the concentration of nitrogen in at.% on the surface and in the subsurface layer decreases from 8 % to 4% and then increases up to a constant value of 6%. Under these conditions relatively small amount of nitrogen are bonded in carbonitrides of CN and C-N type while a considerable part of carbon in the layers is connected to the present of C-C bonds.

A-I/P7 METAL-INSULATOR TRANSITION IN CRYSTALLINE INTERCOLATED WITH COPPER GRAPHITE, V.F. Masterov, A.V. Prichodko, Experimental Phys.Depart, St.Petersburg State Technical University, Russia

Conductivity on microwave frequences (up to 1 GHZ) of crystalline graphite intercolated with copper has investigated in temperature range from 80 to 400K.The phase transition «metal-insulator» was observed in the samples at temperatures 95-130K.The investigation of copper distribution in graphite crystals by scanning electronic microscopy and SIMS have carried out.We interpret the reported phase transition as a effect caused by band structure variation due to a redistribution within the electronic structure of small copper-oxygen clusters.

A-I/P8 STRUCTURE AND INTERMOLECULAR PHONONS STUDY OF SOLID C_{70}, Y. I. Prilutski, Dept. of Physics, Kiev Shevchenko University, Vladimirskaya Str., 64, 252033 Kiev, Ukraine

The low-temperature orientationally ordered crystalline phase of fullerene C_{70} (symmetry group $P112_1/m$, Z=4) iS investigated in the approximation of intermolecular Lenard-Jones (12-6) potential. This model has allowed to approximate good the available experimental data on the neutron scattering.

The vibrational spectrum of solid C_{70} in the field of external phonon modes is calculated using the group theory and atom-atom potential methods. It was shown there are eleven different frequencies of normal vibrations (five translational and six librational modes) which active in Raman region. This fact is in an excellent agreement with available experimental results.

The structure and lattice dynamics of solid C_{70} were studied in dependence on the external pressure.

A-I/P9 STRUCTURAL STUDY OF HCP SOLID C_{70} AT LOW TEMPERATUREE USING X-RAY POWDER DIFFRACTION G. Ghosh. V.S. Sastry, C.S. Sundar, G.V. Narasimha Rao, Y. Hariharan, A. Bharathi, V. Sridahran and T.S. Radhakrishnan, Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102. India.

The current folklore on structural transformations in hcp solid C_{70} believes that, on cooling, C_{70} follows a two step transitions: ideal hcp↔distorted hcp↔monoclinic [1,2]. The first step is thought to imply locking of the long axis of the C_{70} molecule and the second to freezing of rotations around this axis. However, the various reports present neither consistent sets of lattice parameters for the low temperature phases nor a clear structural model. Since the orientational ordering of the prolate spheroidal C_{70} molecules is behind these transformations we believe that kinetics plays a key role. We report here an X-ray powder diffraction study at low temperature using a Siemens D-500 diffractometer and an Oxford continuous flow cryostat. A pure ideal hcp C_{70} powder was taken and was extremely slowly cooled (~0.05 K/min.) in 5 K steps and kept for 2 hours before starting the XRD run for each step. The room temperature hcp phase transforms to a low temperature monoclinic phase in one broad transition spanning 270 K to 170 K. No intermediate distorted hcp structure is observed. The LT monoclinic phase with a=10.99 Å, b=16.16 Å, c=9.85 Å, and ß=107.75° with space group $P2_1/m$ is consistent with a structural model wherein long axes of C_{70} molecules align along [011] and the upper polar caps of C_{70} in the basal layer are in proximity with the lower polar caps of C_{70} in the body centre layer. The ≈100 K width of the transition can be explained using the fact that nucleation of a monocliriic phase creates dilatory stresses in the surrounding hcp matrix and depresses the T_c since dT_c/dP is positive for C_{70}.

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2/ A. R. McGhie et al., Phys. Rev. B 49, 12614 (1994).

A-I/P10 UV IRRADIATION STUDIES ON C_{70} CLUSTERS IN MIXED SOLVENTS, J.A. Nisha, M. Premila, V. Sridharan, C.S. Sundar and T.S. Radhakrishnan, Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

A recent report claims to have formed an all carbon fullerene polymer via cross linking of neighbouring fullerene clusters (C60 or C70) in toluene-acetonitrile mixture upon UV irradiation [1].

Following the same procedure we attempted to polymerise C70. XRD shows the amorphous nature of the product and the absence of crystalline C70. The FTIR of our end product is similar to that reported earlier [1]. However, heating the product even upto 500°C did not revert the spectrum to the monomeric state, which is expected of an all carbon fullerene polymer. Presence of strong VC-N vibrational modes along with signals of C-H,-OH and carbonyl stretching modes are seen in the IR of our as prepared product. The C=O and the-OH modes decrease in intensity on heating, pointing to the presence of moisture in the starting material.

Surprisingly, the IR of our product is similar to that of a fullerene-amine adduct which was previously studied by us [2]. These investigations indicate that the product is not an all carbon polymer as claimed [1]. The presence of strong C-N modes is likely to have arisen due to the photoreaction of nitrogen of the acetonitrile solvent with C70. Hence we infer that the end product is a copolymer of C70 with bridging nitrogen atoms.

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2. J. Janaki et.al., Proc. DAE Solid State Phys. Symp., 39C (1996) 128.

A-I/P11 DEPOSITION AND COVERING OF CARBON FILMS USING HIGA-DOSE IMPLANTATION IN CARBON MEDIUM, A.D Pogrebnjak, V.I. Lavrentiev, R.Kirian, Sumy Institute for Surface Modification, P.O.Box 163, Av. Shevchenco 17, 244030 Sumy, Ukraine; Yu.F.Ivanov, Academy of Engineering and Building, Tomsk. Russia; S.M.Duvanov, Dubna, JINR, Moskovskaia Reg., Russia

Cu(111) and (100) single crystals have been covered by amorphous carbon and titanium carbide films in the vacuum chamber of implanter. RBS, RNR, TEM, SEM, infra-red spectroscopy have been used as analyzing methods. Implantation of Ti ions into Cu crystals under various doses of 5×10^{16} to 8×10^{17} cm^{-2} in carbon atmosphere (medium) has been performed. As a result, a thin amorphous carbon film of 10 to 50 nm thickness (depending on the irradiation conditions), followed by a titanium sublayer, then a sublayer with nanodisperse segregates δCuTi of a sherical form and a layer of high scalar dislocation density have been formed on a surface. Low energy high-current electron beam treatment results in an essential decreasing of carbon film thickness (even its total disappearance in some cases), a dispersion of titanium carbide sublayer, a decreasing of Cu grain dimensions and an increaseing of thickness of defect-containing layer.

A-I/P12 ORIENTATIONAL ORDERING STUDIES IN C_{60} SOLID, V. Sridharan, D.V. Natarajan, C.S. Sundar, K.V. Devadasan, J. Janaki, V.S. Sastry, Y. Hariharan, A. Bharathi, T.S. Radhakrishnan, Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Specific heat and DSC studies have been carried out on C60 single crystals to investigate the orientational ordering. The ordering temperature and total enthalpy change were determined to be 262.3K and 9.3 J/g respectively. Our studies confirm the presence of an additional low temperature peak both in Cp and DSC measurements in agreement with the earlier report [1]. Based on controlled studies on different batches of samples, we rule out defects to be the cause for the additional peak. We attribute the presence of the additional peak to two closely spaced first-order orientational ordering transitions. The total entropy change associated with the entire transition is close to Rln(90/3), corresponding to possible 90 and 3 rotational axes for high and low temperature phases respectively [2]. The entropy change associated with the low temperature ordering peak, as arrived at by fitting the Cp and the DSC curves with two gaussians, is Rln(12/3). We interpret this as to the formation of orientationally twinned structure of Pa3 phase wherein the basis molecles rotate about four equivalent [111] directions. The choice of which of these four one rotate along [111] direction gives rise to four distinct possibilities.

[1] J.E. Fischer et al., Phys. Rev. B53 (1996) 11418.
[2] R. Saito et al., Phys. Rev. B49 (1994) 2143.

A-I/P13 GROWTH OF CARBON-BLACK FRACTAL IN POLYETHYLENE MELT, V. Bouda, J. Kabrt. J. Rajman. Faculty of Electrical Engineering of Czech TU, Technicka 2, 166 27 Prague 6, The Czech Republic

Carbon-back (CB) - polyethylene composite material was produced by polymer/CB mixing in a Brabender cavity mixer and subsequently the plaques 0.5 mm thick were prepared by compression moulding. The CB network was broken up under shear into individual CB clusters during the processing. The plaques were then annealed at 140-200°C to induce different degrees of reagglomeration of the CB clusters in LDPE melt. Both the direct current (DC) and alternating current (AC) conductivity of the samples were measured during the process in situ and in real time. The AC conductivity exhibits a latent period until the rapid increase rate of conductivity. The AC conductivity decreases during the latent period. The internal process during the latent period is interpreted as the relaxation of potential energy of electrostatic repulsion forces between the CB clusters and/or as the decrease of the density of localised conducting states associated with sp^2 bonded carbon. The presence of hydrogen is expected to increase the degree of sp^3 bonded carbon during the latent period. The rapid increase of conductivity after the elapsed latent period is believed to be a manifestation of a CB fractal growth.

A-I/P14 C_{90}, C_{92} AND C_{94}: RELATIVE STABILITIES OF THE IPR ISOMERS, Z. Slanina, X. Zhao and E. Osawa, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi 441, Japan

The complete set of 46 isolated-pentagon-rule (IPR) isomers of C_{90} is described by the SAM1 quantum-chemical method, and their energetics is also checked by ab initio SCF computations (HF/3-21G, HF/4-31G). However, the energetics itself is not able to produce a good agreement with recent observations of Achiba et al. (Mater. Res. Soc. Symp. Proc. 359 (1995) 3). Relative concentrations of the forty six isomers were therefore computed using the isomeric partition function. The procedure changes the stability picture considerably. The symmetries of the five structures most populated in a high-temperature interval are according to the SAMl computations: two times C_2, C_s, C_{2v}, C_1 (two low-energy structures are replaced by species from medium-energy region). One of the fractions of Achiba et al. shows 70 lines in the ^{13}C NMR spectrum, with an origin from a C_2 species (45 lines) and a C_{2v} species (25 lines, 5 weaker). There is however an alternative interpretation of the spectrum: a C_s species (46 lines, 2 weaker) and a C_{2v} species (24 lines, 3 weaker), consistent with our computations. The treatment has also been applied to C_{92} with 86 IPR isomers and to C_{94} with 134 IPR isomers.

A-I/P15 HIP-TREATMENT OF A CARBON/CARBON COMPOSITE, S. Yamada, T. Hoshino and M.Takada, Department of Materials,Teikyo University of Science and Technology, Uenohara.Yamanashi 409-01 Japan

HIP (Hot Isotropic Press)-treatment of a sort of C/C composite was carried out. The starting material was prepared by a normal hot pressing upto 600C under ca.20 MPa, according to the preforming process developed by Chang, Nakagawa and Okura.

The range of opereating temperature and pressure was 1000 - 2000C and 100 - 200MPa, respectively: where «Dr.-HIP» of Kobe Steel Co.Ltd. was employed.

Changes in bulk density, electrical resistivity as well as flexural strength, were determined as functions of temperature and pressure. In parallel, XRD was investigated to elucidate the changes. Additionally, the same starting specimens were graphitized at 2800C under normal pressure to compare the graphitizability with that of HIP-ed ones above mentioned.

A-I/P16 ATMOSPHERE-INDUCED CHANGE OF MICROHARDNESS AND PLASTICITY OF C_2 SINGLE CRYSTALS AND POLYCRYSTALLINE FILMS, I. Manika, J. Maniks, Institute of Solid State Physics, University of Latvia, 8, Kengaraga St., Riga, 1063, Latvia; and J.Kalnacs, Institute of Physical Energetics, Latvian Academy of Sciences, 21, Aizkraukles St., Riga, 1006, Latvia

Microhardness, plasticity and dislocation structure of the indentation zone of C_{60} single crystals have been investigated. A pronounced increase of the hardness and decrease in plasticity of near-surface layers (up to 3μm) of C_{60} single crystals as well as of polycrystalline thin films under atmospheric exposure was observed. Vacuum annealing of atmosphere-aged fullerene crystals resulted in recovering of their mechanical properties. Atmosphere-induced strengthening was supposed to be due to locking of dislocations by intercalated oxygen or, possibly, to oxygen-induced structural change in the fullerene. Temperature dependence of the fullerene hardness in the range of 290-600K was investigated. Decrease in hardness at heating up to 465K and difference in the hardness values for heating and cooling cycles was observed. Hardness increased with increasing the temperature above ~465K. Such an anomalous behavior was interpreted as a result of decomposition of fullerene due to its chemical interaction with oxygen.

A-I/P17 Na_2RbC_2: A NEW lD POLYMERIZED FULLERIDE, G.M. Bendele, P.W. Stephens, Department of Physics, State University of New York, Stony Brook, NY 11794-3800, USA; P. W. Stephens, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA; K. Prassides, K. Vavekis, K. Kordatos, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, BNI 9QJ, U.K; and K. Tanigaki, NEC Fundamental Research Laboratories, Tsukuba 305, Japan

Trivalent cubic fullerides containing Na differ from those containing heavier alkali metals in that they undergo a fcc→pc phase transition similar to pure C_{60} and in that their T_c is lower than expected from the universal relationship between Tc and lattice parameter. Recently, we have shown that the stable phase at low temperature is not the known cubic phase, but instead a new monoclinic phase [1].

From synchrotron x-ray powder diffraction, we find that the structure of the ground state of Na_2RbC_{60} is a single-bonded lD polymer of C_{60} chains derived from the primitive cubic room temperature structure by a 5.7% contraction along one of its cubic face diagonals. The unit cell is monoclinic with lattice parameters a=13.711Å, b=14.554Å, c=9.3731Å, ß=133.53° (at T=180K). The interfullerene distance along the bonding direction (=c) is virtually identical to the intra-dimer distance of the RbC_{60} dimer structure [2]. The fullerene molecules are oriented with a single atom each aligned with the bonding directions and the two polymer chains with buckyballs centered on the origin and the C center are related through a rotation by 180° around b, resulting in space group $P2_1/a$.

We discuss this new structure of Na_2RbC_{60}, paying particular attention to bonding mechanisms, fullerene orientations, bond lengths, and the relation of this structure to other known polymeric fullerides and argue that the contrast between this structure and the [2+2] cydoaddition bonding of the RbC_{60} polymer is due to the different fullerene charge state.

[1] K. Prassides etal., J. Am. Chem. Soc. 119, 834 (1997)
[2] G. Oszlanyi etal., Phys. Rev. B 54, 11849 (1996).

A-I/P18 INCREASED BRIGHTNESS OF AC EL STRUCTURES ON THE BASIS OF ZnS: Cu C_{60}/C_{70} LAYERS, L.S. Yourukova and K.M. Kolentsov, Institute of Solid States Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd, 1784 Sofia, Bulgaria

AC EL structures with a light - emitting layer, based of ZnS: Cu - C_{60}/C_{70} fullerenes are investigated. The electroluminescent mixture (ZnS: Cu plus fullerenes) is prepared at a definite temperature which allows a dense contact of the fullerenes with the electroluminophor grains. The voltage - brightness and the frequency characteristics of these structures show increased brightness compared to the non-containing fullerenes structures. An attempt for explanation of the increased brightness as occurring due to the presence of the fullerenes in structures is made.

A-I/P19 MOLECULAR DYNAMICS OF CsC_{60} IN ITS POLYMER AND DIMER PHASES, J-L. Sauvajol, E. Anglaret and R. Aznar, Groupe de Dynamique des Phases Condensées, Université Montpellier II, Montpellier, France

We present inelastic neutron scattering and Raman scattering studies of inter-molecular vibrational modes of CsC_{60}. In the intramolecular modes frequency range, previous Raman studies have been performed and allowed probe the di- or polymerisation of the fullerene molecules [1,2].
We focus on the interballs modes frequency range and present an investigation as a function of the temperature for both the polymer and quenching-prepared dimer phases. Raman measurements are performed at various excitation wavelengths. The main feature is a peak at 30 cm^{-1} in the polymerized phase, assigned to an interball stretching mode. The same frequency range is investigated as a function of the temperature in inelastic neutron scattering. The polymer and dimer phases display characteristic differences which are emphasized and discussed.
[l] J. Winter and H. Kuzmany, Phys. Rev. B 52 (95) 7115.
[2] D. Bormann, J.L. Sauvajol, C. Goze, F. Rachdi, A. Moreac, A. Girard, L. Forro and O. Chauvet, Phys. Rev. B 54 (96) 14139.

A-I/P20 PHOTOSTIMULATED PROCESSES IN FULLERENES, B.L. Oksengendler(1), N.N. Nikiforova(1), O.E. Sidorenko(2), (1)Institute of Nuclear Physics, Uzbekistan Academy of Sciences, Ulugbek, Tashkent 702132, Republic of Uzbekistan, (2)Institute of Polymer Chemistry and Physics, .Uzbekistan Academy of Sciences, A.Kodyri street, 7 «b», 700128, Republic of Uzbekistan

Electronic and geometrical structure of fullerenes is asaociated with perculiarities of their responce on photoirradiation. Some typical groups of effects can be set apart: ONLY electronic and electronionic. 1. Electronic effects. Electronic spectrum and typical relaxation times were analyzed for different electron exitations. For example, for unusual exitons, where hole's component is delocalized along the surface of fulleren sphere, but electron component is localized in potential well in side the sphere. On the base of this model a set of electronic properties were calculated (electron spectrum, absorption section, Raman scattering cross section, Yahn-Teller effect). 2.Electron-ionic effects. Among different electronic processes, started up by photon irradiation, there are Auger destruction process and strong autolocalization of structure deformation near the impurity states that were investigated. For example, it was shown that photodestruction processes probabilities are substantially different in the regions far and near the isthmus.

A-I/P21 THE INFLUENCE OF PRESSURE ON CONDUCTIVITY OF CARBONACEOUS MATERIALS, Z. Kuvatov, Bashkir State University, Dept. of Physics, 450074 Ufa, Russia

By thermally dehydrogenation of polymers carbon materials may be synthesyzed with various structures. In connection with the problem of obtaining carbon materials with necessary properties, we investigated the influence of pressure on conductivity of products of pyrolysis of polyacetylene obtained at different pyrolysis temperatures T_p. For These samples the curve of conductivity increasing induced by pressure passes through maximum with T_p increasing. It is appears that samples showing maximum baric effect have biggest number of paramagnetic centers too. Therefore it can be concluded, that unpaired electrons take part in carrying of charge and pressure influences on its mobility.

A-I/P22 STUDY OF KARELIAN SHUNGITS MICROPOROSITY, V.V. Petrova, A.A. Savina, Petrozavodsk State University (PSU), Lenin Prosp. 33, 185640 Petrozavodsk, Russia,

Porous structure of different Karelian deposit shungits was studied by X-Ray Small-Angle Scattering method.
The objects being investigated were the thin plates cut out in two manners: parallel and perpendicular to the rock stratum. X-Ray Small-Angle Scattering patterns were obtained with the help of the special chamber KRM-1 at different arrangements of samples relative to the primary beam. The monochromatic Cu Kα-radiation was used.
The interpretation of the patterns was made by two methods. The Gunier approximation allowed us to define the pores shape and calculate sizes and the invariant estimation lets us determinate of summary concentration of micropores. The type of micropores was indentified by iodine filling of shungit samples.
Shungits of different deposits was demonstrated to have sufficient distinctions in character and parameters of microporosity that is derives from their structure peculiarities. Obtained results help to understand differences observed between density values measured by the X-Ray-method and hydrostatic weighing techniques.

A-I/P23 INITIAL PHASE OF C_{60} DEPOSITION ON Si(100) STUDIES IN SITU BY RAMAN SPECTROSCOPY, D. Drews, M. Friedrich, D.R.T. Zahn, Institut für Physik, TU Chemnitz, 09107 Chemnitz, Germany

C_{60} was evaporated from a Knudsen cell onto the (100) surface of Si at room temperature under ultra-high vacuum conditions. The deposition process was monitored in situ by Raman spectroscopy in the spectral region 1350-1600cm^{-1}. Further ex situ investigations were performed using Fourier transform infrared spectroscopy.
In the initial stages of deposition the Raman spectra show a peak at 1469cm^{-1} which is soon replaced by a peak at 1459cm^{-1}. The former has been assigned to the intrinsic pentagonal pinch mode of pure C_{60} while the latter has been reported as the signature of the photoinduced polymerization of C_{60} which is formed under light irradiation with sufficient intensity (~10W/cm^2) [1]. Although the intensity in the monitoring experiment was as high as 60W/cm^2 the deposited C_{60} film appears to be not polymerized at sufficiently low coverages. From the Fabry-Perot interference modulation of the Raman scattering intensity the growth rate of the C_{60} film is calculated. The correlation with the evolution of Raman spectra reveals a critical thickness of about 15nm for the onset of polymerization of the C_{60} on Si(100) under irradiation.
[l] J.L.Sauvajol, F.Brocard, Z.Hricha, and A.Zahab Phys. Rev. B 52, 14839 (1995).

A-I/P24 THE VIBRATIONAL SPECTROSCOPY OF M@C_{82}(M=La, Y): FAR-INFRARED, RAMAN AND NEUTRON INELASTIC SCATTERING RESULTS, S. Lebedkin(1), B. Renker(1), R. Heid(1), H. Schober(2) and H. Riestschel(1), (1)Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, Postfach 3640, 76021 Karlsruhe, Germany, (2)Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

The molecular dynamics in endohedral metallofullerides is of considerable interest due to their unique structures. We describe the improved procedure for producing tens of milligrams of metallofullerenes M@C_{82} (M= La,Y). This allows to study vibrational modes of M@C_{82} not only by Raman, but also by far-infrared and neutron inelastic scattering spectroscopy, requiring relatively large amounts of samples. Particular weight is put on the investigation of low frequency vibrational modes, which include excitations of the metal atom inside the carbon cage. Model calculations (Born-von Karman model) show the principal grouping of vibrational modes and their dependence on the mass of the metal atom in qualitative accordance with the experiments.

A-I/P25 NONLINEAR OPTICAL PROPERTIES OF NEAT AND METAL SUBSTITUTED FULLERENES, J. Callaghan and W.J. Blau, Physics Department, Trinity College Dublin, Dublin 2, Ireland

The third order nonlinear optical properties of C_{60}, C_{70} and Pt and Pd derivatives of these were investigated by picosecond optical phase conjugation at 1064 nm and 532 nm. The magnitudes of the nonlinearities obtained did not differ appreciably from one another and the second order hyperpolarisabilities were of order 9×10^{-47} m^5/V^2. At 1064 nm the metal derivatives exhibited a larger nonlinearity than the intrinsic response from C_{60}, with C_{70} showing the largest response of the materials studies. At 532 nm a large acoustic response was found for all samples arising from laser induced phonon scattering.

Transient absorption and pump-probe studies confirm the location of the triplet states in both C_{60} and C_{70} and have determined the lifetime of the excited singlet state to be 1.2 ns and 0.6 ns, respectively. The metal derivatives possess dual component decays which were assigned as intersystem crossing and triplet decay with lifetimes of approx. 10 ps and 1.5 ns. The large decrease in these lifetimes can be explained with the Heavy Atom Effect.

Optical limiting experiments were carried out at 532 nm. From the intensity dependant transmission measurements, coupled with a population level kinetic study, excited state absorption cross sections and efficiencies for optical limiting were determined. Due to the high molecular symmetry, C_{60} possesses the highest limiting efficiency. Metal derivatives perform better than C_{70}, but less efficiently than C_{60}.

A-I/P26 XPS ANALYSIS OF SIGLE CRYSTAL RbC_{60} SURFACE, T. Danno(1), K. Shiozawa(2), M. Haluska(3) and H. Kuzmany(3), (1)Department of Home Economics, Kochi Women's Universtity, Japan, (2)San Analysis & Consulting Survice Co. Ltd., Japan, (3)Insitut für Materialphysik der Universität Wien, Austria

Surface of Single Crystal RbC_{60} was characterised by means of XPS(X-Ray Photoelectron Spectroscopy). The atomic ratio of Rb to C up to 20Å depth preserved about 3 times higher than the stoichiometry (1/60) from the composition analysis. The top surface was covered by the oxidized carbon material and it decreased by the argon sputtering. The oxidized Rb component was observed at ca. 20Å depth by the shape analysis of Rb3d Spectrum, which shows a weak sholder at the higher binding energy. The stability of RbC_{60} under the ambient atmosphere is explained by the existence of oxidized Rb layer on the surface region.

A-I/P27 INFRA-RED SPECTROSCOPIC STUDIES ON OPAQUE-CARBON BASED MATERIALS WITH SPECIAL REFERENCE TO FULLERENES AND CARBON FIBRES, A. Kumar and G.C. Pandey, Research Centre, Indian Petrochemical Corporation Ltd, Baroda 391346, India

Recording of a good quality IR spectrum of carbon based materials due to their high absorptivity has been one of the major limitations in understanding the structural aspects of such materials. Fullerenes and carbon fibres are a few examples. Recently we have succeeded in recording a fairly well resolved IR sectra of such samples using a modified diffuse reflectance infra-red fourier transform (DRIFT) and newly-developed Mirage-FTIR combination system. The spectral analysis of C_{60} fullerenes both powder and crystalline (obtained without any dilution) has been done in the light of microstructural/morphological variations. The IR spectral features of fullerenes were found to match well with their predicted spectrum and was superior to that commonly reported in literature (as KBr pallet).

Similarly fiarly well resolved IR spectrum of carbon fibres including oxidized/stabilized fibres (commonly known as Panox) and that of high modulus carbon fibres have been recorded by Mirage-FTIR technique. The spectral analysis has been done in the light of extent of removal of non-carbon elements in the carbon framework structure. A correlation betwwen IR spectral characteristic and physico-mechanical properties is being attempted.

A-I/P28 NON-DESTRUCTIVE EVALUATION OF THERMAL DIFFUSIVITY OF FULLERENES AND CARBON FIBRES, A. Kumar and G.C. Pandey, Research Centre, Indian Petrochemical Corporation Ltd, Baroda 391346, India

Microcospic IR photothermal radiometry (PTR) setup has been used as an alternative to conventional laser flash method, for nondestructive evaluation of thermal diffusivity of fullerenes and carbon fibres. Measurements on two C60 fullerene samples (crystalline and powder form - as pallet) were made and the data have been analysed in the light of microstructural variations. The considerable difference (by an order of magnitude) in thermal diffusivity values of the two samples has been explained in the light of structural voids/defects which in case of C60 fullerene (compact) pallet are expected to create a barrier to heat flow and may be responsible for such a low value compared to that of crystalline sample. The extent of (heat flow) barrier will also depend upon the size and number of voids (on the pallet) per unit area i.e. larger the number and size of void, lesser will be the thermal diffusivity.

Thermal diffusivity of carbon fibres representing variations in terms of source, extent of carbonization etc. have been determined by PTR method. The results show that the thermal diffusivity had a direct correlation with the extent of carbonization of carbon fibre.

A-I/P29 STRUCTURES OF SOOT GENERATED BY LASER INDUCED PYROLYSIS OF METAL-GRAPHITE COMPOSITE TARGETS, E. Munoz, A.M. Benito, M.T. Martinez, Instituto de Carboquimica, CSIS, Luciano Gracia 5, 500015 Zaragoza, Spain, J. Fernandez, G.F. de la Fuente, Departamento de Ciencia y Tecnologia de Materiales y Fluidos, ICMA-ETSII, Centre Politecnico Superior, Maria de Luna 3, 50015 Zaragoza, Spain and Y. Maniette, Serveis Cientifico-Tecnics, Universitat de Barcelona, Lluis Solé i Sabaris s/n, 08028 Barcelona, Spain

A novel laser induced pyrolysis (LIP) method for producing fullerene nanostructures has been recently developed, where different lasers and soot collection conditions have been used which differ significantly from those used by other authors.

Carbon soot has been generated by LIP of transition metal containing graphite rods Different types of carbon structures were produced, ranging from amorphous carbon to fullerene nanostructures, varying the temperature of the substrate where the soot is collected, the laser energy and processing parameters, the inert gas pressure and its flow rate and the metal concentration within the metal-graphite composite targets.

A-I/P30 INVESTIGATION OF FULLERENES BY 2-mm WAVEBAND EPR SPECTROSCOPY, V.I. Krinichnyi, Institute for Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia

The fullerenes and their complexes with a partial or complete charge transfer are widely investigated by magnetic resonance techniques in the last decade. NMR spectroscopy allows to study the reorientational motion of a part of C_{60} molecules at temperatures higher then 100 K only [1]. The paramagnetism of some of fullerene systems takes a possibility to investigate these compounds by EPR method [1]. However, the data obtained at usual 3-cm waveband EPR does not permit to determine a correct information on the nature and dynamics of paramagnetic centers in the system under study.

The sensitivity and efficiency of EPR method increases considerably at 2-mm waveband due to a higher spectral resolution and to the appearance of new effects [2]. The present report is devoted to the applicability of a new 2-mm waveband EPR spectroscopy for investigation of various properties of fullerenes. It was shown that the complex of C_{60} with triphenylamine contains photoinduced spins in the ground and excited triple states with different relaxation and dynamics behaviors. These parameters and spin susceptibility are changed dramatically at phase transition at 260 K. The rate (15 THz at 300 K) and activation energy (0.024 eV) of spin rotation in C_{60} molecules were determined as well.

The utility of the new EPR technique in the investigation of other fullerenes and carbone based systems are discussed.

[1] C.N.R.Rao, Ram Seshadri, A.Govindaraj, and Rahul Sen, Mater. Sci. Engin., R15 (1995) 209
[2] V.I.Krinichnyi, 2-mm Wave Hand EPR Spectroscopy of Condensed Systems, Boca Raton, CRC Press, 1995.

A-I/P31 ELECTRON SWARMING IN CARBON NANOSTRUCTURES, S.A. Beznosjuk, M.S. Beznosjuk, D.A. Mezentzev, Department of Physical Chemistry, Altai State University, Dimitrov Street 66, Barnaul 656099, Russia

The successful development of computer simulation of experimental methods of carrying out design at the level of individual atoms in materials stimulated the physics of nanosystems. The required quantum approaches were developed in the 1980s in the form of the rheology of kinematic electron-density waves [1]. This application contains some possible mechanisms of electron swarm traffic confinement in a carbon nanostructure, system of quantum walls.

We took under consideration a simple model of corpuscular electron swarming. The electron corpuscle could intersperse between atoms. For simplicity we have made two basic assumptions. First, we treat the real state of the electron swarm within the so-called jellium approximation. Second, we assume that a set of the single-electron lodges organizes some g-dimensional lattices. An energy of the corpuscular electron swarm per single electron has a form: $E = 0.867xg / (r \times r) - 1.200/ r$, where r denotes a radius of single-electron lodge. Obtained estimates of proper equilibrium parameters of g-dimension corpuscular electron swarms allow us to examine the possibility of their realizing in practical nanostructures. Some results for carbon nanostructures of g-dimension are indicated. Account is taken of quantum topological definitions of the various corpuscular constituents: corpuscular electrons, molecules, coordinate compounds and their clusters.

1. S.A.Beznosjuk, B.F. Minaev, R.D. Dajanov, and Z.M. Muldakhmetov, Int. J. Quantum. Chem..- v. 38.- N6.-1990.- 779-797.

A-I/P32 PHYSICAL PROPERTIES AND PHASE TRANSITION IN AC_{60}, J. Winter, C. Kugler and H. Kuzmany, Institut für Materialphysik, Universiät Wien, Strudlhofgasse 4, 1090 Wien, Austria

The phase transition and physical properties of the alkali metal doped AC_{60} compound with A = K, Rb were studied using Raman spectroscopy. Homogeneously doped single crystal single phase AC_{60} up to the penetration depth of the laser could be obtained by a combination of a doping and an equilibration process above 400 K. The phase transition from a fcc to an orthorhombic structure for the AC_{60} compounds where the molecules are linked togheter and form linear chains and also the conditions for phase separation in the potassium doped system were studied in detail. Quenching and annealing experiments carried out with the RbC_{60} fcc high temperature phase showed significant changes in the spectrum which were interpreted as the Raman response of a metastable monomer and a single bonded dimer phase. Additional experiments were performed to check the possibility to dope neutral polymeric structures as phototransformed C_{60} and different polymeric C_{60} structures obtained by a high pressure and high temperature treatment of C_{60}.

A-I/P33 PREPARATIVE SEPARATION OF HIGHER FULLERENES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY(HPLC) ON ZINC(II)-TETRAPHENYLPORPHYRIN-MODIFIED SILICA COLUMN, Yin-Mei Liu, Ling Zhu, Xungao Zhang, Rongsheng Sheng, Fullerene Institute, Wuhan University, Wuhan, Hubei, 430072,China

A-I/P34 STUDIES OF DIFFERENT FULLERENES DOPED IN POLYSTYRENE BY ABSORPTION AND PHOTOLUMINESCENCE SPECTRA, Gu-Gang Chen, Zhi-Shan Xu, Xun-Gao Zhang, Rong-Sheng Sheng, Fullerene Institute, Wuhan University, Wuhan, Hubei, 430072,China

Thursday June 19, 1997
Jeudi 19 juin 1997

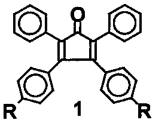
Afternoon
Après-Midi

Poster Session II
16:30-18:00

A-II/P1 CHEMICAL SWITCHING FROM THREE-DIMENSIONAL ALL HYDROCARBON DENDRIMERS TO LARGE AROMATIC GRAPHITE SUBUNITS, K. Müllen, F. Morgenroth, and C. Kübel, Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

A simple divergent synthesis of monodisperse 1,2,4-phenylene based all hydrocarbon dendrimers having diameters of 21 - 55 Å is presented. These dendrimers were prepared via a [2+4]cycloaddition-deprotection-sequence using an excess of tetraphenylcyclopentadienone 1 as monomer and tetraethinylbiphenyl 2 as core. By applying cyclodehydrogenation conditions to the lower generation G_1 the three dimensional structure was converted into the planar polyaromatic graphite subunit $C_{132}H_{34}$.

Molecular mechanics calculations in combination with molecular dynamics simulations were employed to discuss the structure and the shape-persistence of G_2, showing that the conformational freedom of the higher generations G_2 and G_3 is limited.



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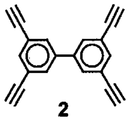

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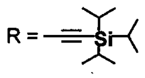

A-II/P2 LASER PYROLYSIS OF CARBON-NTROGEN GAS-PHASE COMPOUNDS: AN ATTEMPTED APPROACH TO CARBON NITRIDE FORMATION R. Alesandrescu, S. Cojocaru, A. Crunteanu, S. Petcu, R. Cireasa, G. Pugna, I. Morjan, National Institute of Physics of Lasers, Plasma and Radiations, P.O. Box Mg-36, Bucharest, Romania; D. Fatu, University of Bucharest, Department of Physical Chemistry, Bd. Republicii 13, Bucharest, Romania; and F. Huisken, Max-Planck Institut für Stromungsforschung, Bunsenstrasse 10, 37073 Göttingen, Germany

In the past few years, the theoretical considerations of Liu and Cohen indicating the extreme hardness of a new carbon-nitride material have attracted an increased interest. Most of the efforts were directed to the growth of CN films by different deposition techniques and surface treatment.

This paper presents a new attempt for the formation of carbon-nitride phases by using the sensitized CO_2 laser pyrolysis of acetylene/ nitrous oxide/ ammonia mixtures. Fine powders were produced in a flow reactor, at different partial pressures of the system reactant-sensitizer (SF_6/C_2H_4). The kinetics of the reaction was monitored by IR spectrophotometry of the exhaust gases. The powders were analysed by X-ray diffraction (XRD), X-ray photoelecton spectroscopy (XPS) anc IR transmission measurements. The majority of the XRD data suggests the presence of the predicted α- and ß-C_3N_4 phases. It was found that minor contamination of powders by fluorine- and sulphur-based by-products, originated from SF_6 decomposition occured. Work is in progress for minimizing the impurities by the improvement of experimental parameters.

A-II/P3 INFLUENCE OF PROCESS PARAMETERS ON CN_x FILMS OBTAINED BY LASER-CVD AT TWO WAVELENGTHS, R. Cireasa, A. Crunteanu, R. Alexandrescu, I. Morjan, C. Martin, I. N. Mihailescu, National Institute of Physics of Lasers, Plasma and Radiations, P.O. Box MG-36, Bucharest, Romania; A. Andrei, Institute for Nuclear Reactors, Pitesti, Romania and F. Vasiliu, Institute of Physics and Technology of Materials, P.O. Box MG-6, Bucharest, Romania

The possibility to produce superhard carbon nitride materials is attracting continuous scientific and application interest. Up to now mainly techniques as plasma CVD, magnetron sputtering. ion assisted dynamic mixing and laser ablation were used to grow CN films.

In this study we used the CVD teclmique for thin film deposition by laser irradiation of ethylene/ammonia/nitrous oxide mixtures with 10.6 µm and 248 nm. A perpendiculary geometry of irradiation on alumina substrates was used. A long pulse regime of the CO_2 laser was heating the substrates and, consequently, thermally decomposing the reactants in order to produce the deposit. The comparison of the pyrolytic process efficiency with the photolytic one (irradiation with KrF laser) is presented. For the photolytic process a temperature rise of the substrate is believed to influence to a certain extent the deposition process.

Because of the known nitrogen defficiency of the CN films, its incorporation on the film was investigated according to the modification of the deposition conditions. The influence of the deposition wavelength and the gas partial presssures on the chemical content and morphology of films is discussed.

A-II/P4 NEW DATA ON BIOLOGICAL ACTIONS OF WATER SOLUTIONS OF FULLERENES AS PROTOTYPES OF NEW CLASS OF DRUGS. G.V. Andrievsky, A.D. Roslyakov, T.V. Gorbach, V.K. Klochkov, A.V. Zhmuro, IT AMNU, 2-a Postysheva str., 310039 Kharkov, Ukraine

During the investigation we took into account the fact that minimal size of fullerene C_{60} aggregates are comparable with a thickness of animal cell membrane. This fact, as well as a property of C_{60} (as a suspension with particles' size 300 nm) to be captured and hold by alive animal cells [2], gives a possibility to classify fullerenes as membranotropic agents. In vitro experiments revealed that FWS (C_{60} = 1-6 µM) : (i) - possess a significant antioxydant; (ii) - decrease human red blood cells' hemolysis in 3-9 times; (iii) - do not inhibit cells respiration, are not hepatotoxic and do not influence negatively blood coagulation. Taking in mind these facts, we made in vivo experiments of biological action of FWS in rats (healthy and with experimental acute autoimmune disorder). It was shown that after single intravenous injection of FWS (C_{60}, 0.3-0.4 mg/kg) after 24 h in animals with experimental acute autoimmune disorder a row of investigated biochemical parameters of blood and heart, liver, renal and cerebral tissues, including basic immunological parameters, returned mostly to normal values. It was revealed that, C_{60} FWS are able to positively influence activity of adrenergic, GABA-, hystaminic- and, especially, serotoninergic systems. A positive effect of FWS, as a result of increased resistance of plasma membranes to damaging factors, manifested in activation of antioxidant and energetic system of the animals tested. Mechanisms of biological activity of FWS as prototypes of the new class of pharmaceuticals based on chemically unmodified fullerenes are discussed.

1. See Andrievsky G., et. al., «Properties of fullerenes in aqueous solutions», the report N... in this Abstracts of ICAM'97/E-MRS'97 SPRING MEETING.
2. Scrivens A., et. al., J.Am. Chem. soc., 116 (1994) 4517.

A-II/P5 PROPERTIES OF FULLERENES IN AQUEOUS SOLUTIONS G.V. Andrievsky, V.K. Klochkov, A.D. Roslyakov, A.Yu. Platov, IT AMNU, 2-a Postysheva str., 310039 Kharkov, Ukraine

Recently [1] a method has been offered for production of highly stable and finely dispersed colloidal solutions of fullerenes in water (FWS). We used this method to obtain both purely aqueous solutions of C_{60} and solutions of C_{60} in water containing either polyvinylpyrrolidone (PVP) or glucose. The properties of the FWS were characterized by the following methods: ^{252}Cf PD-MS, STM, UV-vis spectroscopy, GLC, electrophoresis. FWS, being colloidal systems, were stable during 12 months and more on storage at the normal conditions. The hydrated fullerene aggregates mainly had (approximately) the sizes 10, 40, 120 nm. It was found out that these aggregates consist of more small particles with diameter approximately 3 nm containing 11-13 molecules of C_{60}. In FWS the surface of colloidal particles had been charged negatively and the size of this charge depends on electron-donating properties of solvent components. It is of interest that C_{60}-PVP FWS are convertible colloidal systems i.e., re-soluble after the drying. We specifiide dependence of the sizes of fullerene aggregates from the value λ_{max} of absorption UV-bands of C_{60} in polar and non-polar medium. For bio-medical research, application of FWS as the prototypes of pharmaceutical drugs based on chemically unmodified fullerenes is offered.

1. G. Andrievsky et. al. J.Chem. Soc., Chem. Commun., 12 (1995).

A-II/P6 REALIZATION OF A WIDE RANGE OF GLC/DLC*-PROPERTIES BY PULSED LASER DE- POSITION (PLD), H. Mai and C.-F. Meyer, Fraunhofer-Institut fur Werkstoff- und Strahltechnik, Winterbergstr. 28, 01277 Dresden, Germany

Preparation and characterization of GLC/DLC thin solid films are described. The coating equipment involves a basic UHV-system, various laser types (TEA-CO_2, Nd-YAG & ArF) to provide distinguished photon wave lengths and a particular target handling configuration to achieve a satisfactory thickness uniformity upon technically relevant substrates.

Different wavelengths and power densities of the focused laser beam were applied for the ablation of spectroscopically pure graphite targets. Films were deposited on Si <100> substrates. Condensation proceeds at room temperature and deposition rates of typically 0.1 nm s^{-1}.

X-ray Reflectometry, Ellipsometry, IR- and Raman-Spectroscopy, Electron-Microscopy, Scanning Probe Microscopy and Ultrasonic Surface Wave Spectroscopy were used for the characterization of mechanical and optical properties of the specimens. Selected results demonstrate the correlation between chosen laser parameters and layer properties. This will be demonstrated particularly for mass density (ρ = 2.2 through 3.4 g cm^{-3}), optical extinction coefficient (k = 0.9 through 0.02) as well as Youngs Modulus (E = 200 through 800 GPa) thus representing one of the closest approaches to a «diamond like» behaviour.

*GLC - Graphite Like Carbon, DLC - Diamond Like Carbon.

A-II/P7 SYNTHESIS OF THE DIAMOND CRYSTALS FROM OXYACETYLENE FLAME ON THE METAL SUBSTRATE AT LOW TEMPERATURE. E. V. Grigoryev, V. N. Savenko, D. V. Sheglov, A. V. Matveev, V.A. Cherepanov. A. A. Borisov, A. S. Zolkin, Novosibirsk State University, Pyrogova Street 2, Novosibirsk, 630090, Russia; B. A. Kolesov, Institute Inorganic Chemistry, Novosibirsk, 630090, Russia

Diamond films and particles were synthesized by deposition from oxyacetylene flame on the molybdenum substrates under atmospheric conditions at 650K. It is more then 200K below as usual in such experiments. The study deals with morphological evolution of diamond films in combustion synthesis at different temperatures of the substrate as a basis for understanding the nucleation and growth mechanisms of the diamond phase. The films and particles were studied by scanning and transition electron microscopes and were characterized by Raman spectroscopy in this experiment. The best results, namely, perfect octahedral crystals, were obtained at R (O_2/C_2H_2) = 1.0, gas flow rate F = 2.2 l/min, distance between flame-corn and the surface of the substrate d=2 mm. Raman shift: 1332cm^{-1}, the crystal growth rate: 50 Å/c. Detailed data obtained by scanning electron microscopy are presented on the morphological evolution depending on the synthesis condition.

A-II/P8 RAMAN SCATTERING INVESTIGATIONS OF SEMICONDUCTING DIAMOND-LIKE CARBON THIN FILMS AND FIBERS OBTAINED FROM CAMPHOR, E. Rzepka, A. Lusson, E.A. Ponomarev, C. Lévy-Clément, Laboratoire de Physique des Solides de Bellevue, CNRS, 92195 Meudon Cedex, France; K. Mukhopadhyay, M. Sharon, Department of Chemistry, ITT, Powai, Bombay 400 076, India

Semiconducting carbon-based thin films obtained from camphor soot were studied by microRaman Spectroscopy with a laser wavelength of 632.8 nm. Different spectral contributions were identified between 1000 and 1650 cm^{-1} and discussed. The contributions are the D-like and G-like peaks of polycrystalline graphite at ~ 1345 and 1530 cm^{-1} respectively with a FWHM value ~ 5 times larger than in a:C, and an additional feature at 1240 cm-1 due to disordered sp^3-bonded carbon of camphoric soot. Spectra obtained were typical of amorphous DLC materials (a: DLC) containing a very low level of hydrogen atoms as shown by FTIR spectroscopy. This material seems to be suitable for flat panel display application using field emission.

Thermal annealing by laser light induced a modification in the Raman spectrum. A band appears at 1591 cm^{-1}, close to the peak associated with in-plane stretching mode of sp^2-hybridized carbon atoms (graphite phase).

Thick (20μm) and thin (1μm) fibers were obtained from camphor pyrolysis. Raman spectra were similar to those obtained with laser annealed thin films.

A-II/P9 ELECTRONIC STRUCTURE OF THE POLYMERIZED AMORPHOUS FULLERENE, A.V.Okotrub, L.G.Bulusheva, Yu.V. Shevtsov, Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia

The CKα-spectrum of the amorphous polymerized fullerite was obtained with the use of X-ray spectrometer «STEARAT» by the fluorescent excitation method. The resolution of 0.25 eV for the CKα-spectrum was obtained.

Theoretical X-ray spectra of polymerized fullerene were simulated on the basis of quantum-chemical calculations of C_{120} dimer and of C_{180} trimer by a method PM3 . The full optimization of geometry of these molecules was carried out. The most satisfied accordance of experimental and theoretical spectra is observed for two- and three- dimensional structures. Thus the coordinate value of the C_{60} molecules is in the range of 4-6. For the study of the chemical bonding between molecules fullerene in the polymer chain, fragment-by-fragment analysis of the trimer MO was carried out. Unoccupied orbitals of C_{60} take part on to 15% in the construction of the HOMO' s of polymeric chain. In the structure MO of chain there are MO located on the different molecules C_{60} in significant degree (~80%) and MO, in construction of which, all molecules participate in an equal degree.

A-II/P10 THE SYNTHESIS AND MORPHOLOGY OF CARBON NANOTUBES, Yu.V. Shevtsov, A.V. Okotrub, L.I. Nasonova, Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia, A.L.Chuvilin, Institute of catalysis SB RAS, 630090 Novosibirsk, Russia, A.K.Gutakovskii, Institute of Semiconductor Physics SB RAS, 630090 Novosibirsk, Russia

We used the method of electric arc evaporation of graphite for investigation of processes fullerene and carbon nanoparticles synthesis. For these purposes a 35kW power facility equipped with manipulators, detectors and mass- spectrometer was made. Morphology and atomic structure of the nanoparticles from deposit samples and from soot were studied by the transmission electron microscopy method. The fullerene-containing soot was found to contain the cage carbon particles (monolayered carbon bubbles and tubes) which were formed due to the heating of the particles of amorphous carbon. These particles can organize the ordered structures. The variation of the sintering condition of the amorphous soot particles results to the formation of the multilayered (2-6 layers) closed structures. We proceeded the computer restoring of the separated images of the front and back walls of the tubule. The images demonstrate, the picture of intermittent regions of the strict periodicity. This is the base for the conclusion of the local graphite crystallization of the tubule walls. All nanotubes under investigation was found to have a spiral structure.

A-II/P11 X-RAY SEPCTRA AND ELECTRONIC STRUCTURE OF CARBON NANOTUBES, L.G. Bulusheva, A.V. Okotrub, Institute of inorganic chemistry SB RAS, 630090 Novosibirsk, Russia; D.A. Romanov, Institute of semiconductor physics SB RAS, 630090 Novosibirsk, Russia

The particularities of the electronic structure and electrophysical properties of nanotubes depending on their diameter and spirality was investigated using the quantum chemistry methods. The electron structure calculations have been made by semi-empirical method PM3. The clusters of the tubules (4,4), (5,5), (6,6) and of the tubules (6, 0), (7, 0), (8, 0), (9, 0) were calculated. The ionization potential for HOMO of clusters was shown to be determined by the distortion of the carbon hexagons. We found, that the HOMO structure are the same for the clusters of various diameter: the stripes of zero electron density on the carbon atoms are on the tubule perimeter for (n,n)- type tubules and along the tubule for (n,o) - type tubules. The clusters of spiral nanotubes (6,4), (7,3), (8,2) and (9,1) with fixed diameter (~10A) were calculated. For the central hexagons of these clusters the theoretical CKα-spectra, which reflect the distribution of the electron density of carbon atoms in the cluster valence band were simulated. The theoretical spectra were correlated with the experimental high-resolution fluorescent CKξ-spectra of carbon multylayered nanotubes, obtained by the method of electric arc evaporation of graphite.

A-II/P12 ELECTRONIC STRUCTURE OF $C_{60}F_{24}$, L.G.Bulusheva, A.V.Okotrub, Institute of Inorganic Chemistry SB RAS, pr. Ak. Lavrent'eva 3, 630090 Novosibirsk, Russia.

Seven isomers, possessing the various size of carbon π- system, were constructed. Full geometry optimization for these isomers was carried out by PM3 method and theoretical CKα- and FKα-spectra were calculated. These spectra were compared with the X-ray high resolution fluorescent spectra of $C_{60}F_{24}$ to find the isomer with the best coincidence. The fluorine atoms in synthesized pattern have been found to dispose along a diameter of C60 sphere to form two carbon areas with delocalized electronic density.

A fragment analysis of mentioned above $C_{60}F_{24}$ isomer with the use of the distorted C_{60} frame was made. ρ-type HOMO's of $C_{60}F_{24}$ have been shown to consist of the vacant orbitals of the C_{60} cage with the contribution of 10-30%. Lower energy MO's of $C_{60}F_{24}$ have been found to be formed by 2p-AO's of all carbon atoms of the C_{60} cage and 2p-AO' s of fluorine atoms. These MO's are π-antibonding in respect to the carbon-fluorine interaction. The structure of MO's of $C_{60}F_{24}$ includes MO, located in the narrow energetical range (~0.4eV) with the main contribution from 2p-AO's of fluorine atoms, directing tangentially along the surface of the C_{60} cage. The deeper group of MO's includes σ-bonding and π-bonding orbitals in respect to the interaction between the atoms of fluorines and carbons.

A-II/P13 DIAMONDLIKE CARBON FILM PREPARATION AND SURFACE COATINGS OF OXIDE SUPERCONDUCTING AND FERROELECTRIC FILMS, Shin-ichi Aoqui, Kumamoto Institute of Technology, Ikeda, Kumamoto 860, Japan; K. Ebihara and Y. Yamagata, Department of Electrical and Computer Engineering, Kurokami, Kumamoto 860, Japan

Diamondlike carbon (DLC) films as well as amorphous carbon(a-C) films are investigated as possible passivation and environment protection for YBCO oxide superconducting and PZT ferroelectric thin films. Carbon films show two extreme state of DLC films and a-C films depending on the deposition conditions. The environmental degradation of the YBCO and PZT materials is serious problems in developing high-Tc superconducting devices and ferroelectric IC devices. The pulsed laser deposition (PLD) technique is employed to prepare the perovskite oxide films of YBCO and PZT. These film surfaces were coated by the DLC films prepared using the laser ablation method. Optimum deposition condition of the PLD process for the YBCO, PZT and DCL was investigated. In the case of DLC coatings, a graphite target was ablated using KrF excimer laser of 4 J/cm^2 in 400 mTorr hydrogen ambient gas. An optical band gap of 2.5 eV was attained on room temperature substrate and high quality superconductivity of the DLC coated YBCO films was kept over one month.

A-II/P14 CHARACTERIZATION OF CARBON NITRIDE THIN FILMS DEPOSITED BY AN RF PLASMA BEAM G. Dinescu, E. Aldea, C. Stanciu, C. Ghica, G. Musa, National Institute of Lasers, Plasma and Radiation Physics, Bucharest-Magurele, Romania; M.C.M. van de Sanden, D.C. Schram, Eindhoven University of Technology, the Netherlands

Thin films downstream deposited by a nitrogen plasma jet generated between a graphite electrode and a graphite nozzle have been investigated by ellipsometric spectroscopy, transmission electronic microscopy and microhardness measurements.

Starting from previous results of infrared absorption spectroscopy and XPS investigations, a multilayer structure, with an appropriate chemical composition on each layer, has been considered for fitting the ellipsometric data. This procedure lead to the optical constants and to a composition model for the deposit.

The TEM investigations had shown that the films are amorphous and consisting of an ordered filamentary structure, with filaments having the thickness around 20 nm and being perpendicularly oriented on the substrate surface.

A hardness around two times higher than that of the silicon substrate has been measured.

A-II/P15 CARBON NITRIDE FILM DEPOSITION FROM AN EXPANDING THERMAL NITROGEN PLASMA REACTING WITH SOLID CARBON, A. de Graaf, M.C.M. van de Sanden, D.C. Schram, Eindhoven University of Technology, the Netherlands; and G. Dinescu, A. Andrei, M. Gartner, National Institute of Lasers, Plasma and Radiation Physics, Bucharest-Magurele, Romania

A carbon target has been submitted to an Ar/N_2 expanding thermal plasma leading to the deposition of thin films on a substrate placed downstream the target.

The chemical composition of the deposited films has been investigated by IR absorption spectroscopy, spectroscopic ellipsometry, X-ray photoelectron spectroscopy. Evidence of carbon presence in the film was obtained. Also the nitrogen bonding to carbon was confirmed showing that carbon nitride layers have been deposited.

The spectral emission recorded from the plasma expansion located between the carbon target and substrate strongly exhibits the violet CN radical emission: This emission increases with target temperature.

The experimental results show that the deposition process is based on the reaction of nitrogen excited species with the carbon surface. The carbon atoms from the target are forming chemical radicals which are transported along the flow in the deposition area.

A-II/P16 CARBON NITRIDE FILMS PREPARED BY GUANAZOLE LASER ABLATION IN AMMONIA ATMOSPHERE R. Soto, P. Gonzalez, J. Pou, B. Leon, M. Pérez-Amor. Dpto. Fisica Aplicada, Univ. Vigo, Lagoas-Marcosende 9, 36200 Vigo, Galicia, Spain

Carbon nitride thin films were deposited using an ArF excimer laser to ablate a target of 3,5 diamino 1,2,4 triazole (guanazole) in a reactive atmosphere of ammonia. Films were obtained at room temperature onto crystalline silicon, aluminium and Corning glass substrates.

The dependence of the film properties on the ammonia pressure is reported. Films were characterized systematically by profilometry, Fourier Transform Infrared Spectroscopy and Energy Dispersive X-ray Spectroscopy. Infrared spectra are dominated by a broad absorption band from 1300 to 1650 cm^{-1} and a peak located at 2165 cm^{-1} indicating that nitrogen is bonded to carbon in different configurations. The broad band at high wavenumbers (3100-3500 cm^{-1}) is attributed to NH_x stretching modes revealing the presence of hydrogen in the films. Composition estimated by EDX shows that as the ammonia pressure is increased, higher concentration of nitrogen is incorporated into the films, reaching values up to 53 at.% for NH_3 pressures higher than 1 Torr.

A-II/P17 PARACYANOGEN-LIKE STRUCTURES IN HIGA-DENSITY AMORPHOUS CARBON NITRIDE F. Weich, J. Widany, and Th. Frauenheim, Technische Universität, Institut für Physik, 09107 Chemnitz, Germany

An ab initio based tight-binding molecular-dynamics (MD) method has been used to generate 60 amorphous carbon nitride structures with various stoichiometries (0, 14, 29, 43, 57 % nitrogen) and densities (1.5, 2.0, 2.5, 3.0, 3.5, 4.0 g/cm^3) thus providing for the first time an atomic level insight into the important chemical bonding properties in such materials. At approximately 30% nitrogen content, the character of the material changes from heavily nitrogen doped amorphous carbon to an amorphous carbon nitride. In addition, we observe pronounced trends counteracting the formation of a low-compressibility phase: l) The energetically most favourable density for the amorphous structures shifts downwards from 3.0 g/cm^3 at 0 and 14 % nitrogen to approximately 2.0 g/cm^3 at 43 and 57 % nitrogen, respectively. 2) The sp^2 carbon fraction at any mass density between 1.5 and 4.0 g/cm^3 is strongly enhanced by N-incorporation. 3) In the nitrogen-rich cells at highest densities the network connectivity is considerably reduced compared to pure ta-C. There are even some chain-like and layered structure elements incorporating paracyanogen-like bonding configurations. 4) The trend to the paracyanogen bonding is even more pronounced at densities below 3.0 g/cm^3, confirming experimental Raman and IR findings. During MD-annealing at such densities an increasing number of CN- and N_2-dimers are formed, which under real deposition probably evaporate into the gas phase, thus limit'ing the highest possible N-concentrations in the films to about 40 % in most experimental studies.

A-II/P18 OPTICAL AND ELECTROOPTICAL PROPERTIES OF CARBON DIAMOND LIKE FILMS, V.M.Puzikov, A.V. Semenov, D.I. Zosim, Department of Optical and Constructional Crystals STC «Institute for Single Crystals», 60 Lenin ave., 310001, Kharkov, Ukraine

Experimental results on effect of electric field on optical properties of carbon diamond-like films (DLF) are reported. DLF prepared by the ion beam deposition method demonstrate electrooptical and electrostrictional properties are quadraticaly dependent on the electric field. For DLF of the lst series prepared under optimal conditions the electrooptical C_n and electrostrictional C_h coefficients are $1.22x10^{-19}M^2/V^2$ and $8.25x10^{-19}M^2/V^2$ respectively. For the films of the 2nd series prepared with the increased energy of the deposited ions (~180eV) the coefficients C_n and C_h are $7.11x10^{-17}M^2/V^2$ and $3.57x10^{-17}M^2/V^2$ respectively. The effect of the electric fleld on the reflection coefficients of DLF is characterized by the threshold value of the electric field $0.96x10^8$V/M and $2.63x10^8$V/M correspondingly for DLF of the lst and 2nd series. Beginning from the value of the electric field $1.57x10^8$V/M (lst series) and $3.26x10^8$V/M (2nd series) the effect of memory appears in the films: new states of the reflection function are preserved with the fleld switched off. The effect of the electric field on the reflection function of the more dielectric DLF (lst series) are revealed weaker by an order than that of the less dielectric DLF (2nd series).

A-II/P19 CARBON NANOTUBES OF POLYETHYLENE: SYNTHESIS, STRUCTURE AND FIELD EMISSION, E.F.Kukovitskii, S.G. L'vov, Kazan Physical-Technical Institute, 420029 Kasan, Russia, L.A. Chernozatonskii, Institute of Biochem. Physics, 117334 Moscow, Russia, A.L. Musatov, K.R. Izraeljanz, A.B. Ormont, Institute of Radio Eng. and Electronics, 103907 Moscow, Russia

Crooked carbon nanotubes 10-40 nm in diameter were obtained at 420-450°C by the pyrolysis of polyethylene in He atmosphere using Ni plate as a catalyst. Production of this powder was 200-300 mg per hour (using 500 mg of polyethylene). Their identification was made by electron microscopy, Raman spectroscopy, electron and X-ray diffraction. The oxidation reaction of the nanotube powder studied.

Like-cotton wool nanotube films (about µm thickness) were obtained also on Ni plates. Near surface some tubes come to their ends (20-60 nm in diameter) directed outwards (~10^6/cm^2). We studied their field electron emission at 10-9 torr vacuum. 1-10 mA/cm^2 current density was observed at 4-10 V/µm.

A-II/P20 THE X-RAY EXCITATIONS IN THE POLYMERIZED FULLERENES, V.V. Rotkin, Ioffe Physical-Technical Institute, 26 Politekhnicheskaya st., 194021 St.Petersburg, Russia

Recent development of dimerized fullerene molecule, polymerized chains and arrays of fullerenes on a surface and in bulk monocrystal attracts our attention as extremely nanoscale example of self-organizing structures. These objects possess optical excitation resulting from the electronic collective excitations [1].

We concentrated our research on the calculation of the elementary excitation frequencies in the single cluster [2], in the cluster based material [3], and in the dimerized cluster [4]. Two types of coupled oscillation exist with energy shifted up and down from C_{60} molecule plasmon energy depending on dipole polarization. The generalization of the last result for the 1-D chain of fullerenes or the 2-D plane is straightforward. The 1-D chains were experimentally observed in the doped fullerene solid and the surface of the fullerene solid was found to be polymerized at the UV exposure. The existence of the coupling between the X-ray photon and the transverse collective excitation is shown as the X-Ray polariton [1].

[1] V.V. Rotkin, R.A. Suris, Abstract on The Int.Conf. on Soft X-Rays in 21-st Century, Midway, Utah, USA, 8-11 January, 1997.
[2] V.V.Rotkin, R.A.Suris, Mol. Materials, v.4, 87-94, 1994.
[3] Rotkin V.V., Suris R.A., Sov.- Solid State Physics, {/bf 36}, 12, 1899-1905, 1994.
[4] V.V.Rotkin, R.A.Suris, Sol.State Comm., v. 97, N 3, 183-186, 1995.

A-II/P21 THE ROLE OF THE SUBSTRATE BIAST (DC - or RF) AND SOME OTHER DEPOSITION PARAMETERS IN THE GROWTH MECHANISMS OF CN_xH_y FILMS OBTAINED BY ECR PLASMA ACTIVATED CVD, L.R. Shaginyan, Institute for Problems of Materials Science of Ukrainian National Academy of Sciences, 3 Krzhyzhanovsky St., Kiev 252142, Ukraine

Electron cyclotron resonance (ECR) plasma activated CVD in CH_4-N_2 gas mixture has been used to grow thin CN_xH_y films on steel, Al-Si alloy . The composition, optical and mechanical properties of the films deposited at various process conditions were investigated by electron microprobe analysis (EPMA), IR- spectroscopy and microhardness measurements. It was shown thal the DC-bias does not influence substantially the films properties and such films have a high nitrogen content (N/C~0,6) and polymerlike structure. The RF-bias changed drastically all the films' properties. RF-biased films had a small nitrogen content (N/C~2), were rather hard (4000-7000 N/mm^2), all the bands on the IR spectra of the films became very weak and some of them disappeared. This effect is explained by the ion bombadment influence, which may be effectively realised for dielectric CN_xH_y films only at RF-biased substrate. Variation of RF-biased CN_xH_y films properties is related to the destruction of its polymerlike structure under the ion bombardment and information of highly disordered structure of the film on the base of graphite like cluster containing the carbon and nitrogen atoms.

A-II/P22 THE TRANSFORMATION OF $C_{60}F_{48}$ BY RADIATION DESORPTION OF F ATOMS: XPS AND XAES STUDIES, A.P. Dementjev and M.N. Petukhov, RRC Kurchatov Institute, KurchatovSq., Moscow 123 182, Russia

The study of transformation $C_{60}F_{48}$ after F atoms losses through a radiation desorption is very usefull for understanding chemistry of this compounds. The desorption of F atoms takes place only from the top layers of clean surface, so the surface sensitiv methods can be used. The analysis of top layers of $C_{60}F_{48}$ (powder, films) by XPS and XAES methods was made. It was found that e-, UV, X-ray radiation stimulate the desorption of fluorine atoms from the top layers of clean surface. On basis of analysis of the Cls photoelectron and CKVV Auger spectra conclusion is made, that the most part of $C_{60}F_{48}$ molecules have lost fluorine atoms and passed into a new chemical state [D] having thickness of a few monolayers. The CKVV Auger spectra of [D] state coincides with spectra for Diamond and Polyethylene. This results allow suppose a polymerization with C_{60} as a monomer. The sp^2 and sp^3 hybridization of carbon atoms can be separated by CKVV spectra with high reliability. The mechanism of formation of the sp^3 bonds through a recombination of C60 radicals created from $C_{60}F_{48}$ by fluorine losses is discussed.

A-II/P23 RAMAN STUDIES ON SINGLE WALLED CARBON NANOTUBES PRODUCED BY THE ELECTRIC ARC TECHNIQUE, M. Lamy de la Chapelle, S. Lefrant, IMN-Univ. Nantes, BP 32229, 44322 Nantes cedex 3, France; C. Journet, W. Maser, P. Bernier, GDPC-Univ. Montpellier II, 34095 Montpellier cedex 5, France and A. Loiseau, Lab. Phys. Solide, ONERA, BP 72, 92322 Chatillon cedex, France

Carbon single walled nanotubes (SWNTs) have been produced in high yields using the electric arc technique. TEM studies show that the SWNTs have a narrow diameter distribution around an average value of 1.3 nm.

In this paper we focus on the characterization of these samples by high resolution RAMAN spectroscopy (HRRS). The presence of large amounts of SWNTs in the samples induces a very rich structure in the spectra which is typical for this class of carbonaceous material. Armchair tubes with (8,8) to (12,12) geometry can be detected, being in agreement with the narrow diameter distribution observed by TEM measurements. The ability of HRRS as a highly sensitive fingerprint technique in identifying SWNTs with different diameters and geometries will be discussed.

A-II/P24 CONNECTION OF IR-REFLECTION WITH ELECTRICAL PROPERTIES CARBON NANOTUBE FILMS, V.A. Vdovencov, Z.Ya. Kosakovskaya, V.G. Mokerov, Institute Radio Engineering & Electronics RAS, Mokhovaya str. 11, Moskow 103907, Russia

IR-reflection spectra of carbon submicron films , contained nanotubes, have harrow bands with quantum energies corresponding to optical transitions of the electrons between discrete energy levels. These levels are well discribed by the formula that is characteristic for harmonic quantum oscillator: 0.25 (n+1/2) eV, n=0,1,2... The energy of elementary oscillating quantum (mode) is equal to 0.25 eV, and the observed reflection bands have energies 0.125 eV, 0.25 eV, 0.375 eV. Reflection band, which is supposed to be the phonon, duplicate of the band with energy 0.125 eV, has energy of 40 meV smaller. The temperature dependence of JV characteristics in the range above 300K for investigated nanotube films have the regions described by various activation energies 0.125 eV, 0.25 eV, 0.375 eV. At low temperatures activation energy is near to 40 meV, which we explain by cherge carriers generations by LO phonons. The temperature dependence of Zeebek effect up to 450°C indicates that the films are slightly degenerated semiconductors and have electron-type conductivity. The experimental date are well agreed and lead to the conclusion that temperature dependence of nanotube film electrical characteristics are determined by thermal generation of the electrons from energy levels that are responsible for optic reflection bands.

A-II/P25 MAGNETIC PROPERTIES OF CARBONITRIDE FILMS ELABORATED BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION, M. Trinquecoste, E. Daguerre, L. Couzin, J. Amiell, A. Derré, P. Delhaès, Centre de Recherche Paul Pascal, Avenue A. Schweitzer, 33600 Pessac, France

Several amorphous carbonitride films have been elaborated by Plasma Enhanced Chemical Vapor Deposition. A Radio Frequency discharge has been used under standard conditions with different nitrogenated compounds. It is shown that the influence of molecular precursor is important concerning in particular the magnetic properties: the films issued from pyrrole and cyanuric chloride are exhibiting a large number of spins. However at the opposite of previous works, no cooperative magnetic effects have been found at very low temperature. Finally, it is demonstrated that a further heat-treatment at 1000°C of an ex-cyanuric chloride film appears to lead to a crystalline phase of C_3N_4 which is currently under investigation.

A-II/P26 HFCVD DIAMOND NUCLEATION ON POLYCRYSTALLINE AND MONOCRYSTALLINE (111) COPPER. EVIDENCE FOR TRANSFORMATION OF CARBON PHASES BY ELECTRON SPECTROSCOPIES AND HRTEM, L. Constant, C. Speisser and F. Le Normand, IPCMS - Groupe Surfaces Interfaces, 23 rue du Loess, 67037 Strasbourg Cedex 2, France

Diamond has been deposited on polycrystalline and monocrystalline (111) copper via ot filament chemical vapor (HFCVD) process. The diamond growth is studied by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), directly connected to the growth chamber and by High Resolution Transmission Microscopy (HRTEM) using an extractive replica technique for the preparation of the sample. Both, shape analysis of the AES C KVV line and the C1s relative intensity suggest the following three-step process: first formation of one highly graphitic layer, then very slow growth of graphitic layers, more and more distorted when going away from the copper surface and finally when a critical size corresponding to about 5-6 layers is reached, diamond nucleation and growth. Even on the polycrystalline sample where diamond residues are let by the polishing process, an initial complete transformation into graphite occurs. A very long induction time (more than 10 hours) is required on the monocrystalline sample, unlike polycrystalline one. This is ascribed to the strong interaction of the graphite layer with the copper surface and the lack of defective sites suitable for diamond nucleation on the former surface. This nucleation process is roughly in agreement with the recrystallisation model of diamond nucleation from amorphous carbon proposed by J. Singh and M. Vellaikal, J. Appl. Phys. 73, 2831 (1993). HRTEM examination of the deposit confirms these results with the visualisation of oriented graphitic planes. In addition however spherical agregates of size < 0.1 μm were observed. They are formed with concentric bent graphitic surfaces with sometimes near the center of the sphere a new phase of size some nanometers. The interplanar distance 0.202 nm well corresponds to diamond. An additional and quite original mechanism of diamond nucleation is thus postulated. It occurs through a phase transition inside the agregate owing to the high internal pression of the strongly bent graphitic surfaces, the occurrence of defaults and the behaviour of hydrogen radicals deeply penetrating the agregate.

A-II/P27 CARBON NANOTUBES: THE SOLAR APPROACH, D. Laplaze, P. Bernier, W. Maser, Groupe de Dynamique des Phases Condensées, Université de Montpellier II, 34095 Montpellier, France; G. Flamant, I.M.P. - CNRS Odeillo, 66125 Font-Romeu, France; A. Loiseau, Laboratoire de Physique des Solides, ONERA, 92322 Chatillon, France

Since 1993, we have shown that it is possible to produce fullerenes in rarefied inert gas atmosphere, by the direct vaporization of graphite in focussed sunlight. Having improved the experimental set-up, we are now able to use this method to produce carbon nanotubes.

The material which is vaporized under argon atmosphere at various pressures, is generaly a mixture of graphite powder with cobalt and nickel. Electron microscopic observations show the presence of multi wall as well as ropes of single wall nanotubes and in some cases it also appears some carbon vesicles. The relative proportion of each species seem to be related with experimental parameters like pressure, gas flow rate, composition of the starting mixture.

A-II/P28 THE STATIC WAVES OF ATOMIC DISPLACEMENTS ACCUMULATION EFFECT INSIDE A ZONE OF ELASTIC TO PLASTIC TRANSFORMATION, A.A. Ovcharov, M.D. Starostenkov, General Phys. Dept., Altai Atate Technical University, 46 Lenin St., Barnaul 656099, Russia

The fullerene relaxation under an impulsive pressure deformation was considered in this work. The empiric pair Lenard-Jones potential was used as the interatomic interaction potential satisfiable to the Koshi condition. As the result of research it was obtained an existence of fourth main kinds of crystal relaxation: I) The deformation level range 0-5% - stable phase. Homogeneous deformed crystal is stable. 2) Under the deformation level range 5-15% a horizontal waves of atomic displacements are generated in crystal. First only one wave is appeared, then with the deformation growth waves number increased and their amplitudes are raised. 3) Under the deformation level range 15-17% the vertical waves of atomic displacements are generated in crystal. Their number and amplitudes are substantial less than the same characteristics for horizontal waves. Horizontal waves of atomic displacements are nonstable within this deformation interval. They joined. The process lasts to reach the equilibrium waves number under the assigned deformation level. 4) Under the deformation level range 17.1-17.2% a new wave generation system are observed in crystal - diagonal. The diagonal waves of atomic displacements are generated in crystal. These waves are nonstable. With the deformation growth the dislocation are generated inside these waves.

A-II/P29 PLASMA ENHANCED CVD OF THIN CARBON LAYERS ON COATED SUBSTRATES, H. Schalko(1), M. Hulman(2) and H. Kuzmany(2), (1)Institut für Elektrotechnik, Technische Universität Wien, Güßhausstrasse 27/359, 1040 Wien, Austria; (2)Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, 1090 Wien, Austria

A specially designed system is used to study the parameters of plasma enhanced CVD for the growth of carbon and diamond films on substrates coated with various types of fullerenes. The plasma is generated in a 13.56 MHz discharge chamber under varying gas concentrations of methane and H_2. Discharge power an substrate temperature can be controlled completely separate. Special attention is paid to the coating of the substrate. This coating is performed by molecular beam epitaxy in a separate cell. The coating process is controlled by atomic force microscopy inspection of the coated surface. The deposited carbon layers are analyzed by atomic force microscopy, Raman scattering, x-ray diffraction and electron microscopy. The relative ratio between sp^2 and sp^3 carbon was found to depend critically on the substrate temperature. With increasing temperature the sp^3 concentration increased. Since fullerenes are known to act as seeding for the growth of diamond layers a strong influence of various coatings on the bonding of the deposited carbon films is expected.

A-II/P30 VIBRATIONAL SPECTRA OF SINGLE WALL CARBON NANOTUBES, B. Burger and H. Kuzmany, Institut für Materialphysik der Universität Wien, 1090 Wien, Austria; A. Thess and R. Smalley, Institute of Physics, Rice University, Houston, USA

Single Wall Nanotubes (SWNT) were prepared by condensation of a laser-vaporized carbon-cobalt-nickel mixture. The tubes were analyzed by resonance Raman scattering using excitations between 452 nm and 800 nm. IR spectra were recorded from KBr pellets which were drop coated with a dispersion of SWNTs in methanol prepared by ultrasonic agitation.

In both cases two strong lines dominate the spectra. These lines are at 1495 cm^{-1} and 186 cm^{-1} in the Raman spectra and at 483 cm^{-1} and 1384 cm^{-1} in the IR spectra. The Raman lines of the low energy modes show a strong upshift and increase of intensity upon lowering of the excitation energy, while the G-line shows no dispersion effect. This dispersion effect is strongly related to well known dispersion effects in conjugated polymers. It has been interpreted as a size effect. The results of the studies are compared with spectra of multi wall nanotubes and Graphite.

A-II/P31 SCANNING PROBE MANIPULATION OF CARBON NANOTUBES, D.L.Carroll(1,2), S.Curran(3), P.Redlich(2), P.Ajayan(4), and S.Roth(3); (1)Department of Physics and Astronomy, 118 Kinard Laboratories, Clemson University, Clemson SC, 29634 USA; (2)Max Planck Institut für Metallforschung, Seestr. 92, Stuttgart 70174, Germany; (3)Max Planck Institute for Festkörperforschung, Heisenberg Str.1, Stuttgart 70569, Germany; (4)Department fo Materials Science, Rensselaer Polytechnic Institute, Troy New York, USA

Selection and manipulation of individual and bundles of multiwalled carbon nanotubes as well as Boron Nitrogen doped mulitwalled carbon nanotubes is a technique which can be readily carried out using Scanning Tunnelling probes. This technique is sufficiently flexible to preselect regions on a substrate and deposite the nanotubes upon it. This then allows both the electronic characterisation of carbon nanotubes and a study of the local density of states. The forces involved in manipulating these different forms of nanotubes will be discussed.

A-II/P32 AMORPHOUS AND QUASI-AMORPHOUS STABILIZED CARBON PHASES SYNTHESIZED BY IMPACT AND THERMAL ACTIVATION SYNERGISM, B.F. Dorfman, Atomic-Scale Design, Inc., USA

The stabilized hard carbon phases: diamond-like nanocomposite (DLN), quasi-amorphous carbon (QUASAM) and graphitic-like carbon (GLC) with a similar chemical composition: C3[Si1-xOx]Hy, (x=0.44, y<=0.5), but different fine structure and density have been synthesized in the synergetic conditions of thermal and impact activation of the beam-solid reactions.

The densities of these carbon forms are: dDLN=1.8-2.25 g/cc, dQUASAM=1.35-1.7 g/cc, dGLC=1.8-2.2 g/cc, DLN is a pure amorphous form, while basically amorphous QUASAM reveals a one-axis anistropy becomes stronger in GLC. Having been grown, all these carbon forms are thermally stable in an oxygen-free environment up to ~550 C. However, thick GLC (>=10 microns) is mechanically unstable even at relatively low stress due to graphite-like cleavage, while QUASAM is mechanically and thermally stable in

whole examined thickness range (over 300 microns) up to ~700 C. The chemical bonds between carbon and silica networks are also become stronger with the substrate temperature Ts or accelerating voltage U, or their synergetic sum [T + F(U)] increase. The properties and applications of these carbon phases are discussed.

A-II/P33 CRITICAL PARAMETERS OF PERCOLATION IN METAL DIELECTRIC DIAMONDLIKE COMPOSITES OF ATOMIC SCALE, B.F. Dorfman, Atomic-Scale Design, Inc., USA

The silica stabilized sp2Lsp3 carbon possesses high thermal stability, diffusion resistance, it is free from macropores, but contains from 40-60% vol % of vacancies (~0.2-0.3 nm). It provides a unique dielectric matrix to form the metal-carbon Atomic-Scale Composites (ASC). The maximum metal concentration and the temperature stability of ASC depend on atom radius and metal-matrix interaction. Some metals may be introduced in carbon matrix during its growth over 50 at% while the mechanical properties of matrix and iniform random distribution of metals are preserved. As a result, the Metal-Dielectric Percolation is observed at first in few Me-C ASC.

The theoretical value of the percolation threshold range of metal concentration metal-carbon ASC may be prospective sensor materials due to non-linear transport phenomena. At a higher metal concentration the metal-carbon ASC become amorphous metals which posses a very high thermal-electric shock resistance and low temperature coefficient of electrical conductivity; they are also forming SHottky barriers to Si, GaAs, SiC, and presumably—to diamond. It is particularly important all these phases may be formed in one self-adjustable solid media correspondingly to a cross-sectional design.

A-II/P34 SYNTHESIS OF VARIOUS FORMS OF CARBON NANOTUBES ON LARGE SCALE BY AC ARC DISCHARGE AT LOW He PRESSURE, Zeng Huang, Zhu Ling, Hao Guangming, Sheng Rongsheng, Fullerene Institute, Wuhan University, Wuhan, Hubei, 430072, China

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM B

Epitaxial Thin Film Growth and Nanostructures

Symposium Organizers

G. RITTER, Institut für Halbleiterphysik GmbH, Frankfurt (Oder), Germany

O. TAKAI, Nagoya University, Nagoya, Japan

C. MATTHAI, University of Cardiff, Cardiff, UK

The assistance provided by
Wacker Siltronic
is acknowledged with gratitude.

SYMPOSIUM B

Tuesday June 17, 1997 — Morning
Mardi 17 juin 1997 — Matin

Session I - Growth Methods and Kinetics

B-I.1 - invited - 8:30-9:00

ATOMIC LAYER CONTROL OF DOPING DURING SiGe EPITAXY, **B.Tillack**, Institute for Semiconductor Physics Frankfurt (Oder), Walter Korsing Str. 2, 15230 Frankfurt (Oder), Germany

Atomic layer doping of P and B was realized within SiGe by Low Pressure (Rapid Thermal) Chemical Vapor Deposition, LP(RT)CVD. We control the incorporation of the dopants through surface adsorption equilibrium of PH3 and B2H6, respectively. Doping if performed by interrupting layer growth at low temperature, without source gases for the SiGe growth. As a result, atomic layer doping was achieved with doses below one monolayer at very low temperature (200°C-400°C). The temperature dependence of the incorporated dopant concentration is discussed in terms of surface adsorption/desorption equilibrium.

The results indicate atomic control of doping at very low temperatures which is essential especially for decreasing vertical dimensions of electronic devices.

B-I.2 9:00-9:15

SURFACE REACTION MECHANISM AND MORPHOLOGY CONTROL IN AlP ATOMIC LAYER EPITAXY, M. Ishii, S. Iwai, T. Ueki, and Y. Aoyagi, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-01, Japan

Atomic layer epitaxy (ALE) of III-V semiconductors has recently been extensively studied. In III-V semiconductor systems with an Al component, it is well known that the self-limiting window is narrow. In this report, surface observations of AlP ALE films were made by atomic force microscopy (AFM) in order to understand the surface reaction mechanism, and based on a reaction model, surface morphology control was shown to produce high quality ALE films.

Dimithylaluminum hydride (DMAH) and Phosphine (PH_3) were used as the group-III and -V source gases, and were alternatively introduced into a reactor. The growth temperature was 580-590°C, and the substrate was (100) ± 0.5° oriented non-doped GaP with a buffer layer grown by a conventional MOVPE. The AFM observation was carried out just after the ALE growth.

In the case of ALE with a long DMAH feeding time of 1.0 s, the grown surface is covered with small grains, while a saturated growth rate of 1 ML/cycle is obtained. Assuming an adsorbate inhibition model, this phenomenon can be explained as follows; the DMAH adsorption is avoided on almost all the surface Al atoms with the methyl adsorbate, however, the excess gas may adsorb on bare Al atoms attendant on occasional desorption of methyl, with the result that Al clusters will be formed.

In order to reduce the undesirable methyl desorption during the DMAH introduction, ALE with the DMAH feeding time of 0.5 s is carried out to improve the surface morphology. In this case, atomic steps are observed in all self-limiting conditions with 1 ML/cycle growth rate, indicating that the surface morphology control is successfully achieved and the ideal layer-by-layer growth is obtained.

B-I.3 9:15-9:30

LOW TEMPERATURE HETEROEPITAXY BY LEPECVD, C. Rosenblad, T. Meyer, E. Müller and H. von Känel, Laboratorium für Festkörperphysik, ETH Zürich, 8093 Zürich, Switzerland and A. Dommann, Neu-Technikum Buchs, 9471 Buchs, Switzerland

Low energy plasma enhanced chemical vapor deposition (LEPECVD) is a novel technique for low temperature epitaxial growth. During deposition, a low energetic DC-plasma ($E_{ion} < 10$ eV) is used to dissociate the reactive gases SiH_4 and GeH_4 and supply non-thermal energy to enhance the surface reactions on the growing film, hence allowing the substrate temperature to be lowered substantially below 600°C while still keeping the growth rates in the Å/s range. We have applied LEPECVD to the synthesis of homoepitaxial silicon films and heteroepitaxial $Si_{1-x}Ge_x$/Si superlattices on Si(100). The films have been analyzed by means of high resolution transmission electron microscopy, X-ray rocking curves and scanning tunneling microscopy. The crystal quality and surface roughness of the films is found to deteriorate strongly at ion energies above 10 eV. In contrast to homoepitaxial films which can be grown defect free at sufficiently low ion energies, the $Si_{1-x}Ge_x$/Si superlattices grown at temperatures below 600°C contain defects the exact nature of which is presently being studied. Superlattices grown at a substrate temperature of 500°C show planar abrupt interfaces. Also first results of n-type electrical doping using a flow of PH_3 diluted with H_2 will be presented.

B-I.4 9:30-9:45

SURFACE MORPHOLOGY AND ELECTRICAL PROPERTIES OF $Si_{1-x}C_x$ ON Si GROWN BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION, L. He, Northern Illinois University, Department of Electrical Engineering, 60115 DeKalb, IL, USA, Z.Q. Shi, Hughes STX Corp., Greenbelt, MD, USA, P. Han, and Y. D. Zheng, Nanjing University, Department of Physics, Nanjing, China

Epitaxial $Si_{1-x}Ge_x$ on Si has been investigated with considerable attention due to its narrower bandgap, and larger optical absorption cut-off which could be suitable for fiber-optic communications. The critical thickness of the strain layer, however, decreased rapidly with the higher Ge composition which limits the device application of $Si_{1-x}Ge_x$. The Incorporation of carbon in substitution sites can lead to the relaxation of strained $Si_{1-x}Ge_x$ alloys due to the small covalent radius of the carbon atom. In this work, $Si_{1-x}C_x$ was grown on various n and p-type doped Si substrates by rapid thermal process, very low pressure chemical vapor deposition (RTP/VLP-CVD). The growth temperatures were 650 - 700°C, and pressure was 3.5mTorr. An atomic force microscope(AFM) was used to study the surface morphology variation with the growth parameters such as substrate temperature, mass flow ratio and growth rate. It was found that the surface roughness proportional to the growth rate, and reverse proportional to mass flow ratio. Double-crystal x-ray diffraction was conducted to study the crystal structure and to estimate the C concentration. The current-voltage characteristics was also studied.

B-I.5 9:45-10:00

ULTRA THIN 3C-SiC PSEUDOMORPHIC FILMS ON Si (100) PREPARED BY ORGANOMETALLIC CVD WITH METHYLTRICHLOROSILANE, J. Hofmann and S. Veprek, Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr.4, 85747 Garching, Germany

The large lattice mismatch (≈20%) and different thermal dilatation (~8%) make the pseudomorphic growth of 3C-SiC on Si to appeare impossible. Therefore very thick films (≥20 μm) have to be grown in order to relax the interface defects and obtain good quality heteroepitaxial films [1]. In course of the study of the initial stages of the growth using a UHV-compatible CVD apparatus and in situ low energy electron diffraction (LEED) we find the surprising fact that up to several nm thin films provide LEED patterns corresponding to a 3x2 reconstructed surface (as documented in literature for 3C-SiC surfaces) and appear relatively homogenous. Increasing the thickness upon longer deposition time leads to the disappearance of the LEED pattern and pronounces surface roughening. These results indicate that using novel organometallic CVD techmque [1] might open a way towards the preparation of metastable pseudomorphic 3C-SiC films. Our current work concentrates on the question of the possibility of island growth and latteral defects such as double position boundaries, etc, in order to clarify the latteral coherence of these films.

[1] S. Veprek, Th. Kunstmann, D. Volm, B. Meyer, J. Vac. Sci. Technol., A 15, Jan./Feb. 97, in press.

10:00-10:30 **BREAK**

B-I.6 10:30-10:45

ENHANCEMENT OF 2D GROWTH OF MBE HETRO-STRUCTURES USING LASER ASSISTED MBE TECHNIQUES, A. Dimoulas and A. Christou, University of Maryland, College Park, Maryland 20742, USA and A. Georgakilas, Foundation of Research and Technology Hellas (FORTH), Heraklion, Greece.

UV Laser desorption in-situ to MBE growth effectively prepares the GaAs surfaces for MBE growth and results in two dimensional surfaces during the MBE growth of GaAs and GaAlAs. The objective for incorporating UV laser processing during the MBE growth was to attain complete desorption of hydrocarbons from the GaAs surface, and to control the growth kinetics so that two dimensional structures may result. The optical properties of the resultant undoped and lightly silicon doped GaAs layers were examined by photo luminescence, while lightly doped GaAs layers were investigated in order to understand their transport properties. The Laser assisted grown undoped GaAs layer resulted in a narrow excitonic transition. Heterostructures of GaAlAs/GaAs were also grown using laser assisted techniques for high mobility transistors. The improved 2D transport properties are correlated with TEM results. We report on the performance of structures of delta doped superlattices which were grown by laser assisted techniques. The advantage of such a structure is the elimination of long term transients which are present due to trapping of electrons by ionized donors in the AlGaAs.

B-I.7 10:45-11:00

STM-STUDY ON SILICON (100) GROWN BY MAGNETRON SPUTTER EPITAXY, B. Vögeli and H. Von Känel, Laboratorium für Festkörperphysik, ETH Hönggerberg, 8093 Zürich, Switzerland

Magnetron sputter epitaxy (MSE) is a novel technique for epitaxial growth of group IV heterostructures. Recently, magnetotransport measurements at cryogenic temperatures proved the presence of a two dimensional electron gas in modulation doped strained Si channels and thus the high quality of MSE grown films [1]. However, no direct information on the growth process itself has so far been available. We have now started to investigate the influence of the sputter parameters on the growth process for homoepitaxy of Si on Si (100) by means of a scanning tunneling microscope situated in a separate UHV chamber attached to the sputter system. In comparison to other growth techniques, MSE has a tunable average particle energy from full thermalisation up to 5 eV as an additional growth parameter. First experiments have shown, that at typical growth rates of 2 Å/sec, and with fully thermalised particles, the step structure obtained with MSE is very similar to the one known in MBE at comparable substrate temperatures. Thus, we report on the transition from 2 dimensional nucleation at 350°C to the step flow regime at high temperatures (above 600°C). Furthermore, growth at identical substrate temperature but different average partical energies was performed. The step structure does not seem to be influenced greatly as the average energy is increased. The impact energetic atoms does, however, lead to an increased surface roughness on an atomic scale.

[1] P. Sutter, D. Groten, E. Müller, M. Lenz and H. von Känel, Appl. Phys. Lett. **67**, 3954 (1995).

B-I.8 11:15-11:30

EPITAXIAL THIN FILMS OF HgCdTe ON SILICON SURFACES, G. Wisz, E. Szeregij, M. Kuzma, Instytute of Physics Higher Pedagogical School, 35-310 Rzeszow, Rejtana 16a, Poland, R. Ciach, J. Morgiel, Institute of Metallurgy, Polish Academy of Sciences, Cracow, Poland, T.Ya. Gorbach, S.V.Svechnikov, Institute of Semiconduktor Physics, National Ukrainian Academy of Sciences, Prospekt Nauki 45, Kiev-28, 252650 Ukraine

Anisotropically etched microrelief (AEMR) surfaces of Si have very good properties for epitaxial growth of semiconduktor films. Ultrathin films (thickness 100 nm and less) of Hg_xCd_{1-x} were deposited on AEMR Si substrates by the laser ablation method. Transmision and scanning electron microscopy with a high magnification (10^6) were used for investigations of the composition and the morphology of the films. HgCdTe films have been prepared under various deposition conditions e.g. different substrate-target distances, crystallographic orientations of the surface for various parameters of the anisotropic chemical eaching, different laser parameters. From these measurements the dynamics of the growth was determined. Films reproduce exactly the texture of the surface. The film growth process is the result of a layer by layer mechanism with step migration, without nucleation. Periodic substructures were obtained under some special deposition conditions. The method applied in this work gives the possibility to produce heterostructures. The quality of some heterostrostructures were investigated using electron transmission microscopy technique.

B-I.9 11:30-11:45

THE USE OF ULTRASOUND RADIATION FOR THE PREPARATION OF AMORPHOUS MATERIALS HAVING NANOMETER SIZE PARTICLES, A.Gedanken, Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

The implosive collapse of a bubble created in the liquid is the main event that happens when ultrasound radiation passes through a liquid. This collapse, which occurs in less than a nanosecond, causes very high temperatures (5000K-25000) to develop in the liquid. The outcome of this collapse is very high cooling rates ($>10^{12}$K/sec) that prevent the crystallization of the sonochemical reaction products. The number of molecules that participate in this event is limited and therefore the products of the sonochemical reaction are not only amorphous, but they are also of nanometer size. Using these ideas, which were first described by Suslick [1], we have prepared amorphous metals (Fe, Ni, Co and Pd), amorphous alloys (Fe/Ni, Ni/Co), amorphous metal oxides ($NiFe_2O_4$, $CoFe_2O_4$), amorphous metal nitrides (Fe_3N and Fe_4N) and metal-polymer composite materials (Fe-polymethyl acrylate). In all the cases the products were obtained as powders having nanometer size particles. The amorphous nature of these products was detected by X-ray diffraction, electron diffraction patterns, as well as by DSC (differential scanning calorimetry) studies. We have demonstrated [2] that the particle size of these products can be controlled.

These products serve as catalysts in various chemical reactions and they are also used as substrates for self-assembled monolayer coatings by chromophores such as thiols, alkyltrichlorosilane and others. The magnetic properties of these coated particles are studied for «tailoring» magnetic properties. Our ability to create colloidal solutions using these nanoparticles make them of importance as magnetic fluids.

[1] K.S. Suslick, S.B. Choe, A.A. Cichowlas, M.W. Grinstaff, Nature, 353, 414 (1991).

[2] X. Cao, Yu. Koltypin, R. Prozorov, A. Gedanken, J. Mater. Res. 10, 2952 (1995).

B-I.10 11:45-12:00

TWO-DIMENSIONAL LOCATION CONFINMENT OF CRYSTAL Si GRAIN FOLLOWED BY EXCIMER-LASER MELTING OF Si THIN FILMS, R. Ishihara, P.C. van der Wilt, DIMES, Laboratory of ECTM, TU-Delft, Feldmannweg 17, P.O. Box 5053, 26000 GB Delft, The Netherlands

A single Si grain with a diameter of 1 μm has been successfully formed at edge of well by excimer-laser crystalliztion method. CVD a-Si (70 nm) / SiO_2 (1μm) / c-Si substrate structure in which some parts have thin (500 nm) SiO_2 film with areas of $(4\mu m)^2$ and $(2.5\mu m)^2$ squares was prepared. XeF excimer-laser light was irradiated with an energy density of 370 mJ/cm^2. From the cross sectional TEM image, it can been seen that the grain near the corner of the hole has a size of about 1μm, much larger than in the hole and also away of the hole (50nm for both). The hillock lying at the centre side of the grain's edge is correspond to disk-like features in centre of the $(2.5\mu m)^2$ hole observed in surface image by optical microscope. It can be seen also that the crystalinity at the wall of the hole is degraged. This result was caused from the insufficient laser-light illumination due to effectively thick Si film at the area. From these results, it can be concluded that the grain growth near the corner of the hole was enhanced by lateral heat flux from the inside of the hole to wall the area.

12:00-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Session II - Simulation

B-II.1 - invited - 14:00-14:30

COMPUTER SIMULATION OF ADATOM DYNAMICS ON SiC(001) SINGLE STEPPED SURFACES, Q. Bhatti and **C.C. Matthai,** Dept of Physics and Astronomy, University of Wales, Cardiff, CF2 3YB, UK

Silicon carbide has attracted much interest in recent years because it is a wide gap material displaying a high breakdown field and high electron saturation drift velocity. This coupled with recent advances in growth techniques of SiC has made it a strong candidate material for high-temperature, high power devices. In order to grow high quality single crystal wafers of SiC, one needs to have a good understanding of the dynamics of deposited atoms on the crystal surface. In many experimental studies of layer by layer growth, it has been observed that the step edges play an important role in the growth evolution. Molecular dynamics is a technique that can give detailed information about adsorption and diffusive motions. Although there have been many studies of the adsorption and dynamics on flat surfaces, stepped surfaces have only recently become the subject of research. We have performed molecular dynamics simulations of the adsorption and migration of Si and C adatoms on the single stepped SiC (001) surfaces. Three different step configurations were considered, and for each, the diffusion paths as well as the activation energies for diffusion were determined. The main finding of the work is that the presence of A-steps would be most conducive to Stanski-Krastanov growth.

B-II.2 - invited - 14:30-15:00

SIMULATION OF ATOMIC SCALE SURFACE MIGRATION IN HOMOEPITAXIAL GROWTH USING NEW EAM POTENTIALS FOR FCC METALS, **J.-I. Takano**, Y. Kogure and M. Doyama, Teikyo University of Science & Technology, Department of Materials, Uenohara, Yamanashi 409-01, Japan; O. Takai, Nagoya University, Department of Materials Processing, Furocho, Chikusa, Nagoya 464-01, Japan

The binding energies of gold, silver and copper adatoms and their clusters to each (111) surface have been calculated by use of a newly determined N-body embedded atom potential. The binding energy E_N of an N-adatom cluster can be roughly written as $E_N=3NE_1+mE_2$, where $3E_1$ is the binding energy of a single adatom to the (111) surface and m is the number of bonds within the cluster and E_2 is the binding energy of the bond within the cluster.

We have simulated the motion of a ledge atom, the growth of a kink, the stepdown motion of an atom on each (111) surface by use of an N-body embedded atom potential and the Molecular Dynamics method.

The results of Thin film growth process using the Monte Carlo simulation have been compared with those using the Molecular Dynamics method.

B-II.3 15:00-15:15

CLUSTER-SHEARING AS A NOVEL DIFFUSION MECHANISM OF CLUSTERS ON FCC METAL (111) SURFACES, V. Chirita, E.P.Münger, J.-E. Sundgren, Thin Film Physics Division, Linköping University, Linköping, 581 83, Sweden and J.E. Greene, Coordinated Science Laboratory, University of Illinois, 1101 Springfield Ave., Urbana, Illinois 61801, USA

We use molecular dynamics and the embedded-atom-method to follow the dynamics of small Pt clusters on Pt(1 11). Our simulations reveal a novel diffusion mechanism, which we term double-shearing, involving the successive shearing motion of different portions of the clusters, leading to diffusion over several lattice constants within picoseconds. Using simple bond-counting and energetic arguments, we establish that for clusters with up to tens of atoms, the activation energy for double-shearing has values between ~ 0.9 and 1.5 eV. For clusters with only a few atoms, this mechanism competes with that of diffusion via concerted motion of all cluster atoms, and so contributes significantly to the enhanced cluster mobilities observed during film growth. However, as clusters increase in size, double-shearing compares with other known diffusion mechanisms. Double-shearing is shown to be the preferred diffusion mechanism for clusters of elongated and circular shapes, as well as for dentritic/fractal islands of medium size.

B-II.4 15:15-15:30

MONTE CARLO SIMULATION OF MISMATCH RELAXATION AND ISLAND COALESCENCE DURING HETEROEPITAXIAL GROWTH, M.Djafari Rouhani, R. Malek and D. Estève, Laboratoire d'Analyse et d'Architechture des Systèmes, CNRS, 7 av. Colonel Roche, 31077 Toulouse, France.

We have studied the growth of lattice mismatched semiconductors through the association of the Monte Carlo technique and the Valence Force Field (VFF) approximation. The Monte Carlo technique monitors the atomic motion in the deposited layer using the Arrhenius law and taking into account the impingment of atoms from the gas phase, intralayer and interlayer migrations of atoms and evaporation from the surface. The VFF approximation is used as an energy model to determine the local strain and stress inside the deposited layer by minimizing the total energy. This is performed after each single atomic motion. The strain is assumed to enhance the atomic motion by lowering the activation energy barrier related to the particular event.

Results concerning the case of large lattice mismatches are presented. We have observed the formation of 3D islands showing (111) facets, very soon during the growth. The relaxation of the deposited layer has been investigated and we have shown that complete relaxation may occur inside the islands in a few atomic layers. Further growth leads, under some experimental conditions, to the coalescence of the islands where we have identified favorable sites for the formation of misfit dislocations. We have also shown that vacancies can be formed in the bulk of the deposited layer to relax the local strain.

B-II.5 15:30-15:45

A KINETIC MONTE CARLO STUDY OF THE MORPHOLOGY OF SI THIN FILMS DEPOSITED ON Si(100) AT VARYING ANGLES OF INCIDENCE, S.W. Levine, J.R. Engstrom and P. Clancy, School of Chemical Engineering, Cornell University, 120 Olin Hall, Ithaca NY 14853, USA

Two- and three- dimensional Kinetic Monte Carlo simulations are used to model the deposition of a hyperthermal molecular beam at varying angles of incidence. The simulations incorporate incident atom - substrate interactions, many layer growth and, for the three-dimension model, mimic deposition and growth of Si on a Si(100) substrate. At high angles of incidence, the formation of porous columnar structures seen in the 2-D simulations transform into «flakes» in the three-dimensional model. While the growth angles of the columns and flakes follow the same general trends as previous ballistic deposition simulations with respect to the formation of porous films, current theories do not quantitatively reflect the simulation results. Increasing the substrate temperature increases the widths of the columns and flakes in the direction perpendicular to the path of the beam. Higher substrate temperatures also allow the grown film to remain defect-free for a longer times before columnar structure begins. The effect of sample rotation during deposition of the growth morphology will be shown to produce variations on the columnar structure.

B-II.6 15:45-16:00

COMPARATIVE STUDY OF (001) SURFACE RELAXATIONS OF SOME TITANATES, S. Dorfman, Dept. of Physics, Technion, 32000 Haifa, Israel; D. Fuks, Mat. Eng. Dept, Ben-Gurion Univ. of the Negev, P.O.B. 653, 84105 Beer Sheva, Israel and E. Kotomin, Inst. of Solid State Phys., Univ. of Latvia, 1063 Riga, Latvia and Inst. of Phys. and Astr., Aarhus Univ., 8000 Aarhus-C, Denmark

(001) surface relaxations of the cubic perovskite $SrTiO_3$ and $BaTiO_3$ crystals have been studied in the framework of the shell model. The positions of atoms in several surface layers embedded into the electrostatic field of the remainder of the crystal were calculated. Ti^{+4}, Sr^{+2}, Ba^{+2} and O^{-2} ions in six near-surface layers are displaced differently from their crystalline sites. Such effects create the so-called surface rumpling, a dipole moment and the electric field in the near-surface region. Calculated atomic displacements were compared with the LEED experimental data and showed good agreement.

Our simulations have demonstrated that the cubic perovskite $SrTiO_3$ crystals reveal surface polarization and accompanied by the presence of relevant electric field. This arises due to a disturbed force balance accompanying the surface creation and affect 5-6 planes below the surface. In other words, the surface can serve as important factor imposing a long-range order in paraelectric $SrTiO_3$. As discussed in the literature the (001) surface turns out to be ferroelectric with properties different from the bulk material.

16:00-16:30 **BREAK**

Session III - Nanoparticles and Dots

B-III.1 - invited - 16:30-17:00

LATERAL FORCES AND ATOMIC DESORPTION INDUCED BY THE ELECTRIC FIELD CREATED BY STM TIPS ON METAL SURFACES, F. Flores, **N. Mingo**, Departamento de Fisica, Facultad de Ciencias, Universidad Autonoma de Madrid, Madrid 28049, Spain

The effect of the electric field created by an external voltage applied at the Scanning Tunneling Microscope interface is analyzed by means of a self-consistent LCAO approach. The theoretical method presented in this talk allows us to analyze realistic tip-sample geometries without introducing spurious 2-dimensional periodicities. We present results for both the lateral forces acting on different alkali atoms adsorbed on an Al(100) sample, and the atomic desorption potential induced by the external voltage. The evaporation fields for Na and K are calculated for different tip-sample distances, in good agreement with the experimental evidence.

B-III.2 17:00-17:15

SELF ORGANISED GROWTH AND ULTRAFAST ELECTRON DYNAMICS OF METALLIC NANOPARTICLES, A. Stella and P. Tognini, Università di Pavia, Italy; A. Cavalleri and M. Malvezzi, Università di Pavia, Italy; M. Nisoli and S. De Silvestri, Università di Milano, Italy; P. Cheyssac and R. Kofman, Université de Nice Sophia Antipolis, France

The electron dynamics in metallic nanoparticles (in our case Sn, Ga) subjected to fs pulses presents new and interesting aspects as a function of size. As a matter of fact, by reducing the size from ~ 20 down to ~1 nm, we progressively go: i) first below the light penetration depth (~ 13-14 nm) and then ii) below the electron mean free path (~ 5 nm). This affects drastically the behavior of the electron dynamics in the nanocrystals. More precisely, we observe: with i) the disappearence of coherent acoustic oscillations generated by the fs pulses and clearly observable at large sizes; with ii) the size dependence of the electron thermalization inside the nanoparticles.

The above mentioned effects have been studied both in the solid and liquid state of the nanoparticles.

In order to observe and study such phenomena it is essential that the nanocrystals are grown in a wide size range, with a regular (near spherical) shape and a relatively low size dispersion. The main aspects of such a growth technique will be illustrated in this communication.

B-III.3 17:15-17:30

ELECTRONIC STRUCTURE OF Ag NANOPARTICLES DEPOSITED ON Si(100), Z. Paszti, G. Petö, Z.E. Horvath, A. Karacs, KFKI Research Institute for Materials Science, 1525 Budapest, P.O.Box 49, Hungary and L. Guczi, Department of Surface Chemistry and Catalysis, Institute of Isotopes, 1525 Budapest, P.O.Box 77, Hungary

Small particles in the 1-10 nm size range have properties significantly different from bulk materials. As these are mostly related to the electronic structure, any information on the size dependent changes of the valence band density of states can be very useful for both basic understanding and possible applications. In order to investigate the size sensitivity of the valence band of noble metals, an island-like silver film was deposited onto a Si substrate. Then the sizes of the islands were diminished by low energy ion bombardment. Since Ag does not interact chemically with Si, silicidation can be excluded during the ion bombardment. This sputtering process was monitored by in situ UPS and XPS measurements. The island sizes were determined by TEM before and after the sputtering process. Islands with 100 nm dimensions show bulk electronic structure. With decreasing particle size the lowest binding energy peak of the 4d band gradually decreased, showing that this is the most size sensitive part of the valence band of the silver. The lack of the Fermi edge and a single 4d peak is characteristic of the valence band for silver islands with lateral sizes of 4-6 nm and height of 2-3 nm.

B-III.4 17:30-17:45

ELECTRON DYNAMICS IN SILVER NANOPARTICLES, V. Halté, J.-C. Merle, A. Daunois, M. Albrecht, G. Versini, J.-Y. Bigot, IPCMS, 23, Rue du Loess, 67037 Strasbourg Cedex, France

We have studied the electron relaxation dynamics in the vicinity of the Mie plasmon resonance of silver nanoparticles embedded in a glass matrix. The measurements have been performed at room and liquid helium temperatures using the second harmonic of a tunable amplified Titanium Sapphire laser source delivering 100 fs pulses.

The time-resolved differential transmission has been investigated as a function of pump power and excitation wavelength. The results show that the electron-lattice thermalization time T_1 increases with increasing pump power in agreement with the electron relaxation observed in thin films of noble metals. When the laser wavelength is tuned to the plasmon resonance this thermalization is slower as compared to an off-resonance excitation. This behavior is specific to the resonance of the nanoparticle. A detailed study of the signal characteristics at 0 and 10 ps delays also displays a non-trivial behavior at the resonance. This suggests a description of the plasmon dynamics that goes beyond the RPA model.

B-III.5 17:45-18:00

STRUCTURES AND PROPERTIES OF NANO-PARTICLES SYNTHESIZED BY HYDROGEN ARC PLASMA METHOD, Z.L. Cui and Z.K. Zhang, Research Center of Nanostructured Materials, Qingdao Institute of Chemical Technology, 266042 Qingdao, China

Nanometer size metal particles were synthesized by a hydrogen arc plasma method which possesses the advantages of higher productivity, lower electric consumption and continue working. The microstructures and properties of the nano-particles were studied by TEM, HRTEM, XRD and MS experiments.

The results of the research show that

(1)the shape of the nano-particles are of polyhedron and average particle size is about 50 nm .

(2)the metal nano-particles possess special different oxidation behavior from conventional coarse particles.

(3)the nano-particles possess hydrogen storage function.

(4)the nano-composite particles can be synthesized by this method and possess special shell structure .

B-III.6 18:00-18:15

SEMIMAGNETIC SEMICONDUCTOR CdMnTe THIN FILMS AND NANOSTRUCTURES GROWN BY LASER ABLATION, A. Perrone, A. Luches, Dept. of Physics, University of Lecce, 73100 Lecce, Italy, A. I. Savchuk, I. D. Stolyarchuk, V. I. Fediv, Dept. of Phys. Electronics, University of Chernivtsi, 274012 Chernivtsi, Ukraine and P. I. Nikitin, General Physics Institute, 117942 Moscow, Russia

The $Cd_{1-x}Mn_xTe$ thin films were grown from polycrystalline or single crystal targets with compositions x=0.25; 0.43 by using an XeCl excimer laser (λ=308 nm). For the first time method of laser ablation was used also for fabrication of zero-dimensional structures on the base of semimagnetic semiconductor CdMnTe. Nanocrystals of $Cd_{1-x}Mn_xTe$ (x=0.25) embedded in glass matrix were grown by ablation of semiconductor and SiO_2 targets. X-ray diffraction, optical and magnetooptical studies have been carried out on the obtained thin films and nanostructures. The observed peculiarities of the magnetooptical effects (Faraday rotation and spin splitting) can be attributed to the exchange interaction of the band electrons with the magnetic ions as well as to confinement effect of the exciton states in nanometer-size systems.

This work is supported by Nato Lincage Grant (No.950429).

Wednesday June 18, 1997
Mercredi 18 juin 1997

Morning
Matin

Session III - Nanoparticles and Dots (continued)

B-III.7 - invited - 8:30-9:00

SEMICONDUCTOR QUANTUM DOTS, **M. Grundmann**, N.N. Ledentsov, F. Heinrichsdorff, A. Krost, D. Bimberg, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany, V.M. Ustinov, P.S. Kopev, Zh.I. Alferov, A.F.Ioffe Institute, St.Petersburg, Russia, A.O.Kosogov, U.Gösele, MPI für Mikrostrukturphysik, Halle/Saale, Germany

Semiconductor quantum dot (QD) layers can be fabricated using self-organization phenomena during Stranski-Krastanov growth. The island formation is driven by the lattice mismatch and relaxation of elastic energy. Ensembles with homogeneous QD size and shape can only be explained by taking into account surface and edge energies.

High area density (~10^{11} cm^{-2}) arrays and multiple vertical stacks of small dots with high quantum efficiency can be fabricated using MBE and MOCVD. While details of the growth mechanism and QD ordering are different, InGaAs/GaAs/AlGaAs lasers with low threshold current density and high T_c due to the delta-like zero-dimensional electronic density of states have been fabricated using both preparation methods.

B-III.8 9:00-9:15

THERMAL STABILITY OF STRAINED InGaAs/GaAs QUANTUM DOT SUPERLATTICE, Dong Pan, Y.P. Zeng, M.Y. Kong, Material Center, Institute of Semiconductor, Chinese Academy of Science, P.O. Box 912, Beijing 100083, P.R. China

The thermal stability of a dislocation-free InGaAs/GaAs quantum dot (QD) superlattice grown by MBE has been investigated by cross view transmission electron microscopy (TEM), low temperature photoluminescence (PL) and x-ray double crystal diffraction. After subjected to rapid thermal annealing (800°C,15s), the strain in the quantum dots is found to decrease. The PL spectrum of the annealed sample shows a energy blueshift of 10 meV and the increase of luminescence intensity from quantum dot and GaAs matrix. The interface quality becomes poor due to indium atoms diffusion out from QDs. X-ray diffraction shows that the number of satellite peaks is reduced with the decreased intensity.

B-III.9 9:15-9:30

MBE-GROWTH OF QUANTUM-SIZE Si-DOTS ON SiC(0001)MONITORED BY RHEED, A. Fissel, K. Pfennighaus and W. Richter, FSU Jena, Inst. für Festkörperphysik, M.-Wien-Platz 1, 07743 Jena, Germany

We have investigated the self-assembly of Si quantum-size (10 to 15nm) dots on SiC(0001) by RHEED at substrate temperatures between 700 and 1150K. Due to the large misfit (20%) Si grows in Stranski-Krastanov mode on SiC. The deposition of up to two monolayers results in two-dimensional growth. During further deposition two different growth mechanisms were observed below and above 900K, resp. Below 900 K the occurence of RHEED intensity oscillations of the specular beam indicates a 2-dimensional growth mode. However, during growth interruption the specular beam intensity decreases and simultanously 3-dimensional Si-bulk diffraction pattern occurs indicating an increasing surface roughness due to the formation of Si clusters. The intensities of both the specular beam and the (222)-Si-bulk spot change continuously to a constant value. AFM investigations show that the constant intensity corresponds to an equilibrium cluster structure. The time to reach this value is strongly dependent on temperature. Above 900 K 3D-nucleation takes place within a submonolayer range and the constant values are rapidly reached. From that we have analysed the dynamic processes toward the cluster formation which are important because kinetic limitation may result in different final morphologies. At higher temperatures the surface diffusion is the dominant process with a low activation energy of ~ 0.6 eV. At lower temperatures the situation is more complex because it involves the dissolution of 2- dimensional structures resulting in a higher activation energy of ~ 2eV.

B-III.10 9:30-9:45

OPTICAL GAIN OF CDS QUANTUM DOTS EMBEDDED IN 3D PHOTONIC CRYSTAL, Yu.A. Vlasov(1,2), K. Luterova(1,3), I. Pelant(1,3), B. Honerlage(1), V.N. Astratov(2), A.A. Kaplyanskii(2), V.N. Bogomolov(2),(1)IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France, (2)A.F.Ioffe PTI, St.-Petersburg, Russia, (3)Institute of Physics, AVCR, Prague, Czech Republic

Photonic crystals (PC), i.e. three-dimensional periodic dielectric structures with periodicity matching the optical wavelength, can possess photonic band gaps (PBG), namely, the frequency stop-bands in which the density of photonic states tends to zero. Redistribution of the photonic modes in the vicinity of PBG can result in a total suppression or enormous enhancement of the spontaneous emission rate of the active media, placed within the PC.

PC used in this study was synthetic opal, composed of submicron silica spheres, close-packed in a 3D FCC structure with a period of 200nm, which exhibit a photonic stop-band centred at 600 nm. CdS quantum dots (QD) were embedded in interstitials between the silica spheres by vapor phase synthesis. Optical gain was measured by the variable-stripe-length method using UV excitation of a XeCl excimer laser.

The optical gain of an active material inside the 3D PC was observed for the first time. Unlike typical gain spectra of CdS QD in glass matrices, displaying the maximum gain at the energies of the first quantum-confined transitions, the QD embedded in PC exhibit the maximum gain at the high-frequency edge of the photonic stop-band (2.1 eV) far below the absorption edge of the semiconductor. Observed effects can be ascribed to decrease of photonic group velocity at the edges of the stop-band and to a corresponding increase of the optical path-length resulting in an enhancement of the effective optical gain.

B-III.11 9:45-10:00 NANOCLUSTER COMPOSITE THIN FILMS FOR INTEGRATED NON-LINEAR OPTICAL APPLICATIONS, R. Serna, J.M. Ballesteros, J. Solis, and C.N. Afonso, Instituto de Optica, C.S.I.C., 28006 Madrid, Spain, A.K. Petford-Long, Department of Materials, Univ. of Oxford Oxford OXl 3PH, UK, R.F.Haglund Jr.and D.H. Osborne, Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37325, USA

Non-linear optical materials made of metal nanoclusters embedded in dielectric matrixes exhibit very large third order susceptibilities. However, the fabrication of such materials in waveguide configuration for their use in integrated optoelectronic devices is still a major challenge. We report a new procedure which produces metallic nanoclusters of controlled size embedded in a dielectric thin film in a single step process: pulsed laser deposition. The films consist of Cu nanocrystals embedded in an Al_2O_3 matrix and show excellent non-linear optical properties.

The films are deposited in vacuum,on glass and carbon-coated mica substrates. Ablation is performed by means of deposited an ArF excimer laser (193 nm, 2-3 J/cm^2). The Al_2O_3 is ablated first, leading to the deposition of a continuous layer. Then Cu is ablated during a much shorter time and nanoparticles are formed and deposited on top of the Al_2O_3 layer. This procedure of alternate deposition is repeated up to five times. The structural properties of the films are analyzed by high resolution transmission electron microscopy. The resulting Cu nanocrystals are 2-5 nm in diameter distributed randomly in the matrix.The nanocrystals size can be varied by changing the number of pulses applied to the Cu target. The third order non-linear susceptibility is characterized by the z-scan technique. The linear absorption has been also measured.

10:00-10:30 **BREAK**

Session IV - Atomic Scale Characterization

B-IV.1 - invited - 10:30-11:00 MICROSCOPIC INVESTIGATION OF DIFFUSION, **A. Ourmazd,** Institute for Semiconductor Physics Frankfurt (Oder), W. Korsing Str. 2, 15230 Frankfurt (Oder), Germany

Within a decade, silicon devices will be less than fifty atomic planes deep. To make the manufacture of such devices economically viable, billions must be fabricated simultaneously with high yield. This implies unprecedent microscopic control of important solid-state processes in the immediate proximity of the surface. I will descrie how quantitative electron microscopic techniques can shed light on near-surface, non-steady-state diffusion processes.

B-IV.2 11:00-11:15 NANOSTRUCTURE OF ZnO THIN FILMS PREPARED BY REACITIVE RF MAGNETRON SPUTTERING, O. Takai(1), M. Futsuhara(2), G. Shimizu(1), C.P. Lungu(1), J. Nozue(2), (1)Department of Materials Processing Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan, (2)Paint Design Institute, Nippon Paint Co. Ltd., 1-15, 4 Chome, Minamishinagawa, Shinagawa-ku, Tokyo 140, Japan

We have prepared ZnO thin films by reactive rf magnetron sputtering and studied their nano-structures using some analytical techniques such as, X-ray diffractometry (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

The ZnO thin films were deposited onto sapphire and quartz glass substrates in Ar-O_2 mixtures. In this study we mainly studied effect of the substrate temperature, which varied from room temperature to 873K, on structural properties of the films. The total flow rate was maintained at 10 sccm and O_2 flow, rate was fixed at 5.0 sccm. The gas pressure was constant at 1.0 Pa. The distance between the substrate and the target was 70 mm, and rf power was kept at 75 W.

The ZnO film prepared both on quartz glass and on sapphire substrates showed c-axis preferred orientation which meant that c-plane was parallel to the substrate. The preferred growth became remarkable with increasing the substrate temperature. TEM and AFM observation revealed that nano-structure and surface morphology of the ZnO films deposited on sapphire substrates much differed from the films deposited on quartz glass substrates. The epitaxial growth of ZnO films in reactive rf magnetron sputtering was observed.

B-IV.3 11:15-11:30 ATOMIC SCALE CHARACTERIZATION OF SEMICONDUCTORS BY IN-SITU REAL TIME SPECTROSCOPIC ELLIPSOMETRY, P. Boher and J. L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France

Spectroscopic ellipsometry has long been recognized as a powerful non destructive technique to characterize thin films and multilayers at nanometric scale. In the proposed paper, we want to present a new kind of Real Time Spectroscopic Ellipsometer (RTSE), especially designed for process control. The RTSE is a rotating polarizer instrument coupled with a prism spectrograph. The dispersed light is focused on a low amplified intensifier and detected with a multichannel silicon photodiode array. After amplification the signals are transmitted to a PC through a Digital Signal Processor (DSP) card. The DSP interface allows ten measurements per second on 512 pixels with very good signal to noise ratio. The spectral range extend from 1.5 to 5 eV with a resolution better than 300. During a measurement the processor of the PC is in fact only used for the transfer of the precalculated data (tan Ψ and cos Δ or pseudo optical constants). In this way, data analysis can take place on the previous measurement during the current acquisition allowing real process control. The proposed paper will present in details the RTSE instrument and some results obtained on the growth of semiconductors

B-IV.4 11:30-11:45

INVESTIGATION OF THIN AL LAYER GROWTH WITH IN SITU INFRARED SPECTROSCOPIC ELLIPSOMETRY, A. Hausmann, G. Weidner, M. Weidner, G. Ritter, Institute for Semiconductor Physics, Walther-Korsing-Str. 2, 15230 Frankfurt (Oder), Germany

We have investigated the metalorganic CVD with DMAH (Dimethylaluminiumhydride) of Al layers on sputtered TiN, CVD TiCN, and SiO_2. We have used the high sensitivity of a phase modulated infrared spectroscopic ellipsometer (IREL) to observe the early stages of Al growth. The spectral range of the IREL is from 930 cm^{-1} to 4500 cm^{-1}, the resolution is 8 cm^{-1} and a typical measuring period takes 30s.

The time sequences of the IREL delta values at a suitable wavenumber (e.g. 2600 cm^{-1}) show characteristic features during deposition which correspond to the surface structure at different growth stages (incubation, nucleation, island growth, coalescence, and growing roughness).

The IREL data helped us to find a strong effect of growth temperature (150°C to 250°C) on the nucleation behaviour of Al growth, while DMAH partial pressure (1 µbar to 10 µbar) influences also the layer thickness at coalescence.

Al growth is very sensitive to substrate conditions. The Al layer quality can be improved by using CVD TiCN layer from TDMAT (Tetrakisdimethylaminotitanium) as substrates. A TDMAT gas treatment of SiO_2, substrates allows the growth of Al on such substrates without any interlayer between Al and SiO_2.

We have demonstrated the applicability of IREL measurements for the investigation of early stages of thin Al layer growth.

B-IV.5 11:45-12:00

SURFACE WAVES AS A TOOL FOR THE STUDY OF PHASE TRANSITION OF NANOPARTICLES, P. Cheyssac, Y. El Fidali, R. Kofman, Laboratoire de Physique de la Matière Condensée (UMR 6622), Université de Nice-Sophia Antipolis. 06108 Nice Cedex 2, France, and A. Stella, Universita di Pavia, Italy

Electromagnetic surface waves propagates along the interface between a thin metallic film and a dielectric medium and then are highly sensitive to changes in the properties of the involved media.

In this communication, we will give a brief outline of the principles of the optical technique based upon Attenuated Total Reflexion. A distribution of tin nanoparticles, sizes ranging down to 1 nm, is embedded in a dielectric medium deposited onto the metallic film which guides the surface waves.

We present some results which show that melting and freezing of such small particles can be studied with ATR. The influence of the distance between the particles and the interface will be discussed.

B-IV.6 12:00-12:15

HIGH PRECISION DEPTH PROFILING OF ARGON AND NITROGEN ION ETCHING-INDUCED DAMAGE IN AN AlGaAs/GaAs MULTIPLE QUANTUM WELL STRUCTURE, K. Otte, F. Frost, A. Schindler, F. Bigl, Institute for Surface Modification, Permoserstr. 15, 04313 Leipzig, Germany and G. Lippold, V. Gottschalch, R. Flagmeyer, University of Leipzig, Linnestr. 3, 04103 Leipzig, Germany

In this study we have utilized confocal photoluminescence (PL) spectroscopy on an $Al_{0.35}Ga_{0.65}As$/GaAs multiple quantum well (MQW) structure to compare the damage induced by the standard dry etching technique with argon and the «less damaging» etching with nitrogen. A high depth resolution of almost 2nm has been achieved with this method using a MQW structure with monolayer thickness, a high stretching of the material depth along the surface of the beveled section etched with 500 eV nitrogen and argon ions and the confocal PL measurement.

It has been shown that the nitrogen etching process causes significantly less deterioration on QW PL yield and thus a lower defect concentration compared to the argon etching process. A model including diffusion effects has been used for the interpretation of the experimental results and yields a value for the defect diffusion coefficient of $\sim 4 \times 10^{-15} cm^2/s$ and $\sim 16 \times 10^{-15} cm^2/s$ for nitrogen and argon etched samples, respectively. The results show a strong correlation with RBS/Channeling measurements.

12:15-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-Midi

Poster Session I

14:00-16:00 See programme of this poster session p. B-20 to B-24.

16:00-16:30 **BREAK**

Session V - Semiconductor Interfaces and Quantum Wells

B-V.1 - invited - 16:30-17:00

REFLECTANCE ANISOTROPY SPECTROSCOPY AND THE GROWTH OF LOW-DIMENSIONAL MATERIALS, **Z.Sobiesierski,** DI Westwood, Dep. of Physics and Astronomy, University of Wales College Cardiff, PO Box 913, Cardiff, UK

Reflectance anisotropy spectroscopy (RAS) has proved itself to be extremely sensitive to both surface reconstruction and ultrathin coverages of material on semiconductor surfaces. This in-situ technique therefore lends itself to monitoring the formation of low-dimensional systems in a wide range of growth environments. The following systems have been studied under molecular beam epitaxy (MBE) conditions:

(i) the deposition of sub-monolayer coverages of Si, to form Si δ-layers within GaAs,

(ii) the As/P exchange reaction which leads to the formation of InAs surface quantum wells on the InP(001) surface,

(iii) the self-organised growth of InAs quantum dots via strain relaxation of ultrathin layers (<2ML) of InAs deposited on the GaAs(001) surface,

(iv) the kinetics of hydrogen desorption from vicinal Si(001) surfaces.

In our studies of Si/GaAs, it has been possible to deduce both that RAS is sensitive to coverages ≥ 0.005 ML Si/GaAs, and to estimate the level of activity of Si donors within a single δ-plane. Analysis of time-resolved RAS measurements has led to: an activation energy of 1.23±0.05 eV being determined for the As/P exchange reaction on InP(001); a detailed study of the conditions which influence InAs island formation on GaAs; and the suggestion of a new desorption pathway for H on vicinal Si(001) surfaces.

B-V.2 17:00-17:15

GROWTH AND NANOSTRUCTURE OF InN THIN FILMS DEPOSITED BY REACTIVE MAGNETRON SPUTTERING, O. Takai, K. Ikuta and Y. Inoue, Department of Materials Processing Engineering, Nagoya University, Nagoya 464-01, Japan

InN is one of the less-studied III-V compound semiconductors, probably because the considerable difficulties were encountered in its preparation. It has the wurtzite crystal structure with lattice constants a = 0.353 nm and c = 0.569 nm and the direct energy gap of 1.9 eV. Because of this energy gap, InN has potential applications for visible-light opto-electronic devices. InN was also found to show electrochromic behavior.

InN is known to begin dissociation into its elements at 620°C in vacuum, and the equilibrium dissociation pressure of InN is almost 1 atm at 500°C and rises steeply as a function of the temperature. Therefore, lower temperatures are essential for deposition and crystal growth of InN. Plasma processes have possibility to carry out the low temperature synthesis of InN. In this study InN thin films were deposited by reactive magnetron sputtering onto sapphire, silicon and glass substrates and their structure was analyzed with transmission electron microscope and atomic force microscope. Effects of sputtering conditions such as composition of sputtering gas, gas pressure and substrate temperature on the crystal growth of InN were studied.

B-V.3 17:15-17:30

OPTICAL NONLINEAR PROPERTIES OF $Cd_{1-x}Zn_xTe$ EPILAYERS GROWN ON (100) GaAs BY PULSED LASER DEPOSITION, D. Ohlmann, J.L. Deiss, J.L. Loison, M. Robino, G. Versini, IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France

$Cd_{1-x}Zn_xTe$ is a variable gap II-VI ternary compound which offers a large potential of tunability of the band gap and of the lattice parameter. Epilayers of variable composition were grown by pulsed laser deposition on oriented (100) GaAs substrates by using cold-pressed targets obtained by mixing fine grained ZnTe and CdTe powders. The structural and morphological quality of these layers were controlled and analysed by x-ray diffraction (XRD) and atomic force spectroscopy (AFM).

The linear and nonlinear optical properties of these films of variable composition are studied. The linear transmission spectra show interference fringes of the Fabry-Perot formed by the two surfaces of good optical quality of the sample. Nonlinear properties are studied by pump and probe measurements. The transmission of the sample decreases when it is excited by an intense laser beam. This induced absorption is attributed to impurity or dislocation levels which enable the carriers created by the pump to reach higher energy levels. The high nonlinearity is tunable over a wide spectral range when we choose different concentrations x of Zn.

B-V.4 17:30-17:45

DEFECT FORMATION IN SiGe/Si STRUCTURES GROWN ON GaAs BY RTCVD TECHNIQUES UTILIZING A Si-H TEMPLATE LAYER, A. Christou, M. Al-Sheikhly, University of Maryland, College Park, Maryland, USA; D. Girginoudi, A. Thanailakis and N. Georgoulas, Democritus University of Thrace, Xanthi, Greece

The growth of epitaxial SiGe/Si structures on GaAs has been achieved via the initial deposition of a hydrogenated amorphous silicon layer which acts as the nucleation layer. The substrate temperature was maintained initially at 200°C and then raised to 600°C for the SiGe growth at a pressure of 10^{-3} mbar. The Ge atomic concentration achieved was 10 percent. A dislocation density of 10^7 was maintained within the Si nucleation layer or template layer. Negligible misfit dislocations were present within the SiGe layer (100 cm^2 density) indicating the presence of a coherently strained SiGe. The photoluminescence measurements indicated a bandgap of 1095 meV. The main traps in the SiGe layer were due to the incorporation of carbon and oxygen. TEM examination indicated the presence of oxygen precipitates, misfit dislocations and stacking faults. Background impurity levels of 10^{16}cm^{-3} were achieved.

Of particular interest are films grown on Si (100). The SiGe surface morphology was smooth with no indication of antophase domains. In the optimized samples, Hall mobility was used as measure for film quality in addition to DDX FWHM values, mobility values of 3,000 cm^2/Vs were achieved. Another parameter investigated was the hydrogenated template layer. The role of hydrogen was to enhance the nucleation process for achieving an epitaxial prelayer for SiGe growth. The effectiveness of the template layer was further investigated by electron spin resonance measurements.

B-V.5 17:45-18:00

SILICON BASED MULTILAYERS STRUCTURES PREPARED BY REACTIVE PULSE LASER DEPOSITION, R. Ciach, J. Morgiel, W. Maziarz, Institute of Metallurgy and Material Science of PAN, UL. Rejmonta 25, 30-059 Cracow, Poland; E.G. Manoilov, E.B.Kaganovich, S.V. Svechnikov, Institute of Semiconductors Physics UNAN, pr. Nauki 45, 252650 Kiev, Ukraine; E. M. Sheregii, Institute of Physics of Pedagogical University, UL. Rejtana 16a, 35-310 Rzeszow, Poland

This report is concerned with laser modificated ultrathin Si layers. Two methods were used for their preparation. The periodic stripe pattern on the (100) surface of the p-Si wafer (ρ=7.5 Ωcm) was obtained by the first method that consists from action by single focused laser pulses beam (YAG:Nd^{3+} laser, λ=1.06μm, τ=0.2ms, E=0.2mJ) with next etching.

In the second method the nanocrystalline composite films were prepared by reactive pulse laser deposition (the same laser was used E=0.2J, τ=l0ns, pulse frequency 25 Hz). For example: 1 layer - nc-Si (size of crystalline ~ 3nm) in SiO$_x$ (x=1.5) matrix, 2 layer - nc-Si in SiO$_x$ (x=l) matrix, ... This method allow us to obtain multilayer periodic structures with a period of several nm. The electronography of profile sections of such structures was performed by the PHILIPS CM20 (200 kV) transmission electron microscope, providing a magnification with factor one million The composition of layers was measured by X-ray microanalysis.

B-V.6 18:00-18:15

GROWTH OF Si$_{1-y}$C$_y$/Si- MULTIPLE QUANTUM WELLS USING MOLECULAR BEAM EPITAXY, R. Hartmann, D. Grützmacher, E. Müller, U. Gennser, Micro- and Nanostructure Laboratory, Paul-Scherrerr-Institut, 5232 Villigen-PSI, Switzerland, A. Dommann, Neutechnikum Buchs, 9470 Buchs, Switzerland

Si/SiC Multiple Quantum Well (MQW) Structures of different well thicknesses (3 - 6 nm) have been grown pseudomorphically on Si (100) at growth temperatures between 400°C and 550°C using Molecular Beam Epitaxy (MBE). Solid Si was evaporated by an electron beam, while a graphite filament was used for the C source. More than 2 % of C could be incorporated into substitutional lattice sites giving an additional parameter for the design of Si based structures.

X-ray analyses show that the layers are pseudomorphic and tensially strained due to the smaller lattice constant of C compared to Si. A post-growth rapid thermal annealing (RTA) of 10 min at 800°C didn't affect the layer composition and strain distribution indicating a good thermal stability. The crystallinity and interface quality was additionally confirmed by TEM-measurements. Photoluminescence (PL) studies were done on the samples both as grown and after the RTA-processing. Band edge PL could be observed besides a deep broad band signal at around 0.8eV.

B-V.7 18:15-18:30

SUB-MICRON PATTERNING OF SILICIDE LAYERS BY LOCAL OXIDATION, F. Klinkhammer, M. Dolle, L. Kappius, S. Mesters and S. Mantl, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, 52425 Jülich, Germany

We have investigated the thermal oxidation of epitaxial CoSi$_2$ on Si(100) and Si(111). The epitaxial layers were grown by molecular beam allotaxy with a thickness ranging from 30 to 55nm. Similar to the well estabished masking technology for local oxidation of silicon (LOCOS), the silicide layer is capped by 20nm SiO$_2$ followed by 200nm Si$_3$N$_4$. The nitride is patterned by optical lithography and dry etching. Line width down to 1 μm were generated.

Wet thermal oxidation was used in a temperature range from 850 to 1000°C. On the unprotected regions SiO$_2$ is formed on top of the silicide. During this process Co atoms diffuse from the SiO$_2$/CoSi$_2$ interface through the silicide layer to the CoSi$_2$/Si interface to form CoSi$_2$ again. By this process the silicide layer is shifted into the Si substrate. The silicide layer thins near the edges of the nitride mask and finally it separates. Therefore it is possible to obtain two metallic layers electrically separated by Si and SiO$_2$ with a very small distance of about 100nm.

We have observed a quite different behavior of the separation process of the silicide layers grown on Si(100) or Si(111). This behavior is due to the different interface energies of the CoSi$_2$/Si(111) and CoSi$_2$/Si(100) interfaces. In both cases the separation process is also dependend on the orientation of the nitride-lines to the Si substrate. I-V measurements between two separated pads show typical reverse biased metal-semiconductor-metal (MSM)-Schottky characteristics.

Thursday June 19, 1997 Morning
Jeudi 19 juin 1997 Matin

Session VI - Metallic Thin Layers

B-VI.1 - invited - 8:30-9:00

THE GROWTH OF METALLIC MULTILAYERS ON SEMICONDUCTOR SUBSTRATES AND IN SITU OPTICAL MONITORING, **T.Shen**, Condensed Matter Group, Department of Physics, The University of Leeds, Leeds LS2 9JT, UK

The growth of Co/Cu multilayers on Si(111) substrates has been studied with metal silicides as the initial buffer layers. Epitaxial growth has been observed on both Co- and Cu-silicides. The values of the magnetoresistance of the epitaxial layers were found to be higher for samples grown on Cu-silicides than for those on Co-silicides. The variation in optical reflectance during growth was investigated in situ whilst the specular RHEED intensity was simultaneously monitored. The experimental reflectance data were found to agree well with the prediction of a numerical simulation. Details will be discussed, including the effect of small amount Pb to the optical reflectance and the magneto-transport behaviour of the multilayers.

B-VI.2 - invited - 9:00-9:30

TAILORING EPITAXIAL GROWTH OF LOW DIMENSIONAL MAGNETIC HETEROSTRUCTURES BY MEANS OF SURFACTANTS, J. Camarero, J.E. Prieto, J. de la Figuera, J.J. de Miguel and **R. Miranda**, Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Surfactants have been recently used to custom-modify epitaxial low-dimensional magnetic heterostructures such as thin magnetic films, superlattices and quantum wires. By using a multitechnique approach (STM, TEAS, SXRD, LEED and SMOKE) we describe the surfactant effect of an ordered, compact, layer of Pb on heterostructures based on the Co/Cu(111) system. The Co films grown without surfactants show a 3D pyramidal, rough morphology, consist in fcc-hcp mixtures, are discontinuous and present reacted interfaces. Cu layers deposited on top of these Co films are fcc-twinned and display magnetic bridges and conformal roughness.

The Co films grown with the surfactant grow layer by layer, keep the fcc stacking sequence and present nonreacted interfaces, furthermore the Cu spacer layers are strictly fcc and continuous. This structural perfection allows to modify the magnetic properties, e.g. selecting the easy axis of magnetisation or producing trilayers with complete antiferromagnetic coupling. Finally we will illustrate how the concept of surfactant can be used to fabricate one dimensional magnetic wires on vicinal surfaces.

B-VI.3 9:30-9:45

TEMPERATURE-DEPENDENT INTERDIFFUSION OF ULTRATHIN Fe/Pd (100) FILMS, X. Le Cann, C. Boeglin, B. Carrière, IPCMS Groupe "Surfaces-Interfaces", 23 rue du Loess, 67037 Strasbourg, France, K. Hricovini, LURE, 91405 Orsay, France, and Université de Cergy-Pontoise, 95011 Cergy-Pontoise, France

The magnetism of ultrathin bct Fe films epitaxially grown on a fcc Pd(100) substrate are studied by magnetic circular X-ray dichroism and related to the specific interface morphology of the ultrathin films. In the case of Fe/Pd(100) ultrathin films, the high Curle temperature favors ferromagnetism at room temperature at coverages as low as two equivalent monolayers Fe/Pd(100). The results show a strong in-plane anisotropy and a greatly enhanced magnetic orbital moment (x5) for the ultrathin Fe films.

Soft X-ray core level photoemission studies show a clear temperature-dependent diffusion process. Moreover at 350°C we observe a full Pd monolayer covering the epitaxial Fe film. The originality of this contribution is to show how the interdiffusion at the Fe/Pd interface is related to the strong orbital moment mesured at the $FeL_{2,3}$ edges.

B-VI.4 9:45-10:00

MAGNETIC AND STRUCTURAL PROPERTIES OF ULTRATHIN Cr FILMS ON Co/Pd (111), S. Boukari, E. Beaurepaire, F. Scheurer, B. Carriere, and J.P. Deville, Institut de Physique et Chimie des Matériaux de Strasbourg, U.M.R. 046, 23 rue du Loess, 67037 Strasbourg, France

Our aim is to study the relationship between structure and magnetic properties of ultrathin bcc films of Cr deposited on Co/Pd(111). Films were grown by MBE and their properties analyzed by Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and in-situ Magneto-Optical Kerr Effect (MOKE).

Cr films were grown at 300K and 450K on Co films of thickness 2.5 monolayers (ML) to 11ML. Depending on the growth conditions, the LEED pattern is characteristic either of a pseudomorphic Cr film or a multidomains Cr(110) film. We observe a drastic increase of the polar MOKE signal in the first stage of growth of Cr on a 3ML Co film which suggests that there is a net magnetic moment on a Cr(110) plane. This could be explained by the frustration between the antiferromagnetically coupled Cr(110) magnetic moments and their coupling with Co moments. For deposition at 450K, we observe a decreasing of the longitudinal MOKE signal, in line with the formation of a non-magnetic Cr-Co alloy, as suspected by AES. We also note that a Cr deposit strongly enhances the perpendicular magnetic anisotropy of the film.

10:00-10:30 **BREAK**

B-VI.5 - invited - 10:30-11:00

MICROSTRUCTURE OF Fe/Cu(Au) ARTIFICIAL SUPER- LATTICE, **M. Arita**, A. Kuwahara, Y. Yamada, M. Doi and M. Matsui, Dept. Mater. Sci. & Eng., School of Engineering, Nagoya Univ., Furocho, Chikusaku, Nagoya 464-01, Japan

fcc - Fe in the artificial superlattices of Fe / Cu (Au) gives large magnetization, which are deposited onto Cu (001) by MBE. The magnetization showed various values due to the surface geometry of the substrate: fcc-Fe / Cu superlattices on slightly rough surfaces showed larger magnetization than those on very flat substrates. In order to study the origin of the difference in magnetization, observations of the microstructure have been performed by means of cross-sectional TEM.

Different degrees of surface roughness of Cu (001) were obtained by two methods, i.e. rf-sputtering and ion-beam-sputtering. Fe / Cu (Au) multi-layered superlattices were made by MBE. The TEM samples were prepared by ordinary methods and were observed along [110] using several types of TEM such as JEM2010 and H9000 with the help of persons in Nagoya Univ., Shizuoka Inst. Sci.&Eng., Ciba-Geigy, NTT and JEOL.

The superlattice made on a very flat substrate constituted a flat film with the step of <l nm at the interface between Fe and Cu (Au). Epitaxial growth of fcc-Fe was clearly recognized. On the other hand, the film on a slightly rough substrate showed a wavy contrast with a period of several hundreds of nm and an amplitude of several tens of nm, reflecting the geometry of the substrate. At the interfaces wavy contrast (or step) with a period of ~ 10 nm and an amplitude of several nm was observed while the Epitaxial growth was recognized. The difference of the microstructures in these two samples was mainly the wavy geometry at the interface inside the superlattice. These observed microstructures must play an important role influencing the magnetic properties of the superlattices.

B-VI.6. 11:00-11:15

STUDIES OF THE INFLUENCE OF THE LOCAL GROWTH CHARACTERISTICS ON THE MAGNETIC PROPERTIES OF ELECTROLYTICALLY DEPOSITED Ni FILMS, J. Pflaum, E. Huebner, Th. Zeidler, T. Schmitte, J. Pelzl, Institut für Experimentalphysik III, Ruhr-Universität, 44780 Bochum, Germany; J.-L. Bubendorff, J.-P. Bucher, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67037 Strasbourg, France

In this study we investigate the relationship between local structural properties and the magnetic behavior of thin Ni films. The films were grown by electrodeposition on gold covered mica substrates as well as on gold covered glass substrates. The deposition rate ranges from 0.02nm/s to 2nm/s. Analysis of the local surface texture were performed by Atomic Force Microscopy (AFM) and related to the position and the shape of the resonance line at Ferromagnetic Resonance Spectroscopy (FMR) experiments. Estimating the surface anisotropy, K_S, from the FMR results we obtain a measure for the ratio of the magnetic surface properties to the magnetic volume properties of the Ni films. Additionally, we have used magneto-optical Kerr-effect (MOKE) to study the thickness dependence of the coercive field. From this quality we found that the films on mica substrates offers much more pinning centers for magnetic domains by structural imperfections than the Ni films on glass substrates. To yield insight into the influence of the preparation technique on the structural and the magnetic behavior we compared the results with a series of evaporated Ni films on gold covered glass substrates.

B-VI.7. 11:15-11:30

MAGNETICS PROPERTIES OF ELECTROCHEMICALLY PREPARED CoFILMS AS A FUNCTION OF GROWTH CONDITIONS, J.-L. Bubendorff, E. Beaurepaire, C. Meny, J.P. Bucher, Institut de Physique et Chimie des Matériaux de Strasbourg, 67037 Strasbourg, France; J. Pflaum, E. Huebner, J. Pelzl, Institut für Experimentalphysik III, Ruhr-Universität, 44780 Bochum, Germany

In this study, we discuss the relationship between growth parameters and magnetic properties of electrodeposited cobalt films on Au(111) terraces onto mica. We focus on the role played by the pH, the applied overpotential and the deposition rate. Classical Watts electolytes have been used and the films were covered in situ by a pinehole free Cu protection. The topography of the deposits have been analysed by Atomic Force Microscopy and the growth process determined and controled by in situ Scanning Tunneling Microscopy and cyclic voltametry. Nuclear Magnetic Resonance Experiments show that the cobalt films grow epitaxially and possess hcp-stuctures with the c-axis perpendicular to plane. Magneto-optic Kerr effect measurements and alternating gradient field magnetometry have been used to study the thickness dependence of the magnetic anisotropy. We studie the ratio of fcc over hcp as a function of film thickness. Ferromagnetic Resonance Spectroscopy results will also been presented at the conference.

B-VI.8 11:30-11:45

STRUCTURE OF Fe_xMn_{1-x}/Ir(001) SUPERLATTICES DETERMINED BY X-RAY SCATTERING, EXAFS AND MULTIPLE SCATTERING THEORY, H.M.Fischer, S. Andrieu, M. Piecuch, URA CNRS, BP 239, 54506 Vandoeuvre les Nancy, France, A.Traverse, H. Fischer, M. Bessière, LURE, Université Paris Sud, 91405 Orsay, France

Fe_xMn_{1-x}/Ir(100) ($0 \leq x \leq 1$) superlattices were grown by Molecular Beam Epitaxy. RHEED measurements show that the growth of these alloys on (001)Ir is pseudomorphic to Ir and 2D up to 20 atomic planes at 373K whatever x. X-ray scattering shows the exceptionnel mesoscopic and macroscopic quality of these samples. Extended X-Ray Absorption Fine Structure experiments were performed on these samples in order to determine the alloy structure for each stoichiometry. The usual Fourier treatment of EXAFS oscillations is not an appropriate technique because of the very similar first neighbour distances of the different structures. On the contrary, the application of multiple scattering theory of XAFS allows us to identify the structures. We find that Fe rich alloys ($x \geq 0.7$) have a tetragonal structure with a c/a ratio equal to 1.10, whereas Mn rich alloys are found in a tetragonal structure with a c/a ratio equal to 1,30. The intermediate structure of $Fe_{0.7}Mn_{0.3}$ presents a c/a ratio equal to 1.20. This structural transition is followed by a magnetic transition: the Fe_xMn_{1-x}/Ir(100) ($x \geq 0.7$) superlattices are effectively ferromagnetic, even at 300K. On the contrary, the other superlattices ($x \leq 0.7$) haven't any magnetic macroscopic moment, even at 5K.

B-VI.9 11:45-12:00 MICROSTRUCTURAL PROPERTIES OF EPITAXIALLY GROWN Fe$_x$Mn$_{1-x}$/Ir (100) SUPERLATTICES STUDIED BY HREM, H. Ardhuin, E. Snoeck, M.-J. Casanove, CEMES-LOE, BP 4347, 31055 Toulouse Cedex, France

We report the fine structure of Fe$_x$Mn$_{1-x}$/Ir superlattices where the FeMn alloy layers have various thicknesses and stoichiometries ($0.3 \leq x \leq 0.8$). The different films were epitaxially grown on (100) MgO substrates by Molecular Beam Epitaxy (MBE).

Cross-sectional specimens of these superlattices were studied by High Resolution Transmission Electron Microscopy (HREM), great attention being paid to the evolution of the structural features as a function of x and of the layers thicknesses. The HREM micrographs, combined with image analysis, allowed accurate measurements of the different lattice parameters and of the tetragonality ratio, c/a, in the alloy layers. The elastic strains were estimated from these experiments. The growth and relaxation mechanisms will also be reported.

B-VI.10 12:00-12:15 OPTIMIZED EPITAXIAL GROWTH OF Fe ON Ag (001), D.E. Bürgler, C.M. Schmidt, D.M. Schaller, F. Meisinger, and H.-J. Güntherodt, Institut für Physik, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

We report on a comprehensive study of the growth of 5 nm thick epitaxial Fe(00l) films on Ag(001) substrates which are deposited on Fe-precovered GaAs(001) wafers. We characterize the films in-situ by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and depth profiling to obtain information about the geometrical and chemical surface structure. We find that the surface morphology is improved by either growing or post-annealing the films at elevated temperatures. During deposition at and above room temperature, however, an atomic exchange process is activated that results in a thin Ag film (up to 1 monolayer) «floating» on top of the growing Fe film. We propose and confirm a growth procedure that yields clean, Ag-free surfaces with a morphology superior to the other films. The topography is dominated by a dislocations network which is due to strain relief in the film. This optimized recipe consists of two steps: (i) low-temperature growth of the first 2 nm in order to form a diffusion barrier for the Ag substrate atoms, and (ii) high-temperature deposition of the final 3 nm to take advantage of the improved homoepitaxial growth quality of Fe at elevated temperatures.

12:15-14:00 **LUNCH**

Thursday June 19, 1997 — Afternoon

Jeudi 19 juin 1997 — Après-Midi

Poster Session II

14:00-16:00 See programme of this poster session p. B-25 to B-28.

16:00-16:30 **BREAK**

Session VI - Metallic Thin Layers (continued)

B-VI.11 - invited - 16:30-17:00

STUDYING INTERFACES ON A NM SCALE BY BEEM, **T. Meyer**, Laboratorium für Festkörperphysik, ETH Hönggerberg, 8093 Zürich, Switzerland, H.Sirringhaus, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, G.B. and H. von Känel, Laboratorium für Festkörperphysik, ETH Hönggerberg, 8093 Zürich, Switzerland

Ballistic electron emission microscopy is a technique derived from scanning tunneling microscopy and allows the investigation of the electric and structural properties of metal/semiconductor interfaces on a small scale. In our experiments on thin (2-3nm) metallic CoSi$_2$ films grown epitaxially on Si(111) we have been able to resolve interfacial objects as small as 1 nm. The films were grown by MBE and measured in a low temperature (77K) BEEM-microscope situated in the same UHV environment. Highly doped silicon (111) substrates of both n and p type were capped with an intrinsic silicon buffer layer, on which the CoSi$_x$-film was formed by stoichiometric codeposition and subsequent annealing. During this procedure a network of partial dislocations is formed, relaxing the strain in the silicide. Ballistic-electron-emission-spectroscopy showed that the height of the Schottky barrier is not affected by the presence of dislocations and interfacial point defects. This means that the contrast observed in BEEM-images of these interfacial defects can only be due to electron-scattering, which was confirmed by experiments on n- and p-doped substrates, showing an enhancement and a reduction in the magnitude of the BEEM-current at scattering centers respectively. On samples grown on n-doped substrates the formation of quantum interference states within the film could be observed. Interfacial defects of presummably size could be imaged with a resolution of about 1 nm. They were found to accumulate in the core region of interfacial dislocations. This and the fact that the area-density of point defects is found to be lower close to a dislocation, can be explained in terms of lateral diffusion of point defects within the interface-plane and trapping within dislocations cores [1].

[1] T. Meyer and H. von Känel, Phys. Rev. Lett. 76, April 1977.

B-VI.12 17:00-17:15

TEMPERATURE AND THICKNESS DEPENDENT EPITAXIAL RELATIONSHIP OF Pd(111) ON Cr(110), O. Hellwig, K. Theis-Bröhl, G. Wilhelmi, H. Zabel, Institut für Experimentalphysik, Ruhr-Universität, 44780 Bochum, Germany

Comparing the atomic diameter ratio Kurdjumow-Sachs in-plane epitaxial relationship between Pd(111) and Cr(110) should be assumed. However, depending on growth temperature and film thickness we obtain both, Nishiyama-Wassermann (NW) as well as Kurdjumov-Sachs (KS) orientations. This has been found by surface X-ray scattering as well as from LEED experiments. Both orientations can be distinguished by the number of Pd in-plane domains which is one for NW and two for KS. The samples have been grown by MBE using Nb(110)/Al2O3(1120) as buffer/substrate system. Independent of the film thickness, for growth temperatures above 130°C the expected KS growth has been observed. However, for lower growth temperatures pure KS growth occurs only for Pd film thicknesses below 20 Å. After reaching a temperature dependent critical film thickness a transition from KS to NW orientation takes place. This process is continuous showing several intermediate states. The dependence of the epitaxial relationship on temperature and film thickness has been plotted in a phase diagram. Regions with pure KS and NW growth are separated by a broad transition region of mixed states. Within the transition region the angle between the two KS domains change continuously reaching ~10° for pure KS growth. Additional STM measurements show that Pd forms column shaped islands with varying width and height depending on film thickness, growth temperature and epitaxial relationship between Pd and Cr.

B-VI.13 17:15-17:30

DC MAGNETRON SPUTTERING OF EPITAXIAL Ni FILMS ON MgO SUBSTRATES: STRUCTURE AND SURFACE MORPHOLOGY, E.B. Svedberg, P. Sandström, L.D. Madsen and J.-E. Sundgren, Thin Film Physics, Linköping University, 581 83 Linköping, Sweden, and B. Karr, D. Cahill, I. Petrov, J.E. Greene, Materials Science and Engineering, University of Illinois, Urbana, Illinois, USA

The growth of Ni films by dc magnetron sputtering onto MgO (100) substrates was investigated with the aim of producing epitaxial smooth Ni layers for magnetic multilayer applications. Growth temperatures ranging from 20-700°C for 200 nm thick Ni films were examined. At 100-200°C, smooth, single-crystal layers with a complete (200) texture were obtained, as demonstrated by analyses of (200), (220) and (111) x-ray diffraction pole figures. All higher deposition temperatures produced a (751) texture that was four-fold degenerate and twinned. This change in texture also marked a transition to a faceted surface as shown by atomic force microscopy (AFM). At reduced temperatures, 20°C, a complex texture dominated by (110) orientated grains, was obtained. With different film thicknesses, AFM showed a marked increase in roughness, both in terms of average surface roughness r and height-height correlation, when the thickness was increased. For Ni films grown at 400°C, r increased from 0.5 to 3.0 nm when the film thickness was increased from 10 to 250 nm. Such a dramatic increase was not the case for the single crystal Ni in the 100-200°C range. At 200°C and a thickness of 200 nm, the roughness of the single-crystal layers was an order of magnitude lower.

B-VI.14 17:30-17:45

STRESS-INDUCED COMPOSITIONAL MODULATIONS IN THIN Au-Ni SOLID SOLUTIONS GROWN ON Au (001) BY MBE : A TEMPERATURE X-RAY DIFFRACTION STUDY, G. Abadias, I. Schuster, A. Marty, C. Dressler, P. Bayle-Guillemaud, J. Thibault, CEA-Grenoble, Département de Recherche Fondamentale sur la Matière Condensée, 17 avenue des Martyrs, 38054 Grenoble Cedex 09, France, and B. Gilles, LTPCM-ENSEEG, BP 75, 38402 Saint-Martin-d'Hères, France

Although in the bulk state gold and nickel are nearly immiscible at room temperature, thin $Au_{1-x}Ni_x$ solid solutions with x ranging from 0.2 to 0.5 have been coherently grown on Au (001) by Molecular Beam Epitaxy The thicknesses of the Au-Ni alloys vary from 15 to 30 monolayers and can be controlled using Reflection High Energy Electron Diffraction. The observed enhancement of solubility is due to the epitaxial misfit imposed by the gold substrate to the Au-Ni film.

In this paper we investigate the evolution with temperature of these Au-Ni alloys using a temperature X-ray diffraction technique. The results show a strong evidence of modulations of the Au-Ni alloys structure extended over several angstroms in the growth direction. These stress-induced modulations are temperature and composition dependent and may contribute to the relaxation of the elastic energy of Au-Ni films. The high elastic energy due to epitaxial constraint may be lowered by an «anelastic» process, known as the Zener effect, in which homoatomic pairs of atoms are preferentially oriented in plane.

B-VI.15 17:45-18:00

STRUCTURAL EVOLUTION OF Au (001) /Ni MBE-THIN FILMS AND SOLID SOLUTIONS WITH TEMPERATURE, A HREM STUDY, C. Dressler, P. Bayle-Guillemaud, J. Thibault, G. Abadias, A. Marty, B. Gilles, CEA-Grenoble, Département de Recherche Fondamentale sur la Matière Condensée, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France

Ordering of Au/Ni/Au thin films and AuNi solid solutions has been observed despite their equilibrium phase diagram. Strained Ni thin films epitaxially grown on Au(001) (Ni thicknesses lower than 5 monolayers(ml)) have been annealed at temperatures ranging from 180 to 300°C. Modulations of the contrast in the growth direction (period of a few ml) in high resolution electron microscopy cross section images have been interpreted as the result of chemical modulations of the Au and Ni components. In fact, previous studies at room temperature of these films had shown that the Ni layers remained coherent with the gold layer if the nickel thickness did not exceed 6 ml. It has been shown that the interfaces were not abrupt and that mixing between the two components occurred during growth over 8 to 12 ml: the chemical modulations induced by annealing treatments are localised within these 8 to 12 ml. The occurrence of these modulations has also been checked on AuNi solid solutions epitaxially grown on a Au(001) buffer: if the solid solution is kept strained in the growth plane, the heating gives rise to chemical modulations in the area of the solid solution similarly to the thin films. These modulations are function of the initial Ni concentration and the heating temperature and time. If the thickness of the solid solution is higher than a critical value, the relaxed layer does not show these modulations after heating treatment. This indicates that the ordering is induced by the in-plane strain. The heating favours a strain relaxation of the solid solution in the growth direction, the layer still being coherent in the growth plane with the Au(001) buffer.

B-VI.16 18:00-18:15

LONG RANGE CHEMICAL ORDER AND INDUCED LATTICE DEFORMATION ALONG THE GROWTH DIRECTION IN EPITAXIAL (0001) Co3Ru ALLOY, L. Bouzidi, V. Pierron-Bohnes, N. Ringelstein, J. Arabski and C.C. Cadeville, Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR 46 (CNRS-ULP), 23 rue du Loess, 67037 Strasbourg, France

[0001]Co_XRu (X ~ 3) epitaxial films of about 50 nm thickness have been grown on a Ru buffer at temperatures (T_G) ranging from 450 K to 820 K. Most of these alloy thin films display i) a composition modulation along the growth direction with a periodicity double of that of a disordered hexagonal alloy and ii) an induced decrease of the interplanar distance. The so-observed long range ordering, that was not yet observed in bulk alloys, increases with T_G between 450 and 600 K, then saturates on a plateau and decreases above 700 K. The temperature(T_G) dependence of the 'c' lattice constant between 450 K and 700 K is well described by a double t-T exponential behaviour that yields an activation energy for the ordering process of 1 ± 0.2 eV. This value which is much lower than the usual values of the activation energy in bulk Co-based alloys (~3 eV) can be assiged to a surface diffusion process, illustrating the predominant role played by surface effects (both surface interactions and surface diffusion) in the building of these periodic stackings that are found to be metastable. The decrease of the long range ordering above 700 K is explained by the interplay of bulk diffusion that becomes operating at these temperatures during the deposition time, destroying the native long range ordering induced by surface effects.

Friday June 20, 1997 **Morning**
Vendredi 20 juin 1997 Matin

Session VII - HT Superconductors and Metalloxides

B-VII.1 - invited - 8:30-9:00

INVESTIGATION ON THE RELATION BETWEEN THE THICKNESS AND THE ORIENTATION OF EPITAXIALLY GROWN YBCO THIN FILMS BY LASER ABLATION, **J.H. Park**, S.Y. Lee, Dept. of Electrical Engineering, Yonsei University, Seoul, 120-749, Korea, M.K. Choi and I. S. Yang, Physics Dept., Ewha Womans University, Seoul, Korea

Highly c-axis oriented YBCO thin films have been grown on MgO substrates by laser ablation using halogen lamp as a heater. We have chosen the noncontact method without silver paste to heat up the substrate and to preserve its backside after deposition using halogen lamp for the fabrication of the double-sided YBCO thin films. For the further development to the microwave applications it will be helpful using the halogen lamp to provide good quality of double-sided thin films. A Nd:YAG laser was used to fabricate YBCO thin films. The wavelength of the laser can be chosen among 355nm, 532nm, and 1064nm. By varying the thickness and the film deposition temperature of the thin films, we observed the changes of the film orientations. We can get highly c-axis oriented double-sided YBCO thin films by optimizing the thickness and the deposition temperature of YBCO thin films. The double-sided thin films were systematically investigated using Raman spectroscopy and X-Ray diffraction to ensure the relation between the orientations and the thickness of the thin films.

B-VII.2 9:00-9:15

PREPARATION OF SUPERCONDUCTING MULTILAYER STRUCTURE FOR POWER ELECTRONIC DEVICES, K.Shingai, Y. Yamagata, T. Ikegami and K. Ebihara, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860, Japan

High-Tc superconducting (HTSC) thin films have drawn much attention due to their application in power electronic device such as current leads, current limiters and current switching devices. However, HTSC films with thickness over 400nm hardly obtain high critical current density due to difficulty in controlling the orientation of crystalline grains within these films.

In this study, Y-Ba-Cu-O multi layer structure was prepared using by the KrF excimer pulsed laser deposition technique. This structure shows good c-axis orientation, good surface morphology and high critical current density over 10^5A/cm^2 at 77K for 1 µm films.

In recent years, the investigation of three-terminal superconducting electronic devices for power application has been of great interest. The ferroelectric such as lead zirconate titanate (Pb-Zr-Ti-O) / HTSC stacking structure has paid attention to improve performance of these devices.

Therefore, we also study on the heterostructure of Pb-Zr-Ti-O / Y-Ba-Cu-O grown on MgO(100) substrate. The crystallization, morphology and superconducting properties of these films were investigated. The zero resistance critical temperature Tc(zero) of superconducting channel was 82.0K. It shows that good Pb-Zr-Ti-O / Y-Ba-Cu-O multilayer was obtained.

These multilayer structures will be to contribute for the development of the new application in superconducting electronic devices.

B-VII.3 9:15-9:30

THIN TANTALUM OXIDE FILMS PREPARED BY 172 nm EXCIMER LAMP IRRADIATION USING SOL-GEL METHOD, L.J. Bie, J.-Y. Zhang and I.W. Boyd, Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK; V. Dusastre, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Tantalum oxide film has been extensively studied due to its potential electronic and optoelectronic applications in the semiconductor industry. It is a promising candidate as a capacitor insulator in high density dynamic memories (DRAMs) and in ultra-large-scale-integrated devices due to its high dielectric constant (about 25). Tantalum oxide films can also be employed as non-linear optical materials and in waveguide structures.

Very thin tantalum oxide films (less than 100 Å) were prepared by spin-coating using sol-gel method as well as a novel VUV irradiation step. The layers were formed on Si (100) substrates, using a 172 nm excimer lamp which resulted in homogeneous thin films on the scale of nanometer as indicated by SEM. The effects of spin-on speed, irradiation time and substrate temperature on the film formed have been studied. X-ray photospectroscopy (XPS) was employed to examine the content of different elements during the process and showed that the carbon content, which is considered to be harmful to the electrical properties, can be reduced to the extent of being essentially zero. Ellipsometry, Fourier transform infrared spectroscopy, capacitance-voltage and current-voltage measurements were employed to characterise the oxide films prepared at different substrate temperatures in the range of 100°C to 450°C and indicate that some of them to be of high quality.

B-VII.4. 9:30-9:45 EPITAXIAL GROWTH AND STRUCTURE OF IRON OXIDE FILMS ON Pt (111), M. Ritter, W. Weiss and R. Schlögl, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

The epitaxial growth of a metal oxide has been investigated from the micrometer down to atomic scale by STM in combination with LEED and Auger electron spectroscopy. A unique growth mechanism is observed for iron oxide films grown onto Pt(111) surfaces by repeated cycles of iron deposition and subsequent oxidation. The first monolayer (ML) exhibits hexagonal unit cell with a periodicity of 3.1 Å and a superimposed large hexagonal unit cell with a periodicity of 26 Å. This is explained by a FeO (111) bilayer forming a coincidence structure on the Pt(111) surface due to the large lattice mismatch.

The film continues to grow layer by layer in the FeO structure up to a critical thickness of 3-4 ML, at which the large periodicity induced by the lattice mtsmatch is still visible. Then Fe_3O_4 islands start to grow in (111) orientation, and inbetween these islands the first FeO monolayer gets exposed again due to removal of FeO layers above the first layer. The islands continiously increase in size until they coelesce forming a thick film. Thermodynamic calculations reveil Fe_3O_4 to be the most stable phase under our film preparation conditions. The initial growth of FeO is explained by the stable interface structure that FeO forms at the Pt(111) surface. Upon reaching the critical film thickness the energy balance favours the formation of the Fe_3O_4 islands and leads to a partial removal of FeO layers lying above the first interface layer.

9:45 **BREAK**

☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ **END OF SYMPOSIUM B** ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆

SYMPOSIUM B

POSTER SESSIONS

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session I

14:00-16:00

Growth Methods and Kinetics

B-I/P1 ENERGETICS AND KINETICS OF Yb-Si(111) INTERFACE FORMATION, T.V. Krachino, M.V. Kuz'min, M.V. Loginov, M.A. Mittsev, Ioffe Physico-Technical Institute, Russian Academy of Sciences, Polytechnicheskaya St. 26,194021 St.Petersburg, Russia

In this paper we consider initial stages of Yb-Si(111) interface formation studied by means of TDS, Modulated-Beam Desorption spectroscopy (MBD), LEED, and AES. MBD experiments were performed in wide range of temperatures (including temperatures at which clean Si(111) surface exhibits structure 1x1). The growth mechanism is found to follow the mode similar to Stranski-Krastanov type: 3D islands of Yb silicide phase grow on Yb monatomic interlayer. Adsorbed 2D layer consists of domains surrounded by 2D gas of Yb atoms. Desorption activation energy for isolated Yb atoms Ed=2.9eV is obtained. Formation of 2D domains on Si(111)1x1 results in reconstruction of silicon upper layer. Dimerization of Si surface atoms is accompanied by raising of E_d. A set of 2D domain structures (3x2, 5x1, 2x1) in order of Yb coverage increasing is observed. The least densely packed structure (3x2) with the highest value E_d=4.4eV is arranged in low coverage range. The most close-packed 2D structure (2x1) with E_d=3.2eV is found to be filled up at Yb quantity of $3.6 \cdot 10^{14}$ atoms/cm^2. The latter structure reveals lattice parameters close to bulk Yb silicide film, which allows 3D islands of Yb silicide phase to be formed. Activation energy for Yb silicide film decomposition E_s is equal to be 2.9eV.

B-I/P2 SURFACE ACTIVITY OF RARE EARTH DOPE IN LIQUID PHASE EPITAXY GaAs:Gd, Y.A. Zelenin, V.D. Malyshev, Odessa State Marine University, Dpt.Technical Cybernetics, 34 Mechnicov Street, 270029, Odessa, Ukraine

The surfation effect of rare earth /RE/ dope Gd on GaAs (100) crystal boundary in liquid phase epitaxy GaAs:Gd are investigated by Scanning Electron Microscopy. Changing the grown modes form Volmer- Weber to Stranski - Krastanov and Frank - van der Merve at least, under 0.01 ÷ 0.05 at.% Gd addendum are observed.

Fundamental rebuilding the micro - morphology of apitaxial films in scale (3 ÷ 10)μm are observed in both Bi:Gd and Ga:Gd solvents under 0.03 at.% Gd addendum. The interface surface tension changing is manifested by the displacement of size and shape distribution of alloy melt drops traces the GaAs (5 ÷ 10) μm grain boundary.

Total RE dope effect can be explained assuming spliting ones on two parts:
(a) local, the HSAB complexation residual impurities;
(b) global, the changing grown modes under shift electrons chemical potential of the solution - melt under RE dope - the surface activity. The second side (b) of RE dope effect is the complementary part of the developed Rare Earth Semiconductor Technology REST.

B-I/P3 PREPARATION OF THICK CRYSTALLINE SILICON LAYERS ON GLASS BY LASER IRRADIATION, G. Andrä, J. Bergmann, F. Falk, E. Ose, Institut für Physikalische Hochtechnologie, Helmholtzweg 4, 07743 Jena, Germany

For polycrystalline silicon thin film solar cells a silicon layer 50 μm thick is required consisting of grains 100 μm in diameter deposited on low prized glass substrate. We report on a preparation method combining plasma enhanced CVD of amorphous silicon and laser crystallization.

We start from a-Si:H thin films 200 nm thick which are deposited on glass (Corning 7059) by a plasma CVD process. These films are irradiated by ms pulses of an Ar^+ or a CO_2 laser to result in crystals of several ten μm in diameter. In order to increase the film thickness on this crystalline seed layer further amorphous silicon is deposited by the same CVD process at a rate of 15 nm/min. During the deposition the growing layer is irradiated by excimer laser pulses of about 300 mJ/cm^2 at a repetition rate of 0.01 Hz. Each laser pulse melts the newly deposited amorphous layer down to the crystalline interface which acts as a homoepitactic substrate during resolidification. In this way the whole growing amorphous layer is converted to a polycrystal.

B-I/P4 TEM STUDIES OF UNUSUAL CRYSTALLINE STRUCTURES FORMED IN AMORPHOUS FILMS, V.Y.Kolosov(1) and A.R.Tholen(2), (1)Ural State University, Ekaterinburg, Russia, (2)Physics Dept., Chalmers University of Technology, 41296 Goteborg, Sweden

An unusual internal lattice bending (up to 120 degrees per micron) has been observed in different thin amorphous films subjected to transformation amorphous - crystalline [1]. We will here report about such a transformation in thin films of amorphous iron oxide (Fe_2O_3), which were exposed to the electron beams of different size and intensities inside the electron microscope and transformed to concentric annular areas (width about 1 micron) of "perfect" and "imperfect" crystallline zones of distinct diffraction contrast. The two different zones are thus crystalline both with a constant internal bending of the lattice: the crystals themselves are not bent but regular rotation of the lattice (from <001> to <100> between the centres of any adjacent zones is accumulated inside grains. The grain morphology in the two zones is, however, completely different with quite large grains in the "perfect" zones and fine grains in the "imperfect" zone, where the grains often are crescentlike with their smallest dimension being around 20 nm. (There is also an internal rotation of the lattice from [001] to [100] within the grains).

This unusual microstructures were studied with a Philips CM200 FEG microscope using HREM, EDX, CBED, EELS and bend-contour tecnique, developed earlier [1].

[1] Kolosov V.Yu. Proc XII ICEM, 1990,Vol.1, 574

B-I/P5

GAS PHASE COMPOSITION ANALYSIS WITH ABSORPTION UV SPECTROSCOPY METHOD IN THE SYSTEM GaP-PCl_3-$AsCl_3$-H_2-He, V.A. Voronin, S.K.Guta, Lviv Polytechnic State University , Bandera Street 12, Lviv 290046, Ukraine

In the present paper with the help of the in-situ optical absorption spectroscopy method the concentration's of component's for the system GaP-PCl_3-$AsCl_3$-H_2-He were determined in the source region. The investigation was made in the 220-360 nm region at temperatures from 20°C to 900°C, the Reinold's number having been taken from 0.1 to 0.5. It was shown that homogeneous and nonhomogeneous reactions in the source region had nonequilibrium nature. The kinetics of main reactions were determined for a wide range of flow rates and temperatures.

The conditions at which the oversaturation value of isotemperature gas-phase exist are determined. The kinetics of overstaturated gas-phase during epitaxial growth of $GaAs_{1-x}P_x$ in the chloride gas-transport system at stable temperature was investigated. It is shown that vapour deposition of $GaAs_{1-x}P_x$ in the system under investigation is impossible while chaning the $AsCl_3$ to PCl_3.

Simulation

B-II/P1

DEPOSITION INDUCED ATOMIC MOBILITY IN METAL-ON-METAL SYSTEMS: A MOLECULAR DYNAMICS STUDY, C. Massobrio, IPCMS, 23, rue du Loess, 67037 Strasbourg, France

Adatoms mobility at temperatures lower than those corresponding to thermally activated motion has important implications in the growth of adsorbed nanostructures, since it determines their initial morphology after deposition. Over the years, molecular dynamics simulations have provided a wealth of information on the possible occurrence of this phenomenon for a large variety of metal-on-metal systems. These studies have shown that in most cases transient mobility is absent because of a very efficient transfer of energy from the condensing atom toward the substrate. In a recent series of papers (G. Vandoni et al. Surf. Sci. Lett. 320, L63 (1994), C. Félix et al. Phys. Rev. B 54, 17039 (1996)) devoted to helium scattering studies of Ag atoms diffusion on Pd(100), the extent of aggregation of atoms on the substrate at low temperatures has been explained in terms of a new picture, the 'neighbor driven mobility'. This consists in viewing the localized migration of an adatom around its impact point as due to the attraction of the atoms previously adsorbed. Here we address this issue by molecular dynamics simulations of the system Ag/Pd(100). Our results indicate that the lateral mobility of an adatom is enhanced when a neighbor is found close by, in a way which is strongly dependent on the diffusion barrier.

B-II/P2

MATHEMATIC SIMULATION OF HEAT AND MASS TRANSFER AT GAS EPYTAXY OF GaAs BY MOCVD PROCESS, V.G.Minkina, Heat & Mass Transfer Institute Belorussian Academy of Sciences, 15 P.Brovka St., Minsk 220072, Belarus

Heat and mass transfer is examined during the deposition of epitaxial GaAs layers from a gas mixture of trimethylgallium (TMG) and arsine in a vertical reactor with a substrate holder made in the form of a frustum of a pyramids. Heat and mass transfer in the deposition zone is described by the system of partial differential equations of the conservation of continuity, momentum, energy and mass of components. These equations are solved together with the equations of detailed chemical kinetics of heterogeneous and homogeneous reactions. The dependencies of the physical properties of the gas mixture on composition, temperature and pressure in the reactor are taken into account. Epitaxial layers of GaAs were grown by the pyrolysis of arsine and TMG, using hydrogen as the carrier gas. There is information that hydrogen replacement with nitrogen enables one to obtain better epitaxial films. In this relation, the matter of inert gas (nitrogen or argon) effect on epitaxy process is of interest and is the main subject of investigations in the present work. Initiation of nitrogen (argon) solvent-gas reduces the component diffusion coefficient and consequently the layer growth rate. And the depletion of gas mixture is slowed down, which explains a considerable improvement of growth rate distribution uniformity on the deposition surface. Changing the inert gas concentration, we can control the growth rate and achieve the uniformity of the thickness of the films built up on all substrates. The approximate formulas are obtained to calculate the given process occurring at different Re numbers, concentrations of initiated components and solvent-gas and geometry of reaction channel.

B-II/P3

CALCULATION OF MISFIT DISLOCATION DISTRIBUTION AT THE INTERFACE OF FILM AND SUBSTRATE WITH DIFFERENT ELASTIC MODULI, A.S.Polkovnikov, D.V.Shantsev, Ioffe Physico-Technical Institute, 26 Polytechnicheskaya, 194021 St. Petersburg, Russia

This work present theoretical investigation of the distribution of misfit dislocations in heteroepitaxial films. We calculated elastic stresses in the film of finite thickness and finite width grown on a lattice-mismatched substrate, taking into account stress relaxation on the film edges. A special case of different elastic moduli of the film and the substrate has been considered. For this case the equilibrium position of misfit dislocations is shown to be not in the interface plane. Two systems have been considered: a single misfit dislocation, and a superlattice of misfit dislocations. By minimizing the free energy, we calculated the distance from the interface where a single dislocation is formed. Also we determined the critical thickness of the film as a function of lattice mismatch and elastic moduli. Further, the equilibrium period of a superlattice of misfit dislocations has been calculated. Relevance of these theoretical findings to existing experimental results on epitaxial growth on lattice-mismatched substrates is discussed.

B-II/P4

A MODEL OF COUPLED DIFFUSION OF IMPURITY ATOMS AND POINT DEFECTS IN THE VICINITY OF SEMICONDUCTOR- SEMICONDUCTOR INTERFACE, O.I. Velichko, Belarusian State University of Informatics & Radioelectronics, 6, P.Brovki Street, 220027 Minsk, Belarus and A.K. Fedotov, Belarusian State University, 4, F.Skarina avenue, 220050 Minsk, Belarus

On the basis of nonequilibrium thermodynamics a model of transport processes and quasichemical reactions of particles in semiconductor crystals was developed and a set of generalized diffusion equations was constructed. This set of equations describes impurities and intrinsic point defects diffusion processes in the vicinity of semiconductor-semiconductor interface under conditions of nonequilibrium state and nonuniform distributions of impurity-defect system components. It was assumed that impurity diffusion occurred by formation, migration, and dissociation of impurity atom - intrinsic point defect pairs. A local equilibrium between impurity atoms, intrinsic point defects and their pairs was supposed. The influence of internal stresses and electric field on the pairs and point defects transport processes was taken into account. The comparison with experimental data concerning interface disordering in InGaAs/InAlAs structures under thermal annealing confirms the adequacy of the proposed model.

Nanoparticles and Dots

B-III/P1 MAGNETOSTATIC CONTRIBUTION TO UNIAXIAL MAGNETIC ANISOTROPY CONSTANT OF INHOMOGENEOUS NANOSTRUCTURE FILMS, K.Yu. Guslienko, Institute for Magnetism, ave Vernadskogo 36b, Kiev-142, Ukraine

Explanation of induced magnetic anisotropy is actual problem in physics of magnetic films. One of possible sources of this anisotropy is dipole-dipole coupling of magnetic moments. Magnetostatic coupling in inhomogeneous nanostructure granular, multilayer etc. films is considered and magnetostatic contribution to uniaxial (perpendicular) magnetic anisotropy constant is calculated for different types of the magnetic inhomogeneties on the nanometer scale within strong exchange coupling limit. Developed approach is applicable to the magnetic films with columnar, granular, multilayered and more complex microstructure. In particular, a regular 2D, 3D arrays of ferromagnetic particles in a nonmagnetic matrix and randomly spaced magnetic phases with fixed volume concentration are considered. The typical case of magnetic inhomogeneity such as a film consisting of two mixed magnetic phases with different magnetizations is analyzed in details. Calculation of the magnetostatic coupling is especially actual for granular films and multilayer films because it effects on giant magnetoresistance in these systems. For inhomogeneous magnetic films it is calculated a general expression of the anisotropy constant induced by dipole-dipole interaction. This expression does not depend on details of the magnetization distribution within the film but depends on such easily measured parameters as average magnetization of the film and it dispersion. Calculation of magnetostatic energy of an inhomogeneous film and corresponding anisotropy constant allows immediately to connect magnetic and structure characteristics of the film.

B-III/P2 RAMAN VERSUS INTERBAND ABSORPTION IN GE QUANTUM DOTS, A. Stella and P. Tognini, Università di Pavia, Italy; C.E. Bottani and P. Milani, Università di Milano, Italy; P. Cheyssac and R. Kofman, Université de Nice Sophia Antipolis, France

The non-wetting (or partially wetting) character of Ge with respect to Al_2O_3, SiO, SiO_2 allows to obtain Ge nanocrystals in a wide size range from 10 nm down to 1 nm, a relatively low size dispersion and regular shape, embedded in an amorphous matrix. A key aspect of the sample preparation is represented by the fact that the substrate temperature allows the deposition of the Ge film in the liquid state, so that the shape of the agglomerating nanocrystals is essentially modeled by the surface tension, before solidification through a slow cooling

The growth, which is essentially based on self organisation processes, will be illustrated in this communication together with the main data concerning both interband absorption above the gap and Raman spectroscopy, i.e.:

- a detailed inspection of the optical absorption spectra (from about 1 eV to about 5 eV) versus size gives evidence of the different nature of the quantum behavior of E_1 with respect E_2.
- Raman spectroscopy (through the Γ point scattering peak evolution) gives the possibility of comparing phonon and electron confinement.

B-III/P3 MORPHOLOGY AND OPTICAL PROPERTIES OF SILICON NANOSTRUCTURES GROWN ON DIELECTRICA, M. Andersson, A. Iline and F. Trager, Fachbereich Physik, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Nanostructures of silicon are grown on dielectric substrates, e.g. $CaF_2(111)$, by atom deposition and self-assembly. The morphology of the formed structures is characterised with scanning force microscopy under ambient conditions and the optical properties are characterised by the extinction in the visible and UV-wavelength range. The deposition and growth parameters, temperature, atom flux and deposition time, are varied and especially the substrate temperature (T) has a great influence on the character of the Si nanostructures. At T below ~700K, the deposited atoms form a rough film and, at higher temperatures, clusters with diameters up to approx. 50 nm depending on T and deposition time. The optical extinction spectra from the film samples show a maximum at $\lambda \approx 320$ nm, whereas the clusters samples have an almost monotone increase in extinction with shorter wavelengths. Comparisons are made with spectra calculated for Si films and particles (Mie-theory), and there is a good qualitative correspondence with what is expected from samples with films and clusters, respectively.

B-III/P4 THE STUDY OF DIAMOND AND DIAMOND-LIKE STATES IN THE NANOMETRIC REGION OF THICKNESS, M.N. Petukhov and A.P. Dementjev, RRC Kurchatov Institute, Kurchatov square, Moscow 123182, Russia

Now it becomes evident that further technological advancement in such challenging areas as nanostructure production on the basis of diamond films requires a detailed understanding of the chemical reactions on the surface responsible for nucleation and growth. Auger Spectroscopy has information depth of few monoatomic layers and is capable of yielding information concerning the chemical state of atoms in the near-surface region of a solid. The C KVV Auger line shapes for graphite (sp2 hybridization) and diamond (sp3 hybridization) have different characteristic features and are usable to identify sp2 and sp3 states of carbon atoms. Obviously, AES is preferential method to investigate carbon nucleation at early stage of diamond-like films growth and chemical interaction on the surface of the films.

We have developed photoelectron spectroscopy (XPS) and X- ray-excited Auger electron spectroscopy (XAES) for identification and separation of sp2 and sp3 bonds. The sp2→sp3 conversion of carbon under chemical reaction with O and H atoms have been experimentally found on the surface of growing film during CVD process. The sp3- hybridized carbon atoms due to C-C bonds from sp3 states due to C-O bonds have been separated.

B-III/P5 STRUCTURAL AND OPTICAL STUDIES OF CdS NANOCRYSTALS EMBEDDED IN SILICON DIOXIDE FILMS, A.G. Rolo(1), O. Conde(2), M.J.M. Gomes(1), M.S. Belsley(1) and M.P. dos Santos (1), (1)Universidade do Minho, Dep. Fisica, 4709 Braga Codex, Portugal, (2)Universidade de Lisboa, Dep. Fisica, Ed. C1, Campo Grande, 1700 Lisboa, Portugal

In this work we report on structural and optical spectroscopy studies (X-ray diffraction analysis, Raman, absorption and photoluminescence) of CdS nanocrystals with mean radius value in the range 22 Å to 50 Å, embedded in SiO_2 glass films grown by using the magnetron rf-sputtering technique. The absorption spectra exhibited a marked blue shift of the absorption band edge by 300 meV which was attributed to a quantum confinement of electrons and holes in the CdS crystallites. The fluorescence spectra show a narrow emission peak whose maximum position agrees closely with the value found for the absorption-edge of the corresponding nanocrystals, indicating that the origin of this emission is direct electron-hole recombination in the first quantized conduction-to-valence energy levels. The influence of size confinement effects on the vibrational spectra of nanocrystals was studied by analysing the 1 LO Raman peak.

B-III/P6 SURFACE INVESTIGATIONS OF NANOSTRUCTURED POROUS SILICON, P.V. Galiy, T.I. Lesiv, L.S. Monastyrskii, T.M. Nenchuk, I.B. Olenych, Physical Department, Lviv State University, 50 Dragomanov Str., 290005 Lviv, Ukraine

The additive methods: Auger spectroscopy (AES), PTSEE, ellipsometry and photoluminescence method have been applied for study of por-Si surface The por-Si PTSEE spectra have been studied dependently on porousity degree in the temperature range T=300÷650K and photostimulation in range λ=260÷400 nm. All obtained layers of por-Si had photoluminescent properties stimulated by nitrogen gas laser (337nm) excitation even at room temperature. The changes of refraction index on por-Si samples were studied by ellipsometry in dependence of porous degree (0÷60%) on wave length of He-Ne gas laser (632nm). The quantitative AES analysis by method of pure standards with matrix corrections gives evidence that real surface layer contains mixture of silicon oxides SiO_x and carbon atoms (C)-system SiO_xC_x on por-Si surface. The obtained thickness «adsorbates» films SiO_xC_x was equal 0,31÷0,61 nm. The correlation between porous degree of por-Si and PTSEE glow curve structure was established. The emissively active centres were indentified and their concentration and other kineticts parameters of PTSEE processes were calculated in the result of PTSEE spectra analyses. The influence of «adsorbate» and oxide layers on PTSEE was studied.

Atomic Scale Characterization

B-IV/P1 RAMAN CHARACTERIZATION OF MBE GROWTHED ARRAY OF QUANTUM WIRES ON FACET (311) SURFACE OF GaAs, M.D. Efremov, V.A. Volodin, V.Ya. Prinz, V.V. Preobrazhenski, B.R. Semyagin, Institute of Semiconductor Physics Siberian Branch of RAS, pr. Lavrentjeva 13, Novosibirsk 630090, Russia

Raman technique was applied to study phonon spectra of superlattices grown on facet surface of GaAs (311). Regular corrugation of the interface was expected to bring peculiarities in the phonon spectra with thinning of GaAs layer. Damping of GaAs- like optical phonons within approximately one monolayer of surrounding AlAs was believed to give an appropriate tool for testing of interlocking of facets and forming of quantum wires. A set of superlattices was grown on (311)A GaAs surface with buffer layers of GaAs and AlAs. The thickness of GaAs layers for different samples was varied from 21Å down to 8.5Å at constant thickness of AlAs layers of 27Å. The thickness of layers was determined by growth time calibrated by RHEED oscillations for the case of control growth of the same thickness on (100) surface of GaAs. Using selection rules for (311) oriented surface, different polarization geometry of Raman scattering was applied to study behavior as longitudinal phonons as transverse optical phonons with phonon polarization along and transverse to the direction of quantum wires.

For thick layers of GaAs a decreasing of localized phonon frequencies was observed with reduction of the layers thickness similar to (100) oriented superlattices. With further reduction of the average layer thickness below 15Å threshold an increasing of localized phonon frequencies was detected for the first time. The increasing was explained to be reasoned by interlocking of AlAs facets and forming of GaAs wires, what leads to quantatization of phonons in quantum wires and correspondent increase of phonon frequencies. Calculation of phonon frequencies for two dimensional chains gave the values in quantitative agreement with experimental ones. Observation of the interlocking at threshold of 15Å supports model of corrugated surface of (311) GaAs with height of facets about 10.2Å. A splitting of TO localized modes with phonon polarization parallel and transverse to the direction of quantum wires was observed. The splitting increased monotonically with reduction of the GaAs layer thickness. Anisotropic properties of transverse phonons support the presence of corrugation of GaAs/AlAs interface and formation of quantum wires.

B-IV/P2 RECONSTRUCTION OF THE SI-TERMINATED ß-SiC (100) SURFACE, L. Pizzagalli, IPCMS-GEMME, 23 Rue du Loess, 67037 Strasbourg, France, and C. Joachim, CEMES, 29 rue J. Marvig, 31055 Toulouse, France and A. Mayne, G. Dujardin, PPM, Université de Paris-Sud, 91405 Orsay, France, and P. Soukiassian, F. Semond, L. Douillard, CEA, DSM-DRECAM-SRSIM, 91191 Gif-sur-Yvette, France

SiC is presently a widely studied material because of its interesting properties in various technological domains such as electronic or biotechnology. Up to now, there are some discrepancies between experimental or theoretical works for the caracterization of the structure of clean Si-terminated surfaces. We present here experimental and calculated images of Si-terminated (100) surfaces. The STM experimental images show a Si-dimer resolution and a c(4x2) reconstruction with a long range order. We calculate STM ima,ges of several different surface structures with the Electron Scattering Quantum Chemistry technique and compare with the experimental ones. It is found that a structure forming a c(4x2) pattern, with alternating up and down dimers along the dimer rows, is the best candidate for agreement with the experience.

B-IV/P3 AFM/STM CHARACTERISATION OF NANOSTRUCTURES, V.A. Fedirko, M. D. Eremtchenko, Moscow State University of Technology "Stankin", 3a Vadkovski per, Moscow 101472, Russia; O.I. Khrykin, Institute for Physics of Microstructures Russian Academy of Science, Nizhnii Novgorod 603600, Russia; V.R. Novak, S.L. Vorob'eva, Research Institute of Physical Problems, Zelenograd, 103460 Moscow, Russia

We report on the combined atomic force microscopy and scanning tunnelling microscopy (AFM/STM) investigation of surface nanostructures. C_{60} fullerene molecular layers have been studied. Fullerene layers were formed on a highly oriented pyrolithic graphite wafer by two different Shoefer deposition technique: from surfactant-fullerene mixture and fullerene-indopane adsorption. Scanning tunnelling microscopy shows the regular one-monolayer molecular surface structure for the samples prepared by the Shoefer technique. Local tunnelling electron spectroscopy measurements through the monolayer may be interpreted in terms of the Coulomb-blockade effect. Samples with fullerene-indopane adsorbed layers have cluster structure as revealed by STM and AFM.

InGaAs dot heterostructures on GaAs surface have also been studied using AFM tapping mode of operation. Phase contrast technique enables to distinguish domains of different chemical composition. The results obtained in different AFM modes are compared with one another and with transmission electron microscopy (TEM) images. Spatial Fourier-transform analysis is applied to the images for revealing structure regularity.

Semiconductor Interfaces and Quantum Wells

B-V/P1 FORMATION OF EPITAXIAL $HoSi_2$ LAYER ON Si(100) SUBSTRATE, G. Petö, Z.E. Horvath, E. Zsoldos, N.Q.Khanh, G.L. Molnar, J. Gyulai, KFKI Research Institute for Materials Science, 1525 Budapest, P.O.Box 49, Hungary and J. Kanski, Phys. Dept. Chalmers Univ. of Technology, Göteborg, 41296, Sweden

The condition of epitaxial rare-earth silicides on Si(100) substrate is rather unknown and in some cases, e.g., at $HoSi_2$ case the existence of epitaxial growth has not been reported yet.

5 nm thick Ho film was deposited onto relaxed Si(100) 2x1 surface in 10^{-10} Torr pressure at room temperature of the substrate. The $HoSi_2$ layer was grown in situ by solid phase reaction at different temperatures. The epitaxial growth was monitored by LEED and Angular Resolved Photoemission (ARUPS) in situ and the as-grown film was measured by X-ray Diffraction (XRD), TEM and Rutherford Backscattering (RBS). At 500°C, only Si-Ho reaction was detected without any epitaxial feature, at 700°C annealing a clear but not sharp LEED pattern was observed together with angular dispersion of ARUPS. XRD showed clear epitaxial $HoSi_2$ with relatively large full width at half maximum (FWHM). Electron diffraction confirmed the epitaxial film but RBS channelling showed only slight reduction of Ho signal. These observations could be explained either by strained epitaxy and/or maybe by existence of epitaxial grains misoriented with 0.5-5 degree.

Further annealing at higher temperature (above 800°C) the decomposition of the $HoSi_2$ film was observed with all experimental methods.

B-V/P2 PROPERTIES AND STRUCTURE OF THE FILMS RECEIVED BY THE LASER EVAPORATION IN THE CONDITIONS OF THE STATICAL VACUUM, S.Y. Paranchych, B.M. Grytsyuk, S.V. Nichiy, O.S. Romanyuk, Z.P. Tsaliy, Chernivtsi State University, 2 Kotsyubinsky Str., 274012 Chernivtsi, Ukraine

The methodology of the fabrication of the films by the method of laser evaporation in the conditions of the statical vacuum ($\cong 10^{-8}$ torr) is worked out in the present work and the results of the research of the crystallinity structure, the electrical and photoelectrical propeties of the films $Cd_xHg_{1-x}Se$ and CdSb are presented here.

The fabricated films CdxHgl-xse on the mica bases and NaCl possessed n-type conductivity with the concentration of the carriers $(2\div5)10^{18}cm^{-3}$. The lowtemperatural annealing in the vapour of Se diminishes the concentration of the carriers to $10^{17}cm^{-3}$ and in that time the mobility at the T=300 K exceeds $10^3cm^2/v\cdot c$. The electron diffractometry investigation of the structure showed that the fabricated films were grain-oriented.

B-V/P3

PHYSICAL PECULIARITIES OF SINGLE-CRYSTAL IV-VI THIN FILMS GROWTH ON POROUS SILICON S.P. Zimin, M.N. Preobrazhensky, D.S. Zimin, E.P. Komarov, Yaroslavl State University, Sovetskaya str. 14, 150000 Yaroslavl, Russia and I.V.Saunin, St. Petersburg Electrotechnical University, Prof. Popov str. 5, 197376 St. Petersburg, Russia

Obtaining single-crystal semiconductor layers on relief surface with micro- and nanopores is an important task when creating devices on the base of low-dimensional structures with porous silicon (PS). PbTe film growth on the PS surface with various porosity and pores morphology was studied in this work. Initial single-crystal silicon had [100] and [111] orientation and was doped by P, B or Sb. Microporous and nanoporous PS layers were formed by anodic electrochemical etching technique. Structural characteristics of PS surface and lead telluride film were studied by electronic, optic and acoustic microscopy and by X-ray diffractometry. It is proved that under certain conditions of Hot Wall technique and vacuum deposition one can obtain continuous single-crystal PbTe films with good electrophysical parameters. Basic orientation of PbTe films corresponded to the [100] direction. Film growth processes on pores were studied, influence of plasxa-chemical treatment of PS surface on structural characteristics of lead telluride layers was examined.

B-V/P4

ANALYSIS OF TWO-PHOTON ABSORPTION IN ORGANIC AND INORGANIC QUANTUM WELLS IN A MICROCAVITY, B.S. Monozon and E. Hartung, Dept. of Physics, Marine Technical University, St.Petersburg, Russia; Dept. of Chemistry, University of North Carolina at CH, USA

The analysis of the magneto-optical properties of the organic and inorganic quantum wells (QW) structures will be presented. An analytical model in which the organic and inorganic QWs with resonant Frenkel and Wannier-Mott excitons lie in the center of a single microcavity (MC) on a distance $d << 1$ is developed [1]. A method of approximate solution is suggested for the QWs structures using the system of Schrodinger equations describing the exciton-exciton interaction in the presence of a magnetic field. Application of a magnetic field allows us to distinguish this feature from hybrid Frenkel-Wannier-Mott excitons and evidence its biexciton nature. In the two-band approximation for orientations of the magnetic field close to the boundary of the finite magnetic quantization cone analytic expressions depending explicitly on the QWs system parameters are obtained for oscillator strength of the transitions. It is shown that the optical absorption spectrum has a biexcitonic effect.

[1] V.M. Agranovich, R.Anatasov, F.Bassani, Solid State Comm. 92, 295, (1994).

B-V/P5

DOPED WITH Ga PbTe THIN FILMS ON Si SUBSTRATES, Y.A. Ugai, A.M. Samoylov, A.V. Tadeev, Y.V. Synorov, O.B. Yatsenko, Voronezh State University, Universitetskaya Sq., 394693 Voronezh, Russia

Heterostructures on foreign substrates formed from $A^{IV}B^{VI}$ materials have been attracting great interest both for their fundamental electronic properties and for applications to infrared lasers and detectors. Infrared photoconductivity of both undoped and doped with Ga PbTe thin films on Si high ohmic substrates without anyone buffer layer deposited by modified «hot wall» technique using the thermal evaporation of the elements from separate sources has been studied by IR spectrometer at temperature interval 4 - 300 K.

For further doping procedure have been chosen PbTe/Si films with p-type of conductivity and charge carrier concentration of about 10^{16}-10^{17} cm^{-3} at 77 K. The do-ping procedure of PbTe layers has been performed by annealing under different pressure of Ga2Te molecules in vapour phase. The doping procedure always has led to decrease hole concentration and conversion the type of conductivity of PbTe samples from p to n in some cases depending on the real experimental conditions. As a result for Ga doped PbTe/Si films charge carrier concentration may approach almost intrinsic values of about 10^{13}-10^{14} cm^{-3} at 77K. These doped with Ga PbTe films had a good infrared sensitivity at temperature range 4-200 K and two impurity levels with activation energy E_a=0.045 and E_a=0.105 eV.

B-V/P6

CRYSTAL MICROSTRUCTURE OF PbTe THIN FILMS ON Si SUBSTRATES, Y.A. Ugai, A.M. Samoylov, E.A. Dolgopolova, M.K. Sharov, Voronezh State University, Universitetskaya Sq., 394693 Voronezh, Russia

From the practical point of view the investigation of the microstructure of PbTe/Si thin films seems to be very important because the real parameters of IR detectors would depend from PbTe/Si heterostructures crystallinity perfection.The mirror-smooth surface PbTe thin films (thickness was about 0.5-7 μm) were deposited directly on (100) Si high ohmic substrates without anyone buffer layer by modified «hot wall» technique using the thermal evaporation of the elements from separate sources. The crystal micro-structure of PbTe thin films has been studied by etching pits method, SEM, RHEED and by X-ray analysis which is able to determine the X-ray rocking curve profiles and line width with the high precision.

It has been established that these PbTe/Si thin films have mosaic single-crystal structure with average crystalline dimension of about 2-10 μm in diameter and (100) texture without regard to the Si substrate orientation. The investigation of PbTe/Si thin films dislocation density by etching pits method and by the analysis of x-ray reflection profiles show the average values of about 10^5-10^6 cm^{-2}. The experimental data which have been obtained by these methods are in a good agreement.

B-V/P7

LOW-DIMENSIONAL ELECTRON STRUCTURE FORMED ON HETEROINTERFACE OF n-n-ETEROSTRUCTURES BASED ON PbS AND ZnCdHgTe THIN FILMS, G. Khlyap, A. Andrukhiv, M. Andrukhiv, Pedagog. Inst., Drogobych, 293720, Ukraine

The theoretical and experimental study of low-dimensional electron structure was carried out for epitaxial thin films n-PbS on n-ZnSe substrate and n-ZnCdHgTe on n-HgCdTe substrate obtained by low temperature MBE and modified LPE technology, respectively. The wave functions for electrons and holes and photoluminescent spectra were calculated. The luminescent spectra had maximums; their long-wave decreasing was conditioned by electrons and holes tunneling, and short-wave one was determined by temperature.

B-V/P8

INVESTIGATION OF KINETIC PROCESSES PULSE LASER VAPORIZATION OF CdHgTe AND MnHgTe IN THE MAGNETIC FIELD, B. Kotlyarchuk, D. Popovych, V. Savchuk, V. Savitsky Institute for Applied Problems of Mechanics and Mathematics, National Academy of Sciences of Ukraine, 3b Naukova Str., 290601 Lviv, Ukraine

This work is devoted to investigation spatial-time and spectral characteristics of laser erosive vapour-plasma torch formed at the time of vaporization of mercury chalcogenides targets in the magnetic fields.

The laser vaporization took place in dynamic vacuum ($P \sim 10^{-6}$ Torr) or in the mercury vapour (PHg=10^{-1}-10^{-3} Torr). The magnetic fields of various values (B=1-6 Tesla) and geometry was used in distance target-substrate.

The peculiarities of laser evaporation and condensation in magnetic fields are analysed to control the charge and energetic states of laser plasma. It is determined that kinetic energy of atoms, deposited on the substrate, can be lowered and the ionisation level of evaporated substance remained at the same time under laser evaporation in magnetic fields, applied in the vicinity of evaporating target, parallel to its surface.

Thursday June 19, 1997
Jeudi 19 juin 1997

Afternoon
Après-Midi

Poster Session II
14:00-16:00

Metallic Thin Layers

B-VI/P1 NANOSTRUCTURE STUDY OF Al-BASED SPUTTER-DEPOSITED FILMS FOR LARGE SIZED LIQUID CRYSTAL DISPLAY SUBSTRATE, H. Takatsuji and S. Tsuji, Display Technology, IBM Japan, Ltd, 800, Ichimiyake, Yasu-cho, Yasu-gun, Shiga, 520-23 Japan, K. Kuroda and H. Saka, Department of Quantum Engineering, Nagoya University, Nagoya 464-01, Japan

Aluminum-based metals are expected to be increasingly used for wiring on thin-film transistor (TFT) array which forms on glass substrates, because of their low resistance. However, with using these metals, the stress migration such as hillock and whisker generations are one of the major concern affecting the yield loss in TFT fabrication. It is well known that a resistance to the stress migration relates to the film's nanostructure. Nevertheless, few reports are known about nanostructure study of thin metal films on glass substrates.

In this work, various sputter-deposited Al-based thin films (350 nm thick) on the LCD grade large size glass substrates (550 X 650 mm) was studied by atomic force microscopy (AFM), X-ray diffraction (XRD) analysis and cross-sectional transmission microscopy (TEM), while the resistance to hillock and whisker generations was investigated by means of the nanoindentation techniques which we developed. We find the film's nanostructure depends on the hardware of the sputtering apparatus, the target manufacturing method and the process parameters. Some Al-alloy thin films which were deposited by a magnet-scan-type sputtering apparatus have layered-structure, and one of them has a strong resistance to stress migration with a novel nanostructure. The relationship between the Al-based thin films' nanostructure with a thin under layer of high-melting point metal and the resistance of stress migration is also discussed.

B-VI/P2 EPITAXIAL GROWTH OF Fe/Tb BILAYERS ON Nb(110) /SAPPHIRE (1120), F. Richomme, J. Teillet, Laboratoire de Magnétisme et Applications, UMR 6634, Faculté des Sciences de Rouen, 76821 Mont-Saint-Aignan Cédex, France; T.Ruckert, W. Keune, Laboratorium für Angewandte Physyk, Gerhard-Mercator-Universität, 47048 Duisburg, Germany

The rare-earth/transition metal compounds have been extensively studied because they may exhibit interesting magnetic properties for magneto-optical recording devices.

We observed the epitaxial growth of individual Fe(110) and Tb(0001) thin films on Nb(110)/Al2O3(1120) by molecular beam epitaxy. For the first time, epitaxial bilayers of Fe(110)/Tb(0001) on Nb(110)/Al2O3(1120) have been obtained successfully. The surface crystallography has been investigated by low-energy electron diffraction (LEED). The LEED patterns indicate a high crystalline quality. The composition and the cleanness of the surface was systematically checked by Auger measurements. Ex-situ large and small angle X-ray diffraction was used in order to determine the epitaxial orientation perpendicular to the plane and the film morphology (thickness, crystallite size, ...). In order to determine the optimized conditions of epitaxy, the investigation was performed as a function of the deposition temperature and the thickness of layers during the growth. The reproducible in-plane epitaxial relationships will be described for each type of deposition. All the results will be quantitatively analyzed, correlated and interpreted.

B-VI/P3 EPITAXIAL GROWTH AND PATTERNING OF SPUTTERED Fe FILMS ON GaAs(001), S. Kreuzer, G. Bayreuther and D. Weiss, Institut fiir Experimentelle und Angewandte Physik, Universität Regensburg, 93040 Regensburg, Germany

Fe(001) films, 10-100 nm thick, were epitaxially grown by magnetron sputtering on GaAs(001) and on 100 nm thick Au(001) buffer layers on GaAs(001) in an UHV based sputtering system (base pressure $< 5 \times 10^{-9}$ mbar). Epitaxy of Au was ~ahieved by using a 1- 5 nm thick Fe seed-layer. The growth rates at a power of 1.3 W/cm^2 and an Ar pressure of 4.8×10^{-3} mbar were 0.35 nm/s and 0.072 nm/s for Au and Fe, respectively. In-situ ion etching of the substrate at a temperature around 500°C proved to be essential for epitaxial growth. Excellent epitaxy is inferred from X-ray diffraction and magnetic anisotropy of the films. From X-ray ϕ-scans the epitaxial relationships Fe[100]||GaAs[100] and Fe[100]||Au[110] were determined. Magnetic measurements by vibrating sample magnetometry show a distinct fourfold in-plane anisotropy with the anisotropy constant of bulk Fe. Holographic lithography and ion beam etching were used to pattem the films. Square arrays of dots with periods of 1μm, dot widths of 400 nm and different heights were made. Magnetization measurements show a clear change in the magnetic properties of the films dominated by the shape anisotropy of the dots. The magnetization reversal process is additionaly studied by magnetometric and microscopic techniques.

B-VI/P4 INFLUENCE OF DEPOSITION RATE ON THE STRUCTURE OF THIN METAL LAYERS, P. Haier, N. Esser, W. Richter, TU Berlin, Inst. f. Festkörperphysik, Sekr. PN 6-1, Hardenbergstr. 36, 10623 Berlin, Germany; B. Hermann, K. Lüders, FU Berlin, Inst. f. Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany

It is widely recognized that the growth morphology of thin metal layers depends strongly on the substrate choice and the temperature. We will show here that the deposition rate can also drastically influence the structure and morphology of the layers. This is illustrated for Sb on GaAs(1 10). Layers with a nominal thickness of 30 ML were deposited with varying deposition rates (10 to 0,03 ML/min.) on substrates kept at room temperature. Characterization techniques employed are Raman scattering, Low Energy Electron Diffraction and Scanning Probe Microscopy.

In the larger part of the range of deposition rates, the rhombohedral phase of Sb is obtained. Lowering the deposition rate generally results in larger grain sizes and rougher surfaces. However, in a very narrow range of deposition rate we found a growth mode of Sb which is similar to the pseudocubic phase [1]. This phase was found so far only for thicknesses below 15 ML after annealing at 150°C.

[1] N. Esser, M. Kopp, P. Haier, W. Richter, Journal of Electron Spectroscopy and Related Phenomena, 64/65 (1993) 85

B-VI/P5 LEED, AUGER AND SYNCHROTRON X-RAY DIFFRACTION STUDIES OF THIN Co AND Pt_xCo_{1-x} ALLOY FILMS ON Pt(111), R. Baudoing-Savois, M. De Santis, P. Dolle, Y. Gauthier and M. C. Saint Lager, CNRS Laboratoire de Cristallographie, Associé à l'Université J. Fourier, BP 166, 38042 Grenoble, France

Co films of thicknesses between submonolayer range and about 10 monolayers(ML) were grown on Pt(1 11) at room temperature, by means of an electron bombardment Omicron source.

For all coverages, the LEED diagrams are of good quality. Between 1/8 ML and 5 ML we observe satellites arranged in hexagons: they are centered respectively around the Pt spot positions at low coverage, and around the unrelaxed «bulk» Co spot positions above ≈ 3ML. X -ray scans in the [0k0], [h00] and [hk0] directions exibit also satellites, confirming a non pseudomorphic epitaxial growth. Intensity oscillations of the X-ray specular beam favour a layer by layer growth model and allow calibration of the deposition rate, consistent with our previous Auger results. LEED and Auger data evidenced two different alloy states depending on the annealing temperature (up to 360°C or up to 430°C) which were then analysed in more details by synchrotron X-ray measurements. An oscillatory composition profile is evidenced in the top layers, similar to what happens at the surface of bulk PtCo alloys. In-situ real time X-ray measurements during annealing allowed to follow the changes of the alloy film parameters: lattice, thickness, interface rougness and average concentration; these results will be presented and discussed.

B-VI/P6 EPITAXIAL GROWTH OF VERY THIN FILMS OR RARE-EARTH ON YTTRIUM (0001), N. Witkowski, F. Bertran, B. Kierren, J. Eugène, T. Gourieux, and D. Malterre, Laboratoire de Physique du Solide, BP 239, 54606 Vandoeuvre-les-Nancy, France

In this communication, we present a structural study of ultra-thin films of light Rare-Earth (La and Ce) deposited on Yttrium(0001). Depositions at different temperatures from room temperature to 300°C, lead to an epitaxial growth as demonstrated by Reflection High Energy Electron Diffraction (RHEED). The growth mode was characterized by Auger spectroscopy and shows a layer by layer growth mode in this temperature range. These measurements were completed by atomic-scale characterization achieved by Scanning Tunneling Microscopy.

These results open now the possibility of obtaining very well characterized single crystals of Ce and La by growth of thick films.

B-VI/P7 STRUCTURAL PROPERTIES OF ELECTRODEPOSITED Co/Cu MULTILAYERS, H. El Fanity(1), K. Rahmouni(2), M. Bouanani(1), A. Dinia(2), G. Shmerber(2), C. Mény(2), P. Panissod(2) and A. Berrada (1), (1)Faculté des Sciences, BP 1014 Rabat, Maroc; (2)IPCMS-GEMM, UMR 46 CNRS ULP, 23 rue du Loess, 67037 Strasbourg, France

The elaboration of magnetic multilayers by the electrodeposition technique has recently stimulated new interest. The advantage of this techniques is that, compared to high or ultrahigh vacuum techniques, the required experimental set-up is considerably simpler and cheaper. Co/Cu multilayers have been grown by electrodeposition in a single electrolyte bath based on $CoSO_4$, H_3Bo_3 and $CuSo_4$. X-ray difraction performed on these multilayers have shown polycrystalline fcc structure of both Co and Cu layers with preferential (111) texture. Nuclear Magnetic Resonance spectrum has been recorded at 4.2 K on [Co6nmCu4nm]25 and has shown a resonance line at 216 Mhz which confirms the fcc structure of Co layers. The preliminary analysis of the spectrum shows first that the Co layers are not pure and contain approximately 1% of Cu, second that the interfaces are of good quality. Resistivity measurements performed on this sample presents a giant magnetoresistance effect of about 4% at room ttemperature.

B-VI/P8 INTERFACE STRUCTURE OF MBE GROWN Fe/Cr SUPERLATTICES WITH NON-COLLINEAR MAGNETIC ORDERING, V.V. Ustinov, T.P. Krinitsina, V.A. Tsurin, V.I. Minin, Institute of Metal Physics, Russian Academy of Sciences, 620219 Ekaterinburg, Russia

Recently we have reported peculiarities of Fe/Cr superlattices magnetoresistance resulting from the non-collinear magnetic ordering of Fe layers [1]. In the present work the results of microstructure investigations of these materials and the data on Mössbauer spectroscopy study of the layers and interfaces structure are analysed. The measurements were performed on Fe/Cr superlattices, grown by molecular-beam epitaxy on MgO and Al_2O_3 substrates, with various ^{57}Fe and Cr layers thickness. Electron microscopy investigations showed that these superlattices represent pseudo single crystals consisting of column morphology blocks with low-angle boundaries. As the layer thickness increases the superlattices become more perfect. The Mössbauer spectroscopy showed that in our superlattices the layers interface is in fact a transition region (layer) of ≈ 9Å thickness, whatever Fe and Cr layers thickness. The feature of this region is that the most of Fe atoms in it have an environment characteristic of solid solution of equiatom composition. Spectra parameters also suggest that the interlayer regions are ferromagnetic, their magnetic moment being directed at some angle relative to Fe layers plane. Kinetics of the non-collinear superlattice growth is discussed.

[1] V.Ustinov et al., JETP, 109, 477 (1996), Phys.Rev.B, 54, 15958 (1996).

B-VI/P9 DEPOSITION TEMPERATURE INFLUENCE ON THE EPITAXIAL GROWTH OF IRON ON (110) Nb, A. Mougin, C. Dufour, S. Andrieu, K. Dumesnil, Ph. Mangin, G. Marchal, V. Oderno, L.P.M., U. H.P.-Nancy I, BP 239, 54506 Vandoeuvre Cedex, France

Iron has been deposited on a (110) niobium single crystal film by molecular beam epitaxy. At room temperature and at 200°C, oscillations of the RHEED intensity show evidence of a layer by layer growth. After a deposition of 20Å of iron, the RHEED patterns are characteristic of (110) iron with a parameter very close to the bulk value despite the 15% mismatch between bulk iron and niobium parameters.

When we annealed this film at 400°C, the RHEED patterns change and become characteristic of a rectangular surface lattice (7Å x 4.8Å) presenting twins related by a 110° rotation about the normal to the surface. From Auger spectroscopy, the surface is made of a Nb-Fe alloy.

When 20Å of iron are deposited at 500°C on (110) niobium, the same surface alloy is obtained, without twins in this case.

B-VI/P10 THERMAL STABILITY OF ULTRATHIN AL-FILMS AND AL-CLUSTERS, R. Gröger(1), X. Hu(2), W. Schommers(1), D.H. Shen(2), M. Barczeswki(1), A. Berlinger(1) and P. Von Blanckenhagen(1), (1)Forschungszentrum Karlsruhe, Institut für Materialforschung, Postfach 3640, 76021 Karlsruhe, Germany; (2)On leave from Institute of Physics, Chinese Academy of Sciences, Beijing, China

Al-nanostructures are of technological and fundamental interest in connection with different possible applications, e.g. for creation of conducting lines and single electron transistors.

Al-layers have been produced by molecular beam epitaxy and Al-clusters by local Al-deposition with a scanning tunnelling microscope (STM). The structure of ultrathin Al-layers grown on Si(111) in UHV as a function of temperature and coverage have been studied by low and high energy electron diffraction (LEED and RHEED). A δ-Phase consisting of nanometer-scale clusters has been observed in the coverage range of 1 to 2 monolayers. By application of the STM- field evaporation method individual Al-clusters have been created and deposited at programmed positions on Si(1 11) surfaces in UHV and on hydrogen-passivated Si(lll)surfaces in air. The structure of the Al-clusters were analysed by temperature dependent STM and scanning force microscopy measurements. The structure and dynamics of Al-clusters will be discussed in relation with molecular dynamics calculations performed for a realistic interatomic pair potential for Al.

B-VI/P11 INVESTIGATION OF THE SURFACE MORPHOLOGY OF A EXCIMER VUV LAMP-INDUCED DECOMPOSITION OF PALLADIUM ACETATE FILMS FOR ELECTROLESS COPPER PLATING, J.-Y. Zhang and I.W. Boyd, Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

Excimer UV lamp-induced decomposition palladium acetate films was performed by using novel excimer UV argon and xenon sources which emit radiation peaking at wavelength of 126 and 172 nm, respectively. UV irradiation of a substrate treated with the palladium acetate results in the formation of palladium, which acts as an activator for copper plating by means of an electroless bath. A selective copper pattern can thus be formed in a simple process by means of patterned VUV irradiation using a contact mask. The surface morphology of excimer UV lamp-induced decomposition palladium acetate films on silicon substrates was investigated using an atomic force microscope (AFM) and a scanning electron microscope (SEM). The exposure conditions were found to affect the morphology of the activation layer and the density of the palladium catalyst. The selective electroless copper deposition exhibited good adhesion. The electrical resistivity of the electroless copper was measured by four-point probe and found to be a function of the thickness of palladium. The morphology of the copper layers was also investigated with SEM. The edge of the copper line is remarkably sharp without any metal particles in the surrounding areas that are often present at lines written by focused laser. This UV-induced low temperature metal deposition can provide a particularly attractive approach for the manufacture of thin film micro-circuits and devices.

B-VI/P12 GROWTH AND GIANT MAGNETORESISTIVE BEHAVIOUR IN LaCaMnO/LaSrMnO TRILAYERS BY PULSED LASER DEPOSITION, W. Zhang and I.W. Boyd, Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK; M. Elliott and W. Herrenden-Harkerand, Department of Physics and Astronomy, University of Wales, Cardiff, Cardiff CF2 3YB, UK

Giant magnetoresitance (GMR) effects in metallic multilayer/granular systems have been known for several years. The recent discovery of colossal magnetoresistance (CMR) effects in doped perovskite-type La-Mn-O films grown on $LaAlO_3$ substrates by pulsed laser deposition (PLD), has stimulated even more interest especially for potential magnetic recording applications. Perovskite-type manganese oxides exhibit ferromagnetic ordering in the a-b plane and antiferromagnetic ordering along the c-axis, below the Neél temperature. The ferromagnetically ordered Mn-O monolayer, provides a similar situation to that for metallic multilayers.

In this paper, the growth of LaCaMnO/LaSrMnO trilayers by PLD on Si (100) substrates using a Nd:YAG laser operating at 266nm is reported. The La-Sr-Mn-O layer was chosen due to its high Curie temperature and expectations for improved magnetoresistance properties of LaCaMnO films at room temperature. It is found that the Curie temperature of this trilayer shifts to 250K, compared with 220K in a LaCaMnO single layer. Consequently an improved magnetoresistance, with a value of 40% ($\Delta\rho/\rho_0$) under a magnetic field of 4.7T at 300K, is obtained. The dependence of the electrical and magnetic properties on the growth of the films grown is also described. The strain and magnetorestriction between two layers is used to explain the observed phenomenon.

B-VI/P13 CROSS-SECTIONAL HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY STUDY OF ELECTRODEPOSITED Ni-Cu/Cu MULTILAYERS, A. Cziraki, Eötvös University, Institute for Solid State Physics, Muzeum körut 6-8, 1088 Budapest, Hungary; V. Pierron-Bohnes, C. Ulhaq-Bouillet, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 46 (CNRS-ULP), 23 rue du Loess, 67037 Strasbourg, France; E. Toth-Kadar and I. Bakonyi, Research Institute for Solid State Physics, Hungarian Academy of Sciences, P.O.B. 49, 1525 Budapest, Hungary

We briefly report here a high-resolution transmission electron microscopy (HREM) study on electrodeposited Ni-Cu/Cu multilayers that present giant magnetoresistance. These multilayer samples exhibit a columnar growth morphology. The columns have a convex curvature in the growth direction and a hexagonal or quasi-hexagonal cross-section. They are typically in the (111) orientation and present series of laminar twins. These twins exhibiting sharp twin boundaries parallel with the substrate in order to relax the strain induced by the lattice mismatch (~ 2.1%) between the non-magnetic Cu and magnetic Ni-Cu layers. Since the observed twins are extended defects, they can relax only a small fraction of the lattice mismatch strain. The alternating Ni-Cu/Cu layers are in general parallel to the substrate near the substrate but at the top they follow the convex curvature of the columns. The HREM measurements reveal that these samples have nearly everywhere coherent interfaces between the layers. This suggests that most of the coherency strain still remains unrelaxed.

B-VI/P14 IONIZED CLUSTER BEAMS FOR FORMATION THIN FILMS WITH HIGH ADHESION. ELECTRICAL CONTACTS TO HTSC FILMS, A.S. Zolkin, Novosibirsk State University, Physics Department, Pyrogova Street 2, and A.V. Koshin, Y.G. Shukhov, Institute Laser Physics, Novosibirsk, 630090, Russia

The design and testing of a new two-temperature metal vapour source for ionized cluster beam (ICB) method are described. The vaporized material (Ag atoms and clusters up to 200atom/cluster) from a crucible with vapour (P=1000 Pa) superheating is partially ionized by electrons (J=100mA, E=200-600eV) at the crucible exit (nozzle: d=0.4mm) where the vapour has its highest density and then ionized particles are accelerated in electric field (up to 10kV) and deposited (100 nm/min) on the substrate of HTSC / YBaCuO films, CdHgTe, ceramics, glass and metals. The plasma ion source (E/H, 1mA/cm2, E(i)=600-2000eV) was used for sputtering the degradation layer and for assistance during the deposition as the method for preparing low-resistance contacts on HTSC. Thin metal films (10- 500nm) with high density of covering, low-resistance contacts Ag/Y-Ba-Cu-O (10E-5 - 10E-8 Ohm cm2) and high adhesion and stability to thermal shock were fabricated by ICB. The surface of metal contacts was investigated by the Scanning Electron Microscope in backscatted electrons too, with the computer treatment in order to determine the fulling degree of the development HTSC film surface by silver.

HT-Superconductors and Metalloxides

B-VII/P1 ANNEALING EFFECT OF ANODIZED AL-BASED ALLOY FOR THIN-FILM TRANSISTORS, T. Arai and H. Iiyori, IBM Yamato Laboratory, 1623-14 Shimo-tsuruma, Yamato-shi, Kanagawa 242, Japan

Bottom-gate thin-film transistors (TFTs) have been widely investigated for use in active-matrix liquid crystal displays (AMLCDs). In recent years, much effort has been devoted to developing low-resistivity gate bus lines, to meet the need for large, high-resolution LCDs. Aluminum (Al) is a remarkably good material for gate bus lines. However aluminum easily forms hillocks and whiskers during heating processes such as chemical vapor deposition (CVD) film formation, and causes defects as a result of short-circuits and leakage between the gate and the upper electrodes.

In our study, Al-neodymium (Nd) or Al-gadolinium (Gd) alloy were used as a gate metal, and those surface were anodized to avoid hillock formation during heat process.

The nanostructure of anodized Al gate insulators after annealing was studied by combined atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (TEM). The electrical properties and surface roughness of insulating film were discussed in relation to the annealing conditions. Our result shows that film annealed at 450°C for 1 hour gives smoother surface and exhibited higher breakdown electric fields of over 7.5 MV/cm and lower leakage currents. Excessive annealing makes its surface rough and decrease the breakdown electric fields. The effect of nitrogen addition to the Al-based alloys will be also discussed.

B-VII/P2 EPITAXIAL GROWTH OF YBCO ON HASTELLOY WITH YSZ BUFFER LAYER BY LASER ABLATION, Y.S. Jeong, J.H. Park, S.Y. Lee, Dept. of Electrical Engineering, Yonsei University, Seoul, 120-749, Korea

Good quality superconducting YBCO thin films were grown on Hastelloy(Ni-Cr-Mo alloys) with yttria-stabilized zirconia(YSZ) buffer layers by in situ pulsed laser deposition in a multitarget processing chamber. Generally, Hastelloy exhibit excellent resistance to corrosion, creep, fatigue, thermal shock, impact, and erosion. However, it is difficult to make films on flexible metallic substrates due to inherent interdiffusion problems between metallic substrates and superconducting overlayers. To overcome this difficulty, it is necessary to use YSZ buffer layers since it will not only limit the interdiffusion process but also minimize the surface microcrack formation due to smaller mismatch between the film and the substrate. In order to enhance the crystallinity and the transport properties of YBCO films on metallic substrates, YSZ buffer layers were grown at various temperatures different from the deposition temperature for growing YBCO films. On YSZ buffer layer grown at higher temperature than that for growing YBCO film, the YBCO thin film was found to be textured with c-axis olientation by x-ray diffraction and had a high zero-resistance critical temperature of 85K and a high critical current density.

B-VII/P3 EPITAXIAL PIEZOELECTRIC PZT THIN FILMS OBTAINED BY PULSED LASER DEPOSITION, P. Verardi(1), M. Dinescu(2), F. Craciun(1), (1)CNR Istituto di Acustica «O.M. Corbino», via Cassia 1216, 00189 Rome, Italy, (2)Institute of Atomic Physics, Bucharest-Magurele, POB-MG 16, 76900, Romania

Epitaxial lead zirconate-titanate (PZT) thin films with good piezoelectric properties were deposited in situ on Si (100) and Si (111) substrates with a Nd-YAG laser ablation technique. The experiments have been done at different substrate temperatures. Energy dispersive spectroscopy (EDS) X-ray diffraction and SEM were used to determine the composition, the crystallographic structure and the morphology of the deposited films. All the films exhibited perovskite structures with preferential alignement of the (111) planes parallel to the film surface. Remarkable orientation has been obtained for films deposited at low substrate temperatures, with only very small amounts of non-piezoelectric pyrochlore phase. This is very important for deposition on semiconducting substrates, in order to avoid high temperature stresses and microcracking. Direct measurements revealed good piezoelectric properties in the absence of any subsequent poling, due to the intrinsic orientation of the films.

B-VII/P4 EVAPORATION OF SENSITIVE SUPRAMOLECULAR MEMBRANES ON SEMICONDUCTOR SUBSTRATES FOR ISFET AND EIS CHEMICALL SENSORS, R. Mlika, H. Ben Ouada, Laboratoire de Physique des Interfaces, Faculté des Sciences de Monastir, 5000 Monastir, Tunisie; N. Jaffrezic-Renault, Ingénierie et Fonctionnalisation des Surfaces, UMR-CNRS 5621, Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France; M. Gamoudi, Laboratoire d'Electronique des Solides, UCB LYON I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France

A new supramolecular receptors containing pyrochatechol subunits bounded in α-position of a linear dicarboxylic acid has been synthesized. Thin films based on this receptors were deposited using the technique of thermal evaporation under vacuum onto the gate oxide of ISFET (Ion Sensitive Field Effect Transistor) and the EIS (Electrolyte-Insulator-Semiconductor) structures to fabricate chemical microsensors.

Electrochemical measurements were made to test and calibrate physico-chemical sensors with regards to their sensitivity and selectivity. Both devices have shown Nernstian response towards Iron (III) ions, thus partial selectivity for these ions is shown. The improved lifetime compared with membranes prepared by physical adsorption techniques and the sensitivity observed for these films indicates that these structures are worthy of further developments.

B-VII/P5 GROWTH OF ULTRATHIN ORGANIC FILMS ON Au(111) SURFACES, R. Gerlach, G. Polanski and H.-G. Rubahn, Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, 37073 Göttingen, Germany

The epitaxial growth of ultrathin organic films (alkane thiolates) on single crystalline metal surfaces is investigated via low energy electrons scattering. As an example we discuss the results for nonane tiol molecules $[CH_3(CH_2)_8]SH$, adsorbed on Au(111) surfaces via vacuum deposition. As a function of coverage we observe a change in structure from a $c(21 \times \sqrt{3})$ to a $p(5 \times \sqrt{3})$ structure, which reorientates without further change in coverage into a $c(10 \times 2\sqrt{3})$ structure. An increase in deposited molecules results finally in a $c(4\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure. The latter one is the hexagonally closed packed structure which could also be observed following growth from an ethanolic solution. The structural change is interpreted as being due to an coverage induced increasing tilt angle of the molecules with respect to the surface normal, followed by a rotation of the molecules with respect to the C-C-C plane of the carbon chain. Similar results for alkane thiols of other chain lengths are also discussed.

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM C

Recent Developments in Electron Microscopy and X-Ray Diffraction of Thin Film Structures

Symposium Organizers

A.M. ROCHER, CEMES/CNRS, Toulouse, France

A.G. CULLIS, University of Sheffield, Sheffield, UK

S. RANGANATHAN, Indian Institute of Science, Bangalore, India

K. KURODA, Nagoya University, Nagoya, Japan

The assistance provided by the
HCM Network «Ab-initio calculation of complex processes in materials»
is acknowledged with gratitude.

SYMPOSIUM C

Tuesday June 17, 1997 **Afternoon**
Mardi 17 juin 1997 Après-midi

13:55-14:00 OPENING REMARKS

Session I - First Stage of Growth, Part 1
Chairperson: J. Mayer, Max-Planck-Institut für Metallforschung, Stuttgart, Germany

C-I.1 - invited - 14:00-14:40

X-RAY DIFFRACTION STUDIES OF SURFACTANTS IN EPITAXIAL GROWTH, **E. Vlieg**, FOM-Institute AMOLF, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Due to the availability of synchrotron radiation sources, X-ray diffraction has become a well-established technique for the structural and morphological analysis of surfaces and interfaces. Surface roughness can be studied on a monolayer scale. Due to the penetrating power of X-rays, it is straightforward to study layers that are buried inside a crystal during the growth process, and one can e.g. look at the formation of stacking faults and twinned crystallites.

In this contribution the homoepitaxial growth of metals will be discussed, and in particular the role of additives («surfactants») on the growth behaviour. Systems we have studied include Sb with Ag(111) and Ag(100) and In with Cu(lll) and Cu(100). It turns out that in many cases these additives greatly improve the quality of the grown layers, leading to smoother surfaces and to the suppression of twin formation. The role of Sb during the growth of a Ag(111) crystal is particularly interesting. An Sb pre-coverage of 0.1-0.2 monolayer leads to a change in growth mode from 3-dimensional to layer-by-layer. At a coverage of 1/3 monolayer, the Sb gives a $\sqrt{3}$ reconstruction with a top layer that is entirely in the wrong stacking. When depositing Ag on such a crystal, the top layer stays in the wrong stacking, while the lower layers return to the correct stacking. The stacking fault is thus effectively 'floating' on the surface.

C-I.2 14:40-15:00

MORPHOLOGICAL STUDY OF COBALT AGGREGATES IN MAGNETIC MULTILAYERS BY GRAZING-INCIDENCE SMALL-ANGLE X-RAY SCATTERING, A. Naudon, D. Babonneau, Laboratoire de Métallurgie Physique, URA CNRS 131, Université de Poitiers, UFR Sciences, bat SP2MI, BP 179, 86960 Futuroscope Cedex, France, and F. Petroff and A. Vaures, UMR 137 CNRS/Thomson-LCR, Domaine de Corbeville, 91404 Orsay Cedex, France

There has been interest for a number of years in small magnetic particles. Recently, giant magnetoresistance effects have been shown in $Co/A1_2O_3$ granular multilayers, where the cobalt aggregates are embedded in a non-magnetic matrix. These effects depend on the sizes of the aggregates and the interactions between them.

In order to characterize the morphology of the aggregates and their organization in the multilayer we used the small-angle X-ray scattering technique under grazing incidence (GISAXS). The experiments are then carried out at/or near the critical angle: the result is a considerab]y enhanced surface sensitivity. Full potentiality of this technique is obtained when using a synchrotron source (flux, collimation and choice of the wavelength in order to avoid fluorescence or to perform anomalous measurements) and when patterns are recorded with two-dimensional detectors: gas detectors or Image Plates (IPs). It is then possible to determine the sizes of the aggregates, the correlations in the plane of the layers and the cross-correlations from layer to layer. Results will be shown with different periodicities of the multilayers and a comparison will be made with transmission electron microscopy results.

C-I.3 15:00-15:20

DETERMINATION OF INTERFACIAL ROUGHNESS AND ITS CORRELATION IN SPUTTERED CoZr/Cu MULTILAYERS, J. Langer, R. Mattheis, IPHI Jena, Postfach 100 239, 07702 Jena, Germany; J. Kräußlich, IOQ, FSU Jena, Max-Wien-Platz 1, 07743 Jena, Germany, St. Senz, D. Hesse, MPI Halle, Weinberg 2, 06120 Halle/Saale, Germany; Th. Schuhrke, J. Zweck, Univ. Regensburg, 93040 Regensburg, Germany

Magnetic multilayers exhibiting Giant Magneto Resistance (GMR) are of technological interest. Due to the individual layer thickness in the range of a few Angstroms the evaluation of the structure is quite a challenge. Both crystallographic structure and interface roughness (including in plane and out of plane roughness correlation) are to be determinend. We show how the combination of information yielded by TEM and X-Ray diffraction with a conventional laboratory setup can give a comprehensive picture of the structure. Special emphasis will be laid on the discussion of X-Ray reflectometry scans in nonspecular geometry to determine the interface structure of the individual layers in comparison to what can be gained by TEM (diffraction and bright field imaging).

C-I.4 15:20-15:40 ION ASSISTED DEPOSITION OF Ag(001)/Fe(001) MULTILAYERS: INTERFACE ROUGHNESS, G. Gladyszewski, Department of Physics, Technical University of Lublin, 20618 Lublin, Poland; C. Jaouen, A. Declemy, J.C. Girard, P. Guerin, Laboratoire de Metallurgie Physique, Université de Poitiers, 86960 Futuroscope Cedex, France

The interfacial roughness affects many physical properties of artificially layered structures. Its influence on the specular reflectivity of multilayer X-ray mirrors, an important role in the long-range magnetic coupling in magnetic superlattices causes that a detailed characterization of the interface becomes essential.

One of the multilayer preparation techniques - ion assisted deposition (IAD) allows one to modify the multilayer interfaces during the growth process As reported before, in some systems (for example in Ag/Ni multilayers) a strong improvement of superlattice structure quality occurs in IAD grown samples. In this work, we present results obtained for Ag/Fe multilayers grown on MgO(001) substrates via IAD. The structure charaterization was performed using symmetric and asymmetric X-ray diffraction (XRD) techniques. The Ag(001)<100>//Fe(001)<110>// MgO(001)<100> growth was confirmed. The XRD results were interpreted using the model of non-ideal superlattice structure based on a Monte Carlo simulation. Particular attention is paid to the interface roughness determination. Additionally, the surface roughness was charaterized using atomic force microscopy (AFM). The decrease of the rms roughness for the samples grown in IAD mode in comparison with samples grown without ion assistance was evidenced.

15:40-16:10 **BREAK**

Session I - First Stage of Growth, Part 2
Chairperson: A.G. Cullis, University of Sheffield, Sheffield, UK

C-I.5 - invited - 16:10-16:50 X-RAY SCATTERING STUDY OF QUANTUM WIRES AND LATERAL PERIODIC HETEROSTRUCTURES, **L. Tapfer**, Centro Nazionale Ricerca e Sviluppo dei Materiali (PA S.T.I S.-C N R S.M.), S.S.7 Appia km.712, 72100 Brindisi, Italy

In this work the application of advanced x-ray scattering methods to the analysis of mesoscopic and low-dimensional heterostructures will be reviewed. We will report on the investigation of semiconductor quantum wires, corrugated surfaces and lateral periodic heterostructures by high-resolution reciprocal space mapping, specular and diffuse x-ray reflection. We show that high-resolution x-ray experiments can provide accurate information on the geometrical and structural parameters of low-dimensional heterostructures.

In particular, for periodic quantum wire arrays the shape of the corrugation and the geometrical parameters (width and heigth) can be determined by simulation of the experimental x-ray diffraction patterns using semi-kinematical scattering models. In addition, the strain fields in quantum wires can be determined: a partial elastic lattice relaxation has been revealed in accordance with the predictions of the elasticity theory for low-dimensional structures.

Furthermore, the lateral modulation of the layer thickness and of the lattice strain, which occur in symmetrically strained superlattices grown on slightly off-oriented substrates, is studied by combining high-angle and low-angle x-ray scattering experiments. We show that the lateral modulation can be described in terms of ordered interface roughness. The distribution and correlation of the roughness across the interfaces were investigated by specular and diffuse x-ray reflection.

C-I.6 16:50-17:10 HRXRD FOR THE ANALYSIS OF ULTRA-THIN CENTRE-SYMMETRIC STRAINED RTD-HETEROSTRUCTURES, W. Prost, M. Haase, Q. Liu 1, F.J. Tegude, Gerhard-Mercator-Universität, Halbleitertechnik/Halbleitertechnologie, 1Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany

The application of High Resolution X-Ray Diffraction (HRXRD) to ultra-thin but mismatched and centre-symmetric layer sequences is presented. These layers are indispensable for a variety of (opto-) electronic devices such as graded-index lasers or resonant tunnelling diodes (RTD). Quantum-effect-based devices imply the need of ultra-thin layers which are difficult to analyse by any means. However, most of the high performance RTD layer stacks incorporate a substantial lattice mismatch ($\Delta a/a \geq 1\%$) such that in the HRXRD rocking curve the low-intensity layer peaks become separated from the substrate peak. The measured intensity remains high enough down to the 10 monolayer range to assure a precise assessment. We found that the rocking curves of these layers exhibit a beat under the strained barrier layer peak. We will show that this feature can be described with analytical relations deduced from the kinematical theory under appropriate restrictions. The parameters of this beat depend on the thickness, and composition of the intrinsic RTD layers and can be used to shorten the fit procedure based on the dynamical theory. The presence of thick but lattice matched contact layers results in a intensity modulation and has negligible influence on its mean intensity and phase. In summary, practical lattice-mismatched RTD-device layer structures can now be analysed by a non-destructive method.

C-I.7 17:10-17:30

HRXRD STUDY OF STRUCTURAL PROPERTIES OF MOVPE GROWN $Ga_xIn_{1-x}As$, J. Xu(1), X.J. Cheng(1), X.G. Xu(2), (1)I. Physkalisches Institut, RWTH Aachen, Sommerfeldstrasse 28, 52056 Aachen, Germany; (2)Institut für Halbleitertechnik I., RWTH Aachen, Germany

The goal of this work is to study the concentration distribution on the sample surface in ternary GaInAs layer by high resolution X-ray diffractometry (HRXRD). Little mismatched GaInAs layer which was grown on undoped (001)-InP substrate in a horizontal MOVPE reactor at 40 mPa and 620°C. Tm(In),Tm(Ga) and AsH_3 were used as precursors.

The rocking curves were collected along a line with the step of lmm on the sample surface, which has the size of $2.5*2.5\ cm^2$. From (004) rocking curves the layer strain and Ga concentration depending on the surface position were obtained. Along the gas flow direction Ga content in ternary layer decreases expotentionally. In addition we have also applied the reciprocal space mapping to determin the relaxation, tilt and broadening peak effects. In (224) asymmetrical space mapping no relaxation was observed in about l µm thick GaInAs layer. In (004) space mapping the broadening of (004) rocking curve in both lateral and in-depth compositional gradient were significant presented. On the basis of the X-ray results a simple mathematical model was developed to explain the dependence of Ga content on surface position along the flow direction. Furthermore according to this model some proposals were mentioned, how to improve the uniformity of ternary layer grown in MOVPE system.

C-I.8 17:30-17:50

CHARACTERIZATION OF III-V HETEROSTRUCTURES BY 1-D, 2-D AND 3-D HRXRD SCANNING OF RECIPROCAL SPACE M. Schuster, Siemens AG, Corporate Technology, 81730 Munich, Germany, A. Iberl, J. Fait, J. Phillips, J. Chambers, AXS, Siemensallee 84, 76181 Karlsruhe, Germany, N. Herres, J. Schmitz, FhI IAF, Tullastr. 72, 79108 Freiburg, Germany, P. Phizackerley and H. Bellamy, SLAC SSRL, Menlo Park, CA 94025, USA

Rocking curve measurements (1-D scans through reciprocal space) and reciprocal space mapping (2-D scans) with high-resolution X-ray diffractometers have proven to be an essential analytical technique for the characterization of III-V heterostructures. Whereas, 1-D scans, which are sufficient for the assessment of simple, lattice matched heterostructures, can be performed within minutes, 2-D scans on complicated, relaxed and tilted heterostructures may take hours or days. The use of a detector with 2-D spatial resolution has two benefits: (1) the measuring time can be reduced to the time necessary for a standard 1-D scan, (2) the reciprocal space can be scanned even in 3 dimensions. The requirements of HRXRD at a synchrotron source could be met by a dedicated X-ray CCD detector with a resolution of 1024x1024 pixel (65µm), an intensity range of $1:2^{19}$ and background compensation software.

3-D scans will be discussed, together with 1-D and 2-D scans, on an InAs/GaSb superlattice grown on GaAs(001) by MBE.

C-I.9 17:50-18:10

FINE INTERFERENCE EFFECTS IN X-RAY DIFFRACTION SPECTRA FROM MULTILAYERED STRUCTURES, E. Zolotoyabko, Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

Precise characterization of multilayered structures in many cases requires careful analysis of interference between strong waves originating from the substrate and the thin film components. In this paper some important interference effects will be considered: 1) thickness-dependent shift of diffraction peaks (Fewster-Curling effect); 2) phase sensitivity to subnanometer layers in the interferometer-like scattering geometry; 3) dependence of fringe periodicity on lattice disorder; 4) «cleaning» of the microtilt-induced spectral broadening by quasiforbidden reflections.

Interference effects are not sensitive to the multiple scattering, and therefore are well described in the extended kinematic approximation, which utilizes direct summation of scattered waves [1]. This approach is also suitable for the introduction of short-range variations of structural and geometrical parameters of the multilayered system, which expands the framework of X-ray diffraction studies. In many cases analytical expressions for diffraction spectra can be derived allowing detailed analysis of the characterization problem.

Theoretical findings are illustrated by X-ray diffraction spectra taken from partially disordered SiGe/Si heterostructures, ultrathin GaAs/GaInAs/GaAs quantum wells, Si structures with buried amorphous layers and nearly matched GaInP/GaAs structures.

1. E. Zolotoyabko, Y. Finkelstein, M. Blumina and D. Fekete, Physica B,221 487 (1996).

Wednesday June 18, 1997 — Morning
Mercredi 18 juin 1997 — Matin

Session II - Strain Analysis in Thin Films, Part 1
Chairperson: E. Vlieg, FOM Institute, Amsterdam, The Netherlands

C-II.1 - invited - 9:00-9:40

STRAIN ANALYSIS IN THIN FILMS BY QUANTITATIVE CONVERGENT BEAM ELECTRON DIFFRACTION, **J. Mayer**, S. Krämer, S. Streiffer*, and A. Weickenmeier, Max-Planck-Institut für Metallforschung, Seestr. 92, 70174 Stuttgart, Germany, * now at Dept. of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7907, USA

Lattice strain in metals or alloys is an important factor controlling the performance and failure mechanisms in compound systems. In combination with ceramics or semiconductors, the metal is always the elastically and plastically softer material. Therefore most of the strain is localised within the metal. Convergent Beam Electron Diffraction (CBED) makes it possible to measure lattice strain with high spatial resolution. We have studied Al thin films on SiC and Si substrates. In particular the latter ones serve as a good model system for interconnects in semiconductor devices. The samples were studied in cross-section and plan-view geometry.

The CBED patterns were acquired on an energy-filtering Zeiss EM 912 Omega transmission electron microscope. The energy-filter removes the inelastically scattered electrons which increases the accuracy of the measurements and makes possible to study thicker specimen areas. The CBED patterns were recorded at different temperatures to study the effect of the differences in thermal expansion coefficients. The results indicate that in the thin films strains of up to 0.5% can occur. Strong deviations from a simple equibiaxial strain state were observed in a polycrystalline <111> textured film. A sensitivity to variations in lattice parameter of approximately 10^{-4} was obtained. Possible stress relaxations in the thin TEM sections will be discussed.

C-II.2 9:40-10:00

HRTEM STUDY OF STRAINED Si_{1-x}/Ge_x MULTILAYERS, M. Romeo, C. Uhlaq-Bouillet, J.P. Deville, J. Werckmann, G. Ehret, IPCMS, 23 Rue du Loess, 67037 Strasbourg, France, and R. Chelly, D. Dentel, T. Angot, J.L. Bischoff, LPSE, 4 rue des Frères Lumière, 68093 Mulhouse, France

Epitaxial Si1-x/Gex (0< x <1) multilayers were grown on Si(001) at 670°K using hot wire assisted gas source and ultra high vacuum molecular beam epitaxy. The aim of the study is to determine the surfactant effect of hydrogen present in the first growth technique.

For HRTEM observations, the samples were prepared exclusively by mechanical polishing using the tripod method in order to avoid chemical and structural perturbations introduced by ion milling.

The micrographies were processed with the freeware Khoros. We have evaluated the stress field and studied defects in both samples and thus we have compared the growth techniques.

C-II.3 10:00-10:20

INVESTIGATION OF INHOMOGENEOUS STRUCTURES OF NEAR-SURFACE-LAYERS IN ION IMPLANTED SILICON, J.T. Bonarski, Z. Swiatek, R. Ciach, Polish Academy of Sciences, Institute of Metallurgy and Materials Science, Reymonta st. 25, 30-059 Krakow, Poland; Z.T. Kuznicki, CNRS, Laboratoire PHASE (UPR 292, BP 20, 67037 Strasbourg Cedex 2, France and I.M. Fodchuk, M.D. Raransky, P. Gorley, Chernivtsi State University , Kotsyubinskogo 2, 274012 Chernivtsi, Ukraine

The ion implantation as subject of investigations attracts increasing interest because of its technological applications. For example, the ion implantation and adequate thermal treatment are the basic processes for fabricatin of a new so-called delta-BSF solar cell. In this silicon solar cell the continous sub-structure of modified material (planar amorphous-like layer of nanometric thickness with very thin transition zones) is inserted into the single-crystal emiter. From high resolution electron microscopy studies it is evident that these two Si phases coexist in the form of well-defined layers separated by sharp heterointefaces

The aim of this paper is to contribute to futher structural characterization of silicon monocrystal with buried "amorphous" layer. The whole group of nondestructive x-ray diffraction methods was used in investigation of quality of the a-Si/c-Si heterointerfaces, structural homogenity of the layers and distribution of the stress field. Each measurment was carried out on an initial, as-implanted and annealed material. <100> oriented Si monocrystals were implanted with 180 keV energy P ions at room temperature. The mathematical modelling of defects in real crystals and modelling of x-ray dynamic scattering for interpretation of results were applied. The results reported in this work are compared with similar studies recently published in the literature.

C-II.4 10:20-10:40

INFLUENCE OF CdTe SUBSTRATES ORIENTATION ON THE STRUCTURE REFLECTION OF HgCdTe FILMS OBTAINED BY ISOTERMAL VAPOR PHASE EPITAXY, J.D. Nabitowich, I.O. Rudyj, M.S. Fruginskyj, I.V. Kurilo, State University "Lviv Politechnic", Bandera Str.12, 290646 Lviv, Ukraine

Elementary processes of growth have an influence on the perfection of epitaxy films (EF) which are connected with nucleation character. By the method of replic electron microscopy, diffraction of reflected rapid electrons and electron-probe microanalysis the influence of the crystallographic orientation of CdTe substrate of the EP perfection was estimated. As a rule the two-dimensional mechanism of growth takes place on CdTe substrates (110) Three-dimensional nucleating and connecting with this «island» character of EP growth is observed on the (111) substrates.

The structure and morphology of EP also depends on polarity of (111) facets. The growth velocity on the facet A(lll) is smaller than on facet B(lll) what we connect with different reaction possibility of these facets. Electron-probe microanalysis also showed different reaction possibility of the facets(110) and (111) as to Hg atoms.

The initial conditions of growth and also cooling regime in the final stage of epitaxial growth are influencing on the stage of defectness of transition layer film-substrate and by surface layer of HgCdTe.

10:40-11:10 **BREAK**

Session II - Strain Analysis in Thin Films, Part 2
Chairperson: A. Bourret, CEA, Grenoble, France

C-II.5 - invited - 11:10-11:50

STRAIN ANALYSIS BY X-RAY DIFFRACTION, **P.F. Fewster** and N.L.Andrew, Philips Research Laboratories, Cross Oak Lane, Redhill RH1 5HA, UK

This paper will discuss the precision measurement of strain in materials. The technique of measurement will be discussed and the precautions necessary to obtain reliable results with precisions to one part per million. With X-ray diffraction we can alter the averaging depth by judicious choice of reflections. By combining several reflections from planes that are inclined to the surface it is possible to determine the full lattice distortion.

The measurement of relaxation in semiconductor buffer layers usually involves many assumptions associated with the geometry of the undistorted unit cell. This can be shown to be a problem and a new definition of relaxation associated more directly with the atomic spacings in the plane of the interface will be presented. These methods also give more precise values of the distortions present.

The measurement of the lattice parameters of bulk material will also be discussed, including hazards of sample alignment, complications of interplanar spacings determined from inclined planes and problems of finding a reliable internal reference standard.

C-II.6 11:50-12:10

STRAIN PROFILING IN THIN FILMS BY SYNCHROTRON RADIATION - A NOVEL TECHNIQUE, N.B. Thomsen(1,3), U. Lienert(2,3), S. Garbe(2), V. Honkimäki(2), H.F. Poulsen(3) and A. Horsewell(3); (1)Danfoss A/S, 6430 Nordborg, Denmark; (2)ESRF, 38043 Grenoble Cedex, France; (3)Riso National Laboratory, 4000 Roskilde, Denmark

Residual strain profiles in thin films and multilayers are studied by high resolution, high energy X-rays (synchrotron X-rays). In terms of penetration power and spatial resolution, this emerging technique is bridging the gap between conventional laboratory based X-ray diffraction and neutron diffraction techniques. Accurate knowledge about residual stress/strain conditions in coatings is essential for optimal design of these materials. Two types of coatings were investigated: a nickel/copper multilayer deposited on copper substrate using the so-called dual-bath technique and a chromium-nitride film using the physical vapour deposition, PVD, technique. Both of these types of coatings are known to exhibit strong strain gradients. The initial results provide direction for further experiments towards determining the ultimate capabilities of the synchrotron X-ray technique in strain profiling.

C-II.7 12:10-12:30

LIMITS OF VALIDITY OF THE CRYSTALLITE GROUP METHOD IN STRESS DETERMINATION OF THIN FILMS AND MULTILAYERS, P. Gergaud, S. Labat, O. Thomas, MATOP, URA CNRS 1530, Faculté de St Jérôme, 13397 Marseille Cedex 20, France

The mechanical state of stress of thin films or multilayers is of great importance because of its influence on many physical properties: magnetic, dielectric, elastic, ... For these reasons the determination of stresses in these materials is becoming of increasing importance. Among the methods available for stress or strain determination, the x-ray technique, through the $\sin^2\psi$ method, is of great interest because of the low mean depth penetration of X-ray and because it allows the strain measurements in different phases of a thin film, leading thus, for instance in a multilayer, to a complete knowledge of the state of stress. Usually, the thin films exhibit strong textures inducing some difficulties in the stress calculus. One easy way to solve the problem is to use the crystallite group method. It is a pseudo $\sin^2\psi$ analysis based on the assumptions done in single crystal analysis. Of course, the stronger the texture, the better the validity of the measurements. In this work, we calculate using simulations and modelling (based on Voigt, Reuss and Hill hypothesis) the limit of this technique versus the mosaicity of the texture for both fibre texture and single crystal-like texture. It is shown that the results depend on the symmetry of the state of stress (biaxial, isotropic, with or without shear stress...). These assumptions are in general valid for thin films allowing the use of this technique in many cases.

12:30-14:00 **LUNCH**

Wednesday June 18, 1997 Afternoon
Mercredi 18 juin 1997 Après-Midi

Session III - Coating
Chairperson: P. F. Fewster, Philips Research Center, Redhill, UK

C-III.1 - invited - 14:00-14:40

CORRELATION BETWEEN ATOMIC AND ELECTRONIC STRUCTURE OF DIAMOND GRAIN BOUNDARIES ANALYZED BY HREM AND EELS, **H. Ichinose**, Department of Materials Science, The University of Tokyo, 7-3-1 Hongo, bunkyo-ku, Tokyo 113, Japan; M. Nakanose, Nissan Motor Co. LTD and M. Khoyama, Osaka National Research Institute, AIST, Japan

Atomic and electronic structure of diamond grain boundaries of a polycrystalline thin film diamond are investigated by both high resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS). Atomic structures of CSL boundaries were apparently different from that of other covalent bonding semiconductors such as silicon and germanium. Σ 9 boundary tended to be parallel with (114) plane even though the latter was supposed to contain dangling bonds which cause to elevate boundary energy. A new line attributed to π * state (bonding) appeared in EELDS spectra of (114) Σ 9, (112) Σ 3 and some high angle bondaries. A dangling bond (p_z orbital electron) of a three coordiated atom may easily change into π state in diamond. The change can result in energy reduction of the boundaries to stabilize their atomic structure which is unexpected in other semiconductors and ceramics.

C-III.2 14:40-15:00

EELS ANALYSIS OF HYDROGENATED DIAMOND-LIKE CARBON FILMS, L. Ponsonnet(1), C. Donnet(1), JM. Martin(1), A. Grill(2) and V. Patel(2); (1)Ecole Centrale de Lyon Laboratoire de Tribologie et Dynamique des Systèmes, UMR 5513, BP 163, 69131 Ecully Cedex, France; (2)IBM Research Division, T. J. Watson Research Center, Yorktown Heights, N. Y. 10598, USA

Electron energy-loss spectroscopy has been used to analyse the structure of hydrogenated diamond-like carbon (a-C: H) films deposited by PACVD under a variety of conditions (bias, pressure, gaseous precursors). The ratio sp^3 (tetragonal) to sp^2 (trigonal) carbon sites was quantified from the near edge structure (ELNES) of the carbon K-edge. The results are compared with reference spectra taken on highly oriented pyrolytic graphite and amorphous carbon. In order to better identify the chemical bonding from the carbon K near-edge structure, the first two peaks of the edge were decomposed to obtained the peaks of individual transitions, after subtracting the simulation of the carbon K-edge to extract the core-excitation peaks. The relative contributions of ls/π^* (C=C), ls/σ^* (C-H), ls/σ^* (C-C) and ls/σ^* (C=C) will be discussed. In parallel, EELS spectra were obtained in the low-loss region (from 0 to 50 eV). Several spectral features were observed after decomposition into individual peaks. Small peaks were observed between 4 and 10 eV corresponding to π/π^* orbitals transitions, the main plasmon loss peaking near 23 eV energy-loss. Another kind of peak was seen near 13 eV loss which could be attributed to hydrogen K-edge ionization from gaseous hydrogen indicating that DLC films may have undergone dehydrogenation.

C-III.3 15:00-15:20

IN-DEPTH STRUCTURAL X-RAY INVESTIGATION OF PECVD GROWN DIAMOND FILMS ON TITANIUM ALLOYS, P. Andreazza, C.RM.D., Université d'Orléans CNRS, BP 6759 Rue de Chartres, 45067 Orléans cedex 2, France; M.I. De Barros, D. Rats and L. Vandenbulcke, L.C.S.R, CNRS, 45071 Orléans cedex 2, France

Titanium and its alloys have many attractive properties and important applications, for example in aerospace or corrosive environments. However a greater wear resistance would permit to extend their engineering applications. Diamond coatings have been deposited in a microwave plasma from CH_4H_2 and CO/H_2 mixtures, with that aim. Besides the diamond layer itself, the composition and microstructure of the surface and bulk substrate can be changed and there properties influenced by the thermal treatment and the diffusion of light elements, especially carbon and possibly hydrogen.

In-depth repartition profiles of crystalline phases formed during the diamond films growth are measured here using Grazing Incidence X-ray Diffraction (GIXD), in correlation with Scanning Electron Microscopy coupled with EDX analysis. The GIXD method is particulary well adapted to study surface modifications or depositions of polycrystalline materials. Especially in this case, the formation of different intermediate carbonaceous layers are evidenced in terms of microstructure, from the diamond films to the titanium alloy substrate. In addition, crystalline parameters, microstrains rate and coherently domains sizes evolution of different a and b-Ti alloy solid solutions, titanium carbide and diamond phases has been studied with respect to growth kinetic and deposition temperature, in the range 600-850°C.

C-III.4 15:20-15:40

CROSS-SECTIONAL TEM OBSERVATION OF MULTILAYER STRUCTURE OF A GALVANNEALED STEEL, T. Kato, M. H. Hong, K. Sasaki, K. Kuroda and H. Saka, Department of Quantum Engg, Nagoya Univ., Nagoya 464-01, Japan

An Fe-Zn base galvannealed coating is used widely for an atutomobile sheet. The microstructure has been researched extensively since the mechanical properties of the coating are closely related with the multi-layer microstructure. So far microstructures of the Fe-Zn coatings have been studied only by optical microscopy and SEM. It is only very recently that the microstructures are studied by TEM in any detail. In the present study a focused ion beam (FIB) system has been used to prepare a thin foil specimen if a galvannealed steel for cross-sectional observation by TEM.

Two types of steel which were subjected to different treatments were studied; one is as-dipped and the other is galvannelaed at 773K for 20sec. TEM cross-sectional specimens were fabricated in a Hitachi FB-2000 FIB system. Fabrication took only 3hours. The specimens were examined at an accelerating voltage of 300kV in a Hitachi H-9000NAR microscope.

C-III.5 15:40-16:00 PERFECTION OF $CoSi_2$ LAYERS IN Si (100) OBTAINED BY ION IMPLANTATION,

A.A. Galayev(1), Yu.N. Parkhomenko(2), D.A. Podgorny(2), K.D. Chtcherbatchev(2), A.I. Belogorohov(2), (1)Institute of Chemical Problems in Microelectronics, 86 Prospekt Vernadskogo, 117571 Moscow, Russia,(2)Moscow Steel and Alloys Institute, 4 Leninsky Prospekt, 117936 Moscow, Russia

The effect of dose and annealing on the structure and properties of buried conducting layers obtained by ion implantation have been studied.

$^{59}Co^+$ ions were implanted into Si (100) wafers with resistivity 4.5 Ohm-cm at 180 keV and ion current density of 13 mA/cm^2. In order to anneal radiation defects and initiate cobalt disilicide precipitation the wafers were heated to 450 °C during the implantation. After the implantation, the wafers were annealed in a diffusion furnace in flow of pure argon in two steps: first, for 1 h at 600 °C and then for 30 min at 1000°C.

According to the HREM data on the samples implanted at $3 \cdot 10^{17}$ cm^{-2}, the $CoSi_2$ layer is a continuous, sharp-bounded single crystal. For 10^{17}cm^{-2}, the layer consists of {111}-faced $CoSi_2$ grains. The diffraction peaks are smeared towards the lower angles. These defects are retained at 600 °C but they are disappeart at 1000°C.

The angular distances between the Si and $CoSi_2$ diffraction peaks obtained in different geometries were used to determine the $CoSi_2$ lattice parameters in the directions perpendicular($a_\perp$) and parallel($a_\|$) to the surface. The results were recalculated for unstrained crystal $\alpha_{CoSi_2}^{exp}$ that were used to calculate the relaxation coefficient $R=(\alpha_{CoSi_2}^{exp}-a_{si})/(\alpha_{CoSi_2}^{bulk}-a_{si})$ From the shift of the peak measured relative to their calculated position we calculated the perpendicular($\varepsilon_\perp$) and parallel($\varepsilon_\|$) components of $CoSi_2$ lattice strain in the layer. The above data are in good agreemenb with the Raman spectra.

16:00-16:20 **BREAK**

Poster Session I

16:10-18:00 See programme of this poster session p. C-15 to C-19.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session IV - Advanced Electron Microscopy, Part 1
Chairperson: L. Tapfer, Centro Nazionale Ricerca e Sviluppo dei Materiali, Brindisi, Italy

C-IV.1 - invited - 9:00-9:40

HREM : ULTIMATE PERFORMANCES, **D. Van Dyck**, Department of Physics, University of Antwerp - R.U.C.A., Groenenborgerlaan 171, 2020 Antwerp, Belgium

The factors limiting the resolution in High Resolution Electron Microscopy are discussed. It is shown that EM is approaching its physical limits which are not limited anymore by the instrument but rather by the object. The problem however is how to extract the information from the images so as to fully exploit the resolution capabilities. Since the visualisation of individual atoms becomes possible, we can reconsider the concept of resolution in terms of information theory. New promising developments towards direct retrieval of the object information by processing of the electron images are discussed. These include solutions to the phase problem as well as inversion of the dynamical diffraction in the object. Finally, recent results are shown, which demonstrate the potential of this approach.

C-IV.2 9:40-10:00

NEW METHOD FOR QUANTITATIVE ANALYSE OF STRAIN FIELD IN THIN FILMS FROM HRTEM MICROGRAPHS, E. Snoeck, B. Warrot, H. Ardhuin and M.J. Casanove, CEMES-CNRS BP 4347, 31055 Toulouse Cedex 5, France, R. Kilaas, NCEM/LBL, bldg 72, 94720 Berkeley, CA, USA, M.J. Hÿtch, CECM 15, Rue G. Urbain, 94407 Vitry, France

A new method for measuring and mapping displacement fields and strain fields has been developed. The method is based upon centring an aperture around a strong reflection in the Fourier transform of a HRTEM lattice image and performing an inverse Fourier transform. The phase component of the resulting complex image gives information on local displacements of atomic planes. The 2-dimensional displacement field can then be derived by applying the method to two non-colinear Fourier components. Local strain tensor components $\varepsilon_{xx}(r)$, $\varepsilon_{yy}(r)$, $\varepsilon_{xy}(r)$ and $\varepsilon_{yx}(r)$ can be obtained by analysing the derivative of the displacement field. Applied to HRTEM images of thin films, this technique gives quantitative information on the variations of the strain relaxations in the different layers. Results obtained with this method on epitaxial thin films like: Fe/MgO, Co/Au and GaAsInP/InP will be presented.

C-IV.3 10:00-10:20

THE VOLUME EXTENSION OF THE {1120} STACKING FAULT IN GaN/AIN LAYERS GROWN ON (0001) 6H-SiC, P. Vermaut, A. Béré, P. Ruterana, A. Hairie, G. Nouet, and E. Paumier, LERMAT 6004 CNRS, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

An extensive study combining quantitative high resolution measurement and atomistic simulation was carried out in order to characterize the {1120} prismatic stacking fault (Drum model).

Geometrical models of the fault were allowed to relax with a modified Stillinger-Weber potential. It is rather a short range potential which takes into account the first 4 and 12 second neighbour atoms. In order to apply it to the wurtzite compounds, it was necessary to add a correction term in order to take into account the third neighbour atom which governs most of the anisotropy in the hexagonal system.

A match was next made between the experimental and simulated images. A deviation from the equilibrium interplanar distance was measured accurately along a direction perpendicular to the fault plane.

Instead of finding 0.5 as expected from the Drum model, a value close to 0.6 [1120] was measured. This means that the equilibrium {1120} prismatic stacking fault in epitaxial GaN over 6H-SiC contains a slight volume extension.

C-IV.4 10:20-10:40

QUANTITATIVE LORENTZ MICROSCOPY ON SPIN VALVE, P. Bayle-Guillemaud, CEA-Grenoble, Département de Recherche Fondamentale sur la Matière Condensée, 17 avenue des Martyrs, 38054 Grenoble Cedex 9, France, A.K. Petford-Long, University of Oxford, Parks Road, OX1 3PH, UK, T.C. Anthony and J. Grug, Hewlett Packard Laboratories, Palo Alto, CA, USA

The spin valves (NiFe or Co(8nm)/ Cu(4nm) / Co(8nm)/ MnFe(12nm)) show a change of the resistance (Giant MagnetoResistance) when the two in-plane magnetic vectors of the two magnetic films are oriented parallel or antiparallel under the influence of an external magnetic field. In order to follow the flip process of the magnetic induction as a function of an applied field, quantitative lorentz microscopy has been performed with a conventional TEM equipped with a low-field pole-piece. A magnetising holder allows the in-situ magnetisation of the specimen. For different magnetic field values, Fresnel images are recorded as well as series of Foucault images taken with small incremental tilts of the incident illumination which allowed to produce quantitative maps of the magnetic induction distribution [1] It is then possible to follow the domain wall formation and the domain wall motion as a function of the applied field.

This analysis has been performed on spin valves with different magnetic layers Co, NiFe or NiFe/Co. The series of quantitative maps show the process of rotation of the in-plane magnetic induction. in each case. It is clearly shown that the spin valves response depend strongly of the nature of this layer

[1]: A.C. Daykin et al.: Ultramicroscopy 58 (1995), 365-380.

10:40-11:10 **BREAK**

Session IV - Advanced Electron Microscopy, Part 2
Chairperson: D. Van Dyck, University of Antwerp, Antwerp, Belgium

C-IV.5 - invited - 11:10-11:50

ELECTRON BEAM NANOANALYSIS OF NANOSTRUCTURED MATERIALS, **C. Colliex**, Laboratoire de Physique des Solides, Bat 510, 91405 Orsay, France

The fine electron probe delivered by a field emission source in a STEM, constitutes a unique tool to investigate the local properties of a thin solid specimen. It can be positioned at well on the surface of the sample under analysis, scanned along a profile across a feature of interest, or rastered over a restricted area. For each position, the signals measured through the different detectors are recorded. The Electron Energy Loss (EELS) spectra convey a wealth of useful information covering a wide special range from the eV to the keV domain, i.e. from the gap threshold and interband transitions on one end, to the soft X ray domain with its characteristic electron excitations from well defined core orbitals and their associated fine structures (ELNES) on the other end. Using the acquisition capabilities of the parallel detector, sequences of spectra connected to the successive positions of the incident probe constitute a new type of data set, defined as line-spectra or image-spectra, with axes corresponding to the spatial coordinates on the specimen and to the energy-loss scale. The facility presently operating on the Orsay VG STEM offers optimum resolutions of the order of 0.5-0.7 eV and 0.5-0.7 nm. They are therefore particularly well suited to the exploration of the local composition and electronic properties of nanostructures, such as carbon nanotubes, nanoporous Si, metallic multilayers, heteromaterial interfaces... This contribution will therefore emphasize the new possibilities offered in the domain of high spatial resolution chemical mapping as a support for more refined investigations of the bonding characters and electron states permitted by the identification, measurement and interpretation of the changes in EELS fine structures.

C-IV.6 11:50-12:10

SURFACE OBSERVATION OF SEMICONDUCTORS AND METALS BY ULTRAHIGH VACUUM FIELD-EMISSION TRANSMISSION ELECTRON MICROSCOPE, M. Tanaka(1), K. Furuya(1), M. Takeguchi(2) and T. Honda(2), (1)National Research Institute for Metals, 1-2-1, Sengen, Tsukuba 305, Japan, (2)JEOL LTD. 3-1-2, Musashino, Akishima 196, Tokyo, Japan

Recently, observation and analysis of atomic details of surfaces are achieved in real-space owing to the development of new microscopes. High resolution electron microscopy can obtain atomic scale information on surfaces by direct imaging. A newly developed ultrahigh vacuum field-emission transmission electron microscope (UHV-FE-TEM; JEM-2000VF) enables the imaging and analyzing of clean semiconductor surfaces. It has a 200 keV Schottky-type field-emission gun with a point-to-point resolution of 0.21nm and beam current density of $4x10^8$A/cm^2. The vacuum level around the sample is $2x10^{-8}$Pa. It is equipped with an energy dispersive X-ray spectroscope (EDS) and a parallel electron energy loss spectroscope (PEELS). Field-emission gun provides probe size of 1nm which implement the atomic scale spectroscopy .

With intense electron shower and infrared lamp annealing, the samples are cleaned to form reconstruction such as Au (111) 23x$\sqrt{3}$ and Si (111) 7x7. Field-emission shower also enabled to write nano-sized letters on GaAs(100). The line width of the letters were less than a few atoms.

C-IV.7 12:10-12:30

AES-EELS INVESTIGATION OF THE Si/CrSi$_2$/Si(111) INTERFACE FORMATION, N.I. Plusnin, A.P. Milenin, V.J. Soldatov, and V.G. Lifshits, Institute of Automation and Control Processes, FEB RAS, Radio 5, 690041 Vladivostok, Russia

The formation mechanism, and atomic and electron structures of Si monolayers (ML) deposited at the room temperatures on CrSi$_2$ films grown on Si(111) were investigated by AES, LEED, and EELS methods.

Under r=2Å/min the Cr AES-signal from the substrate and relative amplitude of the bulk plasma losses peak in EELS spectrum decreased faster then under r=0.5Å/min. Accordance of the experimental curve with theoretical one shows that the growth mechanism under r=2Å/min is layerwise and that adsorption of the first 1/3 ML Si (d=3,5Å) atoms takes place only above substrate Cr atoms. The comparison of various growth mechanisms for r=0,5Å/min undoubtedly shows initially the inhomogeneous over thickness intermixing between deposited Si and substrate Cr atoms and then the layer by layer (d=3,5-6Å) and islandlike growth of Si film. Changes of loss energy peak position in EELS, appearance of the new peaks, and kinks in dependences of the bulk plasma losses peaks on thickness show that a two-dimensional layer of Si consisted of surface phases forms at the initial (r=2Å/min) and layer by layer (r=0.5Å/min) growth stages. After that the αSi film grows. Based on the AES and EELS data the electron structure of this two-dimensional layer is similar to the electron structure of Si(111) surface.

12:30-14:00 **LUNCH**

Thursday June 19, 1997
Jeudi 19 juin 1997

Afternoon
Après-Midi

Session V - General Material Studies
Chairperson: C.Colliex, Laboratoire de Physique des Solides, Orsay, France

C-V.1 14:00-14:20

APPLICATION OF FOCUSSED ION BEAM MILLING TOCROSS-SECTIONAL TEM SPECIMEN PREPARATION OF INDUSTRIAL MATERIALS INCLUDING HETERO-INTERFACES, K. Kuroda, M. Takahashi, T. Kato, H. Saka, Department of Quantum Engineering, Nagoya University, Nagoya 46401, Japan and S. Tsuji, Yamato Laboratory, IBM Japan, Yamato, Kanagawa 242, Japan

Transmission electron microscopy (TEM) is well established as a tool for both fundamental and applied research. Specimen preparation is always a crucial question of TEM investigation. Recently a new specimen preparation technique using focused ion beam (FIB) milling was developed. We applied this technique to the fabrication of cross-sectional TEM specimens of industrial materials including heterointerfaces. The following investigations were carried out: interfaces in a hot dip galvanized steel, multilayered structures in thin-film transistors for the liquid crystal display, microstructures of a diamond film on silicon nitride and interfaces in C/C-SiC composites. The largest benefit of FIB lies in its application to heterointerface analysis at a particular position in submicron scale. This technique extends the use of TEM analysis into new areas of characterization of industrial materials.

C-V.2 14:20-14:40

EPITAXIAL GROWTH OF YBaCuO THIN FILMS ON (111) $SrTiO_3$ SUBSTRATES, E. Brecht(1), J. Reiner(1), M. Rodewald(2), G. Linker(1), (1)Forschungszentrum Karlsruhe, INFP, Germany; (2)TH Darmstadt, Fachbereich Materialwissenschaft, Germany

The growth of YBaCuO thin films on (111) oriented $SrTiO_3$ substrates was studied by standard x-ray diffraction experiments performing θ-20, ω- and ϕ-scans, and by complementary cross-sectional HRTEM. The films were deposited by dc magnetron sputtering with the substrate temperature, T_s, in the range of 520°C to 820°C and the film thickness ranging from 6 nm to 180 nm as variable parameters.

At all T_s values the films grow epitaxially with the [113] direction perpendicular to the substrate surface. This means that the distorted single perovskite cells of the triple perovskite «123» structure grow with their (111) planes on the $SrTiO_3$ (111) surface. At low T_s the growth at the interface up to a critical thickness is pseudomorphic and homogeneously strained with narrow mosaic distributions below 0.04°. In films prepared at the highest T_s values broad mosaic distributions of about 1° were observed probably due to strain release by defect incorporation. In the intermediate T_s range internal strain is accumulated in the films. Three domain orientations tilted by 120° according to the three-fold symmetry of the substrate were observed in the film plane. The low T_s films are tetragonal and non-superconducting down to 4 K. Maximum T_c values of 84 K were observed in the films prepared at the highest T_s values. We speculate that the oxygenation of the films and thus the appearance of superconductivity is strain controlled.

C-V.3 14:40-15:00

CRYSTALLIZATION OF FERROELECTRIC PZT THIN FILMS ON MgO SUBSTRATE, A. Di Cristororo, P. Mengucci, A. De Benedittis, Dip. Scienze dei Materiali, Università di Ancona, Italy and B.E. Watts, F. Leccabue, CNR-MASPEC, Parma, Italy

Ferroelectrics thin films are intensely studied because of their potential applicability in non-volatile ferroelectric memory devices (NVFRAM). Lead zirconate titanate (PZT) is one of the best known perovskites used in ferroelectric applications. The most important requirements for obtaining the desired electrical behaviour are the prevalence of the ferroelectric perovskite (PE) phase with respect to the pyrochlore (PY) one and the possibility of growing epitaxial or preferentially oriented thin films. In the present study we report the results of the microstructural characterization of different compositions (PZT 20/80 and PZT 52/48) and thicknesses (100 and 200 nm) deposited by sol-gel on (100) MgO substrates in order to evaluate the influence of these parameters on the microstrucutre and preferential orientation of the deposited films. After deposition, samples were analyzed by grazing angle X-ray diffraction (GAD), scanning electron microscopy (SEM) and cross sectional transmission electron microscopy (XTEM). Results showed that the 100 nm PZT 20/80 film is prevalentely composed of PE with little amount of PY and a preferential (100) orientation. Increasing the thickness up to 200 nm the content of the PY phase increases and the preferential orientation disappeares. XTEM observations allowed to attribute this effect to the presence of a thin layer of PY in between the PZT layer. On the contrary, PZT 52/48 is mainly composed of PE (101) orientated, indipendentely on thickness.

C-V.4 15:00-15:20

MICROSTRUCTURE OF AG/NI MAGNETIC MULTILAYERS WITH DIFFERENT INTERLAYER MAGNETIC COUPLING, A. Rosova, B. Chenevier, D. Boursier, LMGP URA CNRS 1109, 38402 St Martin d'Hères, France; A. Charai, C. Alfonso, EDIFIS, URA CNRS 443, Faculté de St Jérôme, 13397 Marseille, France; O. Thomas, C. Guichet, MATOP, URA CNRS 1530, Faculté de St Jérôme, 13397 Marseille Cedex 20, France; J.-E. Sundgren, E. Svedberg, P. Sandstrom, Dept. of Physics, Linköping University, 58183 Linköping, Sweden

A series of Ni/Ag multilayers was grown at room temperature on oxidized Si (100) substrates by ultra-high vacuum dc magnetron sputtering. The Ni layer thickness is kept constant at 5 nm. The Ag layer thickness varies between 1 and 10 nm to possibly induce a variation of Ni interlayer coupling. X-ray diffraction pole figures and $\theta/2\theta$ scans exhibit a pronounced (111) texture for both Ni and Ag. TEM, HREM and EELS methods were used to characterise the multilayer microstructure. M (H) measurements with the applied field either parallel or perpendicular to the film surface, were performed between 10 and 300 K using a vibrating sample magnetometer. These measurements allowed us to correlate the multilayer microstructure with the magnetic properties.

C-V.5 15:20-15:40 STRUCTURAL CHARACTERIZATION OF InP EPILAYERS GROWN ON (001) AND (111) SURFACES OF GaAs SUBSTRATES, M.B. Derbali, J. Meddeb, H. Mâaref, Laboratoire de Physique des Semiconducteurs, Fac. Sciences de Monastir, Monastir, Tunisia, D. Buttard, Laboratoire de Spectrométrie Physique, Université J. Fourier, Grenoble 1, (CNRS UMR 5588), France

There is an increasing interest in the heteroepitaxial growth of semiconductor on lattice-mismatched substrate. The success of heteroepitaxy adds a new dimension for the system designer who can then take the best features of several semieonductors and combine them together to achieve new devices, such as optoelectronic integrated circuits. Among the heteroepitaxy system under investigation, InP on GaAs has attracted considerable attention. The interest stems from the potential advantages of the integration of InP-based lasers and detectors operating at wavelengths around 1.3 and 1.55 µm with fast GaAs field effect devices for optical communication technologies.

The growth of InP on a GaAs substrate results in a high density of threading dislocations (10^8/cm^2) which arises from the interfacial misfit dislocations due to the large lattice mismatch (3.7 %). Several approaches have been applied to reduce this dislocation density, i.e, thermal cyclic annealing, introduction of strained-layer superlattice,...

In order to improve the InP crystal quality, we have investigated the effect of the substrate orientation. In this communication, we report a reduction in the density of the threading dislocations using (111) surfaces of GaAs substrates. The heteroepitaxial layers of InP were grown by metalorganic chemical vapor deposition on (001), (111)A and (lll)B surfaces of GaAs substrates. The structural properties (residual strain, misorientation and crystal quality) of the heteroepilayers were investigated using high resolution X-Ray Diffraction and Transmission Electron Microscopy .

C-V.6 15:40-16:00 TEM AND HREM INVESTIGATION OF STRUCTURE OF SILICON POLYCRYSTALLINE FILMS AND NANOCRYSTALS INSIDE OF AMORPHOUS SILICON FILMS ON GLASS SUBSTRATES, M.D. Efremov, V.A. Volodin, L.I. Fedina, A.K. Gutakovski, Institute of Semiconductor Physics SB RAS, pr.Lavrentjeva 13, Novosibirsk 630090, Russia; V.V.Bolotov, Institute of sensor microelectronics SB BAS, pr.Mira 55a, Omsk 644077, Russia

The systematic TEM and HREM study of structure of the silicon films on glass substrates in a course of phase transition from the stage of nucleation to the stage of final crystallization was provided. Phase transition was realized using the method of stimulation of nucleation in amorphous phase with rapid thermal annealings and excimer laser treatments. It was demonstrated by HREM, that just after excimer laser treatment silicon nanocrystals were appeared inside of amorphous matrix of the films. Varying the regime of laser treatments allowed to change sizes of observed nanocrystals from 2 to 8 nm and larger. Moreover there was possibility to vary the size and concentration of nuclei independently. There was observed a preference (110) orientation of nanocrystals. Analysis of the electron microscopy contrast showed, that probably nucleation occurred homogenically inside on the film. Applied rapid thermal annealings allowed for nanocrystals to grow conserving preference orientation. Preliminary introduction of nuclei leaded to reduction of incubation time of crystallization and to changing of final structure of the films. There was observed large fields of (110) textured areas with dimension about 20-30mcm arising from introduced nuclei. The preference orientation of crystal grains was detected at thermal, rapid thermal and nanosecond laser annealing, but with reduction of time duration of treatments the increasing of the effect and appearing additional planar correlation in the orientation was observed. Twin defects was observed in the structure of crystal grains of final polycrystalline films. According to obtained experimental data deformation mechanism of appearing of preference orientation was declared and discussed.

16:00-16:30 **BREAK**

Session VI - X-Ray and TEM Studies
Chairperson: H. Ichinose, University of Tokyo, Tokyo, Japan

C-VI.1 - invited - 16:30-17:10 SPECIFICITY OF ELECTRON MICROSCOPY AND X-RAY DIFFRACTION FOR STUDYING THIN FILMS STRUCTURES, **A. Bourret**, DRFMC, CEA Grenoble, 17 rue des Martys, 38054 Grenoble Cedex 9, France

The practical importance of semiconductors or metallic multilayers has generated a large variety of studies on the interface structure between two different crystalline materials. The desired goal is to grow epitaxially perfect crystals on top of each other with no defects in the layers. What happens at the interface is therefore of prime importance to control the defect content. The combination of techniques developed in electron microscopy such as quantitative imaging at high resolution, nanoanalysis with PEELS, filtered imaging and X-Ray techniques such as grazing incidence diffraction at small or large angle, diffuse scattering, reflectivity ... provide adequate tools for studying thin films and interfaces at an atomic scale.

A brief overview of these different experimental approaches will be given in order to show how complementary they are. Interface roughnesses at different scales, interdiffusion and segregation spatial extension, lateral correlation length, atomic steps, internal strains, interfacial defects has already been deduced in a variety of materials. Examples in semiconductor heterostructures and metallic multilayers will be given.

C-VI.2 17:10-17:30 MICROSTRUCTURE AND STRAIN RELAXATION IN $YBa_2Cu_3O_7$ EPITAXIAL THIN FILMS, J.-L. Maurice, M. Drouet, J.-P. Contour, Unité Mixte de Physique, CNRS/Thomson-CSF, 91404 Orsay, France, and O. Durand, LCR Thomson-CSF, 91404 Orsay, France

We report X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations of $YBa_2Cu_3O_7$ (YBCO) thin films grown by pulsed laser deposition (PLD). We used $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) as substrates. The YBCO epitaxial layers were either single or alternating with layers of STO and/or $PrBa_2Ga_xCu_{3-x}O_7$ (PBGCO) in superlattices. In TEM sample preparation, we minimised thinning damage, which tended to be particularly important when PBGCO was present, by using the tripod polisher method.

The observations confirm the existence of twins in the relaxed layers and their absence in the strained ones. In YBCO/PBGCO superlattices, relaxation apparently depends only on the YBCO elementary thickness. It takes place when the latter is larger than approximately 4.8 nm, with no apparent strain in the PBCGO layers.

We finally discuss the relaxation geometry in terms of twins and dislocations.

C-VI.3 17:30-17:50

XRD AND TEM STUDY OF HETEROEPITAXIAL GROWTH OF ZIRCONIA ON MAGNESIA SINGLE-CRYSTAL, R. Guinebretière, B. Soulestin and A. Dauger, Laboratoire de Matériaux Céramiques et Traitements de Surface, URA N°320 ENSCI 47-65, Av. A. Thomas, 87065 Limoges, France

Asymmetric X-ray diffraction apparatus has been builded up in order to characterize polycrystalline or single-crystal like thin films. A four reflections Bartels monochromator associated with a rotating anode source allows to define a strictly parallel X-ray beam. Diffraction lines are detected by a Curved Position Sensitive Detector (CPS 120 INEL) and the samples are put on a five axis specimen holder.

Zirconia thin films have been deposited on magnesia (100) single-crystals substrates using sol-gel precursor solution. Thermal treatment at 600°C induces the crystallization of polycrystalline thin films containing randomly oriented nanocrystals. Annealing at higher temperature give rise to the appearance of a progressive heteroepitaxy and breaking up of the film into isolated islands.

Polycrystalline tetragonal zirconia thin films, several tens nanometer thick, have been studied with a glancing angle equal to several tenth degree. The epitaxial growth has been characterized by XRD under controlled incidence angles and concurrently imaged by TEM on cross sectional samples. The development of heteroepitaxied single crystalline islands results from abnormal growth of interfacial grains having the lowest orientational energy.

C-VI.4 17:50-18:10

STRUCTURAL ASPECTS OF THE INTERFACE LAYER IN SILICON-ON-SAPPHIRE, E. Gartstein, S. Lach, D. Mogilyanski, H. Metzger and J. Peisl, Inst. for Appl. Research, Ben-Gurion University, Beer-Sheva, 84110, Israel and Ludwig-Maximilians-Universitat, Sektion Physik, Gesch-Scholl-Pl. 1, 80539 Munchen, Germany

The structure of Si-on-sapphire (SOS) was investigated by X-ray diffraction and high resolution electron microscopy techniques. The interface layer was observed to develop with thickness of 3.5mn to 5.0nm. From the change in the lattice parameters in the interface layer measured by Bragg and grazing incidence diffraction techniques, it was possible to calculate the strain distribution across the interface. It was found, that whereas the Si epilayer is compressed, the interface layer has a very anisotropic strain distribution with regions both under compression and tension. In addition the twins distribution in SOS was found to be anisotropic. This twinning anisotropicity strongly increases with the thickness of the Si epilayer and causes a damage to the sapphire substrate.

The transmission electron microscopy study showed the formation of the interfacial dislocations at the interface. While the twins can accommodate the long range strain anisotropically in this system, the interfacial dislocations are relieving the short range order strain at the interface.

Friday June 20, 1997
Vendredi 20 juin 1997

Morning
Matin

Poster Session II

9:00-11:00	See programme of this poster session p. C-20 to C-24.
11:00-12:00	***DISCUSSION***
12:00	**LUNCH**

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SYMPOSIUM C

Poster Sessions

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session I

16:10-18:00

C-I/P1

STABLE AND METASTABLE PHASES IN THE VACUUM ARC DEPOSITED THIN FILMS OF Co, B.B. Straumal and W. Gust, University of Stuttgart, Institut für Metallkunde, Seestr. 75, 70174 Stuttgart, Germany; N.F. Vershinin, Institute for Vacuum Technology, Chajanov str. 8/26, 125047 Moscow, Russia; T. Watanabe, Department of Machine Intelligence and Systems Engineering, Faculty of Engineering, Tohoku University, 980-77 Sendai, Japan; V. G. Sursaeva and V. N. Kurlov, Institute of Solid State Physics, Chernogolovka, Moscow District, 142432 Russia

Vacuum arc deposition uses the arc burning in the vapour of the cathode material. The parameters of vacuum arc discharge do not depend on the magnetic properties of the cathode material so critically as in the case of magnetron sputtering. This feature permits one to deposit easily ferromagnetic thin films.

In this work Co thin films of different thickness were deposited onto the NaCl and sapphire single crystalline substrates. The sapphire single crystals were grown with the aid of edge-defined film-fed growth. The substrate temperature during the deposition was kept below 200°C. The microstructure of the Co films was studied using the transmission and scanning electron microscopy. The Co films have a dense columnar structure. The grain size depends on the film thickness. The hexagonal close-packed phase (thermodinamically stable below 422°C in pure bulk Co) and the face-centered cubic phase (stable above 422°C) were detected in the Co films. The influence of mechanical stresses in the film and of the additional annealing on the relative stability of both phases is discussed. The financial support from the Heiwa Nakajima Foundation and the Volkswagen Foundation is acknowledged.

C-I/P2

GROWTH OF Ni FILMS BY DC-BIASED-SPUTTER DEPOSITED ON GaAs(001), J. Yang, K. Makihara. H. Nakai, M. Hashimoto. Dept. Appl. Phys. Chem. Univ.of Electro-Communs, 1-5-1 Chofugaoka, Chofu-shi 182, Japan; A . Barna, P. B. Barna, Inst. Tech.Phys. HAS, 1325 Budapest, POB 76, Hungary

Ni films 100nm thick are deposited on GaAs(001)at 280°C by dc-biased-sputtering at 2.5kV in Ar gas. A bias Vs (0 to -180 V) is applied to the substrate during deposition. The effects of Vs on the Ni film growth on GaAs(001) are investigated by RHEED, XPS, XTEM and XHRTEM.TCR from 150 to 300K and saturation magnetization 4π Mf at 300 K are also measured.

Ni films are polycrystalline mixed with As, while the Ni atoms diffuse into GaAs leaving voids at the interface to result in the epitaxial growth of As_2Ni with $As_2Ni[111] \parallel GaAs[111]$ and $As_2Ni[011] \parallel GaAs[011]$. The diffusion depth ranges from 80 to 200nm as Vs increases up to -180 V while the grain growth of As_2Ni is most enhanced at Vs=-80V.

C-I/P3

TRANSMISSION ELECTRON MICROSCOPY OF THIN-FILM TRANSISTORS ON GLASS SUBSTRATES, S. Tsuji, Yamato Laboratory, IBM Japan, Yamato, Kanagawa 242, Japan, K. Tsujimoto, ITES Co. Ltd., Yasu-cho, Yasu-gun, Shiga 520-23, Japan and K. Kuroda, H. Saka, Department of Quantum Engineering, Nagoya University, Nagoya 464-01, Japan

The recent attention paid to sample preparation of multilayered structure on glass substrates indicates that cross-sectional transmission electron microscopy (X-TEM) are of considerable interest for their potential effectiveness in thin-film transistor liquid crystal display (TFT-LCD) applications. In this paper, we firstly present the significant features of our failure analysis problem which involves some difficulties: fragile location, anomalous, and rare defects. Secondly, we describe an application of focused ion beam etching to specimen preparation for X-TEM observation. We demonstrate that the FIB technique, which allows very localized etching without inducing mechanical stress to thin TEM sample, is very convenient for this delicate location. We also demonstrate that our FIB etching technique is capable of high thinning rates, which allows rapid production of high-quality TEM specimen. Finally, we demonstrate how faulty TFTs including extra thin layer such as contamination, microvoids, and long and fragile protrusions such as whiskers, can be characterized by means of FIB and X-TEM combination.

C-I/P4

TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF THE STRUCTURAL CHARACTERISTICS OF AMORPHOUS TETRAHEDRAL CARBON FILMS, Ch.B. Lioutas, N. Vouroutzis, S. Logothetidis, H. Lefakis, Aristotle University of Thessaloniki, Department of Physics, 54006 Thessaloniki, Greece

Hydrogen free tetrahedral amorphous Carbon films (ta-C) attract an increasing scientific and technological interest due to their special properties, such as high hardness, infra-red transparency and chemical inertness. The structural feature of ta-C films prepared by RF magnetron sputtering, in sequential thin layers, under positiv and negative bias voltage to Si substrate, were examined by transmisssion electron (TEM) microscopy. The microstructure of the films was investigated by cross section TEM. The amorphous character of the films was obvious from bright field images that also revealed the changes of the surface roughness as a function of the deposition steps and bias conditions. No significant diffracted intensity (on Electron Diffraction images) from the film area was detected. However dark field imaging, with the objective aperture on <111> diamond reflection position, revealed that the films were rich in sp^3 C-C bonds throughout the whole film. Similar images with the objective aperture on <002> graphite reflection showed the distribution of sp^2 C-C bonding in the films.

C-I/P5

X-RAY ABSORPTION ANALYSIS OF THE DENSITY AND SYMMETRY OF THE DOPING HOLES IN HTC THALLIUM AND MERCURY CUPRATES THIN FILMS, F. Studer, B. Sekhar, P. Srivastava and C. Martin, CRISMAT-ISMRA, 14050 Caen Cedex, France; C. Gasser and K. Tanabe, ISTEC, Tokyo, Japan

Soft X-Ray Absorption Spectroscopy has been shown to be a unique probe of the electronic states above the Fermi level. Due to its chemical and orbital specificities, soft XAS has been extensively used to investigate the local atomic and electronic structures of solids. Specially in HTC superconductors XAS gives a specific insight on both covalent and doping holes which determine the metallic and superconducting properties. Moreover polarized experiments realized on single crystals and/or thin or thick films allow to determine the symmetry of the empty electronic levels. Among the HTC materials, T1(2212) and Hg(1212) have shown quite similar electronic structure near the Fermi level in band structure calculations, unlike their differences in crystal structure.

In the present work, we report polarized soft XAS experiments on thallium (T12212) and mercury (Hgl212) cuprates thin films in normal and superconducting states using Fluorescence Yield (FY) detection to get bulk information. Two main results have been observed and will be presented:

l) In Hgl212 thin film synthesized in high oxygen pressure, a significant hole density is observed along the z-axis of the structure, perpendicularly to the sample surface. This result is observed for the first time in single Hg-layer cuprate but is in agreement with previous results in the T12212 bilayer cuprate and is connected to charge transfer occurring along the Cu-O-Hg.

2) Below Tc (~ 115K) in Hgl212, a significant increase of the in-plane doping hole density is observed with respect to room temperature. An interpretation of this doping hole density increase can be proposed based on the opening of the superconducting gap and the creation of Cooper's pairs.

C-I/P6

COMBINE CHARACTERIZATION OF CONDUCTIVE MATERIALS BY INFRARED SPECTROSCOPIC ELLIPSOMETRY AND GRAZING X- RAY REFLECTANCE, P. Boher, M. Luttmann and J.-L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France, L. Hennet, Laboratoire de Métallurgie Physique et Science des Matériaux, Université Henry Poincaré, Nancy I, BP239, 54506 Vandoeuvre les Nancy, France

Non destructive, non contact characterization of conductive materials is an interesting challenge, especially in the field of the microelectronics. One way to solve the problem is to use the optical properties of these materials which follow theoretically a Drude law in the infrared region. In this study, spectroscopic ellipsometry in the near infrared (up to 2μm) and in the far infrared (up to 18μm) is used to extract the optical indices. To evaluate the electrical properties the thickness of the layer is also needed. Due to the generally high absorbance of these conductive layers it cannot be extract directly from the ellipsometric measurements. Another possibility is to use a complementary technique like grazing x-ray reflectance (GXR) as we have done in this study. Eleven titanium/SiO2/Si samples with variable titanium thickness have been successively examined. The different thickness have been determined precisely by grazing x-ray reflectance at the cobalt K-α line with the surface roughness of the samples. Conventional x-ray diffraction was also used to determine the crystallinity of the titanium layers. Then IR spectroscopic ellipsometry was used to extract the optical indices of the different titanium layers and their resistivity using the GXR thickness and the Drude model. Values determined by this method compare well with four points probe resistive measurements made on the same samples. The proposed paper will focused on the complementarity of the two techniques and on their domain of validity for this application.

C-I/P7

CRYSTALLIZATION PROCESSES IN COBALT OXIDE THIN FILMS BY X-RAY ABSORPTION SPECTROSCOPY, V.M. Jiménez, A. Caballero, J.P. Espinos, F. Yubero, A.R. Gonzalez-Elipe, Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Avda. Américo Vespucio s/n. 41092 Sevilla. Spain

X-ray absorption spectroscopy (XAS) provides information about the local arrangement of atoms around a given one taken as absorber of the radiation. This technique, in combination with X-ray diffraction has been used to study the crystallization processes that occur upon heating cobalt oxide thin films (CoO and Co_3O_4) at increasing temperatures. The XAS spectra were taken by conversion electron yield detection, a method which is only sensitive to the topmost layers of the materials (of the order of 100 nm). The films have been prepared by Ion Beam Induced Chemical Vapor Deposition, a procedure by which it is possible to control the stoichiometry of the film. The original films were partially amorphous, but they became more crystalline at increasing temperatures. Information about the oxidation state degree of crystallinity and local enviromnent around cobalt have been obtained by analysis of the spectra.

C-I/P8

LATTICE PARAMETER CHANGE IN SUBMICRON Si WHISKERS, A.I. Klimovskaya, Institute of Semiconductor Physics, Kiev, Ukraine and I.P. Ostrovkii, S.V. Fadeev, M.S. Fryginskii, I.O. Rudyi, State University “Lvivska polytechnika”, 12 Bandera str., 290646, Lviv, Ukraine

In this paper the results of structural investigations of grown-on-substrate and free-standing filament-like silicon crystals (whiskers)are presented. The crystals were grown by a method of vapour transport reaction in a sealed tube with using a catalyst of the axial growth of crystals. The investigations were carried out by an x-ray diffractometry with using germanium powder as a calibrated standard, by a method of Bragg reflection from crystalline planes with different Millers indexes and a calculation of corresponding correlation functions, and by a method of electronography. An analysis of the obtained results shows that the lattice parameter of free-standing whiskers decreases with a decrease of their diameter d if d < 1μm. A magnitude of the change of the lattice parameter depends on a doping of the crystals and it is largest for the purest probes. Moreover, the effect found is anisotropic. Structural studies of filament-like whiskers grown on a silicon substrate reveal the lattice parameter change also, while a sign of the change is opposite, i.e., the lattice parameter increases with the decrease of diameter.

A study of a composition of the crystals under investigation by methods an x-ray microprobe analysis, an ion and Auger spectroscopy shows that the found effect cannot be accounted for a large concentration of impurities in the crystals. This effect is unrelated to growth defects also, because the crystals strength in these crystals is larger than that in bulk material. In the paper possible mechanisms of the effects based on an influence of a crystal surface and substrate are discussed.

C-I/P9

ELECTRODE-WIDTH DEPENDENCE ON RESISTIVITY AND STRUCTURE OF ELECTRON BEAM EVAPORATED ALUMINIUM ELECTRODE THIN FILM ON LITHIUM TANTALATE, K. Noguchi(1), H. Nakai(2), H. Ohashi(1), M. Hashimoto(2), (1)Japan Radio Co., Ltd., 2-1-4 Fukuoka Kamifukuokashi, Saitama 356, Japan, (2)The University of Electro-Communication, Chofugaoka 1-5-1 Chofushi, Tokyo 182, Japan

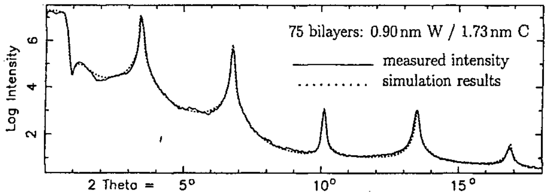
Aluminum electrode thin films (0.90 nm thick) with various widths were simultaneously deposited on a lithium tantalate substrate by electron beam evaporation, and the width dependence of the resistivities of the electrode film was measured by Van der Pauw method. The result shows that the resistivity depends on the electrode width in the width range less than 1 μm. The width dependences for the films with 0.33, 0.53 nm thick were observed similarly. Two kind of specific resistivities were introduced; our results were width-specific resistivity, 2.5x10^{-1} μΩ cm μm and thickness-specific resistivity, 6.8x10^{-2} μΩ cm μm. The resistivity without size effect was determined to be 3.15 μΩ cm. This resistivity is comparable with the bulk resistivity, 2.7 μΩ cm.The morphologies of the electrode films was observed by SEM. Our goal is to observe the cross sectional TEM micrograph of the electrode films, to discuss in compared to the results of resistivity measurements.

C-I/P10 EFFECT OF PHASE TRANSFORMATIONS ON THE FORMATION OF DEFECTS, A.Ya.Gubenko, Moscow Institute of Electronics and Mathematics, Moscow, Russia

In semiconductors, minor changes in impurity concentration (C) and temperature (T) within terminal solid solution ranges lead to phase transformation (PT), whose extension may reach a few percent and oC that occur themselves in C and T ranges (CR and TR). Within these CR and TR, the properties and interatomic forces oscillate with C and T to give alternating peaks and dips of various amplitudes. The occurrence of the PTs is shown to be due to self-maintaining coarce-scale fluctuations, whose sizes oscillate in each successive spike, like properties do, until the parameters of state reach values characteristic of a new phase which is confirmed by the oscillating variation of the second derivative of free energy in C and T. Such a transition from one phase to another may be considered as a self-organization in the matter. The PT causes oscillatory variation, in the CR and TR, of the concentrations of intrinsic point defects and the types and the kinetics of solid-phase reactions. At some C, retardation of solid-phase reactions occurs; at others, these reactions become accelerated. In the former case, the density of microdefects, e.g. in Si, may change drastically with T or concentration of an impurity (with other factors being equal), e.g. it may be smaller by a few orders of magnitude than in the later case. No effect of oxygen and carbon on the kinetics of formation and on the density of microdefects will be observed in this case.

C-I/P11 X-RAY REFLECTIVITY OF MULTILAYER MIRRORS FOR THE WATER WINDOW, H. Grimmer, P. Böni, U. Breitmeier, D. Clemens, M. Horisberger, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland and H.-Ch. Mertins, F. Schäfers, BESSY, Berlin, Germany

Multilayers mirrors consisting of alternating layers of W/C, W/Ti, Ni/Ti or Ni/V were produced by DC magnetron sputter deposition. The figure shows a typical result of Cu Kα characterization.



Detailed results on the roughness of the various interfaces have been obtained using the program SUPREF to simulate the measured results.
The reflectivity for soft X-rays was measured at BESSY with a reflectometer at the beamline PM4. Special attention was given to the fine structure of the reflectivity enhancement at the absorption edges of C (4.36 nm), Ti (2.73 nm) or V (2.42 nm). The measured reflectivities are among the best obtained world-wide for any combination of materials.

C-I/P12 STUDY OF THE HETEROEPITAXIAL GROWTH OF BiSrCaCuO THIN FILMS ON MgO, W. Seiler, J.L. Lebrun, LM3, Ecole Nationale Supérieure d'Arts et Métiers, 151 Boulevard de l'Hôpital, 75013 Paris, France, A. Laurent, J. Perrière. Groupe de Physique des Solides, Universités Paris VII et Paris VI, URA-17, Tour 23, 2, Place Jussieu, 75251 Paris Cedex 05, France

BiSrCaCuO thin films have been grown on single crystal MgO (100) substrates by the pulsed laser ablation method. X-ray diffraction was used to determine the phase formation («2212» $Bi_2Sr_2Ca_1Cu_2O_8$, or «2201 $Bi_2Sr_2Cu_1O_6$), to study the crystalline quality of the films, and to measure the film-substrate in-plane orientation relationships.
Highly textured films were formed, and X-ray diffraction evidences either the growth of pure «2201»films, or a phase intergrowth, i.e the random stacking of «2201» and «2212» cells in the films. The film-substrate epitaxial relationships were studied by asymetric X-ray diffraction. Despite the large lattice mismatch between film (0.54 nm) and substrate (0.42 nm), epitaxial films were grown, and an unexpected in-plane orientation (around 12.5°) was observed, which does not correspond to a simple coincidence of the film and substrate lattices. The precise value of the in-plane orientation (between 11 and 14°) depends upon the growth conditions (substrate T and O_2 pressure). These results will be discussed in relation with the incommensurate modulation in the a-b plane of BiSrCaCuO. In fact, a correlation is observed between the modulation wavelength (measured by X-ray diffraction) and the in-plane orientation.

C-I/P13 STUDIES OF CdTe CLEAVAGE SURFACES AND INFLUENCE OF SUBSTRATES SURFACE DEFORMATION ON HgCdTe EPITAXIAL LAYERS GROWTH, I.V. Kurilo, I.O. Rudyj, P.V. Galiy, T.M. Nenchuk, O.I. Vlasenko, State University "Lviv Politechnic", Bandera Str.12, 290646 Lviv, Ukraine

The physical properties of HgCdTe are determined by point and extend structural defects and background impurities also, which are interacting with point defects that results in deep levels formation in energy gap of the material CdTe substrates technological manufacturing before epitaxial films (EF) growth by isotermal vapour epitaxial method leads to defect structure reconstruction of deformed regions. Therefore the controlled introduction of extend defects into the substrate with the aim of investigation of their influence on nucleating character, elementary processes of growth and structure perfection and EF morphology is of great importance.
The extend defects were introduced into substrate by local deformation with indentor weighted as (5..20)10^{-2} N. The surfaces of substrates without epitaxial growth (control) anc EF were studied with Auger electron spectroscopy (AES) method. The properties of CdTe (110) cleavage surfaces were studied also. The slight stoichiometry deviation (±10%) on the surface of control substrates which were locally indented and admitted to air for a long time has been evaluated according to AES spectra. The insignificant increase of cadmium concentration (2..7%)was observed at indentor mark and its nearly region.
The indentor mark and its nearly region were characterized by higher mercury concentration and lower cadmium one.

C-I/P14 MICROSTRUCTURE IMAGING OF THE YBCO THIN FILM/MgO SUBSTRATE INTERFACE: HRTEM AND FOURIER ANALYSIS OF THE MOIRE FRINGE PATTERN, S. Auzary, F. Pailloux, R.J. Gaboriaud, Université de Poitiers, Laboratoire de Métallurgie Physique, UMR 6630 - CNRS, SP2MI - Bd 3 - téléport 2 - BP 179, 86960 Futuroscope cedex, France

Superconducting properties of YBaCuO thin films strongly depend on the film microstructure.The crystallographic orientation relationship between the deposited film and the substrate together with the crystallographic defects contamined in the films are therefore of prime importance. This study investigates the microstructure of the interface YBCO / MgO by means of TEM.
Observations were essentially carried out by high resolution imaging technique in plan-view samples and then focused on the moiré fringe pattern brought about by the superimposition of both YBCO and MgO lattices.
Structural features and statistic measurements are studied from the Fourier analysis of the moiré fringe pattern.
Results are discussed within the frame of the crystallographic accommodation of the misfit between both lattices essentially in terms of twinning of the YBCO lattice.

C-I/P15 FORMATION AND TRANSFORMATION OF THE DAMAGED SURFACE LAYERS OF CRYSTALS, M.A. Rom, V.F.Tkachenko, "Institute for Single Crystals", 60 Lenin ave., 310001, Kharkov, Ukraine

The developed by the authors X-ray methods allow to recover the profiles of distortions localized in the layers 0 2...100 µm thick They were used for the study of mechanisms of damaged layers (DL) formation in the process of mechanical treatment of crystals. Alongside with the peferentially translational plasticity (sliding typej typical for crystals with the lattice NaCl, CsCl on the mixed crystals CsJ-CsBr one could observe a rotational plasticity (throw-off formation type). In the $K(H_{1-x}D_x)_2PO_4$ the dynamic recrystallization plays a significant role in the formation of DL.

In DL the structural transition single crystal ⇒ polycrystal is observed always. Physico-chemical processes proceeding during the following thermal treatment of crystals define the degree of structure quality and phase composition of DL. In crystals NaCl, CsJ DL is absorbed by the single crystalline matrix. At a constant profile of strong structural distortions in DL of CdS rapidly proceed the processes of diffusion and desorption of Cd atoms, the temperature of KH_2P0_4 decomposition becomes lower. DL moves into the volume of the material (CsJ-CsBr) due to recrystallization with the formation of a stable system of boundaries, in $K(H_{1-x}D_x)_2PO_4$ disdeuteration takes place being accompanied by the generation of new dislocations.

C-I/P16 THREE-CRYSTAL X-RAY DIFFRACTOMETRY FOR HIGH PRECISION STUDY OF SUBSURFACE LAYERS OF CRYSTALS, V.F. Tkachenko and M.A.Rom, "Institute for Single Crystals", 60 Lenin ave, 310001, Kharkov, Ukraine

A three-crystal X-ray diffractometer (TXD) for the solution of a wide class of problems has been designed and created. Two goniometric devices allow to realize different schemes for installation of monochromators, sample under study, to make analysis in the geometry of Bragg, Laue and according to a mixed scheme. When the scheme (n, n, -m) is used the angular resolution of about 0.5 arcs can be achieved. The design of TXD gives a possibility to pass easily to the work with different radiations, monochromators and orders of reflection.

The angular range of the registration of the diffraction reflection curves (DRC) was broadened up to ±172° over the scale of the radiation detector and a linear scanning of the samples was provided. The determination of $\Delta d/d$ value with the error reaching $\sim 10^{-7}$ for perfect crystals and films is realized at a simultaneous illumination with the X-ray beam and registration of DRC of two samples one of which is the studied sample and the other - the reference. This method allows to minimize the effect of the temperature and other factors that are essential in the Bond method. The developed device and methods were applied for the analysis of the kinetics of the epitaxial films growth from the solution-melt and the character of the transitional layer, for the investigation of structure quality of the surface layers of a number of crystals subjected to different external effects.

C-I/P17 X-RAY ANALYSIS OF THE NONUNIFORM SURFACE AREAS OF SOLIDS, M.A. Rom and V.F. Tkachenko, "Institute for Single Crystals", 60 Lenin ave., 310001, Kharkov, Ukraine

The nondestructive diffraction analysis of the damaged surface layers,thin films and coatings characterized by the perfection gradient of structure and phase composition over the depth becomes possible owing to the application of methods of variation of weight function intensity (WFI). The correlation between the profiles of the distribution of the studied parameters over the depth and integral characteristics of the diffraction experiment was established in the kinematic approximation. This allowed to solve a reverse problem - to recover the distribution of phase concentration, crystal lattice periods, parameters of thin structure, texture etc..

The experimental variation of WFI is achieved by the variation of the sliding angle α of the incident X-ray beam on the studied surface or by changing the wavelength of radiation. The variation of α is realized depending on the character of the object under investigation: by the turn of the sample for the analysis of weakly textured polycrystals; by rotation of the sample around the diffraction vector in the asymmetric Bragg's case for the analysis of single crystals and textured polycrystals. The considered approach was realized on single crystals subjected to different external effects and demonstrated high efficiency when studying processes proceeding in the layers 0.2...100 µm thick.

C-I/P18 STRUCTURAL PHENOMENA OF $Bi_2Sr_2CaCu_2O_{8+x}$ THIN FILMS ON (110) $SrTiO_3$ SUBSTRATES, E. Brecht, G. Linker, T. Kröner, R Schneider, J. Geerk, O. Meyer, Forschungszentrum Karlsruhe, INFP, PO Box 3640, 76021 Karlsruhe, Germany, C. Traeholt, National Centre for HREM, Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 Delft, The Netherlands

$Bi_2Sr_2CaCu_2O_{8+x}$ thin films with high structural perfection and superconducting transition temperatures T_c around 70 K have been grown on (110) oriented $SrTiO_3$ substrates using magnetron sputtering. In X-ray diffraction studies two different growth orientations are observed: a) tilted domains with their c-axis almost parallel to $[100]_s$ and $[010]_s$ and b) domains with their c-axis oriented perpendicular to the substrate surface. Both growth orientations exhibit a full in-plane epitaxy within the $(110)_s$ plane with $[110]_F \parallel [001]_s$. In AFM investigations of the film surface morphology the inclined domains are found to form thin plates tilted with respect to the substrate surface, while the c-axis domains have a smooth surface with wide terraces. HRTEM studies support the high crystalline quality and phase purity. From the variation of the layer spacings along the c-axis direction between the alternately stacked atomic layers the Bi-O layer has been identified as the first growth layer at the interface of the c-axis oriented domains.

C-I/P19 STRUCTURE CHARACTERIZATION OF METALLIC MULTILAYERS BY SYMMETRIC AND ASYMMETRIC X-RAY DIFFRACTION, G. Gladyszewski, Dept of Physics, Technical University of Lublin, 20618 Lublin, Poland; S. Labat, P. Gergaud, O. Thomas, MATOP, URA CNRS 1530, Fac. des Sciences de St Jérôme, 13397 Marseille Cedex 20, France

Structural characterization of multilayers is usually performed by the use of X-ray diffraction (XRD) techniques; commonly in the θ-2θ geometry. Interpretation of obtained profiles is not straightforward, require a number of fitted parameters and some of them influence XRD profiles in similar ways and therefore are difficult to separate. Moreover, in the case of most of the multilayered systems a number of local fitting minima exists that cannot be avoided in standard fitting procedures. It is therefore necessary to base the structure characterization on different XRD geometries to obtain additional information about interplanar distances, interdiffusion, roughness. In this work, we present results of the structure characterization of Au/Ni multilayers, based on symmetric and asymmetric XRD. Particular attention is paid to interplanar distances, and composition profiles of studied multilayers. Symmetric XRD profiles are interpreted using the model of non-ideal superlattice structure based on a Monte Carlo simulation. The model allows to fit experimental profiles starting within a wide range of interplanar distances and avoiding any local minima. Asymmetric XRD measurements were performed for different hkl reflections. A stress analysis has been done by plotting d_{hkl} vs $\sin^2\Psi$ (where Ψ is the angle between the surface normal and [hkl]). The perpendicular distance is extrapolated from this curve at $\Psi = 0$. A stress free lattice parameter and the stress in the plane are also extracted. Both asymmetric and symmetric XRD measurements confirm that perpendicular interplanar distances in Au and Ni are larger than the bulk ones. These interplanar distances are discussed in terms of a stress free lattice parameter and a strained one.

C-I/P20 COMPUTER SIMULATION OF X-RAY SCATTERING BY THIN SURFACE LAYERS, R. Barabash, Metal Physics Department, National Technical University of Ukraine, pr. Pobedy 37, Kiev 252056, Ukraine

Theoretical analysis of X-ray scattering by surface layers and thin films was held out in the framework of kinematical theory of scattering. The influence of concentration gradient on the peculiarities of X-ray intensity distribution was taken into account. Thin films as with free as with fixed boundaries were considered. Structure changes due to the diffusion processes in HTSC thin films were analysed. Analitical expressions for X-ray intensity scattering distributions depending on concentration gradient were obtained. It was established, that for X-ray scattering by such layers line profile was not monotonous. It had the point of minimal intensity. The angle position of this point is connected with diffusion coefficient, time and the rate of the movement of boundaries between different phases, formed in surface layers. Computer simulation of X-ray line profiles for different values of diffusion parameters was held out. Instrumental broadening of diffraction line was taken into account. It was shown, that the position of minimal intensity point moved to the side of larger angles with the increase of time or diffusion coefficient. Experimental X-ray scattering intensity distributions were obtained for different compositions of surface layers and different conditions of diffusion processes. They showed good agreement with the results of computer simulation. Diffusion parameters were determined from experimental data using the results of theoretical analysis.

C-I/P21 TEM OBSERVATION OF FIB MICROMILLED SILICIDES AND SEMICONDUCTORS, M. Tanaka, K. Furuya and T. Saito, National Research Institute for Metals, 1-2-1, Sengen, Tsukuba 305, Japan

Focused Ion Beams (FIB) are becoming an effective tool in the formation of submicron devices. However, direct observation of structural changes caused by the FIB irradiation is strongly required because FIB sometimes cause additional phenomena such as radiation damage or beam broadening. In this study, specially designed TEM equipped with FIB (FIB/TEM) is used to observe the structural changes caused by the FIB irradiation to Ni and Pd silicide thin films grown on Si (111), or to Si(100),(111), GaAs(100) and 6H-SiC(001). 25 keV Ga^+-FIB has been irradiated to metal/Si and semiconductor TEM samples to a dose of 1.6×10^{17}ions/cm^2 at room temperature.

Growth of metal silicides was achieved by the combination of EB deposition of metals on Si at room temperature and the subsequent annealing at 573-673 K. Several size of squares were microfabricated by 25kV Ga^+-FIB with the beam size of 0.2μm. TEM observation was carried out simultaneously. Uniform micromilling was achieved in the case of semiconductors, but silicides lose their phases from crystal to heavily damaged states. Post irradiation annealing of silicides resulted in precipitation of Ni rich silicide and the formation of Si rich Pd silicide outside the FIB irradiated area, respectively. The FIB beam broadening is found to be responsible for the reactions.

C-I/P22 X-RAY DIFFRACTION STUDY OF STRUCTURE OF THIN CADMIUM AND COPPER SULPHIDES' FILMS OBTAINED FROM SINGLE-SOURCE PRECURSOR, N.I. Fainer, G.S. Yurjev, Y.M. Rumyantsev, M.L. Kosinova, E.A. Maximovskiy, Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russia

The present work is devoted to study of structure of thin CdS and Cu_2S films by modificated X-ray diffraction method with the weak reflection record from thin films having thickness ~1000-5000 Å. The diffraction measurements were perfomed at both the storage ring synchrotron facility VEPP-3 at INP SB RAS, Novosibirsk, and DRON-4 diffractometer. The geometrical Bragg-Brentano schema of registration of diffraction patterns was identical in both cases.

All thin semiconductor films were synthesized by remote plasma enchanced chemical vapour deposition using dithiocarbamates as single-source precursors at low pressure and low temperatures of growth (373-773 K). It was established that the type of substrate material plays the important role in the formation of structure of cadmium and copper sulphide thin films: polycrystall hexagonal CdS was grown on (100)Si substrates monocrystall cubic type CdS was grown on (100)InP. Mixture of polycrystalline cubic and hexagonal phases of copper sulphide were produced on fused quartz, monocrystalline cubic Cu_2S phase was grown on silicon substrate, polycrystalline hexagonal Cu_2S was grown on CdS/Si(100) heterostructure.

C-I/P23 THE STUDY OF STRUCTURE OF THIN SILICON CARBONITRIDE FILMS BY SYNCHROTRON RADIATION DIFFRACTION, N.I. Fainer, G.S. Yurjev, Y.M. Rumyantsev, M.L. Kosinova, E.A. Maximovskiy, Institute of Inorganic Chemistry, SB RAS, Novosibirsk, 630090, Russia

The thin (1000-2500 Å) films of silicon nitride and silicon carbonitride were grown on (100) GaAs at the total pressure 2×10^{-3} Torr and in the temperature interval of 50-500°C from pure hexamethyldisilasane (HMDS) or its mixture with ammonia using plasma excitation.

The chemical composition, the thickness and refractive index, the surface morphology, low frequency permittivity and conductivity. of these films were determined by different methods. Crystalline structure of the silicon carbonitride films was studied by various methods of X-rays analysis. The diffraction experiments were performed at both the station «Anomalous scattering» of the storage ring synchrotron facility VEPP-3 and DRON-4 diffractometer. The wavelength of X-ray can be varied in the range 0.6-4.0 Å; the diameter of the input X-ray beam was 5×10^{-5}.

The physical and chemical properties of thin silicon nitride(carbonitride) films strongly depend on the gas mixture and the growth temperature. It was established that silicon carbonitride layers deposited from pure HMDS contain a considerable amount of carbon appeared in form Si-C bonds (IR-data) and the nuclei of the second phase with size < 1μm (electron microscopy data). The existence of both hexagonal h-Si_3N_4 and hexagonal h-SiC phases was suggested by X-ray investigation.

Poster Session II
16:10-18:00

C-II/P1 X-RAY DIFFRACTION STUDY OF STRUCTURE OF THIN BORON NITRIDE FILMS OBTAINED FROM BORAZINE, G.S. Yurjev, M.L. Kosinova, N.L. Fainer, Y.M. Rumyantsev, F.A. Kuznetsov, Institute of Inorganic Chemistry, SB RAS, Novosibirsk, 630090, Russia

BN and BN_x:H layers (1000÷5000Å) were synthesized on (100)Si and fused silica substrates by remote plasma enhanced chemical vapour deposihon using as single-source precursor borazine ($B_3N_3H_6$) or its mixture with helium at the low pressure ($3x10^{-3}$ - 10^{-1}Torr) in the temperature region of 100÷600°C.

The physical and chemical properties of boron nitride films were studied by following methods: ellipsometry, IR-spectroscopy and X-ray diffraction. IR-absorption spectra show the presence of B-N, N-H and B- H bonds. It was investigated structure of both the as-deposited films and after thermal annealing (500-700°C). The diffraction patterns were recorded on diffractometer DRON-4 with the automated one circle (detector) and the rotation of the samples relatively to the narrow incident radiatlon beam. The structure of boron nitride films were studied on dependence of the growth temperature and borazine pressure. It was showed the as-grown boron nitrides films grown on (100)Si at low pressure ($5x10^{-3}$ Torr) from pure borazine represented the mixture of hexagonal and cubic modifications of BN. It was observed that BN films has multilayer formation analogous the superlattice structure.

C-II/P2 COMBINED HIGH RESOLUTION X-RAY DIFFRACTION AND EXAFS STUDIES OF $Si_{1-x}Ge_x$/Si HETEROSTRUCTURES, R.Felici, P. De Padova ISM-CNR, Via E.Fermi 38, 00044 Frascati, Italy; R.Larciprete ENEA, INN-FIS, PO 65, 00044, Frascati, Italy; F.Comin, L.Ortega, V.Formoso, L.Ferrari ESRF, BP 220, 38043, Grenoble-Cedex, France

$Si_{1-x}Ge_x$/Si (001), $0.05<x<0.60$, heterostructures are of continuous and increasing interest because of their potential use in Si-based opto-electronic devices. Their properties strictly depend on the compositional gradient and strain due to the deposition techniques and thermal or laser annealing processes.

In this paper we show reciprocal space maps obtained by high resolution x-ray diffraction measured on samples grown with different germanium contents. On the same samples we have performed EXAFS measurements at the Ge k-edge for polarization directions parallel and perpendicular to the surface plane.

We will present the correlation existing between the alloy layer lattice parameters measured by x-ray diffraction and the chemical bond lengths determined by EXAFS.

C-II/P3 STRUCTURAL MODIFICATIONS IN ANODIC AMORPHOUS WO_3 OXIDES IN ELECTROCHROMIC PROCESS, L.A. Aleshina, S.V. Glazkova, L.A. Lugovskaya, V.P. Malinenko, Petrozavodsk State University (PSU), pr. Lenina, 33, 185640 Petrozavodsk, Russia

X-ray research of structure of anodic tungsten oxides in the process of electrochromic coloration and bleaching of films has been carried out in this paper. Investigations have shown that in initial condition samples are amorphous, and arrangement of W and O atoms corresponds to configuration characteristic for crystal modificationof hydrate $WO_3 \cdot 1/3\ H_2O$.

The number of switching cycles varied from 10^2 till 10^5. The character of modiflcations in the X-ray diffraction pattern, taking place at the increase of the number of switching cycles testifies the fact of transition from amorphous W03 •I/3H20 to hydrates with bigger content of water: $WO_3 \cdot H_2O$ and $WO_3 \cdot 2H_2O$. The process of transition is not monotonous. Quantity of phases of this hydrates sharp grows up after 10^4 switching cycles. The analysis of change of distribution of intensity in the process of one and two coloration and bleaching cycles allow us to draw a conclusion that radical modifications in the structure of amorphous WO_3 oxide take place on the stage of coloration in electrolyte.

C-II/P4 STUDY OF STRUCTURAL PROPERTIES OF MOVPE GROWN ZnMgSSe LAYER BY HRXRD AND CATHODOLUMINESCENCE, J. Xu(1), Q. Liu(2), H. Kalisch(3), (1)I. Physikalisches Institut, RWTH Aachen, Sommerfeldstrasse 28, 52056 Aachen, Germany, (2)Gerhard-Mercator-Universität-GH Duisburg, FB 9,Werkstoffe der Elektrotechnik, Sonderforschungsbereich 254, 47048 Duisburg, Germany, (3)Institut für Halbleitertechnik 1, RWTH Aachen, Germany

ZnMgSSe alloy semiconductor is an attractive material for lattice matched waveguiding and cladding layer in blue-green diodes. However, this material system suffers from a number of crystalline defects, which might be responsible for the rapid device degradation. In order to quick, nondestructively study the structural properties such as compositional distribution, defects, strain and their correlation with growth parameters we applied high resolution X-ray diffractometry (HRXRD) and spatially resolved cathodoluminescence(CL) combined with secondary electron(SE) imaging to a series of ZnMgSeS samples grown by LP-MOVPE.

By X-ray diffraction ω-2θ mode was perfomed to study the layer strain and relaxation status. Moreover triple-axis mode was used to seperate the broadening effects of layer peak from in-depth compositional gradient and mosaiic structure. X-ray results show that the stain status and alloy composition in ZnMgSeS layer changed with the thickness. Most of samples have a wide layer peak due to the high dislocation density, which were also observed by panchromatic CL image ($\rho \geq 10^5$ cm^{-2}). Additionally inhomogeneous emission intensity on CL micrographs and wavy surfaces on SE images were also observed at all samples. With the increasing layer thickness the in-depth compositional gradient becomes more significant, and the contrast of intensity inhomogeneity in CL becomes stronger. The rocking curves of single and multi quantum structures indicated their abrupt interfaces, but in-depth compositional gradient in the quaternary layer was also observed in the reciprocal space mapping.

C-II/P5 EELS ANALYSIS OF POLYMERS IN THE TEM, K Varlot(1), J.M. Martin(1), C. Quet(2); (1)Ecole Centrale de Lyon Laboratoire de Tribologie et Dynamique des Systèmes, UMR CNRS 5513, BP 163, 69131 Ecully Cedex, France. (2)Elf Atochem, Groupement de Recherches de Lacq, BP 34, Lacq, 64170 Artix, France

We have performed EELS analyis on different polymers (PET, PMMA, PS) in the analytical TEM in order to evaluate the possibility to obtain chemical information at sub-micrometer scale. At the Carbon and Oxygen K-edges, we used a simulation of the ionisation continuum in order to extract the core-exciton peaks. Then we proposed an identification of the different chemical bondings in agreement with XANES experiments. In the low-loss region, we calculated the dielectric function and related parameters from the EELS spectra.

Moreover, as irradiation damage is the main limitation of EELS analysis in the TEM, we acquired spectra of polymers as a function of the irradiation dose. Irradiation damage is mainly due to inelastic scattering since elastic scattering in low Z-elements at low accelerating voltage is negligible. So degradation mechanisms in polymers under electron beam can be deduced from changes in the core-exciton peaks and the dielectric function.

All these informations obtained by TEM/EELS give a characteristic signature for each analysed polymer.

C-II/P6 SMALL-ANGLE SCATTERING of X-RAYS (S-AS) of GaN, DEPOSITED on SiC and Al_2O_3 SUBSTRATES, M.E. Boiko, Yu.G. Shreter, E.N. Mokhov. A.F. Ioffe Physical-Technical Institute, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia

The modified S-AS have been applied in studying of the defect structure GaN films.

We used for our x-rays measurements thick films (0.2-0.3mm) of the GaN deposited on (0001) plane of SiC substrate and thin (0.003-0.005mm) films GaN deposited on sapphire (alpha-Al2O3). X-ray rocking curves show difference in full width at half maximum (FWHM) of those structures.

(S-AS) shows quite different picture for those samples. GaN films deposited on the SiC had the three-dimensional disoriented domains. GaN domains distribute in liquid cluster model. It is seen by presence of strong incident peak and weak size-peak. The grid of GaN domains looked like the network of 120 or 60 degrees 50 nm cell. Estimation the length (perpendicularly surface) of those hexagonal prism were 200-300nm. The transmission mode S-AS carried out on GaN deposited on sapphire showed that variation of density distributed by a gas- like model.

C-II/P7 LEED, AUGER AND SYNCHROTRON X-RAY DIFFRACTION STUDIES OF THIN Co AND Pt_xCo_{1-x} ALLOY FILMS ON Pt(111). R. Baudoing-Savois, M. De Santis, P. Dolle, Y. Gauthier and M. C. Saint Lager, CNRS Laboratoire de Cristallographie, Associé à l'Université J. Fourier, BP 166, 38042 Grenoble, France

Co films of thicknesses between submonolayer range and about 10 monolayers(ML) were grown on Pt(111) at room temperature, by means of an electron bombardment Omicron source.

For all coverages, the LEED diagrams are of good quality. Between 1/8 ML and 5 ML we observe satellites arranged in hexagons: they are centered respectively around the Pt spot positions at low coverage, and around the unrelaxed «bulk» Co spot positions above ≈ 3ML. X -ray scans in the [0k0], [h00] and [hk0] directions exibit also satellites, confirming a non pseudomorphic epitaxial growth. Intensity oscillations of the X-ray specular beam favour a layer by layer growth model and allow calibration of the deposition rate, consistent with our previous Auger results. LEED and Auger data evidenced two different alloy states depending on the annealing temperature (up to 360°C or up to 430°C) which were then analysed in more details by synchrotron X-ray measurements. An oscillatory composition profile is evidenced in the top layers, similar to what happens at the surface of bulk PtCo alloys. In-situ real time X-ray measurements during annealing allowed to follow the changes of the alloy film parameters: lattice, thickness, interface roughness and average concentration; these results will be presented and discussed.

C-II/P8 NEW X-RAY DIFFRACTION METHOD FOR MATERIALS SCIENCE, Z. Swiatek, J.T. Bonarski, R. Ciach, Polish Academy of Sciences, Institute of Metallurgy and Materials Science, Reymonta st. 25, 30-059 Krakow, Poland and Z.T. Kuznicki, CNRS, Laboratoire PHASE (UPR 292, BP 20, 67037 Strasbourg Cedex 2, France

A new and very promising x-ray diffraction method for the texture and internal stress investigation is described. This method based on the conventional pole figure measurements in the back-reflection technique affords possibilities for investigations of the diffraction effects due to layers on a given depth in a material. The condition of constant information depth is attained by abandoning the Bragg-Brentano focalization geometry using an appropriate offset angle for each sample filt angle. During such measurement after selection of the adequate offset angle its corresponding changes proceeds automatically. In order to obtain satisfactory integrated intensities a pseudo-position sensitive detection technique is applied.

The proposed method in this non-symmetrical mode is recommendable and useful tool for studying texturized and epitaxial thin films as well as multilayer systems.

C-II/P9 CATHODOLUMINESCENCE STUDY OF CRYSTALLINE QUALITY OF (Al, Ga, In)N HETEROSTRUCTURES, Q. Liu, H. Lakner, A. Meinert and E. Kubalek, Gerhard-Mercator-Universität Duisburg, Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany and F. Scholz 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

Group III-nitride heterostructures have recently emerged as important semiconductor materials with applications to high power devices and light emitting devices in the visible and ultra-violet range. For improved device performance and reliability the concentration of deep levels caused by defects needs to be minimized. The goal of this work is non-destructive spatially resolved characterization of defects and microstructures of MOVPE-grown wurtzite (Al, Ga, In)N heterostructures in correlation with growth parameters. We applied spectral and panchromatic cathodoluminescence (CL) combined with secondary electron (SE) imaging to investigate the electro-optical as well as the structural properties of (Al, Ga, In)N heterostructures, such as various energy levels, radiative recombination centers, interfacial quality and crystalline defects. Our CL study on various group-III nitride quantum well structures shows distinct correlations between defects and luminescence behaviours. Panchromatic CL micrographs exhibit typically inhomogeneous emission intensity. Further studies using spatially resolved spectral CL measurements show, that the regulated intensity inhomogeneity (on a -1 µm scale) is related to local variations of the interface quality, while CL-spectra recorded from dislocation sites are dominated by the so-called «yellow-emission». Additionally, high resolution x-ray diffractometry (HRXRD) and scanning transmission electron microscopy (STEM) were used to examine the structural properties and their correlation to CL results.

C-II/P10 TEM AND X-RAY STUDY OF MBE GROWN Fe/Cr SUPERLATTICES WITH NON-COLLINEAR MAGNETIC STRUCTURE, T.P. Krinitsina, V.V. Popov, V.G. Pushin, A.M. Burhanov, V.I. Minin, V.V. Ustinov, Instiute of Metal Physics, Russian Academy of Sciences, Ekaterinburg 620219, Russia

In the present work we report the results of TEM and X-Ray investigations of non-collinear Fe/Cr superlattices, grown by molecular-beam epitaxy on (101)Al_2O_3 substrates. The multilayer structure represents a pseudo-single crystal composed of nanodimensional crystallites with predominantly columnar morphology, separated by low-angle and special high-angle boundaries. These crystallites are partially coherently connected with the substrate, they have equiaxial form in the plane parallel to the substrate plane and in the perpendicular direction their morphology is predominantly prismatic. Three possible orientations of these crystallites relatively to the substrate have been found, namely: {110}, {100} and {311}, the first being dominating. As the Cr layers thickness increases, the crystallites dimensions are found to become somewhat larger and their form approaches to equiaxial. As a result of boundaries migration the nanocrystals gradually acquire the plane facet cut along the planes of {110}, {100}, {112} type. It may be suggested that the correlation length of roughness on interlayer boundaries has the same scale as the transverse size of crystallites (10-20 nm). This may be one of the origins of non-collinear magnetic structure formation in Fe/Cr superlattices.

C-II/P11 X-RAY METHOD OF MICROPORE FILLING EFFICIENCY CONTROL IN ALUMINIUM OXIDE FILMS, V.V. Petrova, Petrozavodsk State University (PSU), Lenin Prosp, 33, 185640 Petrozavodsk, Russia, A.A. Savina, PSU, Lenin St. 33, 185640 Petrozavodsk, Russia.

The procedure of micropore filling effeciency control in porous films by leading a filler into pores is proposed. The method is based on direct measurements of experimental X-ray Small-Angle Scattering (SAS) intensities for samples in an initial state and after chemical-technological treatment .

Process of pore filling is mostly controlled through changes in object mass: the result is estimated by comparison of addition in film mass with the theoretically calculated value. This procedure doesn't provide differentiative information about pore sizes and cannot pretend to high precision because of its small sensitivity.

The merit of proposed method in comparison to the weigh one is that it allows to define volume micropore content by direct measurements of SAS-intensities, get data about a pore size distribution and calculate the filling extent of different size fraction pores from SAS-intensities changes caused by pores filling of matter differed from oxide matrix in whole or in part.

C-II/P12 TEM OBSERVATIONS OF NANOMETER THICK COBALT DEPOSITS IN ALUMINA SANDWICHES, F. Fettar, P. Holody, S.-F. Lee, J.-L. Maurice, F. Pétroff, L.F. Schelp, A. Vaurès, and A. Fert, Unité Mixte de Physique CNRS/Thomson-CSF, 91404 Orsay, France.

We have prepared by sputtering tunnel junctions in which cobalt electrodes are separated by a sandwich made of a thin deposit of Co (nominally 0.2 nm to 2 nm) between two Al_2O_3 layers 4 nm thick. These structures are interesting for spin dependent tunnelling with Coulomb blockade, an effect related to the shape and distribution of the clusters formed by the cobalt.

We present a transmission electron microscopy (TEM) study of these structures. Samples for TEM observations in plan-view and cross section were deposited onto carbon membranes and <100> Si, respectively, simultaneously with the tunnel junctions but without the electrodes.

The cobalt appears to form individual clusters for a nominal Co thickness, t_{Co}, of 1 nm or less. For t_{Co} = 0.4 nm, 0.7 nm and 1 nm, the mean cluster diameter was found to be 2, 2.5, and 5.5 nm, respectively, with a standard deviation of about 0.5 nm in each case. As t_{Co} increases to 2 nm, the cluster shapes become more complex and a percolation threshold is reached.

C-II/P13 CANCELLED.

C-II/P14 NANOCRYSTALLINE Ta SEED- AND CAPPING-LAYERS FOR MAGNETIC THIN FILM MULTILAYERED STRUCTURES*, F. Bensmina(1), P. Humbert(1), M. Benaissa(2), G. Ehret(1), V.S. Speriosu(3) and B.A. Gurney(3), (1)IPCMS, 23 rue Loess, Strasbourg, France, (2)IFUNAM, Mexico D.F., Mexico, (3)IBM Almaden Research Center, San Jose, CA, USA

Sputtered Ta thin flms have been extensively studied for their applications in microelectronics and, more recently, in x-ray optics. In magnetic multilayered structures, Ta thin films can be advantageously used as seed layers to favor a <111> oriented growth of fcc metals, such as Co, NiFe, Cu or FeMn, and as capping layers to prevent air-oxidation of these multilayered structures.

Magnetron-sputtered sandwiches with the structure Ta 50Å/Co 80Å/Ta 50Å and Ta 50Å/Cu 50Å/Co 75Å/Cu 50Å/Ta 50Å were deposited on air-exposed Si wafers. The sandwiches were investigated by HRTEM (topview and cross- sectional samples). With the sputtering conditions used, the Ta layers grow nearly amorphous. The very reproducible morphology however shows short-range ordering characterized by randomly oriented nanocrystals consisting of stacks of a few atomic planes, about 10-20Å wide. Topview electron diffraction micrographs only reveal two broad rings (2.2-2.5Å and 1.35-1.45Å) attributable to Ta. The first diffraction ring is actually composed of at least two line contributions. These results are in agreement with those obtained by grazing incidence XRD. They can be interpreted as resulting mainly from a tetragonal ß-Ta structure affected by the small crystallite size, although the presence of some distorted bcc Ta cannot be ruled out. On the other hand the absence of grain boundaries in the Ta layers explains their efficiency as protective layers. Oxidation indeed proceeds through slow diffusion into the top Ta layer, leading to an amorphous Ta oxide layer of about 30Å in thickness at the air-exposed surface.

(*This work was supported by NATOCollaborative Research Grant No CRG931539)

C-II/P15 STM AND XRD STUDIES OF THE EFFECT OF THE DEPOSITION TEMPERATURE ON THE MAGNETORESISTANCE BEHAVIOUR OF La-Ca-Mn-O FILMS GROWN BY PULSED LASER DEPOSITION, Wei Zhang and I.W. Boyd, Department of Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K, M. Elliott and W. Herrenden-Harkerand, Department of Physics and Astronomy, University of Wales, Cardiff CF2 3YB, UK

Recent studies of La-Ca-Mn-O films grown on $LaA1O_3$ substrates by pulsed laser deposition (PLD) show a strong dependence of the magnetoresistive (MR) behaviour of the films on the preparation conditions. The deposition temperature, in particular, plays an important role in affecting the transport properties and magnetoresistance behaviour of the films. High deposition temperatures produce the largest MR values, whilst the maximum MR values measured at room temperature appeared in films grown at lower deposition temperatures. Therefore an investigation of effect of deposition temperature on the structure, stoichiometry and Curie temperature of the films is clearly necessary to more completely understand this phenomenon.

In this paper, the growth of giant magnetoresitance La-Ca-Mn-O films on Si (100) substrates using an Nd:YAG laser operating at 266nm and standard PLD apparatus is reported for a range of deposition temperatures. The structure, surface morphology and electrical properties of the La-Ca-Mn-O films were characterised by XRD, STM and the four-point probe technique. It was found that the orientation of the perovskite-cubic structure of the films is changed from the (100) to the (110) direction and the peak of the measured temperature versus resistivity curve shifted to low temperatures when the substrate temperature increased from 700°C to 900°C. STM also confirms a significant structure change on the surface of the films. The observed phenomenon can be explained by the onset of lattice distortion during the different deposition processes.

C-II/P16 INVESTIGATION OF CHEMICAL ORDERING IN MBE-GROWN Co_xPt_{1-x} FILMS BY XRD AND HRTEM, M. Maret, C. Uhlaq-Bouillet, W. Staiger, M.C. Cadeville, IPCMS, GEMM, UMR46 CNRS-ULP, 23 Rue du Loess, 67037 Strasbourg, France, and S. Lefebvre, M. Bessière, LURE, Bât 209D, 91405 Orsay, France

From X-ray diffraction, long-range chemical ordering along the growth direction was found in $Co_{80}Pt_{20}$ films, exhibiting mostly hcp stacking and grown around 690 K on 150 Å Ru (0001) buffer deposited on mica(001) substrate, while no chemica] ordering in the (0001) planes was detected. This film structure is clearly different from the fcc $L1_2$-type structure of the Co_3Pt bulk alloy, where all the (111) planes have the same Co3Pt composition. It is indeed in- cluced by the codeposition process and driven by both Pt surface segregation and dominant surface diffusion. An increase of the deposition temperature in the range 500-690 K favors both the growth of the hcp phase and long-range ordering along the growth direction. The microstructure of these films was investigated by HRTEM using TOPCON 002B and JEOL 4000EX microscopes. The cross-section images along the [1120] direction of the Ru buffer show the coexistence of the two types of stacking, hcp and fcc. Image processing by Fourier transform of these different area were performed to give local information on long-range ordering.

C-II/P17

EPITAXIAL STRAIN IN (110) RE-Fe_2 THIN FILMS (RE=RARE EARTH), A. Mougin, C. Dufour, K. Dumesnil, Ph. Mangin, G. Marchal, L.P.M., U. H.P.-Nancy I, BP 239, 54506 Vandoeuvre Cedex, France, and G. Patrat, L. de Cristallographie, BP 66, 38042 Grenoble Cedex 9, France

(110) RE-Fe_2 single crystal thin films (with RE=Y, Sm, Gd, Tb, Dy, $Dy_{0.7}Tb_{0.3}$, Er) have been grown by molecular beam epitaxy. The parameter $a_\perp$ along the growth direction (110) was measured by standard X-ray diffraction, whereas the $a_{//}$ parameter, the distance between the (110) planes perpendicular to the surface, was determined by grazing incidence X-ray diffraction. $a_\perp$ is smaller and, correlatively, $a_{//}$ is larger than the bulk parameter. Consequently, the films are submitted to a ε_{xy} shear ($\varepsilon_{xy} = (a_\perp - a_{//})/2a$, where a is the average parameter) varying between -0.1% and -0.6%. The ε_{xy} shear is shown to induce modification of the easy direction of magnetization compared to bulk compounds. For YFe_2/RE-Fe_2 bilayers, a minimization of the total elastic energy, considering a perfect epitaxy between both compounds, leads to calculated equilibrium shears in good agreement with the experimental ones.

C-II/P18

NANOCRYSTALLINE THIN FILMS OF TITANIUM GROWN ON KBr SUBSTRATE, Ph. Komninou, Th. Kehagias, Th. Karakostas, P. Poulopoulos, M. Aggelakeris, N. Flevaris, Physics Department, Solid State Section 313-1, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece and T. Braisaz, P. Ruterana, G. Nouet, LERMAT 6004 CNRS - ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Thin films of titanium were grown on KBr substrate. Whatever the substrate temperature, diffraction patterns (TEM) exhibit several rings typical of α-Ti showing that the mean grain size is very low (10nm).

The most important characteristic of the nanograins is the formation of twins of the type: $K_1 = \{1101\}$, $\eta_1 = \langle 1012 \rangle$ The observation direction in HREM is along ⟨1123⟩. Although the white or dark spots correspond to two atomic columns, it is confirmed that the twin plane is a mirror plane. Some of these twins contain steps which were associated with the twinning dislocation $b_{2/2}$. In other nanograins, multiple twinning can occur with a twin plane every five or six {1011} planes.

The origin of these twins could be attributed to growth mechanism but the presence of twinning dislocations might suggest than some parts of theses films are under stress.

C-II/P19

TEM AND XRD STUDY OF SOLID PHASE INTERACTIONS IN EPITAXIAL Fe/GaAs (001) STRUCTURES, A. Rocher, CEMES/CNRS, BP 4347, 31055 Toulouse, France, and B. Lépine, S. Deputier, A. Guivarc'h and G. Jézéquel, UMR PALMS, Université de Rennes I, 35042 Rennes, France

The epitaxial growth of iron on GaAs have been largely studied for nearly twenty years and optimum experimental conditions have been proposed elsewhere. However, numerous question subsist : it is difficult to reconcile the interface disruption and intermixing with the epitaxial growth of Fe and to understand the decrease of the average film magnetization for thin Fe layers.

In this context, we studied the solid phase epitaxy of Fe/GaAs. Prepared in UHV conditions, 20-100 nm Fe thick films were deposited on GaAs buffer layers at room temperature and the samples were annealed in situ in the range of 350-500°C. The various specimens were studied by X-Ray diffraction and Transmission electron microscopy (TEM) in order to determine the resulting compounds given by the in situ heat treatment. There is no reaction for heat treatments below 300°C. At the interface only the epitaxial relationship between Fe(001)/GaAs(001) is observed by electron diffraction. At 400°C the interdiffusions appear. They lead to the formation of a layer made of both the ferro-magnetic ternary phase $Fe_3Ga_{1.5}As_{0.5}$ and the antiferromagnetic compound Fe_2As. Both compounds are oriented with the substrate following some intergranular relationships corresponding to a crystalline coincidence with the GaAs. At higher temperatures (500°C), the expected stable phase Fe_3GaAs/GaAs is not obtained because the decomposition of the reacted layer, leading to a probable $FeGa_3$/GaAs structure.

C-II/P20

DETERMINATION OF ORIENTATION RELATIONSHIPS INCLUDING POLARITY FOR HETEROEPITAXIAL STRUCTURES "GALLIUM NITRIDE ON DIFFERENT CUTS OF SAPPHIRE", A.N.Efimov and A.O.Lebedev, Ioffe Institute, Polytekhnitcheskaya, 26, 194021 St.-Petersburg, Russia

Orientation Relationships (ORs) including polarity seem to be extremely necessary, firstly, to understand the nature of an interface between incommensurate crystal structures and, secondly, to know an effect of interface defect structure on output parameters. For example, local domains with an inverse direction of polar axis significantly decrease an effectiveness of devices and at the same time can not be detected by conventional X-ray techniques. To determine ORs with polarity we have successfully used Kossel effect. Electron beam of SEM excites Ga Ka X-rays which passing through both the layer and the substrate create the diffraction patterns. Geometry of Kossel lines is governed by Bragg law while the fine structures of them (i.e. the distribution of contrast across the lines) is described by the dynamic theory of X-rays scattering. It is essential that HKL and -H,-K,-L reflections show different fine structures. Just this fact was used for polarity determination. Interpretation of Kossel patterns was carried out comparing an experimental and computer simulated pictures. Experimental results both original and published earlier by other authors on the orientation relationships including polarity of the layer for GaN epitaxial layers grown on various substrates are summarized.

C-II/P21

OPTICAL AND DIGITAL PROCESSING OF HRTEM IMAGES OF SI THIN FILM DEPOSITED BY RTCVD, F. Pailloux, E.L. Mathe, H. Garem, RJ Gaboriaud, LMP, BP 179, 869690 Futuroscope Cedex, J.C. Muller, CNRS-PHASE, 23 rue du Loess, 67037 Strasbourg Cedex, France

Thin film of Si deposited by RTCVD on (001) Si wafer was investigated by cross sectionnal sample in an 3010 JEOL high resolution microscope, in order to study the epitaxy and extended lattice defects brought about by the deposition process, in the thin film. HRTEM images of extended defects were investigated by optical fourier analysis in different places of the picture wich leads to an explanation in terms of twins and periodicity of twin lamelas.

Further analysis by means of digital processing of the HRTEM pictures is done by `Holographic Reconstruction' and are interpreted in terms of strain field in the matrix.

C-II/P22

DIGITAL PROCESSING OF HRTEM IMAGES OF SEMICONDUCTOR INTERFACES, E Snoeck, A Rocher, CEMES/CNRS, BP 4347, 31055 Toulouse, France

The crystalline structures of interfaces have been studied by High Resolution Electron Microscopy (HREM) for lattice mismatched systems: GaSb/(001)GaAs (8%) and GaInAs/(001)InP (3.1%). Digital processing technique has been performed in order to evaluate the relaxation of the system and the extension of the intermediate zone between the substrate and the epilayer where the crystalline structure is not well defined.

The GaSb grown by MBE at 470°C on GaAs is known to be perfectly relaxed by a Lomer dislocations network directly created during the island growth. The intermediate zone is measured to be few atomic planes thick.

The Ga1-x InxAs is grown on InP by MBE at 450°C with x< 10%. The intermediate zone appears to be thicker than 4nm. The organization of misfit dislocations involved in the relaxation process is studied. Misfit dislocations, poorly organized, are mainly partial and 60° types. Above this interfacial zone, the GaInAs layer appears to be fully relaxed.

C-II/P23 TEM STUDIES OF UNUSUAL CRYSTALLINE STRUCTURES FORMED IN AMORPHOUS FILMS, V.Yu.Kolosov* and A.R.Tholen, Physics Dept., Chalmers University of Technology, Goteborg 41296, Sweden

An unusual internal lattice bending (up to 120 degrees per micron) has been observed in different thin amorphous films subjected to transformation amorphous - crystalline [1].

We will here report about such a transformation in thin films of amorphous iron oxide (Fe_2O_3), which were exposed to the electron beams of different size and intensities inside the electron microscope and transformed to concentric annular areas (width about 1 micron) of «perfect» and «imperfect» crystallline zones of distinct diffraction contrast. The two different zones are thus crystalline both with a constant internal bending of the lattice: the crystals themselves are not bent but regular rotation of the lattice (from <001> to <100>) between the centres of any adjacent zones is accumulated inside grains. The grain morphology in the two zones is, however, completely different with quite large grains in the «perfect» zones and fine grains in the «imperfect» zone, where the grains often are crescentlike with their smallest dimension being around 20 nm.

This unusual microstructures were studied with a Philips CM200 FEG microscope using HREM, EDX, CBED, EELS and bend-contour technique, developed earlier [1].

[1] Kolosov V.Yu. Proc XII ICEM, 1990,Vol.1, 574

* Also at Ural State University, Ekaterinburg, Russia

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM D

Computational Modeling of Issues in Materials Science

Symposium Organizers

H. DREYSSE, IPCMS-GEMME, Université Louis Pasteur, Strasbourg, France

L.T. WILLE, Florida Atlantic University, Boca Raton, FL, USA

Y. KAWAZOE, Tohoku University, Sendai, Japan

M. DOYAMA, Teikyo University of Sciences and Technology, Yamanashi, Japan

The assistance provided by the
HCM Network «Ab-initio calculation of complex processes in materials»
is acknowledged with gratitude.

SYMPOSIUM D

Monday June 16, 1997
Lundi 16 juin 1997

Afternoon
Après-midi

Session I - General Simulation Methods

D-I.1 - invited - 14:00-14:30

MATERIALS SCIENCE BY NUMBERS, **U. Landman**, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

Computer-based simulations open new avenues for investigations of materials properties, allowing elucidation of observations, prediction of novel phenomena, as well as serving as a testing ground for new concepts. In this talk the methodologies of certain classical and quantum mechanical molecular dynamics simulations will be discussed and demonstrated in the context of size-evolutionary patterns of materials clusters, mechanical properties and quantized conductance in nanowires, nanocrystals and their assemblies, atomic-scale friction, and molecular viscoelastic hydrodynamics in lubricated narrow junctions.

D-I.2 14:30-14:45

NEW SIMULATION TECHNIQUE OF GRAIN GROWTH, P. Paillard(1), R. Penelle(2) and V. Pontikis(1,3), (1)Laboratoire de Métallurgie Physique, Université de Lille 1, 59655 Villeneuve d'Ascq, France, (2)Laboratoire de Métallurgie Structurale, Université Paris Sud, 91405 Orsay Cedex, France, (3)Laboratoire des Solides Irradiés,CEA/CNRS/Ecole Polytechnique, 91128 Palaiseau Cedex, France

We present a new simulation technique of grain growth which over-comes limitations of the usual Monte Carlo and Vertex methods. In this technique, grain boundary migration is treated deterministicaly by numerically integrating a classical equation of motion based on experimental data. Moreover, the influence of grain misorientation and of interfacial tension are fully accounted for. Input data such as the grain boundary mobility dependence as a function of temperature and misorientation and the grain boundary excess energy dependence as a function of the misorientation, are key quantities determining the kind of real system being simulated. As a validation test, the results here presented treat of normal grain growth in aluminum in two dimensions. However, the technique can be easily adapted to the three-dimensional case, issue to which work in progress is devoted. Finally, we discuss the applicability of this method to the cases of abnormal grain growth and of primary recrystallization.

D-I.3 14:45-15:00

COMPUTER SIMULATION OF MARTENSITIC TRANSFORMATIONS IN NiAl-ALLOYS, R. Meyer and P. Entel, Theoretische Tieftemperaturphysik, Gerhard-Mercator-Universität - Gesamthochschule Duisburg, Lotharstrasse 1, 47048 Duisburg, Germany

Modelling of alloys with semi-empirical potentials allows computer simulations with many atoms. Such studies may elucidate the relationships between atomistic properties of the materials and the formation of microstructure during diffusionless transformations. We have done molecular dynamics simulations of Ni_xAl_{1-x} alloys which exhibit martensitic transformations in the region $0.60 < x < 0.66$. Results show the formation of premartensitic structures like tweed as well as the development of microstructure on a nanometer scale. Calculations of the static and dynamic structure factor give further insight into these phenomena.

D-I.4 15:00-15:15

COMPUTER SIMULATION OF MARTENSITIC TEXTURES: CONSEQUENCE OF ELASTIC COMPAIBILITY CONDITIONS AND COMPOSITIONAL DISORDER, A. Saxena and A.R. Bishop, Los Alamos National Lab., USA, S.R. Shenoy, ICTP, Trieste, Italy and T. Lookman, Univ. Western Ontario, Canada

We consider a Ginzburg-Landau model free energy $F(e,e_1,e_2)$ for a (2D) martensitic tra,nsition, that provides a unified understanding of varied twin/tweed textures. Here F is a triple well potential in the rectangular strain (ε) order parameter and quadratic e12, e22 in the compressional and shear strains, respectively. Random compositional fluctuations $\eta(r)$ (e.g. in an alloy) are gradient-coupled to ε, $\sim - \Sigma_r \varepsilon(r) [(\Delta^2{}_x-\Delta^2{}_y)\eta(r)]$ in a 'local-stress' model. We find that the compatibility condition [linking ten,sor componets $\varepsilon(r)$ and $e_1(r)$ $e_2(r)$], together with local variations such as interfaces or $\eta(r)$ fluctuations, can drive the formation of global elastic textures, through long-range and anisotropic effective ε-ε interactions. We have carried out extensive relaxational computer simulations using the time-dependent Ginzburg-Landau (TDGL) equation that supports our analytic work and shows the spontaneous formation of parallel twins; branched twins; chequer-board tweed; and hierarchical tweed, with the last texture playing a role in a suggested model scenario for shape memory. The observed microstructure in NiAl and Fe_xPd_{l-x} alloys is explained on the basis of our analysis and simulations.

D-I.5 15:15-15:30

THE MICROSCOPIC THEORY OF DIFFUSION-CONTROLLED DEFECT AGGREGATION, E.A. Kotomin(1,2), V.N. Kuzovkov(1,3) and W.von Niessen(3), (1)Institute of Solid State Physics, 8 Kengaraga Str., Riga 1063, Latvia, (2)Freie Universität Berlin, Fachbereich Physik, Berlin 14195, Germany, (3)Technische Universität Braunschweig, Germany

The kinetics of diffusion-controlled defect accumulation and aggregation under irradiation of solids is of great technological importance. However, the development of rigorous theory is complicated mainly by the necessity to take into account defect interaction which namely leads to similar-defect aggregation and, at appropriate temperatures and irradiation intensities - to metal colloid formation in ionic solids. In this paper, we briefly analyze three types of approaches to this problem - macroscopic, mesoscopic and microscopic, and discuss their advantages and disadvantages. We focus on the microscopic, atomistic formalism of the many-point particle densities [l] which uses only defect diffusion coefficients and attraction energies between similar and dissimilar Frenkel defects - vacancies, v, and interstitial atoms, i, $E_{l,m}$, l, m = v, i. It is shown that the aggregation kinetics is a cooperative process in which the aggregation of vacancies triggers the aggregation of interstitials, and vice versa. Theoretical results are illustrated by extensive experimental data for NaCl and CaF_2 crystals.

[l] E.A. Kotomin and V.N. Kuzovkov, Modern Aspects of Diffusion- Controlled Processes (Elsevier, Amsterdam. l996)

D-I.6 15:30-15:45

EMBEDDED ATOM POTENTIALS IN FCC AND BCC METALS, M. Doyama and Y. Kogur, Teikyo University of Science and Technology, Uenohara, Yamanashi 409-01, Japan

In metals, the interaction cannot be represented by a pairwise potential but many body potentials. By the embedded function, surface problems can be treated. An n-body embedded function is proposed. The total energy is given by $E_{total} = \sum E_i$, $r_{ij} = |r_i - r_j|$, $E_i = F(\rho_i) + (1/2) \sum \Phi(r_{ij})$, $F(\rho) = D \rho \ln \rho$, and $\rho_i = \sum f(r_{ij})$. Here E_{total} is the total internal energy. E_i is the internal energy associated with atom i. ρ_i is the electron density at atom i due to all other atoms. $F(\rho_i)$ is the embedding energy of atom into electron density ρ_i.

$\Phi(r_{ij})$ is the two body central potential between atoms i and j separated by r_{ij}. $\Phi(r_{ij})$ is the contribution to the electron density at atom i due to atom j at the distance r_{ij} from atom i. $\Phi(r)$ and f(r) are represented by $\Phi(r) = A(r_{c1}-r)^2 \exp(-C_1 r)$, and $f(r) = B(r_{c2}-r)^2 \exp(-C_2 r)$. The parameters are determined by use of the formation energy of a vacancy, cohesive energy, C_{11}, C_{12}, C_{44} and the lattice parameters for copper, silver and gold.

For bcc metals $\Phi(r) = A_1(r_c-r)^2 \exp(-C_1 r)$, and $f(r) = B(r_c-r)^2 \exp(-C_2 r)$ or $f(r)= A_2(r_c-r)^2 (r^2+Br+C_2)$ are assumed. The parameters are determined to fit to the formation energy of a vacancy, cohesive energy, C_{11}, C_{12}, C_{44} and the lattice parameters.

A few applications to the calculation of point defects will presented.

15:45-16:15 **BREAK**

Session II - Ab Initio and Tight-Binding Molecular Dynamics

D-II.1 - invited - 16:15-16:45

FIRST PRINCIPLES MOLECULAR DYNAMICS OF ORGANIC AND ORGANOMETALLIC COMPOUNDS, **F. Gygi**, IRRMA, PPH-Ecublens, 1015 Lausanne, Switzerland

Ab initio molecular dynamics simulations of organic and organometallic compounds represent a challenge in the field of electronic structure methods. The presence of first-row elements as well as transition metals requires a highly accurate numerical method. Various approaches have been proposed to deal with this difficulty. We present results of calculations performed within the framework of Density Functional Theory using norm-conserving pseudopotentials. Molecular dynamics simulations of organic molecules, organic crystals, and organometallic complexes will be presented. The effects of Generalized Gradient Approximations (GGA) for the treatment of exchange and correlation in these systems will also be discussed.

D-II.2 16:45-17:00

CORRELATION BETWEEN STRUCTURE AND QUENCH-RATE IN AMORPHOUS CARBON GENERATED BY CONSTANT PRESSURE TIGHT-BINDING MOLECULAR DYNAMICS, L. Colombo, INFM and Dipartimento di Scienze dei Materiali, Universita di Milano, via Emanueli 15, 20126 Milano, Italy, M. Celino and V. Rosato, ENEA C.R. Casaccia, HPCN Project, PO Box 2400, 00100 Rome A.D., Italy

Amorphous Carbon structures have been generated by Tight-Binding Molecular Dynamics simulations in the Parrinello-Rahman-Nosé (NPT) ensemble by rapidly quenching the liquid. Quench rates q in the range $10^{16} < q < 10^{13}$K/s have been used to generate amorphous samples at different densities. The aim of the work has been to infer a possible correlation between the amorphous structure and the quench rate. The generated amorphous structures have been also characterized with respect to relevant properties such as connectivity, fraction of sites with sp2 (sp3) bonding, bond angles and to ascertain the presence of interconnected rings of equally bonded sites. The electronic structure of these objects have been also evaluated and compared to theoretical and experimental data. It has been further discussed the possible use of alternate paths (i.e. reverse Monte-Carlo technique) to efficiently generating amorphous structures with given structural properties.

D-II.3 17:00-17:15

TIGHT BINDING MOLECULAR DYNAMICS SIMULATIONS OF THE VIBRATIONAL PROPERTIES OF α-TITANIUM, J.L. Gavartin and D.J. Bacon, Department of Materials Science and Engineering, The University of Liverpool, Liverpool L69 3BX, UK

Many unusual features of crystalline titanium as well as zirconium and hafnium such as their polymorphism, anisotropy in the elastic and dIffusion propeRties etc., arise from the delicate interplay between the electronic and Vibrational contribution to the corresponding free energies. It is challenging therefore to obtain a reliable calculational scheme that would be capable of accounting for quantum features of the electronic density and, at the same time, could be implemented as O(N) method and used for a long time scale MD simulations. In the present work we employ tight binding molecular dynamic simulations to study the temperature dependence of the vibrational properties of the hexagonal α-phase of titanium. The single modes of vibration are identified by the direct diaganalisation of the correlation matrix of a system of 96 titanium atoms, and subsequent spectral analysis is performed by means of Fourier transform of the corresponding velocity autocorrelation functions. Based on these calculations we analyse the anomalies in the vibrational properties of α-Ti (such as hardening of the (001) TO mode with temperature) and discuss the physical causes of these anomalies. The relative stabilities of other polymorphic modifications of titanium are also discussed.

D-II.4 - invited - 17:15-17:45

MOLECULAR DYNAMICS IN SEMICONDUCTOR PHYSICS, **S. Ihara** and S. Itoh, Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo 185, Japan

Molecular dynamics, which is a powerful method for studying both structural and dynamical properties in condensed matter, is employed as a 'microscope for the motion of atoms'. Information about the motion of individual atoms that is difficult to obtain experimentally can be obtained by this method. Parallel computers of tera-flops speed and tera-byte memory will make it possible to perform multi-million particle simulations using empirical potential. The macroscopic phenomena analyzed by continuum theory can be obtained by coarse-graining the atomic level information provided by this approach. When considering the problem of data analysis, examples in semiconductor physics such as implantation process will be provided.

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session III - Surfaces and Films

D-III.1 - invited - 9:00-9:30

AB-INITIO STUDIES OF ATOMIC AND MOLECULAR ADSORPTION ON SOLID SURFACES, **J. Hafner**, Institut für Theoretische Physik and Center for Computational Materials Science, Technische Universität Wien, 1040 Wien, Austria

Ab-initio local-density-functional studies of atomic and molecular adsorptIon processes on solid surfaces have been preformed using the Vienna ab-initio simulation program VASP. VASP is based on the following principles: finite-temperature local-density theory (including where necessary generalized gradient corrections), ultra-soft pseudopotentials for describing the electron-ion interaction in a plane-wave basis, iterative calculation of the LDF ground state via residuum minimization techniques, optimized charge-density mixing, exact calculation of the HEllmann-Feynman forces and stresses. Applications include: (a) The reconstruction and hydrogen-induced dereconstructions of the low-index surfaces of diamond, (b) the construction of the six-dimensional potential-energy surfaces for the dissociative adsorption of molecular hydrogen on transition-metal surfaces, (c) complex coverage-dependent adsorbate-structures of CO on Rh(100), and (d) the adsorption of thiophene on the catalytically active surface of MoS_2.

D-III.2 9:30-9:45

FULL AB-INITIO CALCULATION OF OXYGEN ADSORPTION ON A (100) SILICON SURFACE - FIRST STAGES OF THE THERMAL OXIDATION, A. Esteve, M. Djafari Rouhani, D. Estève, Laboratoire d'Analyse et d'Architecture des Systèmes, CNRS, 7 Ave. Colonel Roche, 31077 Toulouse, France

A successfull modelling of silicon oxidation has never been achieved (on a macroscopic nor a microscopic basis), despite an important research effort. Coupled atomic mechanisms are certainly involved in this process. Therefore, we are investigating a full ab-initio calculation of the oxygen in interaction with a (100) surface of silicon. Our final aim is to draw a list of elementary mechanisms of the silicon oxidation at the atomic level in view to make a direct simulation of the oxidation dynamics through a Monte-Carlo technique.

The present ab-initio calculation is based on the density functional theory via the Harris functional. The orbitals are expanded in a basis of atomic orbitals (LCAO theory). The unit cell contains eigth layers of silicon, hydrogens atoms to neutralize the dangling bonds in the bulk side (back silicon surface). Our silicon surface is taken to be infinite thanks to periodic boundary conditions. Only the oxygen atom plus the surface layer are free to relax at every step of the energy minimisation, all other atoms are given fix positions. Preliminary results reported concern the calculation leading to the oxygen preferential setting on the surface. The total energy, the angles and bond lengths are evaluated. We shall discuss the results as a function of the experimental conditions.

D-III.3 9:45-10:00

INITIAL STAGES OF THE ADSORPTION AND DIFFUSION MECHANISMS OF Pb ON Si(111)7X7, P. Sonnet, L. Stauffer, L.P.S.E., 4 rue des Frères Lumière, 68200 Mulhouse, France and C. Minot, Lab. de Chimie Théorique, 4 place Jussieu, 75252 Paris, France

We present a theoretical study of the adsorption and diffusion mechanisms of Pb, the Si(111)7x7 surface in the initial stages of the Pb chemisorption in the DAS model. In the framework of the crystalline extension of the Extended Hückel Theory, two adsorption mechanisms are especially studied: adsorption of Pb atoms on Si dangling bonds and Pb adsorption with formation of Pb atom clusters. The second mechanism is found to be more favorable than the first one but the two mechanisms could possibly coexist. This tendancy to agglomeration, in agreement with STM observations, is explained by the strong interaction between Pb atoms emphasized in our calculations. The F half of the unit cell is preferred. The diffusion paths for Pb on Si(111)7x7 are then investigated: jump of Pb atoms between the U (unfaulted) and F (faulted) unit cells are more difficult than jump inside a half unit cell, and jumps from adatoms of the U half unit cell to the F one are favored with respect to the opposite way. Considering the diffusion of a Pb pair between an adatom and a restatom, we show that the interaction between the Pb atoms leads to a significant decrease of the barrier energy computed for a single Pb atom. An interpretation of the experimental data is proposed

D-III.4 10:00-10:15

SEGREGATION OF BORON ON THE CLUSTER MODELLED Si(111)√3x√3R30°-B HYDROGENATED SURFACE, S. Wang, M.W. Radny and P.V. Smith, Department of Physics, The University of Newcastle, Callaghan, NSW 2308, Australia

Since its discovery in 1988, the B-modified si(111) √3x√3R30° surface has attracted a great of attention in semiconductor surface science. While the √3x√3R30° reconstruction is typical for group III elements adsorbed on the Si(111) surface, the B-induced reconstruction is stabilised by significant charge transfer to the subsurface chemisorbed boron from the neighbouring silicon atoms. The thin electrically active layer (the so-called δ-layer) which is produced in this way makes this system of practical importance because of its potential device applications.

First principles all-electron Density Functional Theory cluster calculations have been performed to investigate the chemisorption of atomic hydrogen on the cluster modelled Si(111)√3x√3R30°-B surface. It has been found that a boron atom will most likely occupy a subsurface substitutional S_5 site at low hydrogen coverages (< 0.67 ML), but appear as an adatom at an on-top site directly above one of the first-layer silicon atoms for hydrogen exposures greater than 0.67 ML. The obtained results are compared with the available electron energy loss spectroscopy, temperature programmed desorption, and low energy electron diffraction data.

D-III.5 10:15-10:30

MODELIZATION OF THE MANIPULATION OF SILVER ADATOMS ON Si(001), L. Pizzagalli, IPCMS-GEMME, 23 rue du Loess, 67037 Strasbourg, France and J.C. Okon, C. Joachim, CEMES, 29 rue Marvig, 31055 Toulouse, France

In the last decade, several experimental studies have opened new perspectives for the manipulation of atoms or molecules on a surface with a STM tip. Hence, controlled displacements of molecules or physorbed atoms have been realized. However, to our knowledge, nobody succeeded in controlling the displacement of individual atoms chemisorbed on materials with great technological interest, such as silicon. We investigate the theoretical possibility of manipulating individual silver atoms on a silicon (001) surface with a STM tip. Molecular mechanic calculations have been performed for two different adsorption sites and for various tip heights. We find that if the adatom is located between two dimers belonging to two adjacent dimer rows (cave site), we do not manage to move it for all considered tip heights. But if the adatom is located on the dangling bond of one silicon surface atom (bond site), controlled displacement along the dimer row is possible if the tip height ranges between 2.5 Å and 3 Å above the surface.

10:30-11:00 **BREAK**

D-III.6 11:00-11:15

DIFFUSION ON Ag(100) AND Ag(111) SURFACES, N.I. Papanicolaou, G.A. Evangelakis and G.C. Kallinteris, Department of Physics, Solid State Division, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

The self-diffusion processes of single adatoms on the Ag(100) and Ag(111) surfaces have been studied using molecular dynamics simulation and a many-body potential derived in the framework of the second-moment approximation to the tight-binding model. In the case of Ag(100) face we deduced the migration energies of simple hopping, exchange and complicated exchange mechanisms involving the displacement of more than two atoms. We found that the hopping mechanism is favoured for temperatures lower than 800K with an energy of 0.41eV, in very good agreement with available experimental data and ab-initio calculations. At higher temperatures the exchange type mechanisms become very important. Concerning the Ag(111) face, we found that the dominant mechanism is the hopping exhibiting Arrhenius behaviour with two distinct temperature ranges corresponding to different migration energies. The high temperature range refers to correlated movements. The migration energies found are close to recent experimental results.

This work has been supported by the European Ψκ Network.

D-III.7 11:15-11:30

MODELING OF BORON NITRIDE: ATOMIC SCALE SIMULATIONS ON THIN FILM GROWTH, K. Albe, W. Möller, Forschungszentrum Rossendorf, P.O. Box 51 01 19, 01314 Dresden, Germany

Thin film deposition of superhard boron nitride can nowadays be done by different PVD and CVD methods, but the mechanisms, which are relevant for BN-film growth, are hardly understood. Here computer simulations on atomic scale can be a helpful tool in order to investigate the physical processes involved. This contribution deals with the phase transition from the sp^2-bonded hexagonal to the sp3-bonded cubic structure, which typically occurs during thin films deposition. With respect to the equilibrium phase diagram the limits of empirical models adopted from carbon are discussed. Large scale molecular dynamics studies of boron and nitrogen impacts into h-BN targets are presented using a new classical, interatomic bond-order potential, which was fitted to a fairly complete ab initio-data set. The influences of deposition parameters are studied and the results are compared to experimental findings. Finally, the role of defect production and accumulation for c-BN growth is discussed.

D-III.8 11:30-11:45

A MONTE CARLO SIMULATION OF SILICON NITRIDE THIN FILM MICROSTRUCTURE IN ULTRAVIOLET LOCALISED-CHEMICAL VAPOUR DEPOSITION, J. Flicstein, S. Pata, J.M. Le Solliec, L.S. How Kee Chun, J.F. Palmier and J.L. Courant, France Telecom C.N.E.T. Laboratoire de Bagneux, PO Box 107, 92225 Bagneux, France

A real time Monte Cario simulation is employed to model the low temperature photonucleation and initial stages of film growth during ultraviolet (UV) localised-chemical vapour deposition. This model includes the UV induced effect of activated charge centers (ACCs) creation: ACCs are UV created prior to and during the nucleation on III-V compound substrate[1]. Heterogeneous photolysis of precursor molecules on the irradiated surface and adsorbate dynamics over the surface are also included. The deposition of silicon nitride by heterogeneous photolysis of a mixture SiH_4+NH_3 is used as a test case for modeling and simulation. By modifying the precursor flow ratio, the amount of amorphous material deposited over InP as a function of time for various values of the temperature is obtained over a substrate area of 2000 atomic sites. 2D and 3D predictions of the thin film morphology and its evolution in time during UV irradiation of the surface are presented at constant adsorbate binding energy. Additional picture is obtained about the amorphous material density, the role of surface ACCs on the nucleation and deposition rate, and the aggregate dynamics on the deposition rate. Simulation results indicate that for a given flow ratio and adsorbate-substrate binding energy, there is a critical temperature T_{crit}, such that for temperatures lower than T_{crit} low density silicon nitride is deposited while at $T>T_{crit}$, high density silicon nitride results at constant luminance. The inclusion of two-atom differentiation is shown to alter the layer compacity and is validated by experimental data.

[1]J. Flicstein and J. E. Bourée in Photochemical processing of electronic materials, eds. I. W. Boyd and R. B. Jackman (Academic Press, N. Y., 1992) p. 105-141

D-III.9 11:45-12:00

COMPUTER SIMULATION OF SPUTTERING OF GaP(100) UNDER GRAZING ION BOMBARDMENT, A.A. Dzhurakalov, I.I. Khafizov, Institute of Electronics, 700143 Tashkent, Uzbekistan

In the present work the sputtering processes on the GaP(100) surface under low-energy ion bombardment have been investigated by computer simulation. The trajectories of incident Ne and Ar ions, as well as recoil atoms were simulated in the binary collisio approximation.Energy and angular distributions of recoil atoms as well as sputtering yields versus the angle of incidence, the initial energy and target orientations were calculated.

The computational results show that when movingin surface semichannels and channels formed by Pand Ga atomic chains the projectile ions generate the low energy primary knocked out atoms. At sufficiently small grazing angles the recoil atoms are ejected near the plane which is perpendicular to the plane of incidence. The energies of these ejected particles are lower than 10 eV. The increasing of grazing angles leads to the forming of high energy recoils which are ejected also in plane of incidence. In the angular distributions of ejected particles the maxima corresponding to preferential ejection directions are observed.

D-III.10 - invited - 12:00-12:30

HYDRODYNAMIC INSTABILITY OF LIQUID SILICON DURING CRYSTAL GROWTH,

K.Kakimoto and H. Ozoe, Institute of Advanced Material Study, Kyushu University

The quality of large semiconductor crystals grown from melts is significantly affected by the heat and mass transfer in the melts. This paper reviews the current understanding of the phenomena, especially melt convection, starting from the results of visualization using model fluids or silicon melt, and continuing to the detailed numerical calculations needed for quantitative modeling of processing with solidification. The characteristics of silicon flows are also reviewed by focusing on the Coriolis force in the rotating melt. Descriptions of flow instabilities are included that show our level of understanding of melt convection with a low Prandtl number. Based on geostrophic hydrodynamics, the origin of the silicon flow structure is reviewed and it is discussed whether silicon flow is completely turbulent or has an ordered structure. The phase transition from axisymmetric to non-axisymmetric flow is discussed using different geometries. Additionally, surface-tension-driven flow is reviewed for Czochralski crystal growth systems.

12:00-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Session IV - Complex Materials and Parallel Computing

D-IV.1 - invited - 14:00-14:30

INDUSTRIAL IMPACT OF COMPUTATIONAL MATERIALS SCIENCE, **E. Wimmer**, Molecular Simulations s.a.r.l., Parc Club Orsay Université, 20 rue Jean Rostand, 91893Orsay Cedex, France

With the steadily increasing capabilities of theoretical approaches combined with the sustained advances in computer technology, an increasing number of industrial laboratories are integrating atomistic simulations in their research efforts. The complimentarity between established experimental techniques and novel atomistic simulations offers immediate industrial benefits. Examples include the determination of crystal structures from x-ray powder diffraction patterns combined with total energy minimization techniques, the determination of polymorphism, the analysis of vibrational spectra (IR and Raman), the determination of surface structures for the interpretation of STM images, and the prediction of crystal morphologies. The industrial usefulness of predicting optical properties are illustrated here by the development of high-performance inorganic pigments based on cerium sulfide. The control of defects and buried interfaces is of great practical interest, yet they are difficult to characterize experimentally. Atomistic simulations and property predictions offer a unique opportunity to gain structural information and quantitative thermodynamic data for these important issues in materials science. Future developments of this field will have to face the challenge of connecting the atomistic length and time scales with the mesoscopic and macroscopic domains while increasing the accuracy of atomistic simulations. Clearly, we are only at the beginning of an exciting and rewarding scientific and technological development.

D-IV.2 14:30-14:45

QUANTUM EFFECTS ON PHASE TRANSITIONS IN HIGH PRESSURE ICE, M. Benoit, Laboratoire des Verres, Université Montpellier II, 34095 Montpellier, France; D. Marx, M. Parrinello, Max-Planck-Institut für FKF, 70569 Stuttgart, Germany

The behaviour of ice under pressure is of great relevance in condensed matter physics, planetary physics and biochemistry. The properties of ice are very much depending on the particularities of the hydrogen bond, which is one of the most important interactions in nature.

Here we study the phase transitions between the VIII, VII and X phases of ice under pressure by using an ab initio path-integral molecular dynamics method. Using ab initio methods is essential to describe the hydrogen bonding -in particular the bond breaking and making at high pressure- and path integrals are a powerful way of including quantum effects (such as zero-point motion and tunneling) on atomic nuclei at finite temperature. By comparing results obtained from «standard» Car-Parrinello MD and path-integral MD simulations, we reveal a strong isotope effect on the VIII-VII transition pressure at 100 K. We show that this transition is driven by ionic defect formation in the ordered VIII phase and that hydrogen atoms are tunneling through the double-well barrier. Moreover, we trace back that the symmetrisation transition from the molecular phase VII to the atomic phase X is heavily influenced by zero-point motion at 100 K.

D-IV.3 14:45-15:00

AB-INITIO SUPPORTED MODEL SIMULATIONS OF FERROELECTRIC PEROVSKITES, M. Sepliarsky, R.L. Migoni and M.G. Stachiotti, IFIR, Bv. 27 de Febrero 210 bis, 2000 Rosario, Argentine

While ferroelectric $KNbO_3$ and $BaTiO_3$ present the cubic-tetragonal-orthorhombic-rombohedral phase sequence with decreasing T, their analogous $KTaO_3$ and $SrTiO_3$ are incipent ferroelectrics which exhibit the ferroelectric soft mode but remain paraelectric up to 0 K. Despite the large amount of research attracted by the above phenomenology since long ago, quite a few realistic model simulations are available. Many lattice dynamical calculations have been performed for each isolated material, but the only unified view of their ferroelectric behavior has been provided by the nonlinear oxygen polarizability model. Though initially based on phonon data for the cubic phase, recent ab-initio calculations confirm that the model is basically correct with regards to the energetics involved in the various ferroelectric distortions. Our molecular dynamics simulations confirm the crossover from a soft mode to an order-disorder dynamics in the cubic phase of KNbO3, as suggested from the experiments. Moreover, we observe the appearence of the various phases, and the soft mode behavior of $KTaO_3$.

D-IV.4 - invited - 15:00-15:30

FIRST-PRINCIPLES SIMULATION ON THOUSANDS OF ATOMS, **M. J. Gillan**, E. Hernandez, C. M. Goringe and D. Bowler, Physics Dept., Keele University, Staffs. ST5 5BG, UK

The talk will outline a general framework for constructing order-N (linear-scaling) calculations using density functional theory on very large systems. One possible implementation of the general approach in the CONQUEST code will be described, and practical tests of the linear scaling on systems of up to 6,000 atoms will be presented. Some fundamental issues in achieving rapid convergence to the ground state will be outlined, and practical methods of ensuring this convergence will be described.

D-IV.5 15:30-15:45

ROTATIONAL DYNAMICS IN ORIENTATIONALLY DISORDERD $KClO_4$, F. Affouard, LDSMM, Université Lille I, 59655 Villeneuve d'Ascq Cedex and P. Depondt, LMDH, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France.

A molecular dynamics simulation of a 8 x 8 x 8 cells potassium perchlorate crystal in the orientationally disordered phase was carried out using a CM-5 parallel computer in order to study the individual and two-molecule rotational dynamics of the ClO_4 ions. Symmetry adapted rotator functions and the rotation matrix are used to overcome the difficulty of dealing with orientational variables.

The crystal structure is fcc, with most probable T_d symmetry molecular orientations, in agreement with experiments.

The rotational motion turns out to be diffusive, but molecules which are far from the most probable orientations have greater rotational velocity. The relative orientations of two neighbouring molecules lasts longer than that of a single molecule, showing coupled motion.

These results, along with orientation-translation coupling suggest that molecules not in their most probable orientation push their neighbours aside thus reducing the volume available. This tends to quench the rotational motion of these neighbours in T_d configuration in a way reminiscent of orientational glasses.

D-IV.6 15:45-16:00 STACKING FAULTS IN MG - CALCULATIONS ON A MASSIVELY PARALLEL MACHINE,

N. Chetty, Physics Department, University of Natal, Pietermaritzburg, Private Bag X01, Scottville 3209, South Africa; M. Weinert, Physics Department, Brookhaven National Laboratory, P.O. Box 5000, Upton NY 11976-5000, USA

We study the following low energy stacking defects in hexagonal close-packed (hcp) magnesium using the plane wave pseudopotential technique: two intrinsic faults I_1 and I_2, an extrinsic fault E, and a T_2 fault which is twin-like with mirror symmetry about a faulted plane. In addition, we consider Mg in the face-centered-cubic (fcc) structure. For the defect systems, we have relaxed the Hellman-Feynman forces on the atoms, and we have included volume relaxations of the unit cell. We have a detailed sampling of the Brillouin zone, and we have used various sizes of the calculational supercell. Our resulting energies are converged to better than 2 meV.
To zeroth-order, the ordering of the energies is easily understood in terms of the number of fcc-like atoms in the sequence of (111) planes. However, a simple model based on assigning an on-site energy to each fcc-like atom in the sequence fails to give quantitatively accurate results for the energies of the faults. A second-nearest-neighbor Ising model also gives large discrepancies. We propose a model based on a local bond orientation scheme which reproduces all the calculated results exactly.

Poster Session I

16:00-18:00 See programme of this poster session p. D-22 to D-30.

Wednesday June 18, 1997 — Morning
Mercredi 18 juin 1997 — Matin

Session V - Fracture

D-V.1 - invited - 9:00-9:30

CRACKING A TOUGH NUT* WITH A BIG COMPUTER: STUDYING MATERIALS FAILURE USING MILLIONS OF ATOMS, **F.F. Abraham**, IBM Research Division, Almaden Research Center, San Jose, CA 95120, USA

Continuum fracture theory typically assumes that cracks are smooth and predicts that they accelerate to a limiting velocity equal to the Rayleigh speed, or surface sound speed, of the material. In contrast, experiment tells us that, in a common fracture sequence, an initially smooth and mirrorlike fracture surface begins to appear misty and then evolves into a rough, hackled region with a limiting velocity of about six-tenths the Rayleigh speed. Recent experiments have clearly shown that violent crack velocity oscillations occur beyond a speed of about one-third the Rayleigh speed and are correlated with the roughness of the crack surface. All of these features are unexplained using conventional continuum theory. With the advent of scalable parallel computers, computational approaches are being extended for providing immediate insights into the nature of fracture dynamics. We have studied the rapid brittle fracture of solids using molecular dynamics for 10-millions of atoms and finite-element continuum mechanics. We have been able to follow the crack propagation over sufficient time and distance intervals so that a comparison with experiments is feasible. Most important, we can «see» what is happening on the atomic scale. A detailed comparison between laboratory and computer experiments demonstrates that many of the recent laboratory findings occur in our simulation experiments, one of the most intriguing being a dynamic instability of the crack tip and its associated properties. Microscopic processes have been identified, and an explanation for the limiting velocity being significantly less than the theoretical limit is discovered. The origin of the instability dynamics at the atomic level is best seen in a video of the fracture simulations. In a 100-million atom simulation, we have discovered a dynamical brittle-to-ductile transition in the rapid cleavage of rare-gas solids, immediately leading to the initiation of plastic failure, crack arrest and the spontaneous proliferation of dislocations. We will discuss how this problem scales to the future teraflop regime in scientific computing. Multimedia versions of our 2D and 3D atomistic simulation studies of fracture are available via the World Wide Web:
2D fracture: http://www.almaden.ibm.com/vis/fracture/prl.html,
3D fracture: http://www.tc.cornell.edu/ farid/fracture/100 million/
* NUT: nanocrystal under tension.

D-V.2 9:30-9:45

MODEL STUDY OF NONLINEAR EFFECTS AT FRACTURE OF COMPOSITES AND MULTILAYERS, V. Krivobodrov, Research Center «Composite», P.O. Box 28, St.Petersburg, 194017, Russia

A new structural effect - the dependence of a fracture stress upon a composite (multilayer) sample crossection is theoretically considered. The model is based on the statistical theory of branching processes. The proposed approach allows to introduce a new fracture criterion valid for a wide range of heterogeneous materials. In case of an infinitely large sample the new criterion yields a fracture stress equal to the one predicted by earlier models. For a sample of a finite size the predicted fracture stress is lower than the one calculated according to previous models. The effect can be explained as a nonlinear fracture phenomenon arising out of the nonlinear dependence of microfracture probabilities upon overstressing caused by other microfractures. The fracture stress as a function of a sample crossection is calculated for the heterogeneous materials with different characteristics of strength and plasticity. The composite strength as function of a number of interfacial layers is considered.

The results are essential for strength evaluation of small-sized elements made from composite materials, multilayers, thin films and small clusters of nanoparticles.

D-V.3 9:45-10:00

THERESHOLD EFFECTS IN DISLOCATION MOTION UNDER ULTRASOUND ACTION, J.M. Khalack and V.M. Loktev, Bogolyubov Institute for Theoretical Physics, 14-b Metrologichna str. Kyiv-143, 252143 Ukraine

Numerical modeling of dislocation motion under harmonical force was carried out. Two qualitatively different cases are studied: (1) direct dislocation in Peierls relief and (2) screw dislocation with a jog. (1) Here three regimes of the motion (linear, quasi-linear, and nonlinear) are found. A transition to last regime takes place in an evident threshold manner when Peierls stress is achieved by ultrasound produced amplitude of shear stress in the slip plane. This transition is characterized by sharp (up to 102-103 times) increase of dislocation displacement and velosity, as well as of ultrasound attenuation. (2) For this case the main attention was paid to point defects generation by a jog. There are also three regimes of motion for a jog (when external force increases): (a) jog is immovable and no defects are created); (b) jog changes its equilibrium position, having generated a finite number of vacancies; (c) after the threshold, jog oscillates, continually generating vacancies and interstitials.

An attempt was made to explain the sonoluminescence of semiconductors, where host or impurity electronic subsystem can be excited both by electric field of oscillating dislocation and jog. The model proposed allows to interpret the observable threshold in sonoluminescence excitation and its spectra as spectra of point defects.

10:00-10:30 **BREAK**

Session VI - Polymers

D-VI.1 - invited - 10:30-11:00

NUMERICAL STUDIES OF POLYMER NETWORKS AND GELS, **K. Kremer,** Max-Planck-Institut für Polymerforschung, 55021 Mainz, Germany

The talk will cover a series of recent studies to reveal in more detail the role of trapped entanglements for the properties of polymer networks. Different sources of disorder in the systems have to be considered. Starting from randomly crosslinked polymer melts, systems are systematically idealized via end linked systems to model networks with lattice connectivity. For the latter only links between network loops remain as source of disorder. By this the effect of conserved network loop topology on the elastic modulus could be determined, showing that the classical models of rubber elasticity only account for a small part of the modulus. By swelling and stretching the systems first simulation results on the butterfly effect are obtained.
References: Duering, Kremer, Grest, PRL 67, 3531 (91), JCP 101, 8169 (94); Everaers, Kremer, Macromol. 28, 7291 (95); Putz, Kremer, in preprint (97).

D-VI.2 11:00-11:15

AN EXTENDED BFM MODEL FOR SIMULATION OF COPOLYMERS AT AN INTERFACE, E. James and C.C. Matthai, Dept of Physics and Astronomy, University of Wales, Cardiff, CF2 3YB, UK

The Bond Fluctuation Model has been used extensively in the simulation of many polymer systems. We have extended the original Carmesin and Kramer model so that it allows for a threefold increase in the possible bonding configurations. Although the cpu time per attempted move is slightly greater than before, the increase in ergodicity results in a better acceptance ratio, making this method compuationally more efficient at determining equilibrium configurations. Copolymers at interfaces have been the subject of much study in recent years because of the many possible technological applications. We have used this modified BFM to simulate random AB copolymers at the interface of two good solvents. In the simulations the monomer interactions were represented by a Lennard-Jones type potential together with the excluded volume interaction. We have obtained results for the equilibrium configuration for specific copolymer lengths of up to 128. In addition, we have found that polymer-polymer interactions, modelled by performing simulations on up to 32 different copolymer chains in the solute, has a noticeable effect on the monomer distribution. Finally, the effect of polymer-solvent interactions on the monomer distribution near the interface has been studied.

D-VI.3 11:15-11:30

ULTRA STRONG POLYMER FIBERS, J. Hageman and R. de Groot, ESM, PO Box 9010, 6500 GL Nijmegen, The Netherlands and R. Meier, DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands

Ultra high molecular weight polymers can be processed into ultra strong fibers. In these fibers the polymer chains have near crystalline orientation. The low amount of chain ends and the high orientation results in a large axial elastic modulus, which is even larger than for example the modulus of steel.

It is of great interest to know how much the performance of these fibers can be made even better by increasing the degree of crystallinity and the molecular weight. To answer this question, the ultimate elastic modulus, this is the modulus for the infinite-chain crystalline polymer, should be known. Obviously, this information can not be obtained with experimental techniques, but it can be calculated with the Car-Parrinello technique.

The polymer considered here is polyethylene, the most simple polymer but technologically very relevant. The highest modulus realized experimentally is close to the calculated value for the ultimate modulus.

D-VI.4 11:30-11:45

CLASSICAL AND QUANTUM CONSTANT PRESSURE MONTE CARLO SIMULATION OF ORTHORHOMBIC CRYSTALLINE POLYETHYLENE, R. Martonak(1,2), W. Paul(1) and K. Binder(1); (1)Institut für Physik, KoMa 331, Johannes Gutenberg-Universität, Staudingerweg 7, 55099 Mainz, Germany, (2)Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany

We present a classical as well as a quantum (Path Integral) Monte Carlo simulation of the orthorhombic phase of crystalline polyethylene at zero pressure, using an explicit atom force field with unconstrained bond lengths and angles and periodic boundary conditions. The classical simulations extend over the whole range of temperatures in which the orthorhombic phase is experimentally stable (10 - 450 K), while the quantum ones focus mainly on the low temperature region (50 - 200 K). We used different system sizes and chain lengths (from C_{12} to C_{96} chains) with the total number of atoms between 432 and 3456. We show here the results for structural and thermodynamic quantities, such as the lattice constants a, b, c, the setting angle and internal parameters of the chains, as well as thermal expansion coefficients, elastic constants and specific heat. We discuss in detail the temperature dependence of the measured quantities as well as the importance of quantum effects. In case of thermal expansion coefficients, we compare our results to those obtained from other theoretical approaches as well as to available experimental data.

D-VI.5 11:45-12:00

MD SIMULATION OF ANCHORED POLYELECTROLYTES, C. Seidel and C.C. van der Linden, Max-Planck-Institute for Colloid and Interface Research, Kantstr. 55, 14513 Teltow, Germany

The behaviour of strongly charged polyelectrolyte chains tethered by one end to a solid surface is studied by means of the molecular dynamics simulation approach introduced for polymers by Grest and Kremer [1]. Including individual counter ions we treat the full Coulomb interaction. To sum the contribution of long range interaction under a two-dimensional periodic boundary condition we use a method proposed by Lekner [2] and modified by Sperb [3]. In the brush regime we discuss the stretching of the chains under good solvent conditions. One of the main ingredients of the mean field theory of the polyelectrolyte brush is the assumption of local charge neutrality. We check this assumption on the basis of the simulation results and discuss the role of fluctuations in the counter ion density.

[l] G. S. Grest and K. Kremer, Phys. Rev. A 33, 3628 (1986)
[2] J. Lekner, Physica A 176, 485 (1991)
[3] R Sperb, Mol. Simal. 13, 189 (1994)

12:00-14:00 **LUNCH**

Wednesday June 18, 1997 Afternoon
Mercredi 18 juin 1997 Après-Midi

Session VII - Micromagnetism

D-VII.1 - invited - 14:00-14:30

NUMERICAL MICROMAGNETICS: FROM MODEL TO SOFTLY DISORDERED SYSTEMS, **J. Miltat**, A. Thiaville, Lab. Phys. des Solides, Univ. Paris-Sud et CNRS, 91405 Orsay, France and Michel Labrune, LPMTM, Institut Galilé, Université Paris-Nord et CNRS, 93430 Villetaneuse, France

Micromagnetics is a continuum theory reducing a Ferro- or Ferri-magnet to a 3D vector field with unit length. Torques acting on the magnetization (moment per unit volume) may result from elastic-like interactions (exchange interactions), from the medium anisotropy and/or magnetostrictive properties, from external pressures (applied field), and, lastly, from dipolar interactions, the latter being long range in character. After introducing the basic equations and the general boundary conditions for a finite volume, examples will be shown which undoubtedly establish a close match between theory and experiments, both in the static and dynamic cases. The intrusion of conformation complexity will be illustrated through a further example, dealing with wall structures in exchange coupled multilayers. In a next step, experimental data will be shortly described where an obvious relation between the structural characteristics of the magnetic materials and their magnetic properties will be revealed. Constraints in terms of computing power and methods will be outlined. Lastly, two examples will serve to pinpoint the limits of numerical micromagnetics, dealing respectively with singular points and exchange interactions with «loose» spins at the interface between an Antiferro- and a Ferromagnet.

D-VII.2 14:30-14:45

MAGNETIZATION PROCESSES IN SUBMICRONIC Co DOTS STUDIED BY MEANS OF MICROMAGNETIC CALCULATIONS, R. Ferré, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67037 Strasbourg Cedex, France

The magnetisation nucleation mechanisms taking place in submicronic cobalt dots as obtained by means of 3D Micromagnetic simulations are shown. Attention is focused on the study of the transition from parallel-to-plane to perpendicular-to-plane magnetisation occurring as the thickness of the dot is increased. Simulations show different nucleation and magnetisation reversal mechanisms as thickness varies. For a 35 nm dot, nucleation of stripe domains takes place. Stripe domains evolve with the decrease of the in-plane applied field towards a configuration of «bended stripe» domains as a result of the need for a lateral flux closure. The same nucleation mechanism has been found for thicker dots and is responsible for the appearance of diagonal domains for high thicknesses. For 25 nm thick dots no stripe domains are present and a fully planar magnetisation configuration has been obtained for which flux closure takes place with the formation of two distorted vortices at both sides of the dot formed by two vortices, a cross tie wall and a quasi-Néel wall each. This magnetisation configuration seems to be the analog of the one found in Permalloy thin films [1], but distorted by the presence of the high perpendicular-to-plane anisotropy of cobalt.

[1] A. Tonomura, Rev. Mod. Phys. 59 (1987) 639

D-VII.3 14:45-15:00

MICROMAGNETIC MODELING OF A THIN FILM RELAXATION, J.M. Gonzalez and O.A. Chubykalo, Instituto de Ciencias de Materials de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain; J. Gonzalez, Departamento de Fisica de Materiales, UPV, 20080 San Sebastian, Spain

The magnetization reversal process occurring under constant magnetic field and temperature (magnetic relaxation) was modelized in a thin film with in-plane anisotropy. Our micromagnetic model consisting of a 2D array of moments, oriented in a plane, explicitely considered all the relevant magnetic energy contributions, i.e. Zeeman, anisotropy, exchange and magnetostatic terms. The numerical method used to minimize the free energy of the system was Monte Carlo dynamics in a canonical ensemble. As model parameters, we used real experimental data for highly homogeneous $Co_{83}Zr_5Dy_{12}$ thin film. The demagnetization process was nucleated and started from the formation of domain-wall structures in the corners of the thin film. We were able to follow all the stages of this process, i.e. the nucleation-expansion-propagation-pinning sequence. The curves for the time dependence of the magnetization clearly deviated from the Arrhenius behaviour, namely, we observed a «waiting time» preceeding the nucleation of the reversed regions during which the magnetization was constant.

D-VII.4 - invited - 15:00-15:30

MICROMAGNETIC STUDY OF ULTRATHIN MAGNETIC FILMS, **X. Hu**, National Research Institute for Metals, Sengen 1-2-1, Tsukuba 305, Japan and Y. Kawazoe Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Ultrathin magnetic films and multilayers are of great current interests, both because of their potentials for application and new physics originating from their unique dimension and geometry. Magnetic anisotropy energy with easy direction normal to the film plane occurs at interface or surface quite often, and makes the magnetic structure of the relevant system complicated through the competition with the dipole-dipole interactions. The exchange coupling is not infinite, although fairly large, and thus the simplest, intuitive phenomenological theory fails in many cases. This situation becomes even worse when one considers the response to the external magnetic field. Therefore, the effect of the normal surface or interface anisotropy should be treated carefully. Since this anisotropy is well localized at the interface or surface, this treatment should be general for the study of surface effects of many materials other than magnetic ones, including polymers and liquid crystals among others. Results derived from quantum spin modeling, classical spin modeling, and micromagnetic theory based on continuum model will be presented with discussions on the relations among them.

15:30-16:00 **BREAK**

Session VIII - Magnetism

D-VIII.1 - invited - 16:00-16:30

EFFECT OF CAP-LAYERS ON INTERLAYER EXCHANGE COUPLING, **J. Kudrnovsky** and V. Drchal, Institute of Physics AS CR, Prague, Czech Republic; P. Bruno, Université Paris-Sud, Orsay, France; J. de Vries and R. Coehoorn, Philips Research Laboratories, Eindhoven, The Netherlands; P. Weinberger, Technical University, Vienna, Austria

The effect of non-magnetic cap-layer on periods, amplitudes, and phases of oscillations of interlayer exchange coupling (IEC) is studied theoretically on ab initio level in the frame of the spin-polarized surface Green function technique within the tight-binding linear muffintin orbital method. We build up the multilayer system layer by layer which allows to simplify calculations significantly as well as to study geometrically complex systems. Application of the formalism is made to Co/Cu/Co(001) trilayers with Cu-cap layer interfacing the vacuum through the dipole barrier. We investigate in detail both the asymmetric case with one semiinfinite Co-slab and other Co-slab five monolayers thick as well as symmetric cases of finite Co-slabs of the same thickness. We have found a pronounced oscillatory behavior of both the amplitudes and phases of the exchange coupling with the cap-layer thickness. For the thick cap-layer standard results for Co/Cu/Co(001) trilayer are recovered. The present calculations confirm qualitative conclusions of simple RKKY-like model theories.

D-VIII.2 16:30-16:45

PERIODIC ANDERSON MODEL FOR DESCRIPTION OF NONCOLLINEAR MAGNETIC STRUCTURE IN LOW-DIMENSIONAL 3d-SYSTEMS, V.M. Uzdin, St Petersburg State University, CAPE, V.O. 14 linia, 29 St. Petersburg 199178, Russia and N.S. Yartseva, Institute of Metal Physics, GSP-170, Ekaterinburg, 620219, Russia

Distribution of magnetic moments in the low-dimensional metallic structures have been studied theoretically on the basis of Periodic Anderson Model. Calculation of noncollinear magnetic order was performed in the Hartree-Fock approximation using tight binding real space recursion method. Iteration process includes self-consistent determination of population numbers for the electrons with different direction of the magnetic moments at given atom relatively of fixed axis. The moments of all other atoms are keeping constant in value and direction during self-consistency procedure. Energies of all states corresponding to the different directions of magnetic moments at the atom under consideration have been calculated, and the state with minimal energy being accepted for the next step.

Analytical transformations rested on the generalized «zeros and pole method» for the Green function that allows to avoid some time consuming numerical procedures. It gives possibility to develop efficient algorithm for the calculation of noncollinear magnetic structure of complex space nonhomogeneous systems.

D-VIII.3 16:45-17:00

IMPROVED ANGULAR CONVERGENCE IN NON COLLINEAR MAGNETIC ORDERS CALCULATIONS, D. Stoeffler, and C. Cornea, IPCMS-Gemme, 23 rue du Loess, 67037 Strasbourg, France

Non collinear magnetic orders studies in multilayered systems are essential for the understanding of their magnetic properties. For example, they have to be considered (i) when external magnetic fields are applied, (ii) when biquadratic interlayer couplings are obtained and (iii) when interfacial roughness induces frustrations in the direct magnetic couplings which can be minimized by non collinear magnetic defects. Such studies have been started in our group since two years ago using the tight-binding framework.

In this paper, we present first the method used for determining self-consistently the directions of each magnetic moments and we discuss the angular convergence and its accuracy. We show that usual input/output mixing schemes allow rapid convergences for the charges and the magnitude of the moments but not for the angles even with a complete mixing (the output is directly used as next input). Consequently, if these methods are well suited for collinear studies, new ones have to be developed in order to increase the angular relaxation to the solution of the problem. We present a predictive technique for accelerating the angular convergence based on extrapolations of the variations of each local angle during short iterative calculations giving a convergence speed-up up to 4.

D-VIII.4 17:00-17:15

FAILURE OF TWO-CURRENT MODEL FOR SYSTEMS WITH STRONGLY SPIN-DEPENDENT DISORDER, H. Ebert and A. Vernes, Institute for Physical Chemistry, University of Munich, Theresienstr. 37, 80333 München, Germany; J. Banhart, Fraunhofer-Institute for Applied Materials Research, Lesumer Heerstr. 36, 28717 Bremen, Germany

The resistivities of the ferromagnetic alloy systems Fe-Ni and Co-Ni were studied in detail by application of the Kubo-Greenwood formalism. The electronic structure of the randomly disordered ferromagnetic alloys was computed by use of the spin-polarized Korringa-Kohn-Rostoker Coherent Potential Approximation (KKR-CPA) method.

Two sets of calculations were carried out: one fully relativistic and an other one based on the two-current model. The former one will judge whether the two not directly coupled spin-subsystems could lead to the spontaneous magnetoresitance anisotropy, as it is supposed within the two-current model. Furthermore, all the results obtained are compared with the experimental data.

We found that the two-current model calculations yield spin-resolved resistivities more polarized than could be expected from the experiments. Furthermore they lead to a much lower total resistivity than the relativistic calculations, showing that the scattering processes between the spin-systems are of crucial importance.

D-VIII.5 17:15-17:30

PERCOLATION MECHANISM FOR COLOSSAL MAGNETORESISTANCE, P. Bastiaansen and H. Knops, Dept. of Theoretical Physics, Katholieke Universiteit Nijmegen, PO Box 9010, 6500 GL Nijmegen, The Netherlands

The manganite materials showing colossal magnetoresistance are recently shown to be halfmetallic: they are conducting for one spin direction but insulating for the other. Based on this halfmetallic character, we present a percolation model that explains the observed features of colossal magnetoresistance.

In its simplest form, we show that colossal magnetoresistance can be explained using the percolation properties of the Ising model. The percolation phase diagram of this model is shown to reproduce qualitatively all experimentally observed features of colossal magnetoresistance. In this explanation, colossal magnetoresistance is a critical phenomenon, closely linked with the ferromagnetic to paramagnetic transition in the Ising model. We present results of the Monte Carlo calculations on the resistance of the percolation model.

Thursday June 19, 1997
Jeudi 19 juin 1997

Morning
Matin

Session IX - Electronic Structure - Specific Materials

D-IX.1 - invited - 9:00-9:30

COMPUTATIONAL STUDIES OF NOVEL SEMICONDUCTORS: GROWTH DOPING AND DEFECTS, **R.M. Nieminen**, Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

Semiconductor materials and structures based on III-V and II-VI compounds offer versatile opportunities for optoelectronics applications. However, controlled growth and doping of these compounds are notoriously difficult. Typical difficulties are those associated with native defects and the associated autoconductivities, as well as the metastability of many defect-related phenomena.

This talk summarises recent work on first-principles simulations of defect-related electronic properties and phenomena in III-V nitrides, especially GaN and AlN, and in II-VI materials such as ZnSe. For the nitrides, the calculations, based on density-functional theory and pseudopotentials, shed light on such important issues as (i) the origin of n-type conductivity, (ii) the EL2-1ike metastability of antisite defects (iii) the role of metal vacancies, and (iv) the origin of the broad-band parasitic (yellow/violet) luminescence. For selenides, we demonstrate the preferential existence of vacancies in one sublattice in differently doped samples, and the decoration of these by the dopant atoms. We discuss the implications of the total-energy calculations for the optimal growth of thin films with desired properties. This work has been done in collaboration with Tomi Mattila and Sami Pöykkö.

D-IX.2 9:30-9:45

$AsNCa_3$ AT HIGH PRESSURE, P.R. Vansant, P.E. Van Camp, V.E. Doren, University of Antwerpen (RUCA), Dept; of Physics, Groenenborgerlaan 171, 2020 Antwerpen, Belgium and J.L. Martins, INESC, Rua Alves Redol 9, 1000 Lisboa, Portugal and Instituto Superior Tecnico, Avenida Rovisco Pais 1, 1096 Lisboa, Portugal

An optimization scheme for crystal structure parameters developed by Souza and Martins is applied to the study of ternary calcium nitrides. The forces and stresses are calculated with a pseudopotential plane wave method using the local density approximation and based on an iterative matrix diagonalization scheme for the electronic SCF calculation. The enthalpy is then minimized with respect to the atomic coordinates as well as with respect to the cell metric (i.e. the lattice parameters).

We obtain excellent agreement with experiment for the zero-pressure structure of the perovskite structure Ca_3BiN (cubic Pm3m) and of the distorted perovskite structures Ca_3PN and Ca_3AsN (orthorhombic Pbnm). For the $AsNCa_3$ compound the bandgap energies are investigated as function of the pressure as well as the dependence on pressure of the structural parameters. A new cubic phase consisting of three unit cells is found having a lower enthalpy for pressures above 59 GPa.

D-IX.3 9:45-10:00

ELECTRONIC STRUCTURE CALCULATIONS OF RANDOM ALLOYS: REAL SPACE VS RECIPROCAL SPACE TECHNIQUES, I.A. Abrikosov and B. Johansson, Condensed Matter Theory Group, Uppsala University, Box 530, 75121 Uppsala, Sweden

The coherent potential approximation (CPA) has become a popular technique to study properties of random alloys. However, despite a large number of successful calculations, there were no formal justification of the reliability of this method. Moreover, the underlying single-site approximation has caused some doubts concerning the applicability of CPA for calculating total energy and electronic structure even for completely random alloys.

We have compared results of the CPA calculations with those obtained from the recently developed real-space order-N locally self-consistent Green's function (LSGF) method [1] for a number of different alloy systems. Very good agreement is found for the electronic structures and magnetic properties. Total energies are also well described by the CPA provided the electrostatic contribution is treated in an appropriate manner. On the other hand, restricted averages calculated in the framework of CPA for alloy components show differences from the results of LSGF calculations.

[1]. I. A. Abrikosov, A. M. N. Niklasson, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. Lett. 76, 4203 (1996).

D-IX.4 10:00-10:15

AB INITIO STUDY OF YSi_2 SURFACE, L. Magaud, LEPES-CNRS, BP 166, 38042 Grenoble Cedex 9, France and A. Pasturel, LPN, BP 166, 38042 Grenoble Cedex, France

We present an ab-initio study of YSi_2 bulk and surface cristallographic structures. The calculations are performed using the VASP (Vienna Ab-initio Simulation Package) code which is based on the density functionnal theory and uses ultrasoft pseudopotentials.The calculation of the forces on the ions allows the determination of the equilibrium configurations.Some technical details will be discussed (LDA or GGA, valence orbitals), for bulk Y and YSi_2 and the VASP results will be compared to FPLMTO results.

YSi_2 cristallizes in an hexagonal structure made of alternate Y and Si planes. Bulk compounds are lacunary but STM images showed that no vacancy exists at the surface. We studied the relation between the constrain which appears in Y-Si system and the existence of the vacancies .

In the bulk, the vacancies induce a relaxation of the neighboring atoms (Si and Y) in the hexagonal planes. Long range ordering along the axis perpendicular to these planes is also discussed.

For the surface, the atoms inside the supercell remain on the same plane while the surface layer dissociate in a bilayer, similar to the ones found in bulk Si along the (111) direction. This buckling of the surface is in good agreement with experimental evidence. It is explained by a release of the Si in-plane constrain.

10:15-10:45 **BREAK**

D-IX.5 - invited - 10:45-11:15

ELECTRONIC STRUCTURE CALCULATIONS OF VACANCIES AND THEIR INFLUENCE ON MATERIALS PROPERTIES, **P.A. Sterne**, University of California, Davis CA 95616, USA and Lawrence Livermore National Laboratory, L-407, Livermore, CA 94551, USA

Vacancies play an important role in determining many basic materials properties. This talk provides two examples of how electronic structure calculations can contribute to our understanding of vacancies and their role in determining materials properties. Diffusion and electromigration resistance in aluminium are known to be strongly dependent on vacancies. Electronic structure calculations show that the vacancy-impurity interaction oscillates with distance, and this leads to an explanation for both the increased electromigration resistance and the slow impurity diffusion for dilute copper impurity concentrations in aluminium. Calculations of vacancies in plutonium have been used in conjunction with positron annihilation lifetime measurements to identify the presence of helium-stabilized vacancies. Helium stabilization of vacancies in this case provides the precursor for subsequent vacancy-related changes in materials properties.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

D-IX.6 11:15-11:30

ASW-DFT-LDA STUDY OF C-CONTAINING TiAl, S.F. Matar, Y. LePetitcorps and J. Etourneau, Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS, Chateau Brivazac, 33608 Pessac Cedex, France

Using the ab initio self-consistent ASW method based on the local density functional and examining the bonding characteristics from the COOP (crystal orbital overlap populations), implemented for the first time in such methods, we address the electronic structures and chemical bonding properties of carbon containing TiAl. We firstly examine the hypothetical compounds resulting from the insertion and substitution of carbon. From the results carbon is found to preferably substitute for Al with Ti-C bonds around Fermi level (EF) and forming Ti-rich phases. Then we calculate the electronic structure and chemical bonding properties of the actual temary carbides forming at the interface between the carbon fibre and the TiAl matrix. The strongly covalent Ti-C bonds identified for Ti_3AlC and Ti_2AlC are remiscent of the formation of TiC in the vicinity of the C fibre before the ternary carbides, in agreement with experiment. Valence and conduction bands are separated by non-bonding states around EF in Ti_3AlC while bonding metallic Ti-Al interactions are present in Ti_2AlC at E_F. The role of Al in the bonding within the temary carbides as with respect to TiC is to reduce the directionality of the bonding by its p states which interact with Ti(3d).

D-IX.7 11:30-11:45

ELECTRONIC STRUCTURE OF STANNOUS OXIDE, M. Meyer(1), G. Onida(2), M. Palummo(2) and L. Reining(1), (1)CNRS-CEA, Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau, France; (2)Dipartimento di Fisica, Universita di Roma "Tor Vergata", 00173 Roma, Italy

Stannous oxide SnO is the precursor for the production of the technologically important stannic oxide SnO_2. The oxidation process results mainly in the insertion of an oxygen plane between two tin planes in the layered, tetragonal SnO crystal. In order to well understand this structural evolution, it is crucial to have a precise description of the atomic and electronic structure of the two oxides, and of the relation between electronic and geometric configurations.

We present an ab-initio study of the electronic structure of SnO. Total energies and charge densities are calculated and analyzed as a function of geometry, with a particular emphasis on the importance of low-charge-density contributions to the interlayer cohesion. Density Functional Theory in the Local Density Approximation (DFT-LDA) is used in conjunction with carefully tested smooth pseudopotentials. The resulting DFT-LDA bandstructure is corrected with self-energy contributions evaluated in the GW approach. SnO_2 has already been studied in the past[1] and will be used for comparison.

1 M. Palummo, L. Reining, M. Meyer, and C.M. Bertoni, Proc. of the 22nd ICPS, Vancouver 1994, ed. D.J. Lockwood, World Scientific Singapore (1995), p. 161.

D-IX.8 11:45-12:00

FIRST PRINCIPLES INVESTIGATIONS OF A "QUASI-1-DIMENSIONAL" CHARGE TRANSFER MOLECULAR CRYSTAL: TTF-2,5Cl_2BQ, C. Katan, C. Koenig, GMCM UMR 6626, Université Rennes 1, Campus de Beaulieu, 35042 Rennes, France and P.E. Blöchl, IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Mixed-stack charge transfer compounds exhibit a dazzling variety of structural and electronic phase transition driven by pressure, temperature or photoirradiation. Despite active research over several decades, a detailed understanding of these materials is still elusive. We performed first-principles calculations using the projector augmented wave method in order to get a clear description at a microscopic level of the electronic distribution far from the transition for TTF-2,5Cl_2BQ. Our calculation predict for the first time the low-symmetry structure (ground state) of this compound. We analysed the 1-dimensional and 3-dimensional aspects of the electronic distribution and related them to a simple tight binding scheme which allows us to discuss the pertinence of the 1-dimensional models used to study the phase transitions in this class of materials.

D-IX.9 12:00-12:15

AN AB INITIO OF THE ELECTRON AFFINITY OF DIAMOND SURFACES, M.J. Rutter and J. Robertson, Dept. of Engineering, University of Cambridge, Trumpington St. Cambridge, UK

Diamond surfaces combine chemical inertness with, in some cases, a negative electron affinity. Such surfaces have great potential for use on cold cathodes in flat displays. We present ab initio plane wave electronic structure calculations which enable us to predict the electron affinities of many different diamond surfaces with various terminations and reconstructions. Such calculations give good accuracy and enable the study of perfect surfaces with a range of terminating species so that the effect of the passifying layer can be readily seen. Results for the (100) and (111) surfaces will be presented, giving a range of surfaces more comprehensive than previously published.

We find that the electron affinity varies by over 5.5V between oxygen and hydrogen coverings, and that this magnitude of variation can be understood as simply arising from surface dipoles such as polarised covalent bonds would be expected to produce. A brief discussion is given of some of the technical points of performing such a calculation, which combines ab initio LDA work with experimental results for the band-gap for diamond in order to estimate accurately the position of the unoccupied levels.

12:15-14:00 **LUNCH**

Thursday June 19, 1997
Jeudi 19 juin 1997

Afternoon
Après-Midi

Session X - Electronic Structure - Methodology

D-X.1 - invited - 14:00-14:30

CONCEPTUAL AND COMPUTATIONAL ADVANCES IN MULTIPLE-SCATTERING ELECTRONIC-STRUCTURE CALCULATIONS, **R. Zeller**, Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

It is demonstrated that a physically transparent and exact transformation of the traditional multiple-scattering theory (Korringa-Kohn-Rostoker method) into a tight-binding form exists and that the resulting ab-initio tight-binding method allows density-functional electronic-structure calculations without any loss of accuracy. The complicated traditional KKR structure constants are replaced by exponentially decaying «tight-binding» parameters which are easily calculated in real space with small clusters of repulsive muffin-tin potentials. It is shown that for large systems the main computational effort consists in the inversion of rather sparse matrices and that available standard software efficiently allows to implement the calculations on workstations, vector and parallel computers. For surfaces and interfaces, i.e. for systems with two-dimensional periodicity, the computational effort scales linearly with the number of layers. Thus the ab-initio treatment of high-indexed of surfaces and surface steps becomes possible. It is discussed that additional isolated atoms on surfaces and at steps can also be treated and that recent improvements in full-potential multiple-scattering calculations deliver reliable forces on the atoms and thus allow to determine the geometric arrangement of the atoms.

D-X.2 14:30-14:45

STUDY OF ORDERING EFFECTS IN MULTICOMPONENT ALLOYS BY MEANS OF THE O(N) LSGF TECHNIQUE, S.I. Simak(1), I.A. Abrikosov(1), A.V. Ruban(2) and B. Johansson(1), (1)Condensed Matter Theory Group, Uppsala University, Box 530, 75121 Uppsala, Sweden; (2)CAMP, DTU, 2800 Lyngby, Denmark

We propose an approach which allows one to study ordering effects in multicomponent systems. It is based on the idea behind the Connolly-Williams method (CWM), in which the total energies of alloys with different sets of correlation functions are mapped onto a corresponding cluster expansion. In contrast to the usual CWM scheme we consider a set of alloys at a fixed alloy composition what, in a case of long-range interactions, requires the consideration of big supercells. For this purpose the recently proposed order-N LSGF method [1] turns out to be perfectly suitable. The obtained interaction parameters are inserted in a standard Monte Carlo procedure which is used to study ordering effects as a function of temperature.

This approach has been applied to the Zn_{25} Ni_{25} Cu_{50} alloy, which is known to undergo two order-disorder transitions. Both transitions have been found in our calculations, and calculated transition temperatures are in good agreement with experiment.

[1]. I. A. Abrikosov, A. M. N. Niklasson, S. I. Simak, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. Lett. 76, 4203 (1996)

D-X.3 - invited - 14:45-15:15

LDA AND LDA+U MODELING OF THE ELECTRONIC STRUCTURE OF THE MX CHAIN SOLID, **M. Alouani**, IPCMS, 23 rue du Loess, 67037 Strasbourg, France

The electronic structure of a whole class of low dimensional system, the halogen-bridged transition metal (MX) compounds, is studied by means of an all electron methods based on the local-density-approximation (LDA). These studies have shown that the ligand structure surrounding each chain is essential to obtain the observed dimerized and insulating ground state, and the metal-metal distance along the chains controls the charge-density wave (CDW) in halogen-bridged transition-metal linear-chain (MX) compounds. The strength of the CDW can be understood in terms of a two band Su-Schrieffer-Heeger model with anharmonic potential.

The Spin-density-wave (SDW) NiX systems is studied by means of the mean-field multi-orbital Hubbard model implemented around an all-electron LDA. We have found an absence of lattice dimerization and the ground state is insulating and antiferromagnetic in good agreement with experiment.

Atomic relaxation and defect polarons in the CDW MX systems are studied by means of the Car-Parrinello Projector Augmented Wave molecular dynamics method (CP-PAW). The ground state of polarons obtained by CP-PAW is different from that obtained by simple models.

D-X.4 15:15-15:30

ORDER N TOTAL ENERGY TIGHT BINDING MODELISATIONS OF SILICON, O.B.M. Hardouin Duparc and M. Torrent, Laboratoire des Solides Irradiés, CEA-CERAM, CNRS URA 1380, Ecole Polytechnique, 91128 Palaiseau, France

We present a systematic comparison of several Tight Binding Total Energy modelisations of Silicon. These modelisations include the tight binding electronic cohesive energy and a usually more empirical description of a repulsive term. We examine both the band structure and various structural properties, such as structural stability, bulk modulus, elastic constants, four typical vibrational modes and their Grueneisen constants. We then apply these models to the calculations of the minimized energies and band structures of some multivariant symmetric tilt grain boundaries. We discuss the influence of the choice of the cut off radii.

These calculations are mostly done using the real space order N density matrix technique. We resorted to standard reciprocal space calculations when band strutures or accurate excess energies where needed. Moebius conditions were used for Grain Boundaries.

D-X.5 15:30-15:45

COMPARISON OF TWO O(N) METHODS FOR TOTAL ENERGY SEMI-EMPIRICAL TIGHT-BINDING CALCULATIONS, J. Chen, A. Béré, A. Hairie, G. Nouet and E. Paumier, LERMAT, ISMRA CNRS UPRESA 6004, 6 bd du Maréchal Juin, 14050 Caen Cedex, France

We compare two O(N) methods based on a local evaluation of the density matrix (DM) via the Lanczos-Haydock recursion scheme.

We have recently introduced the first method (*), which computes an approximated DM directly from the local tridiagonalized hamiltonian (LTH).

In the second method the DM is obtained from the diagonalized LTH. The use of the first method is restricted to temperatures higher than 1000K, but there is no limitation for the second one. The methods are compared when applied to grain boundaries in silicon and germanium.

(*) A. Hairie, F. Hairie, B. Lebouvier, E. Paumier, IIB95, Lisbon, Portugal, June 26-29, 1995. Material Science Forum, 1996, 207/209, 105-108.

D-X.6 15:45-16:00

THE NEW COMPLETE MIXED BASIS IN THE ELECTRONIC STRUCTURE THEORY, S.V. Syrotyuk, S.N. Kraevskyi, Department of Electrophysics, State University "Lviv Polytechnic", 290646 Lviv 13, Ukraine

The conventional norm-conserving pseudopotential approach shows the slow convergence. We perceive three reasons of that: 1) the nonorthogonality of the pseudowave states in the crystal; 2) the lack of a small parameter in the Hamiltonian matrix; 3) the difference of the crystal potentials $V_{i+1}(r)-v_i(r)$ is not a small parameter (i denotes the iteration stage number) and therefore one needs many iterations. We suggest the new complete mixed basis(CMB) constructed on core states and plane waves by means of unitary transformation, which is norm-conserving over the crystal. The above-mentioned drawbacks are absent in this new method. Since the operator originated the CMB from nonorthogonal mixed set of states is unitary not only over the valence states but over the core states all the states are treated as pseudostates. The evaluated energy band spectrum of crystal diamond is compared with results obtained in other ab initio an model pseudopotential approachs.

Poster Session II

16:00-18:00 See programme of this poster session p. D-15 to D17.

Friday June 20, 1997 **Morning**
Vendredi 20 juin 1997 Matin

Session XI - Complex Materials and Alloys

D-XI.1 - invited - 9:00-9:30

HYDRODYNAMIC SIMULATIONS OF SPACE EXPERIMENTS, **K. Higashino**, IHI, 229 Tonogaya, Mizuho-machi, Nishitama-gun, Tokyo 190-12, Japan; H. Mizuseki, Z. Zeng, K. Ichinoseki and Y. Kawazoe, IMR Tohoku University, Sendai 980-77, Japan

Space experiment serves a promising research area to develop pure crystals and to determine diffusion constants under low gravity. Especially in this year, an international collaborative laboratory in the space will be established and long term experiment will become feasible. We are incorporated in this project by supplying hydrodynamic simulation to estimate a variety of features of the expected experiments. Among them, here we demonstrate our ability of «predicting before the actual experiments» by showing two typical numerical results. (I) Dynamical flow simulation of shear cell: This experiment is expected to serve a tool to determine the diffusion constant in melt. Since it is necessary to cut the melt in the diffusion process in the space, we should simulate carefully the movement of liquid to avoid danger in the laboratory. (2) Marangoni convection: This is the flow observed in the low gravity experiment according to the temperature distribution at the surface. Because of this flow the resulting crystal has defects, and the effect should be estimated beforehand.

D-XI.2 9:30-9:45

VIBRATIONAL AND STRUCTURAL PROPERTIES OF MODEL GLASSES, P. Jund, D Caprion and R. Jullien, Laboratoire des Verres, Université Montpellier 2, Place E. Bataillon CC069, 34095 Montpellier, France

Model soft-sphere glasses are studied using classical molecular dynamics. To get a better insight on the glass transition we study both, the phonon spectrum and the structural properties using the Voronoi tessellation scheme.

Concerning the vibrational properties the results show a strong dependence on the glass history and more specifically on the quenching process. In particular the transverse branch shows a stronger localization than the longitudinal branch and this may be connected to the presence of «liquid pockets» in the solid glass phase.

The study of the evolution of the local structure using the Voronoi statistics, permits to observe directly the structural freezing below the glass transition temperature Tg. Moreover the geometrical characteristics of the Voronoi cells show a discontinuity at Tg but further studies are necessary to distinguish between an intrinsic effect or hidden cristallization phenomena.

Using the benefits of parallel computing, we are currently applying our simulation tools on more realistic systems like silica glasses.

D-XI.3 9:45-10:00

NUMERICAL SIMULATION STUDY OF THE DISLOCATION CORE STRUCTURE OF DISLOCATION, A. Aslanides and V. Pontikis, Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Plastic deformation of materials is controlled by the interaction, creation and elimination of dislocations. All these processes are driven by mechanisms about which little is known concerning details on the atomic scale. This is the case of the core structure of dislocation.

The importance of core effects causes the inapplicability of the elastic theory and makes a numerical treatment necessary. Two different metals are chosen : Al and Cu, described by two phenomenological semi empirical potentials.

We characterise the equilibrium configuration of an edge dislocation dissociated into two Shockley partials. The influence of the core structure in terms of stresses and strains is comparatively studied in the two materials.

We discuss the validity of the elastic theory of dislocations by comparing our results to the theoretical predictions.

D-XI.4 10:00-10:15

DOMAIN WALL ROUGHENING IN HETEROGENOUS MAGNETIC SYSTEMS IN CIRCULAR GEOMETRY, M. Jost and K.D. Usadel, Theoretische Tieftemperaturphysik, Universität Duisburg, Lotharstrasse 1, 47048 Duisburg, Germany

The interface dynamics of a growing magnetic droplet in a model with non-conserved order parameter and quenched disorder is studied numerically within a discrete time dynamics at zero temperature. As usual in such problems a depinning transition occurs, i.e depending on the value of a homogenous driving field the interface gets trapped by the random impurities or it moves steadily with non-zero velocity.

Starting from a perfect circular droplet the interface soon gets rough and the time evolution as well as the morphology of such a domain wall is analyzed for different driving fields in the pinning-phase with dynamic scaling methods. The results are compared with experimental data of the domain wall roughening in CoPt alloy films [M. Jost, J. Heimel and T. Kleinefeld, to be published]. It is found that the interfaces in the CoPt alloy film are well described by the discussed model. The values of the characteristic exponents give rise to the conjecture that these interfaces can be described by the Edwards-Wilkinson equation with quenched disorder.

D-XI.5 - invited - 10:15-10:30

MECHANISMS OF FORMATION AND TOPOLOGICAL ANALYSIS OF POROUS SILICON - COMPUTATIONAL MODELING, **L.N. Aleksandrov** and P.L. Novikov, Institute of Semiconductor Physics, Academy of Science, Novosibirsk 90, 63090, Russia

Porous Silicon (PS) is promising material for device applications due to visible luminescence, varying dielectric properties, extremely developed specific area. It is also an interesting object for fundamental investigation, since fractal structure of PS exhibits number of optical and transport phenomena, which are not fully understood. The mechanism of formation of porous layer is still a controversial subject. Computational modeling allows to study the physical mechanisms and kinetics of PS formation under anodization in hydrofluoric (HF) acid.

In present work the computer simulation is carried out, which let control the process of PS formation via doping level of substrate, anodic current density, temperature and HF concentration. The modified diffusion-limited model was used, taking into account the relief-selective etching, thermal generation and recombination of holes and quantum confinement effect in crystalline nanoparticles. Computer simulation is performed on two-dimensional (160x80) and three-dimensional (160x160x80) lattice. Plots and plan-parallel cross-sections, respectively, of obtained porous layers are presented. The analysis of simulated structure shows, that the porosity via depth has gradient, which increases with hole generation factor decrease. The fractal dimension, calculated for nanoporous structure, covers range from 1.8 to 3 with size of details, varying from 1 to 10 nm.

10:30-11:00 **BREAK**

D-XI.6 11:00-11:15

EMBEDDED ATOM METHOD CALCULATIONS OF VIBRATIONAL THERMODYNAMIC PROPERTIES OF ORDERED AND DISORDERED Cu_3Au AND Ni_3Al, J. Althoff, D. Morgan, D. de Fontaine, University of California, Berkeley, USA; M. Asta, S. Foiles, D. Johnson, Sandia National Laboratories, Livermore, CA, USA

Recent work had suggested that vibrational effects can play a significant role in determining alloy phase equilibria. In order to better understand these effects, we investigate the vibrational properties of disordered and ordered Cu_3Au and Ni3Al using the Embedded Atom Method. We calculate vibrational thermodynamic quantities within the quasi-harmonic approximation. The vibrational entropy is found to be strongly dependent on volume and cell-internal relaxations. For fully relaxed structures the dependence on lattice decoration of the vibrational entropy is compared to that suggested by recent experimental results.[1] Research supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences.

1. B. Fultz, L. Anthony, and L.J. Nagel, Phys. Rev. B 52, 3315 (1995); L.J. Nagel, L. Anthony, and B. Fultz, Phil. Mag. Lett. 72, 421 (1995).

D-XI.7 11:15-11:30

ATOMIC STUDY OF POINT DEFECTS IN B_2 FeAl, R. Besson, S.M.S., Ecole des Mines, 158 Cours Fauriel, 42023 Saint-Etienne Cedex 2, France and J. Morillo, S.E.S.I., Ecole Polytechnique, 91128 Palaiseau Cedex, France

Using an EAM-type potential supplemented by three-body non central interactions, atomic simulations of point defects formation and migration in B2 FeAl have been performed. The formation energies of single defects agree with previous ab initio calculations. Investigation of multiple defects energetics at T = 0 K yields high values (between 0.2 and 0.3 eV) for the binding energies of double defects that do not contain the Al vacancy. Such defects should be taken into account in any realistic description of the thermodynamic equilibrium state at high temperature. Moreover the complex defect involving first neighbour Al vacancy and antisite appears to recombine spontaneously into a single Fe vacancy. Implications of this instability upon possible diffusion mechanisms in B2 FeAl are discussed.

D-XI.8 11:30-11:45

RESEARCH OF APBs ENERGIES IN ALLOYS WITH L1o-SUPERSTRUCTURE, V.V. Pivenj, M.D. Starostenkov, A.V. Bakaldin, E.V. Chernyh, S.V. Klimenko, General Physics Dept., Altai State Technical University, Lenin st. 46, Barnaul 656099, Russia

It this work proposes pattern of creation the interatomic interaction potentials of Morse's type for ordered alloys with L1o-superstructure. This pattern includes both collection of procedures with experimentally well-known parameters of alloys and collection of procedures which uncritical to parameters (tetragonality values (c/a), energies of sublimation; etc.) The object of pattern's realization to creat and investigate of planar defects on series of alloys and to obtain the features of superstructure.

Orientation dependences were founded in accordance with a computer analysis of APBs energy spectrums in TIAL and PTZN with accounting of tetragonal distortion of the lattice. In process of calculation the isochoric change of lattice's parameters was simulated for various tetragonality values (c/a). The atom's relaxation was made near APB in various orientations {hkl} with the help of founded potentials. It was founded the features of orientation anisotropy of APB-energies. At whole the propose pattern the structure's properties of investigation alloys.

D-XI.9 11:45-12:00

COMPUTATIONAL TREATMENT OF ORDER-DISORDER PROCESSES BY USE OF THE CLUSTER VARIATION METHOD, V.M. Matic, Laboratory of Theoretical Physica and Solid State Physics, Institute of Nuclear Sciences - Vinca, P.O. Box 522, 11000 Belgrade, Serbia, Yugoslavia

We present an implementation of the cluster variation method (CVM), applied to the Ising model, for computational characterization of order-disorder processes in binary systems. We show how the Newton-Ralphson Iteration Scheme (NRIS) is used for numerical solving of system of nonlinear equations, obtained from the condition of minimum of the free energy, in the range of the CVM approximation. An emphasis is made on the problem of the starting iteration point (NRIS being very sensitive of it), for obtaining the low-temperature (ordered) phases. It was shown that an infinitesimally small breaking of symmetry of high-temperature (disordered) phases suppress obtaining solutions which correspond to the metastable phases (saddle points) by NRIS, below the critical temperature T_c. This kind of problems is illustrated by an example of oxygen ordering in basal planes in $YBa2Cu3O_{6+x}$ system, modeled by the two dimensional asymmetric next-nearest neighbor Ising (ASYNNNI) model.

12:00-14:00 **LUNCH**

Friday June 20, 1997 Afternoon
Vendredi 20 juin 1997 Après-midi

Session XII - Clusters

D-XII.1 14:00-14:15 STABILITY AND ELECTRONIC STRUCTURE OF SMALL Na-Cu CLUSTERS: A FIRST PRINCIPLE STUDY, C. Massobrio, IPCMS, 23 rue du Loess, 67037 Strasbourg, France; U. Heiz, Institut de Physique Expérimentale, Université de Lausanne, 1005 Lausanne, Switzerland

Mixed metal clusters of sodium with copper, silver and gold produced by supersonic expansion have been the object of recent experimental investigations (U. Heiz, A. Vayloyan, E. Schumacher, J. Phys. Chem. 100, 15033, 1996). Neutral cluster abundances obtained from the photoionization mass spectra appear to be qualitatively consistent with shell model arguments, which apply to a good extent in both sodium and coinage metals clusters. However, precise knowledge of structural and electronic properties of these systems can only be gained via accurate first principles calculations. Here we present a first principle study of the Na_xCu_y system (x =1-7, y=1-2) performed within the local density approximation of density functional theory by using the Car-Parrinello method. For a given cluster size, we focus on the differences found between the case under consideration and the pure systems. In particular the onset of the three dimensional character is investigated by analyzing the structural transformation undergone when the initial atomic arrangement is taken to be the one corresponding to either Na or Cu clusters having equal number at atoms.

D-XII.2 14:15-14:30 THE EFFECT OF SPILL OVER IN THE ELECTRONIC AND MAGNETIC PROPERTIES OF Ni, Co, and Fe CLUSTERS, J. Guevara, F. Parisi, M. Weissmann, Departamento de Fisica, Comision Nacional de Energia Atomica, Avda. del Libertador 8250, 1429 Buenos Aires, Argentina, and A.M. Llois, also at Departamento de Fisica, FCEN-UBA, Ciudad Universitaria, 1428 Buenos Aires, Argentina.

We calculate the electronic structure of 3d-transition metal clusters using an spd-tight-binding Hamiltonian which considers electron-electron interactions in the unrestricted Hartree-Fock approximation. Our model Hamiltonian takes into account electron spill over at the cluster surface and uses bulk parameter values. We perform calculations for fcc and bcc clusters of up to 177 atoms by making use of symmetry properties. We obtain magnetic moments and ionization potentials for Ni, Co and Fe clusters, and compare with different experimental results. The essential features of the electronic and magnetic properties are reproduced, starting with an spd-bulk parametrization, if a realistic approach for the electron spill over is considered.

D-XII.3 14:30-14:45 GEOMETRICAL EFFECTS ON THE MAGNETISM OF SMALL Ni CLUSTERS, S. Bouarab, A. Vega, M.J. Lopez, M.P. Iniguez and J.A. Alonso. Departamento de Fisica Teorica, Universidad de Valladolid, 47011 Valladolid, Spain

A self-consistent tight-binding method has been used to calculate the average magnetic moments μ of Ni_N clusters between N=5 and N=16. The geometrical structures were taken from the results of molecular dynamics simulations with semi-empirical potentials. The agreement with experiment (minima of μ at N=6 and N=13, and a maximun for N=8) is good and the variations of the average magnetic moment are explained as a consequence of geometrical effects: low coordinated atoms have large magnetic moments. Furthermore, the deviation of the interatomic distances from a smooth behavior also influences the magnetic moments. The contribution of the sp electrons to the magnetism is found to be relevant for Ni clusters with less than ten 10 atoms.

D-XII.4 14:45-15:00 FIRST-PRINCIPLES APPROACH TO THE CALCULATION OF ELECTRONIC SPECTRA IN CLUSTERS, L. Reining, CNRS-CEA, Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau, France and G. Onida, Dipartimento di Fisica, Universita di Roma "Tor Vergata", 00173 Roma, Italy

We present first-principles calculations of absorption and photoemission spectra in small clusters, going well beyond a standard Density Functional Theory - Local Density Approximation (DFT-LDA) approach. Starting with a DFT-LDA calculation, we evaluate self-energy contributions to the quasiparticle energies of an electron or hole in the GW scheme, where the self-energy $\sum = GW$ is constructed from the one-particle Green's function G and the RPA screened Coulomb interaction W.

We discuss the importance of these effects at the example of photoemission spectra of hydrogenated silicon chains, Si_nH_m ($n \leq 5$), taking moreover into account the very important contributions of structural relaxation. On the other hand, a realistic description of the optical absorption spectrum of a small cluster requires also the evaluation of the effects of electron-hole interaction. These excitonic effects can be as large as the self-energy corrections itself.[1] We discuss their contributions to the spectra of the chains.

1 G. Onida et al, Phys. Rev. Lett. 75, 818 (1995).

D-XII.5 15:00-15:15 NON LINEAR DYNAMICS OF ELECTRONS IN METAL CLUSTERS, P.G. Reinhard, Institut für Theoretische Physik, Universität Erlangen, Staudtstr. 7, 91058 Erlangen, Germany and F. Calvayrac and E. Suraud, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

We study the dynamics of the electron cloud in sodium clusters for small and for large amplitude excitations in the Time-Dependent Local-Density Approximation (TDLDA), without recurring to linear approximations. In particular, we discuss the interpretation of strength function and power spectrum as obtained from dynamical calculations. We demonstrate the constructive and destructive interference contained in the various spectral states. We search for special signature of nonlinear couplings in the large amplitude regime, however without finding pronounced effects. We display examples of applications in the case of interactions between clusters and intense laser beams.

D-XII.6 15:15-15:30

KINETIC 3D LATTICE MONTE CARLO SIMULATION OF PHASE TRANSFORMATIONS AT ION BEAM SYNTHESIS OF NANOCLUSTERS, K.H. Heinig, M. Strobel, Research Center Rossendorf, P.O. Box 510119, 01314 Dresden, Germany; M. Palard, CSNSM, bat 108, 92405 Orsay Campus, France

The synthesis of nanoclusters is becoming an expanding field of interest due to potential applications in micro- and optoelectronics. Nanocrystals, for instance, exhibit luminescence that usually does not appear in the bulk material. Nanocrystals can be synthesized by ion implantation, their properties depend strongly on the implantation and annealing conditions. Some aspects of ion beam synthesis remain to be explained. For instance, self-organization in the spatial distribution of nanoclusters has been observed.

Kinetic 3D lattice Monte Carlo (MC) simulations, based on a stochastic cellular automaton, have been performed to determine the dependence of the precipitate radius distribution (PRD) on the ion flux and fluence as well as on the implantation and annealing temperatures. It has been found that there are different implantation and annealing regimes. Unexpected spatial nanocluster size distributions can form at low implantation temperatures which results in a strong depth redistribution of implanted ions during subsequent annealing. Our computer simulations explain for the first time the frequently observed self-organization as an intrinsic property of ion implanted layers.

D-XII.7 15:30-15:45

THE GROWTH DYNAMICS OF ENERGETIC CLUSTER IMPACT FILMS, M. Moseler, J. Nordiek, O. Rattunde, H. Haberland, Freiburg Materials Research Center, Stephan-Meier-Str. 21, 79104 Freiburg, Germany

Thin film growth by energetic cluster impact (ECI) [1] can be described by a stochastic differential equation for the surface profile $h(\mathbf{x},t)$, where $\mathbf{x}$ is a two dimensional position vector parallel to an initially flat surface. Assuming that the impact of a cluster initiates a down-hill mass current proportional to the local slope of the surface, and considering additional diffusion of atoms after the impact, one can derive a linear growth equation:

$$\partial h(\mathbf{x},t) / \partial t = \nu \nabla^2 h(\mathbf{x},t) - K \nabla^4 h(\mathbf{x},t) + \eta(\mathbf{x},t)$$

where ν and K are constants and $\eta(\mathbf{x},t)$ is a stochastic noise. The parameter ν in the growth equation is the strength of the down-hill movement due to the cluster impact and was determined by molecular dynamic simulations of Cu_{1000}, Cu_{2000} and Cu_{3000} clusters impacting with 10 keV kinetic energy on tilted Cu(100) surfaces. From the solution of the spatialy fourier transformed growth equation the power spektrum $\langle h_k(t)h_{-k}(t)\rangle$ was derived. The comparison to experimental powerspectra from atomic force microscopy measurements of copper films shows good agreement.

[1] H.Haberland, Z.Insepov, and M.Moseler, Phys. Rev. B, **51**, 11061 (1995)

D-XII.8 15:45-16:00

A COMBINATION OF ATOMIC AND CONTINUUM COMPUTATIONAL MODELS DESCRIBING THE EVOLUTION OF NANOCLUSTERS, M. Strobel, K.H. Heinig and W. Möller, Research Center Rossendorf Inc., P.O. Box 510119, 01314 Dresden, Germany

Nanoclusters, e.g. generated by ion beam synthesis (IBS), manifest a fascinating state between discrete atomic and continuous solid matter, where physical properties depend sensitively on size. Some of the properties could be used for applications, e.g. the photo- and electroluminescence of nanoclusters of indirect band-gap semiconductors embedded in a SiO_2 matrix is interesting for opto-electronics. Here, we present two models, a discrete and a continuous one, which each is suited to study special processes of ion implantation. The combination of them allows a comprehensive simulation of all aspects of IBS. On the atomic scale our 3D lattice Monte Carlo (MC) model based on a cellular automaton is used to study nucleation and growth of nanoclusters. On the mesoscopic scale, rate equations are used to describe the coarsening of nanoclusters. Special attention is paid to the interface and common simulation ranges of both methods. More realistic initial conditions for the rate equation approach to Ostwald ripening are now available from our MC simulation. Thus for the first time all processes governing the evolution of nanoclusters at IBS can be studied by computer simulations through a combination of atomic-scale and continuum modeling.

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SYMPOSIUM D

Poster Sessions

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Poster Session I

16:00-18:00

D-I/P1 A FIRST PRINCIPLE STUDY OF SMALL Cu CLUSTERS BASED ON LOCAL-DENSITY AND GENERALIZED- GRADIENT APPROXIMATIONS TO DENSITY FUNCTIONAL THEORY, C. Massobrio, IPCMS, 23 rue du Loess, 67037 Strasbourg, France, A. Pasquarello and A. Dal Corso, IRRMA, IN-Ecublens, 1015 Lausanne, Switzerland

Electronic and structural properties of neutral Cu_n (n=2,3,6) clusters are obtained within density functional theory via a) the local density approximation (LDA) and b) the generalized-gradient approximation of Perdew and Wang (GGA-PW) for exchange and correlation. Both sets of calculations are performed by using the method by Car and Parrinello with a plane-wave basis set. Optimization of the electronic and geometrical structures is performed in three stages. In the first, the GGA total energy is calculated on LDA structures previously optimized at both the electronic and structural level. In the second, only the electronic structure is optimized within the GGA scheme. Finally, full GGA optimization including structural relaxation is carried out. A significant reduction of the binding energy (~0.2 ev/atom) is already noticeable in the first case, while no appreciable changes in its value occur at the two further levels. Full GGA optimization results in a moderate increase of bond lengths (~0.1 Å). The differences found between the LDA and GGA ordering energy of the different isomers are discussed in the case of Cu_6.

D-I/P2 PHONON SPECTRA OF ULTRATHIN NON-HOMOGENEOUS CRYSTALLINE FILMS, R. Firstenberg, Institute of Physics, University of Novi Sad, Trg D. Obradovica 4, 21000 Novi Sad, Yugoslavia

This work deals with the application of the molecular dynamics method in simulating ultrathin non-homogeneous crystalline films, and obtaining their phonon spectra.

The whole process consists of the simulation of the movement of atoms in the crystalline lattice and numerical analysis of the resulting displacements. The phonon spectrum can be obtained by means of Fourier harmonic analysis frequencies for which the Fourier transform shows peaks, belong to the modes of the collective vibrations of atoms in the crystalline film. Error estimates were also given in order to minimize the time needed for these calculations.

In order to check the reliability of the applied method, the obtained phonon spectra were compared with the analitical solutions for homogeneous films, determined by rigorous quantum mechanical calculations. The results of comparison have justified the use of classical approach.

The influence of impurities in crystalline lattice on the phonon spectra was examined as well as the possibilities of improving the superconductive properties of these films. The case of one layer of impurities in the film was examined. The behaviour of phonon spectrum in function of the mass of impurity and the thickness of the film has been shown. Some empirical formulae were also given.

D-I/P3 TOWARDS A MACROSCOPIC THEORY OF ANISOTROPIC ETCHING, S. Nedelcu, N. Moldovan, Institute of Microtechnology, PO Box 38-160, 72225 Bucharest, Romania; H. Camon, LAAS/CNRS, 7 av. du Colonel Roche, 31077 Toulouse Cedex, France

Starting from an atomic scale etching theory, a method of solving the coupled equations' system for disappearance probability functions is proposed. These functions have been initially defined for every site of a crystalline lattice. The continuity's hypothesis for the spatial variables is introduced, and one arrives at a non-linear equation for the disappeatrance probability function of a certain atom. We consider this equation as resulting from a variation principle and we draw out the associate Hamiltonian. The prime integrals of the system show us how the canonical equations' solutions depend on the initial given conditions.

The limits of the perturbation theory method applied in order to obtain an analytical solution of the canonical equations are discussed.

Besides, the possibility to introduce the temperature parameter in the model appears.

D-I/P4 COMPUTER SIMULATION STUDIES OF MOLECULAR BEAM COMPOSITION INFLUENCE ON THE GROWING SILICON SURFACE STRUCTURE, R.V. Bochkova, V.I. Dyakonova, V.N. Gorohov, Mordovian State Institute of Teacher Training, 430007 Saransk, Studencheskaya Street 11-a, Russia

Growth of Si films from non-doped or phosphour-doped molecular beam which maintains excited and ionized atoms has been considered. Monte Carlo and molecular dynamics simulation techniques have been used for study of this non-equilibrium process.

Processes of random hits of atoms on substrate surface and probable realizing of elementaly events were determined by Monte Carlo technique. Mechanisms of formation amorphous and crystalline layers were viewed by molecular dynamics technique.

The presense in molecular beam ionized atoms is caused by heightened energy which expense for excitation of neutral atoms of molecular beam and adsorptive layer. In moment of atom strike local raising of temperature happens on crystallization point by energy of bonding and energy of excited atom. Deviation from initial substrate temperature on the surface of film changes with time as $\Delta T = q / \rho c\sqrt{\pi\alpha t}$ where q - density of isolated energy by unity of area, ρ - density of substanse, c - thermal heat capacity, α - coefficient of temperature conduction.

As a result of local excitation of substrate the defects of packing and centres of metastable amorphous states are arised. The probability of hitting to substrate atoms, ions, dimers and complexes from four atoms are taken into account in program.

The dependence of growth rates and defectness of growing film on temperature of substrate and the degree of ionization of molecular beam under different flows and supersaturations are considered. The change of activation energy of surface diffusion from substrate temperature is estimated.

D-I/P5

DESYNCHRONIZATION MODE OF 2D-ISLAND CREATION ON THE STEPPED SURFACE DURING MBE-GROWTH (SIMULATION), Z.Sh. Yanovitskaya, I.G. Neizvestny, N.L. Shwartz, M.I. Katkov, I.P. Ryzhenkov, Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, 630090 Novosibirsk, Russia

The desynchronization mode of 2D-islands creation on the stepped crystal surface during MBE growth was investigated by Monte Carlo simulation. The behavior of perimeter oscillations of islands on flat and stepped surface (100) of simple cubic crystal was compared. Distribution of 2D-islands sizes with the monolayer number in the same coverage phase was considered. During simulation self-organizing stationary asynchronous structure of islands on the stepped surface was observed, causing dumping of perimeter oscillations. This structure caused damping of oscillations of perimeter under conditions when continuous oscillations were observed on flat surface. The number of oscillations was about the ratio of terrace width to the migration length of adatoms. A model of self-organizing asynchronous structure, connected exclusively with steps was proposed. An obligatory condition of its occurrence is coexistence of two modes of monolayer coverage: step flow and two dimensional nucleation growth.

D-I/P6

THE COMPOSITION CHANGES INDUCED BY SURFACE ROUGHENING AND MIXING DURING THE ION PROFILING OF MULTILAYERS, A. Galdikas, L. Pranevicius, Physics Department, Vytautas Magnus University, 28 Daukanto st., 3000 Kaunas, Lithuania, C.Templier, Université de Poitiers, Futuroscope, France

During sputtering of the multilayered structures (depth profiling) since the removal of atoms takes place from the various uncovered (outermost) monolayers having complex topography, the interface between layers is crossed by moving surface boundary at different places at different moments of time. It follows that the time needed to clean the substrate of all atoms of the thin layer is much longer than that under the assumption that the removal of atoms takes place homogeneously, monolayer by monolayer, with constant velocity. In drawing conclusions about how the geometrical distribution of atoms at the interface affects the elemental composition on the surface measured using the ion sputtering technique, one can make mistakes by attributing geometrical effects of the surface topography development to the distribution effects of atoms in the interface region.

In the presented work the effects of the development of surface topography induced during continuous ion sputtering of multilayers in the kinetics of surface composition of constituents of initially ideally layered monolayers is considered by the proposed phenomenological model. On the other hand, it is well known that the interface broadening may occur during the process of ion mixing of multilayers. In order to emphasis the composition changes on the surface produced by surface topography development, the calculated results from the two different models are compared. The first one includes the processes of sputtering and surface mobility of atoms, and second one includes the processes of ion mixing of multilayers and sequential removal of surface monolayers (layer by layer).

The main conclusion made from the qualitative analysis of obtained results is that the effects induced by these two different processes are quite similar and the interpretation of such experimental results in many cases is not so obvious.

D-I/P7

SIMULATION OF THE DEPOSITION AND AGING OF THIN ISLAND FILMS, P. Bruschi and A. Nannini, Dipartimento di Ingegneria dell'Informazione, Università degli Studi di Pisa, via Diotisalvi, 2, 56126 Pisa, Italy

In this communication a program for the simulation of the growth and evolution in time of thin island films in the sub-monolayer regime is presented. The substrate is represented by a triangular or square lattice of adsorption sites. The atoms diffuse over the substrate by hopping to the nearest neighbours at a hopping rate depending on the interactions with the substrate and neighbouring atoms. The electrical resistance of square portions of the island films is calculated by solving the equivalent resistor network obtained by assigning an equivalent conductance to each pair of grains. The intergrain conductances is calculated on the basis of a charging-energy-limited tunnelling model.

The simulations were aimed at studing the influence of process parameters, such as the substrate temperature and deposition rate, on the final morphology and electrical resistance of the samples. The increase of the resistance sensitivity to variation of growth parameters exhibited by samples approaching the percolation threshold is described.

The low stability of metal island films which constitutes a serious limitation to their applications in resistive sensors has been studied with a series of simulations in which the resistance is computed at regular time intervals while the sample evolves at a given storage temperature. The role of the deposition parameters and the effect of different thermal annealing are reported.

D-I/P8

GROWTH PROCESS INVESTIGATION OF SEMICONDUCTOR MICROCRYSTALS, R. Baitsar, S. Varshava, I. Ostrovskii, Scientific Research Department of Semiconductor Microelectronic Sensors, State University "Lvivska Polytechnika", 12 Bandera Str. 290646 Lviv, Ukraine

Growth by CTR method of semiconductor Si and Si-Ce whiskers on the stage of thermodynamical process that takes place in vapour phase in correspondent systems Si-Br and Si-Ge-Br was investigated. The vapour phase content depending on temperature difference between evaporation and crystallization zones (ΔT = 150-400K), transport agent concentration (n_{Br} = 05-3.0 mg/cm^3) were evaluated. The oversaturation at different conditions was estimated. The transport of growth material by both theoretical and experimental way was investigated. The thermodynamical parameters estimated were compared with the parameters of the whiskers grown with certain morphology and shape. The oversaturation values 5-20 corresponding to the growth of thin perfect Si whiskers are provided at temperature of crystallization zone 1000-1100K and temperature difference ΔT = 200K. For Si-Ge-Br system ΔT values should be larger and approach to 300-400K, oversaturation being increased at Si content growth.

By use of the mathematic modeling method of experiment the analytical dependencies of specific resistance on diameter for Si whisker and the dependencies of specific resistance, of tensosensitivity coefficient on impurity (B) concentration and Ge content for Si-Ge whiskers were determined. The dependencies found enable to grow the whiskers with parameters appropriate for their use as sensors of different physical values, e.g., tensoconvertors.

D-I/P9

MONTE CARLO SIMULATION OF PULSED LASER ABLATION INTO AN AMBIENT GAS, T.E. Itina, W. Marine, M. Autric, Laboratoire Interdisciplinaire Ablation Laser et Applications, Case 918, Parc Scientifique et Technologique de Luminy, 13288 Marseille Cedex 9, France

Laser ablation from binary target into a diluted gas background (P<200 mTorr) is simulated by Combined Direct Simulation-Test Particle Monte Carlo method. The spatial and energy distributions of particles deposited at the plane substrate and scattered back at the evaporated surface are calculated. The approach developed has allowed us to consider the influence of the collisions both among the ablated particles and between the ablated and ambient gas particles on the uniformity of film stoichiometry. It is found that the increase of the background gas pressure results in the more uniform distribution of the stoichiometrical ratio of the deposited particles with different masses.

The results of our three-dimensional MC simulation are of a particular interest for the pulsed laser deposition (PLD) of the materials for which the uniformity of thin films is critical.

D-I/P10

SMOOTHING OF THE SURFACE RELIEF DURING MBE PROCESS AS A CAUSE OF RHEED OSCILLATION DISTORTIONS, M.I. Katkov(2), I.G. Neizvestny(1), I.P. Ryzhenkov(2), Z.Sh. Yanovitskaya(1), (1)Institute of Semiconductor Physics, Russian Academy of Sciences, Siberian Branch, 630090 Novosibirsk, Russia; (2)Novosibirsk State University, 2 Pirogova, 63090 Novosibirsk, Russia

Transformation of initial surface band-antiband relief during MBE process and its influence on the reciprocal perimeter change were investigated in this work. Epitaxy on a surface (100) of Kossel crystal was simulated by Monte Carlo method. Consecutive surface configurations were recorded as a computer film. Simultaneously the reciprocal perimeter oscillations of islands and steps, which are correspond surface smoothness like a RHEED specular beam intensity in Brage in-phase condition were registered during simulation. Smooting of the surface relief during deposition process was found to take place on the surfaces with steps of opposite directions. Amplitude modulations of reciprocal perimeter oscillations could be observed in this case. Maxima in amplitude correspond to decreasing of front of growth by one layer. Different growth rates on the lowest and top terraces are responsible for the relief smoothing. This difference is a cause of amplitude modulation of oscillations, as under these conditions addition of two oscillations with close frequences occurs.

D-I/P11 GRAIN EFFECT IN ELECTRONIC PROPERTIES OF SILICON EPITAXIAL NANOSTRUCTURES, A. Filonov(1), A.N. Kholod(1), V.E. Borisenko(1), F. Bassani(2), A. Saul(2) and F. Arnaud d'Avitaya(2); (1)Belarusian State University of Informatics and Radioelectronics, P. Browka 6, Minsk 220027, Belarus; (2)Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Campus de Luminy - Case 913, 13288 Marseille Cedex 9, France

A systematic theoretical study of the properties of grained silicon (111) films have been performed within an improved semi-empirical self-consistent LCAO method. We have attempted to simulate carefully the grain effect in the electronic structure of such nanocrystalline films to see the dynamics of its changes as a function of the boundary formation process.

Grain nature of the nanocrystalline films is found to induce both a direct band gap and its reduction with respect to an isolated grain of the same size. The gap values vary from 2.85 to 1.46 eV depending on the film thickness as well as the lateral size of the grains. Film stacking considerably increases the gap value for the films with the same effective sizes.

Furthermore, the results we have obtained can be explained, in a more simple way, in terms of a confinement effect for interacting clusters and wire-type structures within the Effective Mass approach.

D-I/P12 MODELING OF SILICON NANOCRYSTAL FORMATION IN AMORPHOUS SILICON UNDER PULSE EXCIMER LASER IRRADIATION, M.D. Efremov, O.K. Shabanova, Institute of Semiconductor Physics, Siberian Branch of RAS, pr. Lavrentjeva 13, Novosibirsk 630090 Russia

Modeling of silicon nanocrystal formation inside of thin amorphous silicon films on glass substrates was carried out for the case of thermal treatments and pulsed excimer laser annealing of the structures. Classical nucleation theory approach was applied to evaluate phase composition of the films, size distribution and concentration of critical nuclei. Solution was obtained using computer modeling of Zeldovich equation for kinetics of phase transition taking into account thermoconductivity in the structure, hidden enthalpy of crystallization and mechanical stresses in the structure. Obtained kinetics and size distribution of nuclei was compared with experimental data. The following experimental effects were under consideration: reduction of incubation time of crystallization in the case of preliminary stimulation of nucleation by excimer laser treatments and rapid thermal annealings; retardation of crystallization with the presence of Ge atoms, introduced by ion implantation in the film; HREM observed formation of silicon nanocrystals with sharp size distribution and average size of 2 nm just after nanosecond excimer laser treatment, appearing of strong preference orientation (110) of nanocrystals inside of amorphous films. The influence of mechanical stresses was especially considered as a reason for changing of kinetics of phase transition and for appearing of orientation of nanocrystals inside of amorphous films due to minimum of elastic energy of nuclei with certain orientations in axial field of elastic stresses of the structure. Deformation addends to chemical potential difference in thermodynamic Gibbs potential in a course of phase transition amorphous-crystalline silicon were estimated as 11.4 meV/atom and 0.27mev/atom kbar for local strain around nuclei and integral stresses in the structure accordingly.

D-I/P13 SIMULATION OF EPITAXIAL GROWTH IN III-V PENTERNARY SOLID SOLUTION IN THE TEMPERATURE GRADIENT FIELD, V.N. Lozovskii, L.S. Lunin, A.V. Blagin, P.A. Konstantinov, State Technical University, Dept. of Physics, 132 Prosveshchenya Str. , 345300 Novocherkassk, Russia

III-V - penternary solid solutions are promising materials for optoelectronics as the presence of five components in the solution allows to control three parameters of semiconductors crystal: bandgap energy, lattice constant and thermal expansion coefficient. An important problem in the theory and the technology of these materials is simulation of the liquid phase crystallization in the temperature gradient field. Simulation of InGaAsSbBi epilayer growth by the cellular authomation method allowed to reveal the nature of relief on the surface, the duration of generating the first layer in heteroepitaxy as well as the distribution of epitaxial centres by the dimension related to the period of the contact between the melt and the solid phase.

The experiments have shown that for isoperiodic InGaAsSbBi layers on InSb substrates the mechanism related to nucleation of two-dimensional nuclei on atomic smooth surfaces is realized. The duration of metastable state for the liquid solutions has been found to depend mainly on the temperature gradient.

D-I/P14 COMPUTER SIMULATION OF THE SURFACE BEHAVIOR DURING QUANTUM DOTS GROWTH BY MBE, A.M. Boiko, V.P. Evtikhiev, R.A. Suris, A.F. Ioffe Physical-Technical Institute, 26 Polytekhnicheskaya, 194021 St. Petersburg, Russia

It was shown [1] that the size distribution function (DF) of InAs quantum dots (QDs) grown by MBE on vicinal surfaces of GaAs drastically differs from the distribution function of QD growth on singular (001) surface: the first one is much narrower than the last one. This suggest that the size DF is controlled rather by misorientatied substrate morphology than by Ostvald ripening (OR)

Earlier, using our molecular-dynamic (MD) simulator we demonstrated [2] that under some conditions of the vicinal surface growth the vicinal surface steps become wave shaped. The similar wave like shape of the terraces was observed in [2].

Here we present a size stabilization explanation based on the picture of suppression of adatom diffusion between neighboring cells of waved crystal terraces. Computer simulations demonstrate super liner relation between intercell adatom diffusion current and narrowing down of the necked-down section of the terrace.

1. A.M. Boiko. A. Yu Kaminski, R.A.Suris, "Nanostructures: Physics and technology. 96" p.378.
2. V.P. Evtikhiev, N.A. Titkov, A.Yu Kriganovsky ICSP-23, IOP conference series 1996.

D-I/P15 NUMERICAL MODELLING OF PLUME EXPANSION AND THIN FILM DEPOSITION IN THE PULSED LASER DEPOSITION (PLD) PROCESS, Z. Kantor and T. Szörényi, Research Group on Laser Physics of the Hungarian Academy of Sciences, POB 406, Szedged 6701, Hungary

Pulsed laser induced evaporation of complex materials in vacuum proved to be a straightforward method for thin film deposition. One of the particular advantages of this pulsed laser deposition (PLD) method, the control of the elemental composition of the growing film, is ensured by applying (reactive) atmospheres of pressures up to tenths of millibars. The change of the pressure of the background gas, however, strongly influences both the deposition rate and the lateral distribution of the deposited material on the substrate.

The extension dynamics of the laser generated plasma plume is simulated based on a microscopic collision model using Monte-Carlo calculations. The calculated spatial distribution of the film material as a function of pressure is compared to measured thickness profiles of bismuth films deposited in argon and helium atmosphere. The numerical calculation is successfully applied for the interpretation of the main features obtained in the 10^{-6}—10^{-1} mbar pressure domain, i.e. the decrease in deposition rate and the broadening of the film thickness profiles with increasing pressure.

D-I/P16 METHODOLOGICAL ASPECTS OF CALCULATIONS OF THERMODYNAMIC FACTOR IN INTERDIFFUSION, S. Dorfman; Dept. of Phys., Technion, 32000 Haifa, Israel and D. Fuks, Mat. Eng. Dept, Ben-Gurion Univ. of the Negev, P.O.B. 653, 84105 Beer Sheva, Israel

The diffusion behaviour can be studied in binary systems for which appropriate radioisotopes for both constituents of the alloy are available. With respect to the Fe-Al system appropriate and inexpensive radioisotopes are vailable for Fe component (e.g. ^{59}Fe) but not for Al. In the framework of the Boltzmann-Matano method the diffusion behaviour of Fe-Al intermetallics can be gained and interdiffusion coefficients D can be determined. The interdiffusion coefficient is related via the modified Darken equation to the tracer diffusivities of the constituents. The thermodynamic factor Φ entering the Darken equation is proportional to the second derivative f the Gibbs free energy, G, of the alloy on the molar fraction of one of components. These relations can be used to deduce the tracer diffusivity of Al provided that the tracer diffusivity of Fe, the interdiffusion coefficient and the thermodynamic factor are known. According to the Darken equation Φ may be determined as a derivative of the Gibbs energy, G, multiplied by the concentrations of components and devided by RT. The mixing energy, which enters G, could be calculated on the basis of the thermodynamical data or by means of non-empirical calculations. We suggest to use for these ab initio calculations the modern non-empirical methods.

D-I/P17 THE WATER ADSORPTION ON THE Si(111)7X7 SURFACE, A THEORETICAL STUDY, H. Ezzehar, L. Stauffer, P. Sonnet, Laboratoire de Physique et de Spectroscopie Electronique, 4 rue des Frères Lumière, 68200 Mulhouse, France and J. Leconte, C. Minot, Laboratoire de Chimie Théorique, 4 place Jussieu, 75252 Paris Cedex 05, France

We present a theoretical study of the initial steps of the water adsorption on Si(111)7x7. Water dissociates on the surface. In a first step, partial dissociation generates radicalar species, H· and HO·, that are adsorbed on the dangling bonds of the surface. The first sites to be saturated are those of adatoms from the faulted half of the Si(111)7x7 unit cell. When three molecules per unit cell are adsorbed, one restatom site is involved together with adatom sites and the adsorption implies an electron tranfer from one unit cell to another. For the following adsorptions, a restatom site is involved simultaneously with an adatom site. The OH· goes on the restatom site since H·, more selective, goes preferentially on the adatom site. Complete dissociation of H_2O seems to be even more favorable. Water adsorption can displace the hydrogen atoms, initiating an oxidative process.

D-I/P18 WITHDRAWN.

D-I/P19 WITHDRAWN.

D-I/P20 SELF-ORGANIZATION KINETICS IN FINITE PRECIPITATE ENSEMBLES DURING COARSENING, V.A. Borodin, RRC Kurchatov Institute, 123182 Moscow, Russia; K.H. Heinig, S. Reisss, Research Center Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

A rate equation approach is applied for the description of the self-organization (layering) phenomenon predicted in recent computer experiments. This layering was observed in finite precipitate systems during annealing and is caused by Ostwald ripening. We demonstrate that the layering is triggered by local inhomogenieties in the spatial distribution of precipitate sizes and should not be treated in terms of the frequently considered «spinodal decomposition» approach. The change of the spatial profile of precipitate size starts from the boundary of the system and occurs within a «reaction shell» having a thickness of the order of the diffusional screening length. During annealing this «reaction shell» shifts progressively into the system, leaving behind layers of precipitates. The layering is shown to occur only in sufficiently large systems with characteristic dimensions of at least several diffusional screening lengths. The reason for the weak sensitivity of interlayer distance to variations of system parameters is elucidated.

D-I/P21 COMPUTATIONAL MODEL OF NONEQUILIBRIUM PHASE TRANSITIONS IN A Si-Ge SYSTEM, P. Prikryl, Math. Inst. Acad. Sci., Zitna 25, 115 67 Prague 1, Czech Republic and R. Cerny, Dept. Phys. Fac. Civil Engng., Czech Tech. Univ., Thakurova 7, 166 29 Prague 6, Czech Republic

A computational model of a Si-Ge system melting and solidification induced by pulsed-laser irradiation is formulated using the methods of continuum physics. Phase transitions in the system are modeled using the theory of transition states so that undercooling or overheating of the interface and nollequilibrium phase diagrams are taken into account.

The numerical solution of the mathematical model is performed using the Galerkin finite element method in a 1-D approximation and the moving boundary problem is solved by a front-fixing technique. Computer implementation of the numerical model is then performed and a Fortran computer code is developed.

In a practical application of the computational model, the melting and solidification of both Si-Ge alloys of various composition and thin Ge layers on the Si bulk induced by ArF excimer laser are simulated. The results of numerical simulations are compared with the available experimental data.

D-I/P22 ENERGY OF TWO STRUCTURES OF $\sum = 11$ TILT GRAIN BOUNDARY IN SILICON AND GERMANIUM WITH TIGHT BINDING METHODS, J. Chen, B. Lebouvier, A. Hairie, G. Nouet and E. Paumier, LERMAT 6004 CNRS - ISMRA, 6 boulevard du Maréchal Juin, 14050 Caen Cedex, France

Atomic structures of grain boundaries are often studied with empirical potentials. In the special case of $\sum = 11$ [011], the energy difference between the two possible structures known as A and B structures is weak when it is calculated with those potentials. However, it shows that a structure is the more stable one at zero temperature.

Another way to determine the relative stability of the two structures is to use the tight binding method. The results on silicon obtained with Wang Chen and Ho method as well as with Goodwin, Skinner and Pettifor one are contrary to those obtained with the usual empirical potentials: B is the more stable structure at zero temperature. In germanium, the method of Mercey and Chou leads to the stability of A structure with respect to B one.

Those results raise two questions: why do tight binding methods give results different from those of empirical potentials? What is the origin of different behaviour of silicon and germanium which are usually considered as very near each other?

D-I/P23 COMPUTATIONAL MODELING OF CO_2 LASER PULSED ANNEALING OF HgTe FILM ON CdTe SUBSTRATE, V.G. Savitsky, P.E. Storchun, Institute of Applied Physics at Ivan Franko State University, 49 Pushkin Street, 290044 Lviv, Ukraine

Application of laser powerful single-pulse irradiation provides a possibility of quick non-equilibrium thermal annealing for investigation of defect formation processes in HgTe monocrystalline thin films. Two layer structure - thin HgTe monocrystalline film (d=10μm, $h\upsilon co_2 > E_g$) on massive CdTe substrate (d=2mm, $h\upsilon co_2 < E_g$) - was proposed to achieved homogeneous quick HgTe film annealing. During $C0_2$ laser irradiation, two concurrent processes occur - HgTe heating and heat flow into CdTe substrate. Interaction between above processes ensures the homogeneous heating of the HgTe film.

Computer modeling was carried out to predict temperature distribution over the two layer structure. One-dimensional heat diffusion differential equation was discretized by finite difference scheme over a non-uniform grid. Results of numerical simulation of temperature distribution are presented for single-pulse irradiation by CO_2 laser from the substrate side as well as from the film for different duration of the pulse.

D-I/P24 DETERMINATION OF THE CZOCHRALSKI SILICON AND MO-VPE $Ga_{1-x}Al_xAs$ AVERAGED STOPPING POWERS FOR CHANNELED IONS USING CALCULATIONAL AND EXPERIMETAL METHODS, M.A. Misdaq, R. Elassali, Nuclear Physics Techniques Laboratory, Faculty of Sciences Semlalia, B.P. S15, University Cadi Ayyad, Marrakech, Morocco

Non-doped Czochralski silicon and MO-VPE $Ga_{1-x}Al_xAs$ averaged stopping powers for channeled beams of light ions along the <100> and <110> major axes habe been evaluated by using a Monte Carlo calculational method adapted to the experimental conditions. Stopping powers of the studied materials have also been measured by combining charged particle activation analysis (CPAA) with ion channeling for $Ga_{1-x}Al_xAs$ and performing transmission of particles experiments on silicon crystals. Calculational and experimental methods have been found in agreement with each other. Variation of the calculated $Ga_{1-x}Al_xAs$ and silicon stopping powers as a function of the energy of the channed ions along the <100> axis have been investigated.

D-I/P25 INVESTIGATION OF THE GROWTH OF ZINC TELLURIDE FROM GASEOUS PHASE, B.J. Datsko, N.A. Ukrainets, M.I. Dronyuk; G.A. Ilchuk, I.F. Viblyi, V.O. Ukrainets, Department of Physics, State University "Lvivska Politeknika", 12 Bandera str. , 290646 Lviv, Ukraine

It is known that investigation of condition of growth of semiconductor materials from gaseous phase based on calculation of its equilibrium composition and experimental studing of mass-transfer .For purpose of the optimization of conditions of ZnTe-growth the mathematical model of $ZnTe\text{-}NH_4Br$-system and the investigation of the partial pressures of the component in temperature region (800-1400)K and at owerall pressures (10^3-10^5)Pa were carried out. On the basis of the obtained results the optimum condition of the growth are established, nameli velocities of ZnTe-mass-transfer depend on temperature and concentration of mass-transferer.

D-I/P26 MODELING OF THE ELECTRONIC STRUCTURE, ELECTRONIC CHARGE DENSITY AND OPTICAL CONSTANTS OF $In_{1-x}Ga_xSb$ TERNARY ALLOYS, V.G. Deibuk, R. Tsirulkevich, State University of Chernivtsi, Kotsyubynskogo 2, 274012 Chernivtsi, Ukraine

The $In_{1-x}Ga_xSb$ alloys are attractive semiconductor materials for optoelectronic devices in the near-to-far-infrared spectral region. Using the empirical local pseudopotential scheme with spin-orbit interaction, the band structure and charge density for the $In_{1-x}Ga_xSb$ alloys are calculated. In order to take into account lattice antistructure defects we used a modified virtual crystal approximation.

The exact electronic structure is used for calculation of the dielectric function $\varepsilon(E)$ in random-phase-approximation by means of the Baldereschi mean-value-point technique for Brillouin-zone averages.

The optical constants such as the complex refractive index, absorption coefficient and normal-incidence reflectivity are analyzed. Our results are found to be in good agreement with recent experimental data.

D-I/P27 THE ELECTRON AND HOLE EFFECTIVE MASSES IN SILICON WITHIN AB INITIO PSEUDOPOTENTIAL APPROACH, Y.S. Budjak, I.S. Sobchuk and S.V. Syrotyuk, Department of Electrophysics, State University "Lviv Polytechnic", 290646 Lviv 13, Ukraine

The electron and hole effective masses in silicon have been evaluated on base of crystal wave functions obtained by direct solving of energy band spectrum and eigenfunction problem within ab initio pseudopotential approach. The effective mass tensor has been calculated at different points of the Brillouin zone. The obtained values are in good agreement with experiment.

D-I/P28 NUMERICAL MODELING OF P-TYPE DOPANT DIFFUSION IN III-V SEMICONDUCTORS, J. Marcon, S. Gautier, S. Koumetz, K. Ketata, M. Ketata, LCIA, INSA de Rouen, BP 8, 76131 Mont Saint Aignan, France; J.G. Caputo, LMI, INSA de Rouen, France and P. Launay, CNET, Laboratoire de Bagneux, BP 107, 92225 Bagneux, France

Indium phosphide and related compounds are promising materials for optoelectronic device applications. Considerable effort has been devoted to producing materials reliable Heterojunction Bipolar Transistors. Epitaxial layers (Be doped InGaAs and InGaAsP) are widely used for the preparation of these high quality devices.

The device performance could be strong improved by the dopant diffusion during the technological processes. This require to control the p-type diffusion in III-V semiconductors and leads to models consisting on partial differential equations.

This work introduces numerical algorithms related to analysis of dopant diffusion profiles. Several diffusion models (based on Frank/Turnbull and Kick-out mechanisms) are implemented in simulation programs. A good agreement has been obtained between calculated and experimental profiles. The parameter values (equilibrium concentrations, diffusivities, ...) are discussed and compared with other published data.

D-I/P29 COMPUTER SIMULATION OF ATOMIC ARRANGEMENT IN ALUMINA, L.A. Aleshina, K.L. Kovalev, A.D. Fofanov, Petrozavodsk State University (PSU), pr. Lenina 33, 185640 Petrozavodsk, Russia

Computer simulation of possible short-range order in cation sublattice of $\gamma\text{-}Al_2O_3$ has been carried out. The character of short-range order appearing under different stereochemical limits has been revealed. It has been shown that this short-range order does not appropriate any cristallyne modification of Al_2O_3 oxide.

This atomic arrangements were used as initial configurations for following randomisation of the models.

Disordering of the oxygen fcc-sublattice has been accomplished, aimed at approximation towards the structure of the amorphous oxide. The molecular statics method has been applied. As a result of disordering the amorphous phase scattering maximum arises at the x-ray pattern calculated for the computer model. The position and shape of this maximum depends on stereochemical limits in cation arrangement.

D-I/P30 INVESTIGATION OF THE ELECTRONIC STRUCTURE OF VACANCIES IN ZnSe, V. G. Deibuk, A.S. Melnitchouk, Department of Theoretical Physics, State University of Chernivtsi, Kotsyubynskogo 2, 274012 Chernivtsi, Ukraine

The energy spectrum of vacancies in ZnSe is studied. The position of one-electron vacancy levels relative to the valence-band edge is determined in the framework of molecular cluster approach.The electronic structure of ZnSe with Zn vacancy is modelled by that of 17-atom cluster with the central atom of zinc being removed.The boundary conditions on the cluster surface are taken into account. The Hartree-Fock-Roothaan set of equations was solved using charge self-consistent procedure.

Electron-electron correlation and configuration mixing are taken into account. Many-electron states are constructed using group theory considerations and thus neutral and charged vacancy levels are obtained. A comparison with experimental data is made.

D-I/P31

DOUBLE DOPING OF n-ZnSe SINGLE CRYSTALS DURING CuCl SALT VAPOURS HEATING AND THE INVESTIGATION OF THEIR KINETIC PROPERTIES, V. Kasiyan, D. Nedeoglo, State University of Moldova, 60 Mateevich Str., 2009 Kishinau, Moldova

Galvanomagnetic phenomena and photoconductivity relahation in the n-ZnSe crystals doped with donor (Cl) and acceptor (Cu) impurities in equivalent amounts were investigated in temperature range from 77 K to 500 K. The crystals were doped during their annealing in vapours of CuCl salt. It was shown that simultaneous doping of n-ZnSe with donor and asseptor impurities in equal amounts leads to formation of crystal regions which consist of cluster accumulations of ionized copper acceptor impurity surrounded by space charge regions created by ionized chlorine atoms. The observed peculiarities of the transport phenomena and the character of relaxation process are explained in the framework of the two-barrier model of a non-uniform semiconductor with high-ohmic inclusions in low-ohmic matrix. In the high temperature range (T>400 K) the reversal of Hall coefficient sign connected with the transition to the hole-electron impurity conduction was discivered after double doping of the n-ZnSe crystals.

D-I/P32

THE NEW METHOD OF THE VAPOUR PRESSURE INVESTIGATION OF LOW-VOLATILE PHASES, A. Zavrazhnov, D. Turchen, E. Goncharov, M. Fedorova, Voronezh State University, 394000 Voronezh, Russia

The method which makes it possible to generalized the vapour pressure investigations on the low-volatile phases is under discussion in the present paper. The essence of this method is in the possibility to obtain of the phase diagram as a result of the measurement of the P-T dependence in the equilibrium, that appeares when the non-saturated vapour of the foreign volatile substance injects with the charge of the investigated system.

This substance is chosen so that the temperature control equilibrium could: a) - allow to control the shift of the charge composition at a sacrifice in selectively absorbtion one of the phase-formed elements of the charge by the vapour; b) - be accompanied by the change of the quantity of the moles in the vapour phase. One way to express this equilibrium is: $(1/x)\ A_nB_{m(s)} + (L\text{-}I/I)AC_{L(g)} = (1/x)\ A_{n-x}B_{m(s)} + (L\text{-}I/I)AC_{L-1(g)}$ (1).

It has been shown, that the integral vapour pressure in the equilibrium (l) is an amplified signal from the immensely small values of the partial pressure of the intrinsic components of investigated system. At the present work the method of thermodynamical calculation, which is able to obtain the binary phase diagram from the experimental data beloning to the equlibrium (1).

D-I/P33

COMPUTATIONAL MODELLING OF EUTECTIC TRANSFORMATION IN TERNARY SYSTEMS WITH INTERSTITIAL ELEMENT, O.M. Barabash, Insitute of Metal Physics, National Ukrainian Academy of Science, Vernadsky pr. 36, Kiev 252142, Ukraine

Phase equilibrium in ternary systems with interstitial elements were simulated using quasichemical model of substitutional solid solutions which contains interstitial element in its octahedron intersites. In the framework of this model there were determined interstitial atom's concentration and temperature of alloy's desintegration depending on the concentration of alloying element. The melt was described by means of regular solutions model. The expressions for free energy as for interstitial phase as for intermetallic were written in the supposition, that solubility of other elements in this phase is small. Peculiarities of eutectic reaction resulting in the formation of two solid phases from the melt were studied: metallic matrix and fibres or lamellae of interstitial phase. In usual binary or quasibinary systems this reaction is nonvariant and takes place at constant temperature and concentration. In multicomponent systems such transformation occupies the whole region of concentrations and occurs in certain temperature interval. Computer simulation was performed using the system of the equations which determined equilibrium between the melt and solid solution; and also between the melt as with interstitial phase, as with carbon, as with intermetallic compound. The results of computer simulation in three and four component systems were experimentally confirmed.

D-I/P34

APPLICATION OF A SIMPLE MODEL TO THE STUDY OF NON-ADIABATIC ELECTRONIC TRANSITIONS IN SOME MATERIALS, D. Mathieu, CEA-Le Ripault, DXPL/CPX, Laboratoire d'Ingénierie Moléculaire, BP 16, 37260 Monts, France and P. Martin, CISI, Aéropôle, Im. Rafale B, 1 rue Charles Lindbergh, 44370 Nantes-Bouguenais, France

Recently, a simple TDSCF model has been presented, devoted to the study of the parameters influencing the rate of non-adiabatic electronic transition in some materials (D.Mathieu, in: Programme and Abstracts of the Conference «Ab initio calculation of complex processes in Materials pp 79-80, Schwäbisch-Gmünd, Germany, 1996). In order to retain the simplicity of the model, only weak non-adiabaticity can be treated. However, this is no severe limitation for our purpose, namely the investigation of the electronic response of energetic materials to strong impacts. Results of early simulations on model systems are presented here, after a brief description of the approximations involved and the computational implementation. Since clusters are used as model systems for condensed matter, the convergence of the results with respect to clusters size is monitored. In addition, it is shown that relevant parameters are the ratio between electronic and nuclear frequencies and the range of variation of interatomic distances. The rate of non-adiabatic transitions further depends on several factors whose influences are discussed.

D-I/P35

MESOSCOPIC STUDY OF LASER ABSORPTION BY A TRANSPARENT CERAMIC, R. Mendes Ribeiro, M.M.D. Ramos, Departamento de Fisica, Universidade do Minho, Larga do Paço, 4709 Braga Codex, Portugal, A.M. Stoneham, Physics Department, University College London, Gower Street, London WC1E 6BT, UK

The understanding of the processes occurring on the target in Pulsed Laser Deposition (PLD) is crucial for a fast optimisation of the deposition parameters in order to obtain high quality thin films. Phenomenon occurring in the target like the ejection of large particulates that deposit on the substrate or the formation of a rough cone shape morphology that affect the deposition process can not be understood in the framework of atomistic simulations, since the processes involve very large volumes. Integration of the heat equations don't seem to be the appropriate approach for the study of PLD, since it ignores the actual means by which the energy is transferred to the target and ransported through it.

Mesoscopic modelling provide solutions in an intermediate scale where both results from atomistic studies and methods characteristic of macroscopic modelling are used. We are developing a mesoscopic model for PLD. In this paper, we show the results for the evaporation of a transparent material in which only structural defects can absorb light. The preliminary results show that the electric fields generated play a dramatic role in the process.

D-I/P36

EXACT GROUND STATE CALCULATION FOR 2D RANDOM-FIELD SYSTEMS: EVIDENCE FOR A PHASE TRANSITION, U. Nowak and J. Esser, Theoretische Tieftemperaturphysik, Universität Duisburg, 47048 Duisburg, Germany

Exact ground states are calculated with an integer optimization algorithm for the two dimensional random-field Ising ferromagnet (RFIM) with Gaussian-distributed random fields. We investigate the critical behavior at zero temperature by a detailed finite size scaling analysis.

It is widely believed that in the thermodynamic limit, the two dimensional RFIM has no ordered phase for any finite strength of the random fields. Nevertheless, within our simulations we find some evidence for the existence of a zero-temperature phase transition. The critical value of the width of the random field distribution determined by finite size scaling analysis is $fc \approx 0.6$. By our method, four critical exponents of this unexpected transition can be calculated unindependently, fulfilling appropriate scaling relations.

D-I/P37 A COMPARATIVE STUDY OF THE ELECTRONIC BAND STRUCTURES OF SOME MERCURY AND THALLIUM CUPRATE SUPERCONDUCTORS, F. Studer and B.R. Sekhar, CRISMAT-ISMRA, 14050 Caen Cedex, France

Understanding of the nature of the electronic states near the Fermi level in HTSC materials is one of the vital informations in elucidating a comprehensive theory for high Tc superconductivity. Many of the predictions of band structure calculations on these materials have been shown to be correct by recent high resolution photoemission and resonance Raman scattering experiments. Particularly, the nature of Fermi surface and anisotropy of the superconducting gap in certain high symmetry directions of the Brillouin Zone have been found to be in general agreement by both calculations and experiments. Thus these band structure calculations have been quite sucessfull in representing the electronic structure of HTSC materials, within the inherent limitations of the method. Among these materials, the Tl and Hg cuprates take much attention due to their similarities in electronic structure near the Fermi level. This similarity arises mainly from the hybridization of Hg states with the apical oxygens. Here we present a comparative study of the band structures of some Tl and Hg cuprate superconductors calculated using local density approximation (LDA) and the linear muffintin orbital method (LMTO) in the atomic sphere approximation (ASA). We discuss the observation of the Tl/Hg-O band crossing E_f and the degree of self doping in these materials. We have also compared our results with those of calculations using other methods.

D-I/P38 AB INITIO STUDY OF THE ELECTRONIC AND ATOMIC STRUCTURE OF THE Ag/MgO(100) INTERFACE, Yu.F. Zhukovskii(1,2), E. Heifets(3), E.A. Kotomin(1,4), and R.M. Nieminen(2), (1)Institute of Solid State Physics, University of Latvia, 8 Kengaraga, 1063 Riga, Latvia, (2)Laboratory of Physics, Helsinki University of Technology, 1 Otakaari, 02150 Espoo, Finland, (3)Dept. of Chemistry, University of California, Davis CA 95616, USA, (4)Institute of Physics and Astronomy, Aarhus University, 8000 Aarhus-C, Denmark

Adhesion properties of noble metals on oxides are studied rather poorly. In this paper, we present results for the atomic and electronic structures of the Ag/MgO(100) interface calculated using an ab initio Hartree-Fock computer code CRYSTAL with the DFT electron correlation corrections. One to three silver layers atop three layers of MgO substrate are calculated using a slab model. The band structure, electron density distribution and densities of states are analyzed in detail for isolated and interacting slabs of silver and MgO. The energetically most favourable adsorption position for Ag atoms is found to be above the O atoms of the substrate with the binding energy of 0.20 eV per interface atom and the equilibrium Ag-O distance of 2.64 Å for a Ag monolayer, and 0.4 eV for three Ag layers. The adhesion energy arises mainly due to the electrostatic interaction of substrate atoms with a complicated charge redistribution in the metal film, characterized by large quadrupole moments and electron density redistribution towards the gap position in the middle of the nearest Ag atoms. To improve the quality of the results, we introduced in the present study special pseudofunctions centered in such the gap positions with a preliminary optimized basis set for both silver bulk and slabs.

D-I/P39 A COMPARATIVE STUDY OF THE ATOMIC AND ELECTRONIC STRUCTURE OF DEFECTS IN OXIDE CRYSTALS: AB INITIO AND SEMI-EMPIRICAL STUDY, E.A. Kotomin(1,2), N.E. Christensen(2) and R.I. Eglitis(1,3), (1)Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga 1063, Latvia, (2)Institute of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark, (3)Universität Osnabrück - Fachbereich Physik, Germany

We give a review of recent large-scale atomistic simulations of point defects in three oxide crystals: highly ionic MgO, partly ionic Al_2O_3 (corundum) and rather covalent perovskite $KNbO_3$. The ab initio, full potential LMTO method and semi-empirical method of the Intermediate Neglect of the Differential Overlap (INDO) were used and combined with cluster and supercell models for defects. We discuss advantages/disadvantages of different models and methods and illustrate this by results for similar defects - F centers (O vacancy which trapped two electrons) in the three materials mentioned. It is demonstrated how the electron density distribution and absorption/luminescence energies depend on the covalency of the chemical bonding of a host crystal. We apply these methods for the detailed theoretical simulation of diffusion motion of F-type centers and interstitial O atoms in oxide crystals. On the basis of our calculations, we suggest the mechanisms of defect diffusion, calculate the relevant activation energies and give interpetation of existing experimental data.

D-I/P40 SPIN DYNAMICS STUDY IN SOLID C_{60}: AB-INITIO MOLECULAR ORBITALS CALCULATION OF ONE- AND TWO-CENTER INTEGRALS, Y. I. Prilutski, Dept. of Physics, Kiev Shevchenko University, Vladimirskaya Str., 64, 252017 Kiev, Ukraine

Calculation of one- and two-center integrals which arise at the investigation of spin dynamics (spin-lattice relaxation processes, photoconductivity, transfer energy) in solid C_{60} is carried out. Ab-initio MNDO and group theory methods were used for our computer simulation. Representations of group I_h for fullerene C_{60} were shown to have standart basis sets of matrix elements of irreducible representations that may be used as coefficients of molecular orbitals expansion in terms of atomic ones. The results of calculation have been compared with available experimental data on the spin dynamics in solid C_{60}.

D-I/P41 THE MONTE CARLO MODELLING OF FLUCTUATIONS OF HOT ELECTRON CURRENT IN MILLIMETRE-WAVE UNIPOLAR DEVICES, V. I. Yatskevich, Belarusian State University of Informatics and Radioelectronics, vul. Petrusya Brouki 6, 220027 Minsk, Belarus

The main source of the noise in semiconductor devices is the current fluctuation which generates in both semiconductor material, and contacts. The diffusion noise arises in semiconductors where the electric field becomes stronger. Using the Monte Carlo techniques we investigate in this work the hot electron diffusion noise in the GaAs millimetre-wave unipolar devices—diodes and transistors. The doping levels in the analysed devices are 7.10^{23} (m^{-3}) and more. The devices' length is 1.2 µm.

The influence of ionised impurity scattering on the noise in the GaAs unipolar devices is discussed in this work. The accent in this work had been put on the fact that the electron scattering on ionised impurities plays an important role in hot carrier diffusion noise of the millimetre-wave devices based on high doped gallium arsenide. It is shown that the main influence of this scattering on noise properties in the device has up to three times saturation field. The noise characteristics investigations in the millimetre-wave FET with quarter-micrometer gate were analysed.

D-I/P42 MODELING OF InSb AND InAs WHISKERS GROWTH, I.A. Bolshakova, T. A. Moskovets, I.P. Ostrovskii, A. S. Ostrovskaya, A.I. Klimenko, State University «Lvivska polytechnika», 1 Kotlyarevgkii str., 290013 Lviv, Ukraine

The present work deals with modeling of growth process of InAs and InSb whiskers. They are used as miniature sensors for magnetic field measurement. For this purpose it is very important to obtain the whiskers with sizes and properties predicted beforehand.

The whiskers are grown by CTR method in a sealed tube with use of iodine as a transport agent. The whisker diameters range from 3 to 10 µm for InSb and from 20 to 80 µm for InAs. Due to mathematic simulation of growth process the main kinetic parameters of the systems have been estimated. The calculation was carried out assuming both VLC and VC mechanism of whisker growth. The dependence of growth rate on the whisker diameters has been determined. For the whiskers of low diameters (InSb system) only Hibbs-Tomson effect was taken into account. As a result, their growth rates increase at a diameter growth. For whiskers of large diameters (InAs system) it should be accounted the effects taking place in liquid-crystal interface as well as a distribution of vapour oversaturation along the tube. The whisker diameters are larger, the growth rates are lower.The kinetic coefficients found (b = $1.1\text{-}10^{-1}$ cm/c for InAs and b = $3.7\text{-}10^{-2}$ cm/c for InSb) indicate that growth rate of InAs is larger than the correspondent rate of InSb whiskers, which is in good agreement with the experimental data.The activation energy of whisker crystallization has been estimated (E= 69 kJ/mol for InSb and 134 kJ/mol for InAs). A comparison of these data with activation energy of bulk material growth indicates in participation of VLC mechanism of whisker growth.

D-I/P43 COMPUTER MODELING OF MICROSTRUCTURE-PROPERTIES OF BARIUM TITANATE CERAMICS, Z.S. Nikolic, V.V. Mitic, Lj. Kocic, Faculty of Electronic Engineering, University of Nish, PO Box 73, 18000 Nish, Yugoslavia and M.M. Ristic, Serbian Academy of Science and Arts, Knez Mihailova 35, 11000 Belgrade, Yugoslavia

Processing of ceramic materials depends on an improved understanding of essential basic mechanisms and their influence on microstructure evolution and on the final materials properties. A particularly interesting approach to better understanding of action of elementary mechanisms and the causality between barium titanate ceramics microstructrures and its properties would be the determination of the qualitative and quantitative effects by applying modeling and simulation of some characteristics of microstructure. Computer modeling offers the possibility of model experiment interaction too. In that sense, we have applied the numerical modeling and the fractal geometry method for controlling barium titanate microstructure characteristics. The computer calculated properties were compared with experimentally observed data.

D-I/P44 THEORETICAL STUDY OF CHARGE-INDUCED DEFECTS AT METAL-POLYMER INTERFACE, M.M.D. Ramos, J.P.P. Almeida, Departamento de Fisica, Universidade do Minho, Largo do Paço, 4709 Braga Codex, Portugal

Conducting polymers have attracted much attention concerning the possibility of their use as active components of electronic devices. As in other areas, theoretical modelling can play an important role in understanding of charge injection at metal-polymer interface.

We use a molecular dynamics method with semi-empirical quantum chemistry at CNDO (complete neglect of differential overlap) level to study the chemical interactions between aluminium and transpolyacetylene atoms during the interface formation.

Our results show charge transfer between metal and polymer. When polyacetylene is put in contact with aluminium, charge flows from or to polyacetylene shifting one-orbital energies until the Fermi level of both materials is in coincidence. Charge injection leads to a charge-induced structural relaxation of the free-defect trans-polyacetylene backbone and a polaron type defect is created.

D-I/P45 COMPUTER MODELING OF VIBRATIONAL MODES FOR ANISOTROPIC CRYSTALS, O.V. Stachiv, C.C. Tovstyuk, State University "Lviv Politechnika", Bandera Steet 12, 290646 Lviv, Ukraine

The applied computer program of phase velocities, phonon frequences and polarization vectors of accustical phonons for solid states with certain symmetry and any singony is represented. The continual approximation and Jakobi method are assumed. The input datas are: elastic tensor, density, atom weight. The vibration spectra of Te, graphite ß modification of such layered crystals as GaS, GaSe, InSe . The results show a specific, non-monotonic dependance of vibrational modes in layered crystals LC, which differs from other anizotropical crystals. It also shows the absence of pure logitudinal mode and presence of one pure transvertional mode with perculiar points in LC. For some crystals the perculiar axis, which are not following from symmetry conditions are followed. The computer program includes reference datas for 20 materials and subprogram of heat capacity and Debye temperatures. It can be useful while experiment results treating for different materials.

D-I/P46 THE ENERGY BAND STRUCTURE EVALUATION FOR DIAMOND WITHIN THE NEW COMPLETELY ORTHOGONALIZED PLANE WAVES METHOD, S.V. Syrotyuk, Y.E. Kynash and I.S. Sobchuk, Department of Electrophysics, State University "Lviv Polytechnic", 290646 Lviv 13, Ukraine

The energy band spectrum of diamond crystal has been evaluated within the new completely orthogonalized plane waves(COPW) method, in which the unknown crystal states are represented on mixed basis of core and COPW-states. The linear transformation creating COPW-states from plane waves(PW) is unitary, and therefore we deal with charge density in contrast with OPW approach. The COPW basis is norm-conserving over the crystal in contrast to the ab initio atomic pseudowave functions that show this property only in the free atom. The COPW pseudopotential does not depend on searched energy in contrast to OPW one. Other advantages of suggested method are analysed. The obtained data are compared with those evaluated by means of model local and non-local pseudopotentials, ab initio atomic core norm-conserving pseudopotentials and other approaches.

D-I/P47 ELECTRONEGATIVITY EQUALIZATION SCHEME AS ALTERNATIVE TO MIEDEMA - de BOER RELATION FOR MULTI-COMPONENT ALLOY, Y.A. Zelenin, Odessa State Marine University, Dpt.Technical Cybernetics, 34 Mechnicov Street, 270029, Odessa, Ukraine

The relationship between fundamental R.G.Pearson - R.G.Parr /PP/ Hard-Soft Acid-Bases/HSAB/ Electronegativity Equalization principle in the form /EE/ Charge Transfer Energy equation /CTE/ of W.J.Mortier type and empirical A.R.Miedema - de Boer /MB/ relation for entalphies of formation of the binary alloy are established.

It is shown that there is clear correspondence between these theoretical methods, namely—the EE-scheme of PP type gives identical to MB relation for binary alloy, if one consider the chemical hardness is equal to the volume of Wigner - Zeitz crystal cell in negative 1/3 power. The novel analytical formulas for CTE of three - component alloys is obtained and written in MB functional form.

It is important to note that, the new CTE functional is not of an additive or catastrophic evident type. The extension of the present approach on a multi - component alloys are briefly discussed.

D-I/P48 ANALYSIS OF TELEVISION IMAGES OF PHYSICAL OBJECTS WITH THE HELP OF THE METHOD OF CUTS, T. Protasova and A. Borisenko, Sumy State University, 2 R.-Korsakov St. 244007 Sumy, Ukraine

When taking analysis a image of a physical object, for example, a thin film, in many cases it is necessary to pick out more informative tones of the image and to remove noises. The method of cuts is proposed for that procedure. A half-tone image is separated into bright levels (cuts), the damaged and useless levels are taken out, and analysis is carried out for the rest ones. Besides the different cuts can be combined building a necesssary for analysis configuration that can improves quality and decrease time of analysis.

D-I/P49 PHYSICAL MODEL AND COMPUTER SIMULATION RESULTS OF DEGRADATION OF THE Si/SiO_2 STRUCTURE DURING ANNEALING AND HYDROGEN PLASMA TREATMENT, G.V. Gadiyak, Institute of Computational Technologies, Russian Academy of Sciences, Siberian Branch, Lavrentjeva 6 Street, Novosibirsk 630090, Russia

In this paper it is suggested a theoretical model and numerical results for description of the behavior of each of the three Pb varieties and new defect centers L. (P_b) at the (111) interface, P_{b0} and P_{b1} at the (100) interface). It was used the following set of the chemical reactions:

$$P_b + H \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_b - H, \qquad (1)$$

$$P_b - H + H \overset{k_3}{\Rightarrow} P_b + H_2, \qquad (2)$$

That to explain experiments the author introduced new hydrogen-related defects L near Si/SiO_2 interface. They are trapping centers for hydrogen and take place the same (2) chemical reaction. For P_b and new defect centers L we used rate equations and for mobile species (atomic and molecular hydrogen) we used diffusion equations which was solved numerically. We can explain experiments by vacuum annealing and remote hydrogen exposed samples and obtained good agreement with experiment.

D-I/P50 THEORETICAL MODEL AND COMPUTER SIMULATION RESULTS OF ENHANCED DIFFUSION OF HIGH-TEMPERATURE IMPLANTED ALUMINIUM IN SILICON CARBIDE, G.V. Gadiyak, Institute of Computational Technologies, Russian Academy of Sciences, Siberian Branch, Novosibirsk 630090, Russia; A.V. Suvorov, Cree Research Inc., Durham NC 27713, USA

Wide application of SiC films in microelectronics devices makes especially important predictions of the doping profiles during and/or after thermal treatment. A macroscopic kinetic model of enhanced diffusion of aluminum in SiC films during ion bombardment at high temperature has been considered. The set of equations describing the kinetic model takes into account generation Si- and C- dangling bonds during bombardment, breaking of Si- bonds, formation of C-Al and Si-Al bonds, formation of mobile Si and C atoms, diffusion of the mobile species (Aluminum, Carbon, and Silicon) to the surface their reactions with Si- and C- dangling bonds as well as their evolution from the film. Numerical simulation of the equations has allowed to find the total concentration profile of Al implanted into SiC, the concentration profile of Al atoms on C- and Si- dangling bonds, the concentration profile of mobile Al atoms and the flux of Al from the film. We obtained a good agreement with experimental data.

D-I/P51 NEW THEORY OF THE THERMAL OXIDATION OF SILICON, G.V. Gadiyak, Institute of Computational Technologies, Russian Academy of Sciences, Siberian Branch, Lavrentjeva 6 Street, Novosibirsk 630090, Russia

The growth kinetics of SiO_2 films on silicon is developed. Our model is based on an oxygen incorporating into Si-Si bonds during thermal oxidation and chemical reactions being occured in narrow reaction layer. A simple model of oxidation takes into account the reactions occurring in bulk and at the two interfaces of the oxide layer as well as the diffusion process for atomic oxygen and diffusion approximation for calculation of the coefficients of kinetic reactions. We compare the predictions of an oxidation rate model that we have developed with the available experimental data for both the thin and thick oxide regimes, O_2 and N_2O ambient as well as Deal-Grove and other models. The relationship is shown to be in excellent agreement with oxidation data obtained over a range of temperature (800-1200 C), and oxide thickness (6-400 Å) for O_2 and N_2O ambient oxidation and different pressures.

D-I/P52 PERSONAL COMPUTER-AIDED DESIGN OF PLASMA SPRAYED MATERIAL LAMELLAR STRUCTURE, O.P. Solonenko, A.L. Sorokin, A.P. Zinoviev and S.M. Gel'fand, Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences, Institutskaya 4/1, 630090 Novosibirsk, Russia

The problem - oriented dialogue programme complex for direct computational experiment in the chain «plasma torch - powder injection - high-temperature dusted jet - coating» is described in the context of formation of the lamellar structure of sprayed materials. Particular emphasis has been placed on the physico - mathematical models forming the base of the above- mentioned subsystems, and on the level of their up-to-date program realization for computer- aided design and optimization of the plasma spray and related technologies.

The dialogue programme complex provides: (i) engineering calculation of linear scheme dc plasma torches, (ii) simulation of powder injection into plasma flow and calculation of gasdynamic parameters of the heterogeneous plasma flow for the nozzle exit section, (iii) 2d Eulerian and Lagrangian modelling high-temperature subsonic jet of complex gas composition with admixture of polydisperse particles, including the interaction with a normally placed substrate, (iv) simulation of unsteady-state conjugate conductive-convective heat transfer between flattening and solidifying melted particle and substrate, (v) prediction of the regularities of sprayed material formation (lamellar structure, macroporosity, dynamic of coating growth) dependent on the statistical distributions of particles velocity, temperature, aggregate state, and size over the spraying spot.

D-I/P53 MOLECULAR DYNAMICS SIMULATION OF SHOCK LOADING OF EAM IRON, A.B. Belonoshko, Institute for Earth Sciences, Uppsala University, 75236 Uppsala, Sweden

The Earth's core is believed to consist mainly of iron. Knowledge of iron melting curve is of primary importance for construction of global Earth models. There are two experimental approaches allowing to study iron melting at pressures of Earth's core: the shock wave (SW) and diamond anvil cell (DAC) techniques. A more detailed understanding can be gained through atomistic modeling of relevant processes. We modeled shock wave experiments on iron melting using a parallel implementation of EAM molecular dynamics method on IBM SP2 computer. We concluded that there is a possibility that as called the «low» melting curve corresponds to plastic flow of material generated by non-hydrostatic stresses. Therefore, it is possible, that iron melting curve is significantly higher than it was established during last several years with diamond anvil cell technique.

D-I/P54 MOLECULAR DYNAMICS SIMULATIONS OF SPALLATION IN METALS AND ALLOYS, W.C. Morrey and L.T. Wille, Department of Physics, Florida Atlantic University, 777 Glades Road, Boca Raton, FL 33431, USA

We report on the results of large-scale molecular dynamics simulations of the mechanical behavior of two-dimensional metallic systems. The specific impact phenomenon studied is that in which a flyer of mass M moving with x-velocity v impacts a target of mass 2M moving with x-velocity -v. Simulations of such a spallation experiment have been performed for a generic metal, modelled with an Embedded Atom Potential and also for a Cu-Ni alloy system, modelled with truncated Lennard-Jones potentials.

Our simulations indicate cold-welding upon impact, and shock wave generation, followed by rebound from the boundaries. The alloy was less ductile than the generic metal and consequently the system came apart due to the cooperative effect of the reflected shock waves.

D-I/P55 SIMULATIONS OF THE ELASTIC RESPONSE OF SINGLE-WALLED CARBON NANOTUBES, C.F. Cornwell and L.T. Wille, Department of Physics, Florida Atlantic University, 777 Glades Road, Boca Raton, FL 33431, USA

Using the Tersoff-Brenner potential we have performed molecular dynamics simulations of nanotubes in compression. These large-scale simulations are performed on a MasPar massively parallel computer. The elastic response is investigated and an expression for Young's modulus is derived from the simulations. Typical failure modes are also shown and discussed.

Thursday June 19, 1997
Jeudi 19 juin 1997

Afternoon
Après-Midi

Poster Session II
16:00-18:00

D-II/P1 STRUCTURAL AND ELECTRONIC PROPERTIES OF YPO_4 AND $Ca_{10}(PO_4)_6Fe_2$, V. Louis-Achille, L. De Windt and M. Defranceschi, IPSN, CEA-FAR, BP 6, 92265 Fontenay-aux-Roses, France

Calculations have been performed using the local density approach with 'soft core' pseudopotential and a plane wave basis for the structural and electronic properties of two iono-covalent type solids: the xenotime YPO_4 which is structurally related to monazites and the fluoropatite $Ca_{10}(PO_4)_6F_2$ which is the simplest apatite.

The geometry is optimised mixing two numerical criteria : the minimisation of the total energy and the annulation of the pressure calculated from the stress tensor. The computed lattice parameters, bulk modulus and cohesive energy are in good agreement with the experimental data.

The interplay between ionic and covalent bonding is investigated through the electronic properties. The self-consistent band structures have been calculated along the high symmetry directions of the irreductible Brillouin zone. Calculations have been performed on densities of states. The results are analysed and discussed.

Finally, a prospective discussion on the potential of such materials in accepting structural defaults is given.

D-II/P2 INTERACTION OF CU(111) SURFACE STATES WITH DIFFERENT EXTENDED DEFECTS, A. Barral and A.M. Llois, Departamento de Fisica, FCEN-UBA, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Nowadays it is possible to probe and manipulate surfaces in the nanometer and even atomic range using scanning tunneling microscope. It is then interesting to follow the evolution of surface states and the appearance of quantum well states on transition metal surfaces in the presence of a variety of extended defects. In this contribution we study the interaction of the Shockley surface state in the Γ point of Cu(111) with periodic arrangements of adsorbed atoms. Numerical results are obtained for periodic arrays of rows and 2D-patterns using Cu and Fe as adsorbates and also for steps of varying width. We use an spd tight-binding hamiltonian for which the local basis is enlarged to account for electron spill over.

D-II/P3 ENERGY ELECTRONIC BAND-STRUCTURE OF METALLIC LITHIUM IN THE FIELD OF EXTERNAL EXCITATION, V. Popov, General Physics Department, Altai State Technical University, Lenin St 46, Barnaul 656099, Russia

Modern band theory assumes that the energy structure of electrons experiences no significant changes when the atoms are thermally excited. The present paper discusses the most important variations in the band structure of the electrons in metallic lithium. Lithium was chosen as the object of investigation for two reasons. First, this metal has been studied fairly well both experimentally and theoretically, so that it can be considered a suitable test material. Second, thanks to the anomalies in the elastic properties of lithium at high pressures and low temperatures discovered in experiments and the theoretical predictions of the transition of lithium to a magnetically ordered state at large values of the lattice constants there is an unflagging interest in this material.

A procedure is developed that allows for exact calculations of the band energy of a solid in the Hartree-Fock approximation The starting point is a self-consistent calculation that employs a Gaussian basis of functions. The method is used to establish the energy structure of the electrons in metallic lithium as a function of temperature. The calculated density of states, Fermi surface, optical conductivity, the K-edge of the X-ray emission spectrum, and other properties of the electrons agree with the experimental data. Small variations in the band energies for lithium are discovered. The most important ones are the broadening of the core electron states and the transition of outer-shell electrons from s-symmetry states to p-symmetry states as the temperature grows

We investigated the influence of vacancies and s-, p-, d-impurities on the electronic band structure of metallic lithium. The influence of d-impurities is the most significant.

D-II/P4 COMPUTER SIMULATION OF A THERMOACTIVATED PROCESS OF ATOMIC STRUCTURE RECONSTRUCTION IN THIN FILMS, M.D. Starostenkov, O.V. Andruhova, N.V. Lomskikh, A.V. Borisov, N.M. Gurova, Dept. of General Physics, Altai State Technical University, Lenin St. 46, Barnaul 656099, Russia

In quasi-two-dimensional approximation using stochastic methods a thermoactivated process of structure reconstruction in binary thin films with compositions AB and A_3B and stable of stratified and netlike thin films (monoatomic layers are altemate with the chess structure AB) was investigated depending on external and internal conditions, atomic interaction radius and vacancies concentration (diffusion occur by vacancies mechanism). Possible mechanismes of atomic disorder in thin films were established: point defects, clusters and segregations, micro-domains and antiphase boundaries with structures peculiarity on them. The temperature dependencies of some characteristics (long- and short- order parameters, corelation functions, APB thickness and length ...) It was established the geterophase fluctuation is preceded to phase transition (diffuse phase transition take place). Depending on topology of monoatomic phase it is observed: l) at the case of stratified structure the erosion of monoatomic phase follow more slow than in netlike case; 2) at netlike case monoatomic phase is condense in the center of the periodical unit.

D-II/P5 COMPUTER MODELLING OF GRAIN BOUNDARIES IN Ni_3Al, M.D. Starostenkov, B.F. Demyanov, S.L. Kustov, E.G. Sverdlova, E.L. Grakhov, General Physics Dept; Altai State Technical University, Lenin st. 46, Barnaul 656099, Russia

In this work studies simmetric tilt grain boundaries (GB) with an axis of turn [001] in Na_3Al with L12 superlattice. Computer simulation of GB with S=5 (012) and S=5 (013) was carried out using Morse's empirical central-force potentials The calculations of energy of GB was carried out in rigid model, in which the atoms are in sites of crystalline lattices. The initial structures of GB were chosen coincidence with geometrical model of a coincidence site lattice (CSL). For each GB was constructed g-surfaces.

The g-surfaces for GB (012) and (013) have the essentially different forms of rellef. Each g-surface has the several minima corresponding to the different stables GB. For plane (012) there are three types of GB: GBl and GB2 have a plane of symmetry one-atomic and two-atomic accordingly, third type has antiphase GB. The results of accounts are compared to CSL model. Accounts have shown, that the atomic configuration GB appropriating to model CSL is unstable. Such GB has higher energy. The transition in stable state is realized by displacement on some vector f. The power barrier of transition is absent. In plane (012) all GB have three variants of transition distinquished by a direction displacement and a depth of a power minimum. The directions of displacement are: [021], [12 2 1], [14 2 1]. Energies of GB dependent from vektors of displacement and limited from 9.22 to 5.34 Jm^{-2}.

D-II/P6 EVOLUTION OF SOLITON OF TENSION IN POLYMER CRYSTAL. N.K.Balabaev, Institute of Mathematical Problems of Biology, RAS, Pushchino Moscow Region; L.I.Manevitch and E.A.Zubova, N.N. Semenov Institute of Chemical Physics, RAS, Moscow, Russia

It is believed now that a number of important processes in solid polymers can be realized only by motion of specific - «zero-dimensional» - structural defects which can propagate along the chains of a polymer with a constant velocity. As an example, it turns out that if one is pulling a chain from a crystal, a minimum expenditure of energy is achieved by passing a soliton of tension through the chain and not by shifting the chain as a whole. The solitonic mechanism of pulling of a chain can be of considerable importance in the processes of mechanic degradation, premelting and plastic deformation of polymer crystals.

Up to now all the results in the area have been derived in the approximation of «immobile neighbours», i.e. are rested on the assumptions that chains neighbouring to one with a soliton hardly change their positions, and that their motion has no effect on the dynamics of solitons In the present work we first compare the evolution of a subsonic soliton of tension by its passing through a chain surrounded by immobile and mobile neighbours. To do that we have elaborated the three-dimensional molecular-dynamical model of polyethelene crystal with provision for the both possibilities.

D-II/P7 ELASTIC AND SUPERELASTIC PROPERTIES OF FEM-BASED PERCOLATION SYSTEMS: LONG STRIP AND BAR TRANSFER MATRIX SIMULATION. V.G. Oshmyan and S.A. Timan, N.N. Semenov Institute of Chemical Physics, Moscow, Russia

Numerical modeling of elastic percolation requires solving of extremely large algebraic systems with jumps in coefficients. Iterative methods become unsatisfactory as convergence is too slow.

Transfer matrix algorithm has been applied to simulate elastic and superelastic behavior of FEM-based percolation systems on 2D square and triangular lattices. Each cell of underlying lattice is considered as finite element and is filled by rigid or soft isotropic elastic solid with respective probabilities p and (1-p). Elastic thresholds p_e and critical exponents of macroscopic stiffness T (elastic problem) and S (superelastic problem) have been estimated using phenomenological renormalization of computer simulation data on long strip and bar geometry.

In the case of the square lattice, computed value of S is in a good agreement with results predicted by spring-like models, whenever estimate of T is considerably lower. Unusual Poisson ratio extreme-type dependence upon p with minimum at elastic threshold and sharp maximum near geometrical one is discovered.

Comparison of results of numerical simulation on triangular and square lattices should clarify the fundamental problem of universality of mechanical critical exponents.

D-II/P8 COMPUTER MODELING OF DIELECTRIC PROPERTIES OF BARIUM TITANATE CERAMICS, V.V. Mitic, Z.S. Nikolic, Lj. Kocic, Faculty of Electronic Engineering, University of Nish, PO Box 73, 18000 Nish, Yugoslavia and M.M. Ristic, Serbian Academy of Science and Arts, Knez Mihailova 35, 11000 Belgrade, Yugoslavia

There is a growing interest in the electronic industry for new high performance ceramic materials such as barium titanate ceramics. In that sense, the subject of the present investigations was computer modeling of the interrelation between the structure, influence of additives, and final dielectric properties of barium titanate ceramics. The effects of the pressing pressure, sintering temperature and additives CeO_2 and $MnC0_3$ on the barium titanate structural characteristics were investigated. SEM has been used for detailed examination of microstructure. The interrelations between technological parameters, such as pressing pressure and sintering temperature, and structure, as well as structure and dielectric properties of pure barium titanate and with additives can be significance in farther defining of dependencies between material structure constituents, grain and pores, and dielectric properties of barium titanate ceramics.

D-II/P9 COMPUTER MODELLING OF DIELECTRIC LAYERS EMPA, V.A. Moshnikov, A.I. Rumyantseva, A.I. Rybnikov, NPO CKTI Polytechnicheskaya st. 24, St Petersburg, Russia

EPMA of dielectric and high resistance semiconductor layers could be realized with the help of model based on standard Monte-Carlo procedure. The main approximations are: local electric charge is concentrated in sphere with a center on a depth Zo; the charge distribution law is exponential. Value of electrical field strength, calculated in three-dimensional space is used for correction of calculated formula for electron brake ability in given point of space and also for determination of power losses before electrons entry the sample. The feature of this model is the availability of condition of self-coordination between experimental data and model's parameters (sphere diameter, depth of sphere center, etc.).

D-II/P10 NEW MANGANESE OXIDE PHASE FOR LITHIUM BATTERIES, D. Bloch, D. Warin, CEA/CEREM, Laboratoire de Stockage Electrochimique de l'Energie, 38054 Grenoble, France and F. Le Cras, P. Strobel, CNRS, Laboratoire de Cristallographie, 38042 Grenoble, France

The Li-Mn-O spinel phase appears of great interest for constituting the cheap cathodic material of lithium batteries for electric vehicules, this phase must be synthesized at sufficiently low temperature in order to achieve a good electrochemical activity during cycling of the battery.

This paper discuss the successive reactions which occur during the complete solid state transformation of ß-MnO_2 in presence of lithium salt into a Li-Mn-O spinel phase at temperatures as low as 150°C. A new intermediate manganese oxide based phase is detected with an original crystal structure between initial ß-MnO_2 used as the precursor and the final spinel phase obtained usually in a presence of excess of lithium salt at higher temperatures.

The physico-chemical and structural characteristics of this new phase have been measured. The electro chemical behaviour during lithium intercalation has been investigated with liquid and solid polymer electrolytes: the performances have still to be improved in the case of the liquid electrolyte.

D-II/P11 THEORETICAL INVESTIGATION OF OXYGEN DEFECTS IN SiC, A. Gali(1), P. Deak(1), R. Gutierrez(2), A. Sieck(2), Th. Frauenheim(2); (1)Technical University of Budapest, Department of Atomic Physics, Budafoki ut 8, 1111 Budapest, Hungary, (2)Technische Universität Chemnitz, Institut für Physik, Reichenhainer-Str. 70, 09107 Chemnitz, Germany

SiC exhibits wide range of physical and chemical properties to make it suitable for use in high temperature, high power and high frequency semiconductor applications. However, relatively little is known about how common impurities may influence its electronic properties. Oxygen inevitably appears in SiC, due to the natural surface oxides and the manufactured oxide layers in semiconductor devices. Almost nothing is yet known about the behaviour of oxygen in bulk SiC. To examine it, we have calculated various oxygen point defects in SiC with semi-empirical PM3, ab initio LDA, and Density-Functional based tight-binding methods. We have determined the equilibrium sites of oxygen and its effect on the electronic structure. The barrier energies of single oxygen interstitial, and the local phonon modes were also calculated.

D-II/P12 POSSIBLE n-TYPE DOPANTS IN DIAMOND AND AMORPHOUS CARBON, S. Pöykkö, M. Kaukonen, M.J. Puska and R.M. Nieminen, Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

It has been extremely difficult to produce n-type conducting diamond, whereas it seems that n-type conducting tetrahedrally bonded amorphous carbon (ta-C) can be obtained using phosphorous or nitrogen as dopant. In this work we have studied substitutional, group V, VI and VII atoms N, P, O and Cl and complexes formed by these impurities and native defects in diamond and ta-C using first-principles electronic structure methods. Electronic structure calculations reveal the differences between ta-C and diamond in the microscopic level and should thus ease the experimental search for a way to produce n-type conducting diamond.

D-II/P13 TREATMENT OF ELECTROSTATIC INTERACTIONS AT THE Si - SiO_2 INTERFACE, S. A. Prosandeyev, Department of Physics, Rostov State University, 5 Zorge st., 344090 Rostov on Don, Russia; G. Boureau and S. Carniato, Laboratoire de Chimie Physique, Matière et Rayonnement, Université Pierre et Marie Curie, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Silica in equilibrium with silicon is known to be partly cristalline. Because of crystallographic constraints, models proposed so far (cristoballite as well as tridymite) deal with polar surfaces of silica, which are expected to be highly unstable. In this paper, using both exact treatments of simplified models and Monte-Carlo simulations of the real system with effective potentials, we show how the system compromises to decrease the electrostatic energy. We also investigate the role of electrostatic interactions on the formation of oxygen vacancies at the Si-SiO_2 interface. Using a tight binding approach, implications of these interactions on mid-gap surface states in silica are also discussed.

D-II/P14 SIMULATION OF SILICA AND OF ITS INTERFACE WITH SILICA, N. Capron, A.K. Lagraa, S. Carniato and G. Boureau, Laboratoire de Chimie Physique, Matière et Rayonnement, Université Pierre et Marie Curie, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

In spite of the spectacular development of ab initio calculations, effective potentials retain attractive features: they are quick, convenient and cheap. This is particularly true in the field of the simulation of defective silica and of its interface with silicon. From surface-sensitive, high resolution Si2p core level spectroscopy with synchroton variation, it has been shown, several years ago, that silicon at interface presents different oxygen states. In a first step, we have defined criteria and evaluated the ability of different effective potentials and of ab initio calculations to simulate the defective silica. In a second step, we have performed Monte-Carlo simulations of the Si/SiO_2 interface using different effective potentials, including tight binding potentials and compared the obtained informations with the results of ab initio simulations.

D-II/P15 A COMPUTATIONAL MODELLING FOR THERMOPLASTIC AND MECHANIC-THERMOPLASTIC DEFORMATIONS OF ORGANIC MATERIALS-AN ATTEMPT, N. Moldovan(1), J. Mohr(2), M. Ilie(1), S. Nedelcu(1), P. Ruther(2), (1)IMT-Bucharest, PO Box 38-160, 72225 Bucharest, Romania, (2)FzK, Postfach 3640, 76021 Karlsruhe, Germany

Two phenomena have been studied, as being involved in the intermediate or final steps of polymer microlenses manufacturing process: a thermoplastic one (the partial melting of PMMA cylinders) and a mechano-thermoplastic one (the compression molding of PC cylinders).

Experiments have been performed, physical models have been elaborated, numerical approaches have been done in order to define the process parameters and to predict the final shape of the microstructures .

The results are compared and discussed, the limits of the proposed models are revealed.

The work was accomplished in the frame of the PECO-HCM program «Microfabrication with synchrotron radiation» (1995-1997)

D-II/P16 AB INITIO CALCULATION OF EXCITONIC EFFECTS IN REALISTIC MATERIALS, S. Albrecht(1), G. Onida(2), L. Reining(1) and R. Del Sole(2), (1)CNRS-CEA, Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau, France, (2)Dipartimento di Fisica, Università di Roma "Tor Vergata", 00173 Roma, Italy

Ab initio calculations, based on the Density Functional Theory (DFT) in the Local Density Approximation (LDA), allow for the description of the ground state properties of a wide class of materials. Also one-quasi-particle excitations, like the insertion of an electron or hole which determines the bandstructure, can be obtained with good precision by adding self-energy corrections to the DFT-LDA eigenvalues. A realistic description of two particle excitations, like the creation of electron-hole pairs in absorption experiments, has up to now been hardly feasible for systems where the electron and the hole interact. In this work we show how such excitonic effects can be included in ab initio electronic structure calculations, via the solution of an effective two particle equation. Results are presented for the calculation of the binding energies of excitons in lithium oxide Li_2O. The application to the construction of the absorption spectrum of semiconductors is discussed. It is shown how this method allows to analyse the nature of the excited states and the effect of the electron hole interaction on their charge distribution. This point is illustrated at the example of a silane (SiH_4).

D-II/P17 LDA AND TIGHT-BINDING: TOTAL ENERGY CALCULATIONS OF POLY-PARA-PHENYLENE, M.Miao, V.E. Van Doren, P.E. Van Camp, University of Antwerpen (RUCA), Dept. of Physics, Groenenborgerlaan 171, 2020 Antwerpen, Belgium; G. Straub, Los Alamos National Laboratory, MS B221, Los Alamos NM 87545, USA

The total energy of PPP as a function of the dihedral angle has been calculated in a LD approximation (Perdew-Zunger) as well as in a simple tight-binding model. The LDA calculations predict a stable conformation of the chain for a torsion angle of 34.8° and a potential well depth of 1.5 kcal/mole with respect to the energy of the planar conformation. The LDA direct band gap is 2.54 eV in good agreement with experimental results. The tight-binding model uses only nearest neighbor interactions and universal coupling constants as determined by Harrison and Straub. This model shows clearly that the torsion is due to the attractive Π-binding and the steric Coulomb repulsion. It also shows that the band structure strongly depends on the geometry.

D-II/P18 CALCULATION OF $A(Xe)_N$ ATOMIC WIRE RESISTANCE, L. Pizzagalli, IPCMS-GEMME, 23 rue du Loess, 67037 Strasbourg, France; C. Joachim, CEMES, 29 rue Marvig, 31055 Toulouse, France and X. Bouju, C. Girard, LPM URA 772, Université de Franche-Comté, 25030 Besançon, France

Recently, Yazdani and co-workers have succeeded in measuring the resistances of $(Xe)_1$ and $(Xe)_2$ wires with a STM tip [Yazdani et al, Science 272 (1996) 1921]. We calculated the resistances of Such $(Xe)_N$ nanoscopic wires within a STM junction modelized by a tip of ten copper atoms and a copper surface. In order to improve the understanding of the experimental curves, the dynamical behavior of the Xe atoms is considered for the shortest wires, $(Xe)_1$ and $(Xe)_2$. In this last case, we start molecular mechanics calculation with one Xe atom on the surface and the other under the tip apex. We find a resistance of 0.06 $M\Omega$ for the $(Xe)_1$ wire, in agreement with the experience. We show that the resistance of the $(Xe)_2$ wire ranges between 10 $M\Omega$ and 30 $M\Omega$ and that a precise determination is not possible due to mechanical deformations and interference effects. Finally, we study longer wires and found that their conductive properties are close to the properties of an alkane chain.

D-II/P19 COMPUTER SIMULATION STUDY OF NONREGULATING SOLIDS STRUCTURE, V.V. Glazkov, R.V. Bochkova, V.I. Dyakonova, Mordovian State Institute of Teacher Training, 430007 Saransk, Studencheskaya Street 11-a, Russia

It is not insufficient the dates of direct experimental results for full characterizing the structure of nonregulating solids. Computer simulation is the important method which successfully amplifies the results of direct experimental methods and in series of cases gives more full results.

The simulation results of structure of silicate glasses $0.69SiO_2$ $0.27M_2O$ $0.04Nd_20_3$ (M=Li, Na, K) and $0.69SiO_2$ 0.27P $0.04Nd_20_3$ (P=Mg, Ba) are described in present report. Structure models were built by Monte Carlo method which based on application of known effective empirical potential of interaction. The simulation procedure consists in following.

N points which symbolized atoms are randomly scattered in cube with side equal L. The length of cubic side is determined by density of simulated glass. The potential energy of all ions interaction is calculated as the sum of energies of pair interactions.

The basic part of algorithm is composed from relaxation of model giving atom configuration which may be considered as element of canonical ensemble under temperature T. The relaxation process is realized by random displacement of ions.

Periodical boundary conditions are used. After each test displacement the change of full configuration energy of system ΔE is calculated. If the energy lower then initial the test displacement is took into account. If the energy raiser then initial but quantity $\exp(-\Delta E/kT)>t$ (t - random number from interval [0,1]) the test displacement is took into account too. Test displacement is rejected if this conditions are not implemented.

Analysis of builting models is consisted in calculation of their structure characteristics: pair correlation function, dependence of middle coordination number on distance and others.

D-II/P20 A NEW MODEL OF DLA UNDER HIGH MAGNETIC FIELD, H. Mizuseki, K. Tanaka, K.Kikuchi, K. Ohno and Y. Kawazoe, Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

A new Monte Carlo model is introduced to describe the Diffusion-Limited Aggregation (DLA) with extra forces arising from the Lorentz' s and/or Coulomb forces. Furthermore, we simulate a behavior of multiparticle diffusive aggregation to examine the resultant pattern of crystal in the electrochemical deposition. Specific patterns grown under the external force are produced by Monte Carlo simulation. In the present model, the basic movement of particles is the random walk, with different transition probabilities in different directions, which characterize stochastically the effect of the extra forces. In case assuming high magnetic field, pattern-formations which are qualitatively different from the standard DLA model are observed and they are successfully compared with preexisting experiments [1]. The present numerical results of electrochemical deposition show that the generated patterns strongly depend on the force of ion and the concentration of it [2].

[l] I. Mogi et al., J. Phys. Soc. Jpn. 60 (1991) 3200.
[2] Y. Sawada et al., Phys. Rev. Lett. 56 (1986) 1260.

D-II/P21 ANGLE DEPENDENCE AND DEFECT PRODUCTION IN METAL-ON-METAL CLUSTER DEPOSITION ON SURFACES, C. Félix, Bell Lab., Lucent Technologies, Murray Hill, New Jersey 07974-0636, USA and IPE, EPFL, 1015 Lausanne, Switzerland; C. Massobrio, IPCMS, 23 rue du Loess, 67037 Strasbourg, France; B. Nacer and T. Bekkay, Univ. Cady Ayyad, Faculté des Sciences Semlalia, Dépt. de Physique, LPSCM, Marrakech, Morocco

Cluster deposition experiments on solid surfaces are of fundamental and technological importance since they allow to fabricate unconventional structures characterized by novel and interesting properties. Atomic-scale simulations can be a useful complement to these investigations, by providing guidelines to optimize the experimental parameters. Here we use molecular dynamics to analyze the dependence on the impact angle of the distribution of defects originated by the deposition of a Ag_{19} cluster on Pd(100) at four different initial kinetic energies (0.1 eV, 2 eV, 20 eV, 95 eV) . For increasing energy the cluster undergoes, upon deposition, a transition from a three-dimensional, multilayered adsorbed structure to a two dimensional one. Interestingly, implantation of Ag atoms and promotion of Pd substrate atoms is common to all energies and angles, and for a given initial total kinetic energy, it increases with decreasing impact angle. Our results are discussed in light of experimental findings recently obtained on the same system.

D-II/P22 THE INFLUENCE OF ELECTRON SPECTRA MODELING ON CRYSTAL POLARIZABILITY, O.V. Stachiv, C.C. Tovstyuk, State University "Lviv Politechnika", Bandera Steet 12, 290646 Lviv, Ukraine

The electron-phonon interaction and it`s influence on vibration modes of layered materials is investigated. The Frelich approximation and comparison of Fivas one-partical dispertion and parabolical laws are included. The vibration modes renormalization and relaxation time dependence on interlayered mixing is investigated. The results show the existance of peculiar point in vibration spectra for Fivaz modes modulation and it`s absence for parabolic once. For assimptotical cases two- and three-dimentional isotropic spetra we `ve got the same vibration modes dependences and relaxation time. The spectra modeling influences sufficiantly relaxation time.

D-II/P23 THE EVALUATION OF MICROSTRUCTURE OF GAS SENSITIVE LAYERS BASED ON SnO_2<J>, D.V Sharonov, M.V. Bestaev, D.Tz. Dimitrov, V.A. Moshnikov, M.F. Panov, Dept.of Microelectronics, State Electrical Engineering University, 5 Prof. Popova St., 197376 St Petersburg, Russia

Results on simulation of production of micropores in thin film samples are presented. Microstructure variations dependent upon the initial supersaturation level of the vacancy solution are considered. The time and size distributions of the pores are estimated. The calculation results have been used to improve the selectivity of the gas sensitive SnO_2 layers. The initial supersaturation level was obtained by varying the concentration of the high partial pressure impurity. The pores were produced by sublimation of the impurity while isothermal annealing in the inert gas flux. The calculation results have been compared with the microscopy and ellipsometry experimental data.

D-II/P24 FIRST-PRINCIPLES INVESTIGATIONS OF THE ELECTRONIC, OPTICAL AND CHEMICAL BONDING PROPERTIES OF SnO_2, Ph. Barbarat and S. F. Matar, CEA Le Ripault, Dépt. Matériaux, BP 16, 37260 Monts, France

The electronic structure of the rutile-type oxide SnO_2 is examined self-consistently using the augmented-spherical-wave (ASW) method within the density-functional theory (DFT). The influence of hybridization between the different l-states on the chemical bonding is discussed from the density-of-states (DOS) and the crystal-orbital-overlap-population (COOP) results. A description of the nature of chemical bonding in SnO_2 is provided along with the investigation of the optical properties. An overall agreement was found between the calculated and the experimental optical properties in the ultraviolet spectrum.

D-II/P25 ON A MULTIPLE SCALE CONTINUUM ENERGY FORMULATION, APPPLICATION OF INTERFACIAL PROPERTIES IN MATERIALS SCIENCE, N. Daher, Laboratoire de Physique et Métrologie des Oscillateurs du CNRS, associé à l'Université de Franche-Comté-Besançon, 32 av. de l'Observatoire, 25044 Besançon Cedex, France

In the last decades some efforts have been devoted to the study of surface and interface phenomena in complex structures where mechanical, thermodynamical and electromagnetic properties are simultaneously taken into account with their coupled effects and interactions. In addition, some relations between discrete, atomic and continuum models have been developed. In particular, phenomenological approaches based on the laws of continuum physics including discontinuities and interfacial, physical properties have been devised. It has been shown that the different models suffer from some mathematical inconsistencies and there is also a need for a generalization of the Green-Gauss and transport theorems well-known in the bulk but only partially established at interfaces.

Firstly, we recall the different inconsistencies, then, a general solution is presented. Finally, a special attention is devoted to the modeling of complex structures such as those exhibiting an electromagnetic ordering encountered in media like ferroelectric dielectrics and semiconductors. Moreover, volume and surface phenomenological parameters are related to discrete atomic models.

D-II/P26 COMPUTER SIMULATION OF TRANSPORT AND NOISE PROPERTIES OF NON-LINEAR INHOMOGENEOUS MEDIUM, D.V. Shantsev, O. Shalaev, R.A. Suris, Ioffe Physico-Technical Institute, 194021 St Petersburg, Russia

We report on computer simulation of transport and noise properties of non-linear inhomogeneous medium. We considered a model system with nonlinearity given by the following simple law: resistance is zero when current I is less than some critical current I_c and resistance is constant for $I>I_c$. Such a model system can be relevant for describing properties of a wide class of physical materials, for example, weak links in films of high temperature superconductors. An inhomogeneous medium consisting of elements with different critical currents has been studied. Analytical results for the system can be obtained for the region close to the percolation threshold only. Direct computer calculation is also impossible because of discontinuity of I- V characteristics. We developed a new method allowing the determination of current density spatial distribution in such a medium. It is based on subsequent consideration of media consisting of elements with nonlinear I-V charcteristics of special form. Calculations for 2D square networks of up to 30x30 elements have been conducted and validity of theoretical predictions in the framework of percolation theory and effective medium approach is discussed. It is shown that such a system exhibits anomalous noise behaviour near the percolation threshold.

D-II/P27 MODELING OF CHARGE ACCUMULATION IN MNOS STRUCTURES WITH NONSTECHIOMETRIC OXIDE SUBLAYER, J.O. Lichmanov, RPC «Lepton», p/b 19, 103489 Moscow, Russia; V. M. Maslovsky, O. I. Kazmin, S. A. Kazmina, A. N. Subotchev. Zelenograd State Research Physical Problems Institute, 103460 Moscow, Russia

This work is devoted to development of model for charge accumulation in silicon nitride of MNOS-structures while tunnel injection of carriers to silicon nitride through oxide layer take place. Some regions of this oxide adjacent to interphase boundaries are nonstechiometric. In this work it was used model [l] where electrons are captured both by positively charged centers and by neutral traps. To determine injection current dependence on electric field magnitude in oxide it was used preliminary determination of tunnel penetration of barrier with arbitrary form that is dependent on initial nonstechiometry and electric field magnitude. To compute tunnel penetration of barrier with arbitrary form it was used splitting of such barrier on set of rectangular barriers. The results of numerical modeling show the possibility of rather significant reduction of accumulation time and increase the steepness of the temporal characteristics of charge accumulation. When nonstechiometric region width w is nearly zero numerical modeling shows the results that similar to the results obtaining for the case of Fowler-Nordheim injection current. When nonstechiometric region width w is 1 nm the accumulation time is decreased more then order of magnitude.

1. V.M. Maslovsky, E.V. Simanovich. Prolonged storage of electrons in MONOS-structures. Mat. Res. Sos. Symp. Proc. V.284 (1993)159-166.

D-II/P28 THE AB-INITIO STUDY OF THE ELECTRONIC STRUCTURE OF LITHIUM AZIDE, A.B. Gordienko, A.S. Poplavnoi, Kemerovo State University, Krasnaya 6, Kemerovo 43, 650043, Russia

The results of the implementation of computational scheme based on the density functional theory which incorporates the basis of true psedo-atomic orbitals and the application of this approach for studying the electronic structure and related properties of lithium azide (LiN_3) are presented. The compounds similar to that of LiN_3 refer to the ion-molecular crystal type and can serve as the model objects to study the reguliarities of chemical reactions in solids. To investigate the energy structure of these crystals one has to apply the computational methods which are adaptable enough to describe highly localized states of the molecular anion that is placed into a crystal. The pseudo-atomic-orbital scheme with no parameters, used by the authors, appears to be a suitable one.

The results obtained for LiN_3 e.g. total energy, band structure, charge density, full and projected density of states have been compared with experimental data as well as with those of full-electron calculations for crystals and isolated molecules (N_3^-) and are in a good agreement.

D-II/P29 MESOSCOPIC ENSEMBLE, Y.A. Zelenin, Odessa State Marine University, Dpt.Technical Cybernetics, 34 Mechnicov Street, 270029, Odessa, Ukraine

The novel intermediate averaging type of pure quantum mechanical states for molecule as a whole, but not for macroscopic body as a whole in classical thermodynamic, are enunciated in Mesoscopic Ensemble definition contrary to J.W.Gibbs Macroscopic Ensembles /ME/.

The main distinction and analogies are: i. System under averaging- the single molecule. Total ME is only single copy of Canonic J.W.Gibbs ensemble - the single macroscopic body. ii. External condition - the first coordination shell of molecule in condensed phase includes: external electrostatic potential, electron chemical potential, the covalence affinity. iii. meso-state definition - average occupancies of natural state of molecule: atomic net charges and bond order matrix, average nuclear coordinates. iv. phase - determined experimentally molecule immersed in condensed body.

The total basis of molecular responses for single diatomic-bond model and Legendre transformed Total Energy functional are presented. General form equation connected Mesoscopic and Macroscopic level of averaging presented. The interplay between Isomorphic (1994) DFT R.G.Parr's Ensemble and Mesoscopic Ensemble are briefly discussed.

D-II/P30 MODELING OF KINETIC OF IZOVALENCY DOPING OF GaAs BY Bi IN THE PROCESS OF GROWTH FROM CHLORIDE GAS-TRANSPORT SYSTEM, V. A. Voronin, S. K. Guba, Lviv Polytechnic State University, Bandera street 12, Lviv 290046, Ukraine

In the prezent work we have decided the problem of nonequilibrium izoelektron doping in the chloride gas-transport system. This decision is based on the using of adiabatic parameter, which reflect the existence of the slowand quick of the heterogeneous chemical reactions described the processes of growth and doping the rezults of the kinetic processes analysis are the equations connected the concentrations of the izovalency admixture and the lokal concentrations of the components and of the temperature.

D-II/P31 A NEW METHOD FOR STUDYING THE INFLUENCE OF THERMAL TREATMENT ON OCCUPANCY PERCENTAGES OF OXYGEN ATOMS IN THE (CZOCHRALSKI) SILICON LATTICE, M.A. Misdaq, H. Erramli, R. Elassali, R. Charik, Nuclear Physics Techniques Laboratory, Faculty of Sciences Semlalia, B.P. S15, University Cadi Ayyad, Marrakech, Morocco; G. Blondiaux, CERI-CNRS, 3a rue de la Férollerie, 45071 Orléans Cedex, France

Occupancy percentages of oxygen atoms at trace levels in the Czochralski silicon lattice have been determined by irradiating the crystal with a 3.1 MeV ^{3}He beam and exploiting ratios of channeled to random yields for the <100>, <110> and <111> directions. The ^{16}O (^{3}He, p) ^{18}F nuclear reaction was used and the ^{18}F yield was measured by direct gamma-ray spectrometry. The influence of thermal treatments on oxygen atom occupancies of interstitial sites has been investigated by analysing virgin and thermally treated (under a nitrogen atmosphere) silicon samples.

D-II/P32 MONTE CARLO SIMULATIONS OF SYSTEMS WITH MAGNETOVOLUME INSTABILITIES, M.E. Gruner and P Entel, Theoretische Tieftemperaturphysik, Gerhard-Mercator-Universität - GH - Duisburg, 47048 Duisburg, Germany

We perform Monte Carlo simulations of a spin-analogous model which describes coupled spatial and magnetic degrees of freedom and chemical disorder on a fcc lattice. Our calculations reproduce the anomalously low or high thermal expansion (Invar or anti-Invar effect, respectively) and other magnetovolume effects like a softening of elastic constants or a broadened and flattened anomaly of the specific heat at the magnetic phase transition as observed e.g. in several iron and manganese based alloys and complexes. In analogy to the 2- γ-states model proposed by Weiss, which describes the behaviour of some iron based alloys, we connect this anomalous behaviour of manganese alloys with two different states of the manganese atom: One state with a large magnetic moment and a large lattice constant (High Moment State, HM) and another with a small magnetic moment and a smaller lattice constant (Low Moment State, LM). The model which we use is an Ising-like model which can reproduce both, the HM state and the LM state. The elastic properties of the alloy are described with the help of Lennard-Jones pair potentials being different for the HM state and the LM state, respectively.

D-II/P33 SEMI-EMPIRICAL TIGHT-BINDING INTERATOMIC POTENTIALS BASED ON THE HUBBARD MODEL, Q. Xie, Max-Planck-Institut für Physik komplexer Systeme, Bayreuther Strasse 40, Dresden, 01187, Germany

By use of the perturbation method for the Hubbard model, we discuss the contribution of the interatomic electron correlations to the cohesive energy in terms of the bond order potential. With this idea and the first-order approximation for the bond order, we present a semi-empirical tight-binding model for the interatomic potential. Based on this model, the influence of the on-site Coulomb interaction on materials properties such as the phase stability, the vacancy formation, the Cauchy pressure and the elastic anisotropy ratio is studied, and it is shown that although being a pair functional one, the present model can be used to describe the bcc transition metals without resorting to angular bonding. Moreover, the model is applied to calculating the epitaxial Bain paths of vanadium, niobium and tantalum, and it is predicted that vanadium and niobium have a metastable tetragonal phase while tantalum has a plateau across the fcc phase. The model implicates that the effect of electron correlations may play an important role in the prediction of mechanical properties of the solids with half-filled or nearly half-filled bands.

D-II/P34 SPIN-FLIP CONTRIBUTION TO THE CONDUCTIVITY OF MAGNETIC MULTILAYERS, R. Gomez Abal, A.M. Llois and M. Weissmann, Departamento de Fisica, Comision Nacional de Energia Atomica, Avda. del Libertador 8250, 1429 Buenos Aires, Argentina

The conductivity of magnetic multilayers, such as Co/Ni, Co/Cu and Co/$Cu_{1-x}Ni_x$, is calculated within the semiclassical approximation. The band structure is obtained with a tight-binding Hubbard Hamiltonian solved in the Hartree-Fock approximation. Once selfconsistency is reached, the spin-orbit coupling term is added and a further diagonalization is performed.

As it is well-known, quantum well states appear in the band structure of superlattices. By calculating the conductivity as a function of the energy we find that there is a large influence of these quantum well states when their energy is close to the Fermi level and the spin-orbit coupling is taken into account.

D-II/P35 COLOSSAL MAGNETORESISTANCE IN MANGANITES, P. de Boer and R. de Groot, Electronic Structure of Materials, Katholieke Universiteit Nijmegen, PO Box 9010, 6500 GL Nijmegen, The Netherlands

The ferromagnetic manganites $A_{1-x}B_xMnO_3$ (A a trivalent element and B divalent) have been subject of intensive study in the past few years. These manganites exhibit colossal magnetoresistance (CMR), i.e. their resistance can drop several orders of magnitude under influence of an external magnetic field.

Electronic structure calculations show that these manganites are half-metallic: they are conducting for one spin direction but insulating for the other spin direction. The half-metallic behaviour is essential for the physical properties: The colossal magnetoresistance results from a percolation problem near the Curie temperature, where the correlation length diverges.

D-II/P36 ON THE STABILITY OF ANTIFEROMAGNERIC CONFIGURATION OF A ONE MONOLAYER Fe FILM ON Co(001), A. Mokrani, LPME EA 1153 DS4, 2 rue de la Houssinière, 44072 Nantes, France and O. Elmouhssine, G. Moraïtis, J.C. Parlebas, C. Demangeat, IPCMS-GEMME, 23 rue du Loess, 67037 Strasbourg, France

Würsch et al. [to appear in Phys. Rev. B 55 (1997)] have recently observed through spin-polarized low-energy electron diffraction combined with in situ Kerr magnetometry and a model calculation that a six monolayer (ML) thick fcc Fe film undergoes a reversible transition from a room-temperature paramagnetic state to a low-temperature phase including antiferromagnetically coupled planes. In order to study the possibility of an intralayer antiferromagnetic coupling of the atoms, the magnetic structure of a one ML-thick Fe film on a fcc Co(00l) substrate, is calculated ab initio. Two different types of intralayer spin ordering of the Fe atoms are investigated: the ferromagnetically ordered Fe layer with both parallel and antiparallel couplings to the Co magnetization and the c(2 x 2) ferrimagnetic spin configuration. The calculations are performed using the tight-binding linear muffin-till orbital method in the local spin density and atomic sphere approximations.

D-II/P37 NON COLLINEAR MAGNETISM AND EXCHANGE COUPLINGS IN FeCo/Mn SUPERLATTICES, C. Cornea and D. Stoeffler, IPCMS-Gemme, 23 rue du Loess, 67037 Strasbourg, France

Recent experimental works on FeCo/Mn multilayers have exhibited a large biquadratic couplings and a net magnetic contribution of the antiferromagnetic Mn spacer. We realize a systematic study of the non collinear magnetic behaviour of Fe_xCo_{1-x}/Mn_n superlattices for various Fe concentrations x and Mn thicknesses n. The electronic structure is determined in the tight-binding framework using the real space recusion technique including non collinear magnetism.

In this paper, we present calculations of the coupling energy as a function of the relative orientation between the magnetization direction $\Delta\theta$ of successive Fe_xCo_{1-x} layers. For these studies we have to determine self-consistently the magnetic moment vectors distributions for each value of $\Delta\theta$ in the range $[0, \pi]$ with a very good accuracy in order to obtain very well converged total energies $E(\Delta\theta)$. We do first the calculation for $\Delta\theta = 0$, $\pi/2$ and π and we interpolate the converged charges, magnetic moments and angles for having nearly converged stating points for the other angle values. It is then possible to obtain rapidly $E(\Delta\theta)$ curves with a lot of calculated points allowing a precise analysis of the coupling energy. We show that non collinear magnetic solutions are the most stable for Fe_xCo_{1-x} layers with high Co concentrations.

D-II/P38 DETERMINATION OF MAGNETIC MOMENT VECTORS DISTRIBUTIONS IN FeCo/Mn SUPERLATTICES, C. Cornea and D. Stoeffler, IPCMS-Gemme, 23 rue du Loess, 67037 Strasbourg, France

It has been shown recently that FeCo/Mn multilayers present very interesting magnetic properties related to non collinear orders in the Mn spacers (large biquadratic couplings, net magnetic contribution of the antiferromagnetic Mn spacer). A complete electronic structure study of Fe_xCo_{1-x}/Mnn superlattices is under progress since two years in our group in the tight-binding framework using the real space recusion technique.

In this paper, after a brief presentation of the calculations we do, we focuss mainly our attention on the angular convergence of the magnetic moments directions and we discuss the accuracy for the determination of the energy. We compare usual input/output mixing schemes to more complexe predictive techniques for the angular relaxation. We show that the more rapid and easy to use convergence scheme consists in a combination of (i) usual mixing for the charges and the magnitude of the moments and (ii) extrapolations of the variations of each local angle during simple mixed iterative calculations. We give a few examples of comparisons between convergences obtained using only mixing and using the new mixing/extrapolation combinated techniques. We discuss also the stability and the acceleration of the angular convergence for the second technique.

D-II/P39 MAGNETIC STRUCTURE OF DEFECTS AT THE Fe/Cr INTERFACE ROLE OF NONCOLLINEARITY, N.S. Yartseva, Institute of Metal Physics, GSP-170, Ekaterinburg, 620219, Russia, V.M. Uzdin, St Petersburg State University, CAPE, V.O. 14 linia, 29 St. Petersburg 199178, Russia and C. Demangeat, IPCMS, 23 rue du Loess, 67037 Strasbourg, France

Different kinds of space defects on the background of ideal smooth interface in Fe/Cr multilayers, such as steps, embedded clusters, pinholes, random interface roughness, are investigated within model Hamiltonian approach. Calculations of magnetic structure are performed in the Habbard Model (HM) and in the Periodic Anderson Model (PAM) in mean field approximation by recursion method in the real space. Modification of the PAM for a description of non-collinear structure is developed. It allows to compare the results of calculations obtained in collinear approximation in the HM and the PAM with the results of noncollinear PAM theory for the same kinds of defects. Such comparison shows the restrictions of collinear approach for a description of real interface structure and clarifies the role of magnetic frustrations in a formation of noncollinear order. Information about the angular dependence of hyperfine fields on Fe atoms in Fe/Cr superlattices obtained by means of Mössbauer spectroscopy technique is discussed within the frame of developed theory of noncollinear magnetic structure.

D-II/P40 NON-COLLINEAER DISTRIBUTION OF MAGNETIC MOMENTS IN IMPERFECT Fe/Cr SUPERLATTICES, M. Freyss, D. Stoeffler, H. Dreyssé, IPCMS-GEMME, 23 rue de Loess, 67037 Strasbourg, France

The determination of the electronic structure of very large and complex systems is out of reach of the ab initio methods, which require too large a computing time. On the other hand, semi-empirical methods allow the calculation of the magnetic order in systems with numerous atoms and without symmetry properties.

By means of such a method, namely a d-band tight-binding model, we were able to calculate the non-collinear magnetic order in Fe/Cr superlattices with interfacial monoatomic steps. The study of such a system is of particular interest because of the many recent experimental results. In particular, the observed non-collinear exchange coupling between the Fe layers is believed to be due to the presence of steps at the interface. No experimental technique has yet permitted to determine the distribution of magnetic moments in such a system and to understand the influence of the steps on the magnetic order and the exchange coupling.

Our calculations show how the magnetic moments in the Cr spacer rearrange so that the magnetic defect induced by the step is very localized. Moreover, we show that the presence of steps do yield a non-collinear coupling between the Fe layers, as before assumed.

D-II/P41 RELATIVE STABILITY OF AN ON-TOP AND AN INVERTED Mn MONOLAYER ON Ag(100): EXPERIMENT AND THEORY, O. Elmouhssine, G. Moraïtis, J.C. Parlebas, C. Demangeat, IPCMS-GEMME, 23 rue du Loess, 67037 Strasbourg, France and P. Schieffer, C. Krembel, M.C. Hanf, G. Gewinner, LPSE, 4 rue des Frères Lumière, 68093 Mulhouse, France

Mn films with a thickness of one monolayer have been deposited in ultra-high vacuum, at room temperature (RT), on a Ag(100) single crystal. Photoemission and ion scattering spectroscopy data indicate that after Mn evaporation a substantial fraction of the Mn atoms is located within the second topmost atomic layer. If the film is left at RT or mildly (330K) annealed, the Mn atoms tend to exchange further with Ag atoms, increasing the Mn concentration in the second atomic plane. Eventually the second atomic plane of the sample is constituted mainly by Mn atoms, whereas the first atomic layer is almost a pure Ag plane, i.e. an inverted atomic Mn monolayer is formed. In order to directly compare experiment and theory, we have performed calculations to study the stability of $Ag_1/Mn_1/Ag(100)$ versus $Mn_1/Ag(100)$. The calculations are performed with the 'ab-initio' tight-binding linear muffin-tin orbital method. The case of 2ML-thick MnAg alloy on Ag(100) is also investigated. The surface and interface magnetism as well as the relation between magnetism and stability of Mn films are discussed.

D-II/P42 MAGNETISM OF EPITAXIAL 4d TRANSITION METAL MONOLAYERS ON GRAPHITE, P. Krüger, J.C. Parlebas, G. Moraitis and C. Demangeat, IPCMS, 23, rue du Loess, 67037 Strasbourg, France

Recently, Pfandzelter et al. reported the first observation of monolayer ferromagnetism of a 4d metal (Phys. Rev. Lett. 74 (1995), 3467). They grew ruthenium on the graphite (0001) surface, found that the growth was lateral until the first monolayer was completed, and that the overlayer was ferromagnetic below 250 K using spinpolarized secondary electron emission spectroscopy.

Here we investigate the possibility of magnetism in 4d transition metal monolayers adsorbed on graphite with the experimentally determined atomic density by first principle calculations. The electronic and magnetic structure of the overlayers is calculated by means of the tight-binding linear-muffin-tin-orbital method. For free monolayers having the same structure as the epitaxially adsorbed ones we find ferromagnetism with large magnetic moments in the cases of ruthenium and rhodium (1.9μ_B and 1.2/μ_B respectively). For the adsorbed ones the possibility of magnetism is studied as a function of adsorption height. The magnetic moments of the overlayer atoms show strong adsorption height and site dependance.

D-II/P43 MAGNETIC PROPERTIES SIMULATION OF Co/Ru INTERFACES, K. Rahmouni, S. Zoll, N. Persat, D. Stoeffler, A. Dinia, IPCMS-GEMME, UMR 46 CNRS-ULP, 23 rue du Loess, 67037 Strasbourg, France

The Co/Ru multilayers have been extensively studied and have shown very interesting magnetic and magnetoresistive properties, like a very high antiferromagnetic interlayer exchange coupling and a very small giant magnetoresistance (GMR). Most of the studies have pointed out that these properties are very sensitive to the quality of the interfaces. To confirm this correlation between the shape of the interfaces and the magnetic properties, we have performed GMR and magnetization simulations on Co/Ru multilayers with mixed interfaces using a linear concentration profile. The magnetic moments profile is determined from the electronic structure with an ab-initio calculations using a large cell: $Co/Co/Co/Co_{0.75}Ru_{0.25}/Co_{0.5}Ru_{0.5}/Co_{0.25}Ru_{0.75}/Ru/Ru$

The GMR is obtained using a semi-classical description of the two spin channel currents. The results of the calculation will be presented in details to show the strong dependence between the magnetic properties and the nature of the magnetic/non-magnetic interfaces. Indeed the decrease of the magnetic moment in the intermixed interfaces may explain the reduced interlayer exchange coupling and GMR as it was expected for perfect Co/Ru interfaces.

D-II/P44 COMPLEX MAGNETIC BEHAVIOR AT THE SURFACE OF B2 ORDERED FeCr ALLOY, F Amalou, H Bouzar, M Benakki, A Mokrani, Institut de Physique, Université de Tizi-Ouzou, 15000 Tizi-Ouzou, Algérie and C Demangeat, G Moraitis, IPCMS GEMME, 23, rue du Loess, 67037 Strasbourg, France

Using a Tight-Binding Linear Muffin Tin Orbitals model, we have investigated the local polarisation at the (001) surface of B2 FeCr alloy. Our calculations were performed using local density approximation and general gradient approximation with Langreth-Mehl-Hu functional for p(lxl) and c(2x2) configurations.

We have considered the two cases of Fe top layer and Cr top layer. For Cr top layer and for p(lxl) configuration, we found the local polarisation at the surface to be ferromagnetically coupled with the subsurface layer and high magnetic moments (2.52μ_B) compared to the bulk values, the magnetisation of the subsurface Fe layer is found to be strongly depressed (0.79μ_B). In the case of Fe top layer, the magnetic moments are: -2.03μ_B for iron surface atoms and O.65μ_B for chromium subsurface atoms, and the local polarisation at the surface is found to be antiferromagnetically coupled with the subsurface, in contrast to parallel coupling between Fe and Cr in bulk FeCr.

D-II/P45 MAGNETIZATION REVERSAL IN FINITE AND INFINITE SQUARE PRISMS, R. Ferré, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67037 Strasbourg Cedex, France

We present first 3D micromagnetic calculations on finite, as well as infinite square prisms as function of the prism width. We observe strong differences between reversal mechanisms in infinite prisms and nucleation/reversal processes in finite prisms. For infinite prisms, the nucleation mechanisms observed are in agreement with former analytical solution of the linearized Micromagnetic equations on cylinders and rectangular prisms [1,2]. For finite prisms, we report substantial differences in the angular dependence of the nucleation fields in comparison to that obtained for finite prisms. Particularly, a nucleation/reversal mechanism triggered by the wire extremities, has been obtained for small prism sizes. This nucleation mode can be regarded as a generalization of the buckling mode to finite lengths. Contrarely as obtained for infinite prisms with large widths, domain nucleation and wall propagation has been found to be the ad hoc reversal mechanism after a curling like nucleation for finite prisms.

[1] A. Aharoni and S. Shtrikman, Phys. Rev. 109 (1958) 1522
[2] W.F. Brown Jr., J. App. Phys. 33 (1962) 3026

D-II/P46 MONTE CARLO SIMULATIONS OF MAGNETIC PROPERTIES IN MULTILAYERS, L. Veiller, D. Ledue and J. Teillet, L.M.A. U.M.R. C.N.R.S. 6634, Faculté des Sciences de Rouen, 76821 Mont-Saint-Aignan Cedex, France

We have used Monte Carlo simulations to study the behaviour of a multilayer system consisting of ferromagnetic Heisenberg layers (A and B) with different interaction constants (J_{AA}, J_{BB}) coupled ferrimagnetically together ($J_{AB} < 0$). Each layer is made up of N atomic planes which are LxL in cross section. Periodic boundary conditions are applied in the plane of the system and free boundary conditions are applied in the bottom and the top planes. Mixed interfaces of the type $A_\rho B_{1-\rho}$ are included to the system. Magnetic exchange interactions (limited to the nearest neighbours) and a crystal-held interaction term are included in the Hamiltonian of the system.

The effects of lattice sizes and exchange interactions on the transition temperature are examined. In particular, substantial changes in specific heat have been noticed. The effects of disordered interfaces and magnetic anisotropy on the transition temperature and spin orientations are also investigated.

Results will be related to the experimental works of rare-earth / transition metal multilayer films.

D-II/P47 RELATION BETWEEN THE MAGNETIC MOMENT AND THE IONICITY IN NiO, S. Doyen-Lang, D. Fristot and J. Hugel, Université de Metz, IPC-LSOM, 1 bd Arago, 57078 Metz Cedex 3, France

The magnetic moment has been investigated in terms of the ionicity within the local spin density approximation. The Kohn-Sham equations have been solved self consistently using a simplified version of the discrete variational method based on a numerical LCAO scheme. The simple LSDA results show close connection between the moment and the ionicity since both quantities vary in proportion. A high charge transfer demands a wide 2p orbital extension for the oxygen. The ionic character splits the 3d metal levels according to the ligand field theory.

The LSDA+U treatment allows the theoretical and experimental gap to match when U is regarded as a parameter. The U correction enhances the crystal field effect by enlarging the gap between the last occupied minority t_{2g} subband and the first empty e_g one. As a result the U values are not spread over a large energy interval but range between 5 and 6 e.V.

D-II/P48 STUDY OF MAGNETIC PROPERTIES OF MOLECULAR SYSTEMS BASED ON ANILINE AND AMINONAPHTHALENESULFONIC ACID, I. Lado Tourino(1), F. Tsobnang(1), M.R. Soriano(2), A. Le Méhauté(1), (1)Institut Supérieur des Matériaux du Mans, 44 avenue F.A. Bartholdi, 72000 Le Mans, France; (2)Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Departamento de Quimica Inorganica, Analitica y Quimica Fisica, Ciudad Universitaria, Pabellon II, 1428 Capital Federal, Argentina

A Density Functional Theory (DFT) study using Becke's exchange functional together with the LYP (Lee, Yang and Parr) correlation functional has been carried out to explore the magnetic properties of molecular magnets based on aniline and aminonaphthalenesulfonic acid.

In this study we consider a model system consisting of two aniline radicals stacked along an axis perpendicular to their molecular plane. Both the effect of distance between aniline molecules and the relative positions of the amide groups on the magnetic coupling have been studied.

The influence of metallic ions placed between the aniline radicals as well as the effect of their position on the magnetic properties of our system has also been analyzed.

D-II/P49 MOLECULAR MODELS OF SLIPPAGE FOR STRAINED PASSAGE MACROMOLECULES IN AN ORIENTED CRYSTALLINE POLYMER, U. Gafurov, Institute of Nuclear Physics, 702 132 Tashkent, Uzbekistan

An elementary act of polymer plastic deformation and of its creep is slippage of molecular chains. An oriented crystalline polymer with homogeneous chemical structure is studied. Models of the thermoactivated slippages of stressed macromolecules and of the relaxation of local loads on amorphous parts of these molecules are presented. The crystalline polymer is considered as two-phasic one with interchanging amorphous and crystalline regions in a microfibrille. For calculations Frenkel-Kontorova's soliton model is used. It is assumed that polymer crystallits are long enough the continuous matter approximation to be applicable.

In dependence on external load and amorphous region length two cases are realized. The first case takes place when the load is moderate. In this case the load on the amorphous section of a slipped out chain are completely relaxed and this section could change its conformation state. In the second case slipped out amorphous part of a macromolecule is in strained state but its strain is less than one of the macromolecule before its slipping out. The energy activation depen- dencies on molecular parameters and the local load are different for the two cases.

D-II/P50 THE MOLECULAR MODEL OF TENSION AND SLIPPAGE OF THE STRAINED PASSAGE MACROMOLECULES IN ORIENTED LINEAR CRYSTALLINE POLYMERS. COMPUTER SIMULATION, U. Gafurov and E. Pestrikova, Institute of Nuclear Physics, 702132 Tashkent, Uzbekistan

The biphase model of linear oriented crystalline polymer as linear polyethylene with real sizes crystalline and amorphous regions was used. This model considered passage macromolecules with strained section in one amorphous regions possessing the free conformational coiled sections in adjacent amorphous regions and the molecular chain with cross chemical bonds or strained loops (entanglement) on crystallite surfaces. With help of computer simulation the numerical calculate of local loads distribution along crystalline section of the strained passage macromolecules to and afterwards thermofluctuation kink formation was conducted. The condition of balance of strained chain in polymer crystallite was made with application of the Frenkel-Kontorova crowdion model. The kink formation is accompanied mechanically stimulation molecular chains slippage and local loads relaxation on them amorphous sections as well as by conformation reorganizations of these sections in some conditions. Is shown that the nature of distribution of local loads, kink form and it evolution in different degree and considerably besides of molecular parameters depend from longitudinal size of crystallits, load on amorphous sections of macromolecules.

The macromolecules slippage with non-loaded section on opposite end of crystallite the kink energy loss is accompanied. While the slippage of fixed passage molecular chain of cross bonds or strained loop (entanglement) on of polymer crystallite surface by increase of energy initial kink is accompanied. At unsufficiently high initial local loads on streined amorphous sections the molecular chain again pull in crystallite. For such chains with growth their tension at increase of external load or at redistribution of local loads in chains sliding processes are created of condition for termofluctation rupture their stressed amorphous sections.

D-II/P51 ROTATION MODEL OF SELF DIFFUSION MOBILITY OF MACROMOLECULES IN CRYSTALLYTES OF FLEXIBLE-CHAIN LINEAR POLYMER, U. Gafurov and V.S. Presman, Institute of Nuclear Physics, Tashkent, Ulugbek 702132, Uzbekistan

The model of the rotation mobility and selfdiffusion of linear macromolecules in the crystallits of flexible-chain polymers (type of polyetylene) has been proposed. It has been taking into account the interconnection of molecular degrees of freedom such as rotations of molecular groups and chain deformation in the intermolecular field. Varying the summary potential energy the expressions corresponding to the condition for chains equilibrium have been found for the considered model. Thus we have got complex nonhomogeneous equation with mixed terms. However, if accept that the solution changes slowly enough, one can restrict oneself only to terms including derivative of the lowest order and their products. In this case the solution is analogous to one of Frenkel-Kontorova's equation.

Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM E

Material Aspects for Electric Vehicles including Batteries and Fuel Cells

Symposium Organizers

Th. HARTKOPF, Technische Hochschule, Darmstadt, Germany

A. MORETTI, RENAULT, Research Department, Trappes, France

J.G. WURM, Waterloo, Belgium

M. WAKIHARA, Tokyo Institute of Technology, Tokyo, Japan

SYMPOSIUM E

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session I

E-I.1 9:00-9:30

TEMPERATURE DEPENDENT ELECTRIC BREAKDOWN STRENGTHS OF OIL IMPREGNATED POLYPROPYLENE CAPACITOR FOILS, A. Schneuwly, P. Gröning, L. Schlapbach, Institute of Physics, Pérolles, 1700 Freiburg, Switzerland. In collaboration with ABB Dattwil and Condis SA in Rossens, Switzerland

Today, thin metallized polymer foils are used in high power capacitors for the dielectric material. The firm Condis uses in its technology segmented, metallized polypropylene (PP) foils. To avoid air enclosures in the capacitor rolls, oil is used as impregnation medium.

To study the influence of the impregnation oil on the polymer foil we measured the diffusion of the oil into the PP foil and determined the electrical behaviour. With oil diffusion, the electric field in the polymer becomes homogeneous, and the breakdown strength of the PP foils increases. Calorimetric analysis shows that the PP foil absorbs about 5 wt.% oil.We studied the electric breakdown strength for impregnated and dry PP capacitor foils at various temperatures. With increasing temperature the breakdown strength decreased. The results show a discontinuity of the breakdown strength in the temperature region around 50°C.

Calorimetric analysis yields information about structural properties of PP capacitor foils. At 50°C a phase transition occurs in the PP because of a recrystallisation of partially crystalline fields. We have found important links between temperature induced structure modifications and the electric breakdown strength. Calorimetric analysis of PP foils after washing out the additives with CH_2Cl_2 proved, that the phase transitions in the PP is due only to the additives. Furthermore, the breakdown strength of PP foils without additives showed no discontinuity at 50°C.

E-I.2 9:30-10:00

USING OF THE ALUMINIUMOXIDE SUBSTRATES FOR THE MICROWAVE ICs, Ul.M. Biahun, V. V. Murav'ev, Ul. M. Parkun, A. A. Tamelo, V. I. Yatskevich, Belarusian State University of' Informatics and Radioelectronics, vul. Petrusya Brouki 6, 220027 Minsk, Belarus, and Al. M. Nikitin, Minsk Research Institute of Radio Materials, 220115 Minsk, Belarus

High quality parameters of satellite and cell communications will be achieved by using hybrid technology of creation of the microwave units of microwave devices. Using high heat conduction aluminum base of substrate is very important at creation microwave circuits including a combination discrete active devices and monolithic circuits. Moreover using aluminiumoxide technology brings the achievement of thin layer dielectric (150μm), that is the reason of decrease of radiation of the parasitic modes, decrease of jagged AFC at connection of the amplifiers with previous monolithic cascades. Al substrates with a high quality dielectric layer based on an anodic Al oxide with the following parameters: maximum dielectric layer thickness - up to 150 μm, dielectric constant - 4÷6, break-down voltage is beyond 1000 V. It allows effectively to use superficial wiring technique, to produce high-integrated microelectronics assemblies in a frequency range between super-lower and super-high frequencies and at improved thermal, mechanical and radiation characteristics and increased ecological purity.

E-I.3 10:00-10:30

MATERIALS SCIENCE FOR THE FUTURE UKRAINIAN MICROELECTRONICS, N.N. Berchenko, M. Skulskyj, «Lviv Polytechnic» State University, 290646 Lviv, Ukraine

For a long time in the training of specialists in the Semiconductor Electronics Department of the «Lviv Polytechnic» Materials Science was limited to studies of Si for integrated circuits and III-V for optoelectronics. Only now Materials Science begins to play here its own role. It is explained not only by the fact that spectrum of materials advanced electronics now uses has extended overwhelmingly, but also by microelectronics industry collapse in the former USSR. Today Materials Science is developing in increasingly more twisted spiral: discovery of new effects necessitates creation of materials with qualitatively new physical properties, but new ideas and visions, in turn, emerge from their research and so forth. This leads to the prediction of new effects or more profound understanding of existing effects (porous Si is a recent example) and so ad infinitum. Future materials scientist must be able to be actively included in any stage of the process what requires broadening of his knowledge of fundamental disciplines crucial for prognostication of new material properties and technological processes and characterization methods which become increasingly more and more sophisticated. But it is a specifics of a specialist for Ukraine that he in first turn must be oriented on applied «small» science where scientific products can be developed without expensive subsidies in modestly equipped laboratories. And he should be trained to be able to accomplish this, beginning from initial conception to marketing of new products.Curriculum specially designed for accomplishing this purpose we would like to present to the attention of the symposium.

10:30-10:45 **BREAK**

E-I.4 10:45-11:15 SURFACE SCIENCE AND ITS ROLE IN ADVANCED MATERIALS EDUCATION, N.N. Berchenko, «Lviv Polytechnic» State University, 290646 Lviv, Ukraine

All-round investigation of the processes occuring at surface and different interfaces has always been occupying a noticeable place in the training of specialists in the Semiconductor Electronics Department of «Lviv Polytechnic». Principal attention, though, was paid to the problems concerning technological characterization and failure analysis of Si integrated circuits. Today Surface Science significance in Microelectronics goes on to increase. A striking example of this can be the emerge of nanotechnology with interface or surface itself constituiting all the working volume of device. However, diversification of surface research into areas outside classical solid state technology, what opens to it really unconfined expance throughout practically all the branchesof science and industry, from medicine to archaeology, becomes a critical factor for its future. This fact was accounted for in the new program for both graduate and postgraduate level at «Lviv Polytechnic»designed namely to train specialists able to apply methods, tools, and theories of Surface Science to multidisciplinary activities and support traditions of Surface Science research at «Lviv Polytechnic». Inconclusion it should be claimed that advanced Surface Science, however no other discipline is, perfects analytical problem-solvings kills that are generic and widely applicable and it can be used as a methodological base for other courses.

E-I.5 11:15-11:45 NEW PHOSPHATES FOR HIGH-TEMPERATURE PROTON CONDUCTORS, A.A. Belik, B.I. Lazoryak, Chemistry Department, Moscow State University, Vorob'yevy Gory, 119899 Moscow, Russia; and A.I. Beskrovnyi, Laboratory of Neutron Physics, Joint Institute for Nuclear Research, P.O. Box 79, Dubna, 101000 Moscow, Russia

X-ray and neutron diffraction study, Mossbauer and IR spectroscopy, thermal analysis, magnetic susceptibility and electrical conductivity measurements have been performed on the phosphates $Ca_9Fe(PO_4)_7$ and $Ca_9FeH(PO_4)_7$. Structural transformations in $Ca_9Fe(PO_4)_7$ during reduction are clarified and the hydrogen ions in the structure of $Ca_9FeH(PO_4)_7$ are localised. The reaction of $Ca_9Fe(PO_4)_7$ with hydrogen are studied. The reduction occurs at a wide range of temperature (450-1000°C) and hydrogen concentration (5-100%).

The redox reactions in double calcium and iron phosphate proceed reversibly without destruction of the crystalstructure. $Ca_9Fe(PO_4)_7$ are stable in air or in an inert atmosphere and $Ca_9FeH(PO_4)_7$ are stable in an inert atmosphere up to 1500°C. The oxidation of $Ca_9Fe(PO_4)_7$is not observed below 580°C in air.

$Ca_9FeH(PO_4)_7$ in hydrogen-containing atmosphere is suggested to use as a material for high-temperature proton conductors.

11:45-12:15 ***DISCUSSION***

12:15-14:15 **LUNCH**

Tuesday June 17, 1997 — Afternoon
Mardi 17 juin 1997 — Après-Midi

Session II

E-II.1 - invited - 14:15-15:00

PLENARY TALK, **G. Maggetto**, Vrieje Universiteit Brussels, T.W. -ETEC, Pleinlaan 2, 1050 Brussels, Belgium

E-II.2 15:00-15:30

SILICON PRODUCTION IN RUSSIA: POLICY AND STRATEGY OF BILATERAL PROJECTS WITH FOREIGN COMPANIES, A.M. Prokhorov, General Physics Institute.Moscow, Russia; G.N. Petrov, T.M. Tkacheva and G.K. Ippolitova, ELLIAN-NT, Co. Ltd,.Moscow, Russia

As a result of the USSR decay all economic and industries alliances between the plants and studies institutes in the Republics of the former USSR were broken. So at present there are two ways to recover silicon production in Russia: first way - to build all facilities on a new base - is uneconomic and unprofitable; the second one includes the «bridges» with old partners and simultaneously creation of new relationships with our colleagues from other countries. Russian scientists and engineers have successful experience in investigations of natural quartz with the history of its origin; analyze of carbon thermal reduction conditions and metallurgical silicon; the development of ecologically pure and reliable technology of polycrystalline silicon growth; development of new growth technology for 8'-12' silicon single crystals based on the magnetic fields application and includes the design of new furnace; investigation of MCZ Si crystals properties including the properties of high resistivity MCZ Si after the neutron doping both by feast and by thermal neutrons irradiation; development of new ID slicing machine (for 8" Si ingots) with low vibration in the cut-area. This knowledge and «know-how» are the base of bilateral Russian-Kyrgyzian project one of the goal of which is the using of the plant build during USSR existence and cooperation with several European companies.

E-II.3 15:30-16:00

$Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ - ELECTROLYTE FOR ALL OXIDE LITHIUM ION CELLS, U. Herterich, T. Brousse, R. Marchand and D.M. Schleich, Laboratoire de Génie des Matériaux, ISITEM, BP 90604, 44306 Nantes, France

For application in all oxide lithium ion batteries we are interested in solidel ectrolytes with high values of ionic conductivity and no electronic conductivity. Recently the perovskite lithium ion conductor $Li_{.33}La_{.56}TiO_3$ has been investigated in our laboratory. Although this compound has high values of lithium ion conductivity (of the order of 10^{-4} S/cm at room temperature) the usable electrochemical window is restricted to voltages higher than 1.5V vs. Li due to the reduction of Ti^{+IV} to Ti^{+III}.

For Nasicon-type $Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ high values of lithium ion conductivity had been reported (1). Our own measurements have shown values of the order of 10^{-4} S/cm at room temperature due only to bulk conductivity. Moreover this compound should have a large electrochemical window as all the components are in highly stable valence states. Thereforewe consider $Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ to be a good candidate for the desired electrolyte. Sintered pellets of the material could be prepared by pressing powders to a pressure of 10000 kg/cm^2 and subsequently annealing at 860°C for several hours in air. These pellets with densities of 85-90% of the theoretical value were coated with different types of thin film anodes and thin film cathodes and studied electrochemically.

(1) H. Yamamoto, M. Tabuchi, T. Takeuchi, H. Kageyama and O. Nakamura, 8th Int. Meeting on Lithium Batteries, p. 316, Nagoya (1996).

16:00-16:15 **BREAK**

E-II.4 16:15-16:45

ELECTROCHEMICAL PERFORMANCE AND CHEMICAL PROPERTIES OF OXIDIC CATHODE MATERIALS FOR 4V RECHARGEABLE Li ION BATTERIES, A. Ott, P. Endres, V. Klein, B. Fuchs, A. Jäger, H.A. Mayer, S. Kemmler-Sack, Institut für Anorganische Chemie der Universität, Auf der Morgenstelle 18, 72076 Tübingen, Germany; H.-W. Praas, K. Brandt, VARTA Batterie AG, Gundelhardtstr. 72, 65779 Kelkheim, Germany; G.Filoti, V. Kunczer, Institute of Physics and Technology of Materials, 76900 Bucharest, Romania and M. Rosenberg, Ruhr-Universität Bochum NB03/32, 44780 Bochum, Germany.

The correlation between electrochemical performance and Li content was studied for possible electrode materials for 4V rechargeable Li-ion batteries from the system $Li_{1+x}Mn_{2-x}O_{4-\delta}$ and $Li_{1-x}XNi_{1+x}O_2$.

In the spinel phase $Li_{1+x}Mn_{2-x}O_{4-\delta}$ the electrochemical performance can be roughly divided in three regions: In region I ($x \leq 0.05$) the experimental capacity is inferior than the theoretical value; in region II ($0.05 \leq x \leq 0.2$) both values are practically in agreement, whereas in region III ($0.2 \leq x \leq 0.33$) the rechargeable capacity is higher than calculated with $\delta = 0$. The rechargeable capacity of materials from the system $Li_{1-x}XNi_{1+x}O_2$ with α-$NaFeO_2$ structure increases with increasing x with an optimum for $x \approx 0$.

For both systems the methods of preparation are reported together with the characterization of the materials by X-ray investigations and Rietveld refinement, several analytical methods, cyclic voltammetry, magnetic measurements, Moessbauer studies of ^{57}Fe doped samples, ^{7}Li NMR and ^{1}HNMR and FTIR investigations. Both systems are frustrated antiferromagnets with a ground state with strong spin glass character. The charge distribution between Li and Mn or Ni is discussed.

E-II.5 16:45-17:15

APPLICATION OF PLASMA SPRAY DEPOSITED COATINGS FOR SEAWATER ACTIVATED BATTERIES, S. Tamulevicius and R. Dargis, Kaunas University of Technology, Studentu 50, 3031 Kaunas, Lithuania

Batteries which use seawater as electrolyte are attractive power sources as they have moderate cost, excellent safety characteristics, indefinite shelf life time under dry conditions, and they are environment friendly.

The Ni/Al coatings which were applied as the cathodes for the seawater activated batteries were produced by plasma spray deposition.

Voltage - time ($U = E - IR(t)$) dependence was measured for the galvanic pair Mg - Ni/AI, where I was constant current, E - electromotive force of the galvanic pair and R(t) - variable resistance. It was noticed that U(t) inclination depends on the anode corrosion rate, and mass of the anode is the only parameter that restricts life time of the seawater activated cell.

Current density of this cell was fount to be a linear function of the temperature of the seawater.How output power density depends on the space between electrodes and number of cells also was investigated for the cells with different are of electrodes.maximum output power density like $4.5 * 10^5$ W/m^3 we got for these cells.

We have demonstrated that plasma spray technology can be used effectively to produce Ni/Al cathodes for the seawater activated cells.

17:15-17:45 ***DISCUSSION***

Wednesday June 18, 1997
Mercredi 18 juin 1997

Morning
Matin

Session III

E-III.1 9:00-9:30

SOLID - STATE THERMO- AND RADIATIONSTABLE POLYMER ELECTROLYTES FOR VARIOUS ELECTROCHEMICAL DEVICES, V. A. Solomin, V.V. Lyapunov, B.A. Zhubanov, Institute of Chemical Sciences Kazakh National Academy of Sciences, 106 Sh. Ualikhanov Str., 480100, Almaty, Republic of Kazakhstan

The solid-state polymer electrolytes (SPE) are of perspective as a materials for various electrochemical applications due to their comparatively high conductivity and satisfactory mechanical properties, good chemical stability in redoxreactions and low gas permeability. In this study, proton-conducting properties of SPE based on polynaphthoyleneimidosulphonic acids were examined. The latter are thermostable polymers combining relatively good hydrolytic resistance with high mechanical properties, service characteristics, enhanced thermooxidative and radiation stabilities. Polynaphtoyleneimidosulphonic acids (PNIS) were synthesized according to the procedure elaborated by the authors.These are high molecular mass film-castable polymers soluble in DMFA, DMAA, and N-methyl pyrrolidone. The results obtained suggest that PNIS-based membranes may appear to be promising as a «new generation» of materials for solid-state polymer electrolytes, which are to be used in a number of electrochemical devices working at temperatures up to 350°C.

E-III.2 9:30-10:00

INTERFACIAL ELECTRIC PROPERTIES OF BETA"-ALUMINA AND ELECTRODE BY AC IMPEDANCE, Qi Fang(1), Jun-Ying Zhang(2), (1)Department of Materials, Imperial College, London SW7 2BP, UK. (2)Department of Electronics & Electrical Engineering, University College London, Torrington Place, London WClE 7JE, UK

Beta»-alumina has been extensively studied in last two decades, due to its potential applications for many industries, such as chemical sensors, AMTEC, particularly as a high energy battery - sodium-sulphur battery for electric vehicles. However, the obstruction of Na-S battery going to market is mainly price, reliability of the material as well the electrical properties. The aim of this work is to study the interfacial electric property between beta»-alumina and electrode and to enhance cell power density. A testing cell Na(l)/beta»-alumina/ Na-M, where M = Sn, Pb, Mo TiN and TiB$_2$, was set up and run with temperature range of 400° - 800°C. The performance of the test cell and the interfacial electric properties are described by measuring current-voltage characteristics and AC impedance. The AC impedance data demonstrated that wetting of the beta»-alumina electrolyte plays an important roll on reducing the cell resistance for molten Na-Sn or Na-Pb electrode, and the molten alloy electrodes have a smaller cell-resistance, 0.3 - 0.35 Ω cm^{-2} at 700 °C after 10-20 h. The comparison with the sputtered thin, porous film electrodes, showed that the microstructure and thickness of electrode, and the interfacial resistance between electrode and surface of beta»-alumina is crucial to enhance cell power density.

E-III.3 10:00-10:30

SURFACE SCIENCE AND ITS ROLE IN ADVANCED MATERIALS EDUCATION, N.N. Berchenko, «Lviv Polytechnic» State University, 290646 Lviv, Ukraine

All-round investigation of the processes occuring at surface and different interfaces has always been occupying a noticeable place in the training of specialists in the Semiconductor Electronics Department of «Lviv Polytechnic». Principal attention, though, was paid to the problems concerning technological characterization and failure analysis of Si integrated circuits. Today Surface Science significance in Microelectronics goes on to increase. A striking example of this can be the emerge of nanotechnology with interface or surface itself constituiting all the working volume of device. However, diversification of surface research into areas outside classical solid state technology, what opens to it really unconfined expance throughout practically all the branches of science and industry, from medicine to archaeology, becomes a critical factor for its future. This fact was accounted for in the new program for both graduate and postgraduate level at «Lviv Polytechnic» designed namely to train specialists able to apply methods, tools, and theories of Surface Science to multidisciplinary activities and support traditions of Surface Science research at «Lviv Polytechnic». In conclusion it should be claimed that advanced Surface Science, however no other discipline is, perfects analytical problem-solving skills that are generic and widely applicable and it can be used as a methodological base for other courses.

10:30-10:45 **BREAK**

E-III.4 10:45-11:15

BIPOLAR PLATES MATERIALS DEVELOPMENT USING Fe-BASED ALLOYS FOR SOLID POLYMER FUEL CELLS, R. Hornung, Siemens AG, Corporate Technology, Paul-Gossen-Str. 100, 91052 Erlangen, Germany and G. Kappelt, Institute for Material Sciences, Department of Corrosion and Surface Techniques, Martensstr. 7, 91058 Erlangen, Germany

The development of alternative electricity generator technologies such as fuel cells has been stimulated by the discussion about the reduction of pollutant and CO$_2$ emissions. Due to its high efficiency and the relatively low working temperature of 80°C the solid polymer fuel cell (SPFC) is mainly intended for transport applications. Designing the SPFC you can distinguish between the functional materials (catalyst, membrane and carbon paper) and the construction materials for the bipolar plates. At the moment an Au-plated Ni-based alloy is used for the bipolar plates. The coating is applied by sputtering in order to reduce the contact resistance between the carbon paper and the bipolar plate. The construction materials are exposed to very different potentials by the electrochemical contact with the electrodes. From here great demands are made on the bipolar plates with regard to the corrosion behaviour and the contact resistance. An increased contact resistance influences the cell performance negatively.

The susceptibility to pitting corrosion and uniform corrosion of economical alternative Fe-based alloys was investigated by polarization curves. The experimental results will be presented.

E-III.5 11:15-11:45 SYNTHESIS AND CHARACTERIZATION OF $LiMn_2O_4$ FOR USE IN Li-ION BATTERIES, D.I. Siapkas, I. Samaras, C.L. Mitsas, T. Zorba, G. Moumouzias, D. Terzidis, S. Kokkou, A. Zouboulis, A. Voulgaropoulos, K.M. Paraskevopoulos and E. Hatzikraniotis, Dept. of Physics, Solid State Section, University of Thessaloniki, Thessaloniki 54006 Hellas, Greece

Lithiated manganese dioxide ($LiMn_2O_4$) is an exceptionally promising cathode material for lithium-ion battery technology. Because of its electrochemical performance in conjunction with the low price and toxicity of the starting materials (chemically or electrochemically obtained MnO_2) used in the synthesis of this compound, it seems to have a considerable advantage over established materials such as $LiNiO_2$ and $LiCoO_2$, already in use in commercial lithium-ion batteries.

In this work we present the preparation of $LiMn_2O_4$ and its characterization by a multitude of methods including XRD, FTIR spectroscopy, SEM and EDS, BET and electrochemical testing. In spite of the complexity of the synthesis process and the many parameters influencing it, we have succeeded in correlating structural and physical properties of the product with its electrochemical performance. Thus the material produced exhibits a specific capacity of 120 mAh/g, within the 4 V plateau, which is reduced by about 20% after 100 cycles.

In addition, in order to enhance the performance and stability of the lithium-ion system a wide variety of commercial carbonaceous materials as well as different non-aqueous solvents and lithium salts are currently investigated with respect to their compatibility.

11:45-12:15 ***DISCUSSION***

12:15-14:15 **LUNCH**

Wednesday June 18, 1997 — Afternoon
Mercredi 18 juin 1997 — Après-Midi

Session IV

E-IV.1 - invited - 14:15-15:00 PLENARY TALK, **J.J. Payan**, Vice President Research, RENAULT, Direction de la Recherche, 9-11 Avenue du 18 Juin 1940, 92500 Rueil Malmaison, France

E-IV.2 15:00-15:30 PAIRWISE INTERACTION AND STRUCTURAL DIAGRAM OF SEMICONDUCTOR QUASI-BINARY SYSTEMS, N. Korenchuk, Technological University of Podillya Region, 280016 Khmelnitsky, Ukraine

In an approximation of pairwise interaction of the nearest atoms disregarding correlations the equations of curve phase equilibriums of binary and quasi-binary have been obtained by means of the statistical mechanics methods. The model parameters are the ones of the interaction in solid and liquid phases. On the basis of the analysis of the phase equilibrium curves equation of quasi-binary systems and behaviour of liquidus and solidus curves close by pure components melting points the classification of diagrams of various quasi-binary systems condition in the model parameters has been carried out. The calculation method of various types model parameters of comdition have been offered, nad electronic computer calculations of interaction parameters in the solid and liquid phases for condition diagrams: eutectic type, «sigar» type; diagrams of continueus series of solid and liquid solutions with common minimum temperature point on the curves of solidus and liquidus for more then 50 types of various condition diagrams have heen made. The possibility to present the result obtained for all the types of condition diagrams in a single figure is considered. These results are of great significante both for research and teaching purposes.

E-IV.3 15:30-16:00 FROM NICKEL-CADMIUM TO LITHIUM-ION THROUGH NICKEL-METAL HYDRIDE, SAFT SERVES THE EV MARKET, J.P. Cornu, SAFT, Electric Vehicle Division, 156 avenue de Metz, 93230 Romainville, France

For the last 20 years, SAFT has maintained a constant effort of research and development in the field of electrochemical generators for Electric Vehicles. At the present time, more than 100 scientists and technicians are working in SAFT's R & D team.

Today, SAFT has selected the Ni-Cd, NiMH and Li-Ion couples for Electric Vehicles. The SAFT Ni-Cd modules are already in mass production and allow 100 km range to a European compact car.

Work in progress will improve some others performances in a near future but the Ni-Cd batteries will meet more than 80 % of the urban market needs. The Ni-MH and Li-Ion couples are in development. With Ni-MH, the range of a 4 passenger car will be extended, before the end of the century, to 160 km (100 miles). Two modules have been designed and are still tested on prototype vehicles. To fulfill the long term requirements of EV application, ambient temperature Li-Ion battery, using liquid electrolyte, appears today to be the most promising system. Thanks to its 30 years experience in lithium batteries and a dedicated R&D program on rechargeable lithium over the past five years, SAFT has developed a chemistry and process resulting in full-scale 100 Ah cells unit and module prototypes. These prototypes are described, and results are presented. From these results, complete battery systems can be calculated, with promising characteristics (range up to 300 km).

16:00-16:15 **BREAK**

E-IV.4 16:15-16:45 MECHANICALLY RECHARGEABLE ZINC-AIR CELLS, I. Iliev(1), A. Kaisheva(1), Z. Stoynov(1), H.J. Pauling(2); (1)Central Laboratory of Electrochemical Power Source, Bulgarian Academy of Sciences, 1113 Sofia Bulgaria; (2)ChemTEK, Labor für Elektrochemie GmbH, Karlsruhe, Germany

A mechanically rechargeable zinc-air ZOXY® cell is developed. Air electrodes incorporating new concept and technology providing a low polarization and stable long-term operation are used . Porous zinc electrodes (mercury free) with highly developed surface area and extremely high discharge rate capability in wide temperature range are used . The developed zinc- air ZOXY® cell is mechanical rechargeable: once the zinc anode has been discharged, it is removed out of the cell and a «fresh» zinc electrode is introduced by which the cell is operational again. The removed zinc anode, is «recharged» electrochemical in a separate cell. This «recharge» procedure can be repeated 5 - 8 times without significant losses of the amperhour capacity of the zinc electrode. A recycling process is under development by which zinc is electrochemically deposited and new zinc anodes are produced. A battery from 300 ZOXY® cells is tested on an electrically driven car. At minus temperatures (0° to -10°C) the stretch covered by one battery discharge was 764 km.

E-IV.5 16:45-17:15 ZEBRA BATTERY MEETS USABC GOALS, C.-H. Dustmann, AEG Anglo Batteries GmbH, Söflinger Straße 100, 89077 Ulm, Germany

The ZEBRA battery system is the most promising candidate to power future electric vehicles. Not only because its energy density is threefold that of lead acid batteries (50 % more than NiMH) but also because of all the other EV requirements such as power density, no maintenance, summer and winter operation, safety, failure tolerance and low cost potential.

The electrode material is plain salt and nickel in combination with a ceramic electrolyte. The cell voltage is 2,58 V and the capacity 32 Ah. Some hundred cells are connected in series or in series parallel to form a battery with about 300 V OCV.

The battery system including battery controller main circuit-breaker and cooling system is fully engineered and ready to be mounted a vehicle. The background of these features will be presented.

E-IV.6 17:15-17:45 ALKALINE BATTERIES FOR HYBRID AND ELECTRIC VEHICLES, F. Haschka, Deutsche Automobilgesellschaft mbH (DAUG), Forschungslaboratorium, E. Kessler-Str. 5, 73733 Esslingen, Germany

The USABC PNGV Program and the EZEV regulation in California have accelerated the development of hybrid vehicles. Hybrids offer flexible and unrestricted mobility as well as pollution free driving mode in the city. To achieve these requirements, high power storage systems are demanded. Alkaline systems (e.g. nickel/cadmium, nickel/metal hydride) will meet the requirements of advanced hybrid cars. DAUG has developed nickel/cadmium an nickel/metal hydride cells in Fibre Technology of different performance types (up to 700W/kg peak power) and proofed in electric vehicles of different projects. Aspecial bipolar cell design will meet even extreme high power requirements. The cells make use of the Recom design ensuring high power charge ability at low internal gas pressure.

17:45-18:15 ***DISCUSSION***

Thursday June 19, 1997
Jeudi 19 juin 1997

Morning
Matin

Session V

E-V.1 9:00-9:30

STRUCTURAL AND GIANT MAGNETORESISTANCE CHARACTERISATION OF Ag-Co MULTILAYERS, M. Angelakeris, P. Poulopoulos, O. Valassiades, J. Stoemenos and N.K. Flevaris, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece; O. Kalogirou and D. Niarchos, Institute of Materials Science, NCSR-«Demokritos», 15310 Athena, Greece

Ag-Co multilayers were prepared on various substrates (Si, polyimide and glass) by e-beam evaporation under ultra high vacuum. X-ray diffraction and high resolution electron microscopy studies showed a deterioration of multilayer structure upon reducing the individual Co-layer thickness to 0.5 nm. Furthermore, the saturation field in the parallel field geometry increases, as SQUID magnetometry revealed, while magnetoresistance reaches 16% at room temperature and exceeds 30% at 30 K. Magnetoresistance values were found to depend strongly on individual layer thicknesses as well as on the total film thickness.

E-V.2 9:30-10:00

MAGNETOSTRICTIVE PROPERTIES OF TbDyFe THIN FILMS PREPARED BY e-BEAM EVAPORATION, O. Kalogirou, A. Speliotis, D. Niarchos, Institute for Materials Science, NCSR-«Demokritos», 15310 Ag; Paraskevi, Attiki, Greece; P. Poulopoulos, M. Angelakeris and N.K. Flevaris, Dept. of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

(TbDy)/Fe multilayers were prepared by e-beam evaporation under ultra high vacuum (base pressure ~5xl0^{-9} mbar) using a cast $Tb_{0.2}Dy_{0.8}$ composite-type target and an α–Fe target. Substrate temperature was 320 K. Deposition rate was ~1.5 Å/sec, for both (TbDy) and Fe. The nominal composition of the multilayers was: $[(TbDy)(39Å)/Fe(29Å)]_{73} \approx 5000$ Å. The multilayers were deposited on Si(l 0 0) and kapton. The e-beam evaporation technique was also used to prepare a terfenol-D thin film. A cast composite-type target with the terfenol-D stoichiometry was used. The deposition conditions were: base pressure = 1.2xl0^{-8} mbar, P_{dep} = 0.8-1.2xl0^{-7} mbar, $\theta_{dep} \approx 600$ K, deposition rate ~7.5 Å/sec. The total film thickness was 0.47 μm. RT Moessbauer spectroscopy on the kapton-deposited multilayer showed the multilayer character of the samples. The magnetic moments lied on the film-plane. The (TbDy)/Fe multilayers were subsequently annealed under vacuum of 2xl0^{-6} mbar at 500°C and 550°C for 15 min and 1.5 hours, respectively, to obtain an interface mixing of the layers. The samples annealed at 550°C for 1.5 hours, as well as the as-deposited terfenol-D films, present magnetostriction $\lambda_{//} \approx 200$ ppm at 4 kOe at RT. The annealed samples retained the planar anisotropy.

E-V.3 10:00-10:30

COMPETITION BETWEEN Co-Cr HYBRIDIZATION AND LOW-COORDINATION EFFECTS IN THE MAGNETISM OF A Co MONOLAYER DEPOSITED ON Cr SUBSTRATES, A. Vega, S. Bouarab, L.C. Balbas, Departamento de Ficica Teorica, Universidad de Valladolid, 47011 Valladolid, Spain and C. Demangeat, H. Dreyssé, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67037 Strasbourg Cedex, France

We present a tight-binding study of the magnetism (local magnetic moments, magnetic order and average magnetization) of a Co monolayer grown on the Cr(001) and Cr(107) substrates. It is found that the Co-Cr hybridization strongly reduce the spin-polarization at the Co overlayer in agreement with recent experimental observations. At the same time, the presence of local steps at the surface, occuring for instance at the (107) substrate of Cr, leads to an in- crease of the spin polarization at the less coordinated Co-atoms. The competition between both effects is discussed through the different magnetic configurations obtained as solutions of our self-consistent tight-binding model. Results are compared with available experimental data where magnetically dead Co layers are found when deposited on Cr(001).

10:30-10:45 **BREAK**

E-V.4 10:45-11:15

MAGNETIC DICHROISM IN CORE LEVEL PHOTOEMISSION FOR THE STUDY OF Fe-Pd AND Fe-Au INTERFACES, X. Le Cann, C. Boeglin, B. Carrière, IPCMS-GSI, 23 rue du Loess, 67037 Strasbourg, France and K. Hricovini, LURE, Université Paris Sud, 91405 Orsay, France

Magnetic dichroism with polarized light is a powerful technique to study in a chemically selective manner magnetic local properties. In a previous work, we have performed this technique in the absorption mode in order to investigate the magnetism of ultrathin films of $Fe/Pd_{(100)}$. By applying the magnetooptic sum rules on the dichroic spectra, we find a strong enhancement of the orbital moment for a 2ML Fe film compared to the bulk bcc Fe value. Our study in the photoemission mode on the 2p and 3p Fe core levels shows a discrepancy with our absorption results. The asymmetries measured for 2 or 3ML Fe films or for a thick Fe film covered with lML Pd are in fact highly reduced compared to those for bcc $Fe_{(100)}$.This difference could take its origin in the specifity of the photoemission mode, more surface sensitive than absorption. We could attribute this reduction to an interface located hybridization of the 3d-Fe and 4d-Pd bands. In the present work, we have performed magnetodichroic experiments in core level photoemission on the 2p and 3p Fe core levels with a circurlarly and linearly polarized light on thin layers Fe/Pd and Au/Fe. The aim of this study is to probe the effects on the asymmetry related to the interfaces.

E-V.5 11:15-11:45 REAL-LIFE EV BATTERIES CYCLING ON BENCH, J.P. Büchel, W. Bögel, H. Katz, Technische Hochschule Darmstadt, Institut für Elektrische Energiewandlung, Fachgebiet: Regenerative Energien, Landgraf-Georg-Str. 4, 64283 Darmstadt, Germany

Based on technical and commercial experience, Renault Electric Vehicles has identified real-life parameters and constraints on EV batteries, such as ambient temperature, depth-of-discharge, time ratio on charge/discharge/standby, power amount and frequency demands, charge conditions, ... which may influence the life time of traction batteries on EVs, and might explain the differences observed between bench and in-vehicle measurements.

A bench test procedure has been issued, which allows to quantify the relative importance of individual parameters on battery performances.

We propose to discuss this approach for several battery systems, such as Lead-Acid, Nickel/Metal Hydride, Sodium/Nickel Chloride and Lithium-ion.

E-V.6 11:45-12:15 INDUSTRIAL AWARENESS ON LITHIUM BATTERIES IN THE WORLD, DURING THE PAST TWO YEARS, H. Katz, W. Bögel, J.P. Büchel, Technische Hochschule Darmstadt, Institut für Elektrische Energiewandlung, Fachgebiet: Regenerative Energien, Landgraf-Georg-Str. 4, 64283 Darmstadt, Germany

The main lithium systems, available for electric vehicles powering, have been listed, and their possible structures and compositions have been investigated.

The papers presented during the main Battery Symposia of the last two years, as well as the patents laid in the United States, and main development programs in the United States, Europe and Asia have been examined and analysed. A synthetic data base of lithium systems investigation fields has been drawn, in order to know more about potential leaders in lithium industry, research and development, manufacturing, intended uses, and recycling.

12:15-12:45 ***DISCUSSION***

12:45 ***CONCLUSIONS***

LUNCH

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Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM F

Advanced Materials Education and Training

Symposium Organizers

J. AMOUROUX, ENSCP, Paris, France

P. Van ROSMALEN, Research Institute for Knowledge Systems bv., Maastricht,
The Netherlands

M. MENDEZ NONEIL, Centro de Investigacion y de Estudios, Mexico, Mexico

S. SOMIYA, Teikyo University of Science & Technology, Yamanashi, Japan

SYMPOSIUM F

Monday June 16, 1997
Lundi 16 juin 1997

Afternoon
Après-midi

Session I

F-I.1	14:15-14:35	GENERAL PRESENTATION OF THE SESSION, J. Amouroux, Lab. Génie des Procédés Plasmas, ENSCP/UPMC, 11 rue P. et M. Curie, 75005 Paris, France
F-I.2	14:35-15:05	MODELLING OF SAFETY AND ACCIDENT IN INDUSTRIAL PLANT, G. Crean, NMRC, University College, Lee Malting, Prospect Row, Cork, Ireland
F-I.3	15:05-15:30	MODELLING OF TRANSPORT PROPERTIES OF GASES AND THERMAL PLASMA, P.Fauchais, L.M.T.C.T.S. Université de Limoges, 123 Av. A. Thomas, 87060 Limoges Cedex, France
F-I.4	15:30-15:55	MODELLING OF THIN FILM DEPOSITS FOR PV CELLS, D. Rapakoulas, Lab. of Plasma Chemistry, University of Patras, PO Box 1407, 26500 Patras, Greece
	15:55-16:15	**BREAK**
F-I.5	16:15-16:40	MODELLING AND LONG TERM PREDITION OF HIGH TEMPERATURE CORROSION PROCESS, W.J. Quadakkers, Research Center Julich, Institute for Reactor Materials, PO Box 1913, 5170 Julich, Germany
F-I.6	16:40-17:15	MODELLING OF SURGERY ACTS IN CONNECTS WITH INRIA (EUREKA PROGRAMM), M. Nord, Pediatric Surgeon, IRCAD-EITS, Hôpital Civil, Hôpitaux Universitaires, 67091 Strasbourg, France
F-I.7	17:15-17:30	MOLECULAR MODELISATION METHODS : POSSIBILITY AND LIMITATION, M.Masella, D.C.M.R., Ecole Polytechnique, 91118 Palaiseau, France

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session II

F-II.1 9:00-9:25 MODELLING OF SPACE MATERIAL, S. Cavadias, Lab. Génie des Procédés Plasmas, ENSCP/UPMC, 11 rue P. et M. Curie, 75005 Paris, France

F-II.2 9:25-9:50 MODELLING OF PROCESSES BY DIFFERENT CODE, A. Isambert, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, 92295 Chatenay Malabry, France

F-II.3 9:50-10:15 NEW EDUCATION CODE FOR ENGINEERING PROCESS AND SCALE UP IN CHEMICAL PLANT, J. Zollinger, Batch CAD Ltd. , Tanners Yard, Gilesgate, Hexham NE46 3NL, UK

10:15-10:30 **BREAK**

Session III

F-III.1 10:30-10:55 MULTIMEDIA TRAINING COURSES ON SURFACE ANALYSIS IN MICROELECTRONICS, F. Pêcheux,(1) Y. Hervé,(1) H. Marchal,(1) N. Hertel,(2) J.-P. Stoquert,(1) R. Stuck,(1) P.Siffert,(1) (1)CNRS/PHASE, BP 20, 67037 Strasbourg Cedex 2, France; (2)ISA2, University of Aarhus, Ny Munkegade, 8000 Aarhus C, Denmark

The paper presents a set of multimedia courses on material characterization in microelectronics. So far, XS/ESCA, RBS, and SIMS have been implemented. The courses are the result of a common work between ISA and PHASE, and are validated through the European project MODEM, « Multimedia Optimisation and Demonstration for Education in Microelectronics ». A special entity named « the virtual campus » in the MODEM terminology will at term integrate these courses and, thanks to Internet, make them available for the whole European Community, for both academic (postgraduate) and industrial purposes.

The courses, developped with Asymetrix ToolBook, contain four parts, one for each method presented and a generic header concerning the other methods. Each part is based on a generic template that covers six different topics:

1/ History: The history of the method. How it has been discovered ?
2/ Overview: A brief survey of the method. What it is used for, what it can('t) do ?
3/ Theory: The underlying principles and models.
4/ Instrumentation: A description of the components of a real experimental set-up.
5/ Protocol simulator: An interactive presentation showing the protocol of use of the set-up.
6/ Evaluation: A list of exercices (MCQs) and problems. The problems involve the cooperative use of specific tools like a pocket calculator, a table of elements or kinematic factors.

One of the major interest of the courses is the protocol simulator available for each method. The simulator is not intended to be a realistic model of the underlying physics, but rather aims at giving the future user a good look and feel of the actual experimental set-up. Thanks to an appropriate design methodology and to a specific programming interface, it is pretty easy to adapt the simulator to any real set-up implementation.

F-III.2 10:55-11:20 NETWORK-BASED TRAINING FOR MICRO-ELECTRONICS USING SIMULATION TOOLS, J. Hensgens, P v Rosmalen, J. Hovius, T. Mouthaan, J. v Merrienboer and H. Leemkuil. RIKS Maastricht / University of Twente, PO Box 463, 6200 AL Maastricht, The Netherlands.

Simulation-based training supports active learning enabling students to acquire complex knowledge and skills. Such training is inevitable whenever knowledge of and experience with professional simulation and modelling tools is essential for the job fulfilment like in micro-electronics. Telematics enables more openness and flexibility for courses: adjustments to specific users, update to meet rapid knowledge changes and it opens new training facilities at distance e.g. tele-teaching, tele-conferencing or tele-assistance. MODEM - Multimedia Optimisation and Demonstration in Microelectronics - will exploit both technologies to establish a European wide training service for the micro-electronics industry and higher education. The tele-based architecture creates opportunities for on-line support to enhance the supposed learning effects for students using simulations. Human resources are connected to the network to support the learners. MODEM uses a virtual campus within a spatial metaphor to simplify access to its services. The architecture of the virtual campus and its simulation-based corners learning environment funded on top of existing software will be described. Would-be scenarios, also used to find the system requirements, will give some insights into the MODEM environment. Within this context we will discuss a combined use of multimedia, simulations and telematics, how this leads to different educational settings. The resulting active learning approach can be interwoven with peer learning as well as group exercises. An interactive course is implemented on optimisation of solar Cells and a first evaluation using micro-electronic students is conducted to investigate the usability.

F-III.3 11:20-11:45 INTELLIGENT POLYMER AND THEIR DEVELOPMENT, Y. Ossada, Biological Sciences, Hokkaido University, Sapporo 060, Japon

11:45-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Session IV

F-IV.1 14:00-14:25 A MATERIALS SCIENCE EDUCATIN NETWORK, P. Schepp, Deutsche Gesellschaft für Materialkunde EV, Hamburger Allee 26, 60486 Frankfurt, Germany

F-IV.2 14:25-14:50 DATA BANK SYSTEM, M. Madiou, Société ORACLE

F-IV.3 14:50-15:10 MULTIPURPOSE COMPACT COMPUTERIZED EXPERIMENTAL SET-UP FOR EDUCATION, TRAINING AND STUDYING THE POWDERS BEHAVIOUR IN THERMAL PLASMA FLOWS, O.P. Solonenko, A.A. Mikhalchenko, V.P. Lyagushkin and E. V. Kartayev, Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences, Institutskaya 4/1, 630090 Novosibirsk, Russia

A new computer-aided diagnostic method for simultaneous in-flight measuring the vector of velocity, surface temperature and size of single particles in plasma dust-laden flows was presented by us in previous publications. Now it is possible to create a special compact computerised set-up including the above-mentioned diagnostic apparatus, supplemented by the (i) - dc microplasma torch (less then 1.5 kW power), and (ii) - injector of powder materials providing the generation of a dusted microplasma jet of specific operating gas and particles' material.

The possible applications of this diagnostic set-up are the following (i) - fundamental investigation of basic phenomema concerning the plasma-particle interaction, (ii) - optimization and design of different technologies are occurring in the presence of disperse phase (spraying, spheroidization, densification, evaporation, atomization of the powders, etc.), (iii) - education and training in the new diagnostic methods and their application for examination of the behavior of different powder materials at high temperature. Such development is particularly attractive for the Universities (Faculties of Mechanical and Chemical Engineering, Materials Science, etc.).

15:10-15:30 **BREAK**

Poster Session

15:30-17:30 See programme of this poster session p. F-5 to F-6.

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Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

SYMPOSIUM F
POSTER SESSION

15:30-17:30

F-P1 SEMICONDUCTOR MATERIALS IN MODERN MICROELECTRONICS (ELECTIVE COURSE IN NON-PROFILE INSTITUTE) G.K. Ippolitova and P. I. Pospelov Moscow Institute (Technical University) of Roads, Moscow, Russia

This course was chosen because the increasing of the microelectronics role in the life and industry. This course includes the description of Si - the main material in semiconductor industry now. In the course the problems concerning raw materials, silicon crystals growth, the special feature of silicon single growth of large diameter (more than 8") ingots; the electrophysical, optical, mechanical and other properties of silicon and the methods of their determination are discussed. In this course the possible use of amorphous and porous silicon is discussed. The microelectronics development demands also the using of such compound semiconductors as AsGa, InP, InSb, various triple or more solid solutions. The epitaxy technology and the ways of its developments and using are also discussed. One part of this course includes the information about of quantum-dimension devices productions and the problems connected to the super thin layers fonnation and the layers of super-lattice. In separate part of course the VLSI production is discussed and the problem of new types of devices formation in the area of optoelectronics and ULF-devices.

F-P2 MATERIAL, SCIENCE AND PHYSICS OF SEMICONDUCTORS FOR MECHANICAL ENGINEERS, T.M.Tkacheva and V.V. Gorbachev, State Academy of Print Arts, Moscow Russia

In the State Academy of Print Arts the course «Material Science and Physics of Semiconductors» is one of the special courses that future mechanical engineers study. The base of this course is the fundamental knowledge about the processes in solid state: the crystal lattice feature, energetic levels, the alliance between the chemical bonds and the properties of charge carriers, the influence of impurities on the properties of semiconductor; the defect formation and its annealing; the differences between the elementary semiconductors such as Si or Ge and the various compounds; the main feature of compounds; surface phenomenon; the comparison of bulk and surface importance for every kind of semiconductor devices; methods of diagnostic semiconductor parameters. One part of this course consider briefly the chemistry phenomenon concerning semiconductor material science, the other one is the brief review of the semiconductor growth methods. The practice laboratory help the students to try the parameters measurements and the computer modeling help them to imagine rather complex processes such as crystal growth.

F-P3 DISSOCIATION OF WATER VAPOR ON SILICON SINGLE CRYSTALS PRELIMINARY MODIFIED BY LOW ENERGY INERT GAS IONS. EVIDENCE FOR O ATOM DIFFUSION FROM CHEMISORBED LAYER INTO THE BULK DURING HEATING OF THIS SYSTEM, A.D.Lozovskii, Karpov Institute of Physical Chemistry, Vorontzovo Pole st.10, Moscow 103064, Russia.

Modern understanding of the wet oxidation of Si single crystals is not complete yet. Preliminary ion beam modification of the surface is a good tool for controlled influence on this process. A series of experiments (H2O chemisorption on Si(100)-(2x1) at T=300 K, heating up to definite T=Th with definite law of heating, cooling to T=300 K) was made. Characteristic time of O-ion signal decrease (method of secondary ion mass spectrometry) versus T appeared to increase. It may be caused by O atoms profile becoming wider due to their interdiffusion. Another evidence can be obtained through measuring of the ratio of H2 thermal desorption peak square for Si(100)/H2O system to that of Si(111)/H2O (saturation at T=300 K). It appears to be equal to 2.8, while that of SiO desorption peaks is equal to 4. Special experiments have shown that there is no interdiffusion or segregation of H atoms during thermal desorption from Si/H2O systems. Therefore such discreapancy is caused by nonzero probability of O atom diffusion from adsorbed layer into the bulk. Preliminary argon ion beam modification of single crystal Si surfaces (E=2 keV) has shown that for Si(100) such probability increases at $>2*10^{14}$ cm^{-2} and for Si(111) decreases at $>6*10^{14}$ cm^{-2}. The difference between thus oriented surfaces vanishes due to silicon amorphization under the influence of ion beam.
Moreover taking interdiffusion of O atoms into account we have obtained better fit of theoretical SiO thermal desorption kinetics to experimental one.

F-P4 ELECTRICAL BEHAVIOUR OR MULLITE MATERIALS OBTAINED BY A NOVEL COPRECIPITATION METHOD USING OF CLAY MINERALS AND ALUMINIUM SALT J. Pascual-Cosp(1), J. R. Ramos-Barrado(2), R. Lopez(2), J. Ruiz(1), J. Zapatero(1), P. J. Sanchez-Soto(3), A. Justo(3) and J.L. Perez- Rodriguez(3). (1) Departamento de Ingenieria Civil y de Materiales, ET.S.I.I. Universidad de Malaga, 29071 Malaga, Spain. (2) Departamento de Fisica Aplicada, Facultad de Ciencias, Universidad de Malaga, 29071 Malaga, Spain. Instituto de Ciencia de Materiales, C.S.I.C. Universidad de Sevilla, Spain

The electrical and dielectric properties of samples of mullite obtained by a novel coprecipitation method, using layered clay minerals and aluminium salts coming from aluminium wastes, and organic compound as coprecipitation agent are measured by impedance spectroscopy using a Solartron 1260 controlled by computer for a temperature range between 673K and 1073K, and frequency range between 10Hz and 1MHz.
The activation energy of d.c. and the critical frequency for the transition from conductor to dielectric behaviour presented a strong dependence on the microstructure and sintering temperature.

F-P5 CRYSTALLIZATION FEATURES AND STRUCTURE OF CHROMIUM-MOLYBDENUM CAST IRON, S.Pietrowski, Inst. Mat. Eng. Technical University of Lodz, ul; Stefanowskiego 1, 90-924 Lodz, Poland

It has been proved by means of differential thermal analysis (DTA) that in chromium molybdenum cast iron with increasing chromium and molybdenum content in the range of 6.5÷13,6% Cr and 0.4÷4.0% Mo the following eutectic mixtures are crystallizing subsequentty: $M_3C+\gamma$, $M_7C_3+\gamma$ and $M_{23}C_6+\gamma$ The last eutectic mixtures is crystallizing only of Mo contentis greater than 1.5 wt % Mo. At that condition an additional thermal effect can be disclosed on the crystallization diagrams of the alloy.

F-P6 EDUCATION IN MATERIAL SCIENCE IN MEXICO, M. Mendez Noneil, Centro de Investigacion y de Estudios, Avanzados del i.p.n., av. inst. politecnico Nasional, 2508 col San pedro Zacatenco, 07300 Mexico, Mexico.

F-P7 RUSSIAN TECHNOLOGY SCHOOL, G.K. Ippolitova, T.M. Tkacheva, G.N. Petrov, ELLINA-NT, Dm. Ulianova St., 1/61, apt. 179, 117333 Moscow, Russia

Russian Technology School is founded by Russian Academy of Sciences, General Physics Institute and ELLINA-NT, Research and Production Co. This School suggests the postgraduate education and consulting service in the field of semiconductor physics and semiconductor material science for specialists and administration of semiconductor industry. Professors of this School are the leading scientists and specialists of Russia and invited persons from the other countries. The School organizes the help for pass the necessary exams and the consults the writing of manuscripts prepared as Ph.D. or M.Sc. manuscripts. The main topics of School are: metrology of semiconductors parameters at the manufacture; quality control of the raw material for semiconductor production; modern effective technologies for «electronic» and «solar» silicon; methods of increasing the thermal and radiation stability of semiconductors; save-energy and ecologically pure technology of polycrystalline silicon production; the alliance between the raw material impurities content and the impurities content of single crystals/ Separate course is organized concerning the facilities constructions, e g. new slicing machine for silicon single crystal ingots of 8" in diameter. Another separate course is organized concerning the protection of intellectual property in Russia and comparison with the world experience.

The durations of courses are three months; nine months; one and a half of year (M. Sc. Preparation) and three years (Ph.D. Preparation).

F-P8 MATERIALS SCIENCE EDUCATION IN ESTONIA, T. Kaps, E. Mellikov, A. Opik, P. Kulu, Tallinn Technical University, Ehitajate tee 5, EE 0026 Tallinn, Republic of Estonia

Two different conceptions are spread in materials science education nowadays. The first future-oriented, necessitating a change from the industry economy model towards that of the research and information network economy is typical for developed countries. The second aimed only at the fulfilment of the actual practical requirements of various industries is typical for developing countries.

After restoring of independence and not very long period of changes materials science higher education in Estonia is introducing into the new stage of developing - the period of future-oriented science based materials science education. The new education system bases on results of PHARE project ES-9502 «Higher Education and Science Reform» and PHARE TEMPUS project S_JEP-11212-96 «Restructuring of Higher Education System on Material and Genetic Technologies in Estonia» and consists in the organising of Centre of Competence in Materials Science and graduated schools at TTU. The report deals with our results and problems in the field of: a) the relations in triangle basic subjects - materials science - materials technology - in new curricula for Bachelor, Master and Doctor studies; b) the relations between advanced materials higher education, scientific research and industry in Estonia; c) the possibilities of use of multimedia, Internet and the World Wide Web and computer-aided learning and d) the possibilities of Estonia to join with the all-European Materials Science Education network.

Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM G

Biomaterials: Perspectives for Research & Industry at the Century Change

Symposium Organizers

F. BURNY, University of Brussels, Brussels, Belgium

L. HENCH, Imperial College of Science, Technology and Medicine, London, UK

D. MUSTER, LEED Biomatériaux, CHRU, Strasbourg, France

T. YAMAMURO, Research Institute for Production Development, Kyoto, Japan

SYMPOSIUM G

Tuesday June 17, 1997 **Morning**
Mardi 17 juin 1997 Matin

Session I - Orthopedic Biomaterials, Part 1

G-I.1 - invited - 8:45-9:15

DEVELOPMENT OF BIOACTIVE BONE CEMENT AND ITS CLINICAL APPLICATIONS, **T. Yamamuro**, T. Nakamura, K. Kawanabe, Department of Orthopaedic Surgery, Faculty of Medicine, Kyoto University, Sakyo-ku, Kyoto, 606 Japan

Two types of bioactive bone cement, dough type and injection type, were developed by combining AW glass-ceramic powder and Bis-GMA resin.During their hardening process which last for a fewminutes, they do not generate high heat, maximum 37°C on the cement surface. Their mechanical strength after hardening (compressive strength 220-270 MPa, bending strength 120-135 MPa, fracture toughness 1.6 MPa $\cdot$ $m^{0.5}$) is significantly greater than that of PMMA cement. When they are implanted into the living bone tissue, they directly bond to bone within 4-8 weeks through an apatite layer which is spontaneously formed at the bone-cement interface in vivo. The new bioactive bone cement has been used in a few cases of hip replacement since 1993. Their radiological as well as clinical results are satisfactory to date in all cases. The bioactive bone cement has also been used in fields of plastic surgery, neurosurgery, and maxillo-facial surgery with satisfactory results.

G-I.2 9:15-9:30

THE CALCIUM PHOSPHATE BIOACTIVE CONCEPT APPLICATIONS TO ARTIFICIAL BONE IMPLANT COATING AND INJECTABLE BONE SUBSTITUTE, G. Daculsi, J.M. Bouler, Centre de recherche sur les matériaux d'intérêt biologique UPRES EA 2159, Faculté de chirurgie dentaire, Place Alexis Ricordeau, 44 042 Nantes, France.Nantes, France

In the last twenty years calcium-phosphate-materials found wide clinical applications for repair of bone defects, bone augmentations and coatings for metal implants. Calcium- phosphates provide special properties in such indications, based on their chemical composition and micro-structural appearence which is closely related to those of bone mineral. According to the specific properties of HA and B-TCP we have developed a concept of controlled bioactiviry (Daculsi et al, J. Biomed. Mater. Res., 1989, 23: 883-894).

The biphasic calcium phosphate, a mixture of Hydroxyapatite (HA 60%) and Tricalcium phosphate (TCP 40%) prepared in a microporous associated to macroporous form have demonstrated the efficiency for osteogenesis on/and at the expense of the material (Triosite TM) The concept have been applied to resorbable plasma coating on titanium for hip prosthesis and also for the mineral charge associated to a polymer for a new ready for use Injectable bone substitute.

We shall expose the bioactive concept, the experimental study in vivo and in vitro, and the clinical results in human.

G-I.3 9:30-9:45

DISSOLUTION BEHAVIOUR OF CALCIUM-PHOSPHATE COATINGS OBTAINED BY LASER ABLATION, L. Clèries, J.M. Fernandez-Pradas, G. Sardin, J.L. Morenza, Universitat de Barcelona, Departament de Fisica Aplicada i Electronica, Av. Diagonal 647, 08028 Barcelona, Spain

Pulsed laser deposited calcium-phosphate coatings on titanium alloy have been tested under simulated physiological conditions, in order to evaluate the changes in morphology, composition and structure.

The coatings were deposited under different sole water vapour atmosphere pressures and substrate temperatures. Different morphologies and structures, ranging from amorphous and mixed crystalline phases to pure crystalline hydroxyapatite (HA), were obtained.

The coated samples were immersed in a Ca-free Hank's balanced salt solution for up to 5 days. Characterization was performed by XRD, SEM and FT-IR spectroscopy before and after immersion. The morphology and structure of the pure HA coatings is preserved during the exposure time in solution, whereas the existence of other phases causes their partial or complete degradation.

G-I.4 9:45-10:00

IN VITRO EVALUATION OF A BIOACTIVE HYDROXYAPATITE AGGREGATES. S. Caropreso(1), R. Filocamo(1), M. Fabbri(2), L. Cerroni(2), C. Piconi(2) and S.G. Condo(2), (1)Dept. Exp. Med.Biochem. Sci. University of «Tor Vergata» Rome, Italy; (2)Fin-Ceramica s.r.l. Faenza (Ra) Italy

Porous hydroxyapatite is useful to prepare both aggregates for bone substitution and substrates of controlled porosity as drug release system .

In the present study some in vitro results are reported concerning the interaction of hydroxyapatite based porous bodies(HA) with predetermined porosity (40%), containing tricalcium phoshate lower than 4% and an osteogenic cellular line (MC3T3-El). Laser transmitted light and reflected light microscopy observations were performed on cells in presence of the tested material.MTT and crystal violet tests and LDH activity were determined on cells incubated with HA conditioned medium. On cells coltured in presence of the porous aggregates were evaluated also alkaline phosphatase, protein content and cAMP. Cellular proliferation was reduced respect to the control, but it was not related to cytotoxic effect of the material because no increase of LDH was observed. Osteoblast cells showed intense phagocytosis of microparticles derived from HA dissolution and after 10 days samples were widely populated by cell aggregates, light micrographs showed cells anchored and spread over the surface of the underlying HA aggregates, with a flattened and stellate shape.

G-I.5 10:00-10:15

STUDY OF THE INTERFACE REACTIONS BETWEEN CELLS AND A BIOCOMPATIBLE CERAMIC, P. Mengucci, G. Majni, Dept. Materials Science; and M. Mattioli Belmonte, A. De Benedittis, G. Biagini, Inst. Normal Human Morphology, University of Ancona, Italy

The capacity of cells to bond with biomaterials appears to be based on the ability of these materials to form dynamic interfacial zone. Several investigators are carrying out in vivo studies on the formation of interfacial structures between the implant surface and the bone, mainly in orthopaedics and dentistry. Also cell culture models are important instruments for investigating interface reactions, and they may be used as a first screening for biomaterials. In this context the present study reports the preliminary results of the modifications induced by the growth of a Chinese Hamster Ovary cell line on the surface of a biocompatible ceramic cordierite. Samples were analysed after 8, 14, 22 and 30 days of growth by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and grazing angle X-ray diffraction (GAD) in order to evaluate both the surface morphology and the modifications of the composition of the ceramic support. EDS and GAD analysis were carried out under different instrumental conditions for the evaluation of the modifications occurred through the thickness of the material. Results showed that the main compositional variations below the cells are related to the decreasing of the K and Ca content near the material surface with respect to the bulk. This suggest that these elements could be directly involved in the cellular response.

10:15-10:45 **BREAK - VISIT OF THE POSTERS**

See programme of the poster session p. G-9 to G-12.

Session II - Orthopedic Biomaterials, Part 2

G-II.1 - invited - 10:45-11:15

SOME MATHEMATICAL TOOLS FOR THE DESCRIPTION OF THE ASYMPTOTIC BEHAVIOUR OF THIN ADHESIVE LAYERS, **A. Brillard**, Laboratoire de Mathématiques, Faculté des Sciences etTechniques, 4 Rue des Frères Lumière, 68093 Mulhouse Cedex, France

The purpose of this talk is to present some mathematical tools which can be applied in order to describe the asymptotic behaviour of a thin layer bonding two adherends, when the thickness 2ε of this small layer goes to 0. The adhesive is given a Norton-Hoff nonlinear elastic incompressible behaviour, while the adherends are supposed to be linear elastic bodies. In order to describe the limit of the stress tensor σ^ε and that of the displacement $u\varepsilon$ in the three-body system, when ε goes to 0, we first look for estimates on $(\sigma^\varepsilon, u^\varepsilon)$ in Sobolev spaces.
The first mathematical tool is the so-called asymptotic expansion method which requires the transformation of the thin layer into a layer of thickness 2, in order to work in fixed domains. First one writes the solution $(\sigma^\varepsilon, u^\varepsilon)$ of the transformed problem now posed in the fixed domains as the series
$(\sigma^\varepsilon = \sigma^0 + \varepsilon\sigma^1 + e^2\sigma^2 + \dots; u^\varepsilon = u^0 + \varepsilon u^1 + \varepsilon^2 u^2 + \dots,$
then one puts these expressions in the transformed problem and finally identifies the coefficicnts of the different powers of ε.
The second mathematical tool is based on the possibility to write the original problem as a minimization problem Min $F^\varepsilon(u)$, where F^ε is defined on some
Sobolev space and V^ε denotes a closed subspace of this Sobolev space, corresponding to the naturally imposed constraints. This tool consists in the description the asvmptotic behaviour of the fimctional F^ε when ε goes to 0, using epi-convergence arguments, in order to determine the behaviour of u^ε.

G-II.2 11:15-11:30

TISSUE ADHESIVES - THE STATE OF THE ART ADHESIVES IN ORTHOPEDIC SURGERY, F. Burny, M. Donkerwolke, D. Muster, Brussels, Belgium and Strasbourg, France

G-II.3 11:30-11:45

MATERIALS SELECTION AND DESIGN FOR ORTHOPEDIC IMPLANTS WITH IMPROVED LONG-TERM PERFORMANCE. J. Vander Sloten, L. Labey, R Van Audekercke, G. Van der Perre, K.U.Leuven, Division of Biomechanics & Engineering Design, Celestijnenlaan 200A, 3001 Heverlee, Belgium

Although more than 90% of the joint replacements currently performed is successful during more than 10 years, the large number of replacements that is performed annually and the high cost and limited success rate of revision operations demand further improvement in the design of orthopedic implants. Failure is generally due to aseptic loosening of the implant. Three main causes for this phenomenon have been identified. Stress shielding of the bone surrounding the prosthesis due to a mismatch in mechanical properties can lead to bone resorption. Relative movement of the prosthesis leads to the development of a soft tissue interface. The presence of wear particles triggers cell processes that cause osteolysis. Despite impressive efforts to improve prosthesis designs, in hip surgery for instance, the cemented Charnley prosthesis introduced in '67 remains the gold standard. This might be due to the fact that one has generally concentrated on a single problem, neglecting the others. Biomaterials scientists tend to tackle the problem of prosthesis fixation by developing new, bioactive materials ignoring biomechanical effects such as stress shielding or micromotion. The only way to proceed with new prosthesis designs with a chance for success is the integration of biomaterials and biomechanics.

G-II.4 11:45-12:00

SMART ORTHOPAEDIC IMPLANTS, F. Burny, R. Bourgois, M. Donkerwolcke, F. Moulart, R. Puers, K. Van Schuylenbergh, Brussels, Belgium and Leuven, Belgium

G-II.5 12:00-12:15 Y-TZP CERAMICS FOR ARTIFICIAL JOINT REPLACEMENTS, C. Piconi, ENEA, Dpt. Innovazione, 301 Via Anguillarese, 00060 Roma, Italy; W. Burger, H. Richter, CeramTec AG, 23/29 Fabrikstrasse, 73207 Plochingen, Germany; A. Cittadini, G. Maccauro, V. Covacci, N. Bruzzese, Catholic University, 1 L.go F. Vito, 00168 Rome, Italy; G.A. Ricci, ENEA, Dpt. Innovazione, 301 Via Anguillarese, 00060 Roma, Italy; E. Marmo, FN Spa, 15062 Bosco Marengo (AL), Italy

Due to their excellent mechanical properties, Tetragonal stabilized zirconia ceramics (Y-TPZ) are used in ball heads for Total Hip Replacements. Many Y-TZP materials available on the market show ageing after hydrothermal treatment. High UHMWPE wear was reported after a short implantation period of steam sterilized Y-TZP ball heads. This effect may be related to ball head surface phase transformation, due to corrosive attack. This study is aimed to evaluate the stability of Y-TZP ceramics.

Y-TZP made out Yttria coated powders were aged at 140°C under 0.2 MPa water pressure, in Ringer's solution at 37°C, in NZW rabbits. Samples made out Yttria coated powders show lower strength degradation than samples made out coprecipitated powders.

Activity performed in the framework of the Project Brite-EuRam BE 5172.

G-II.6 12:15-12:30 DEVELOPMENT OF PLASMA-SPRAYED BIOCERAMIC COATINGS WITH BOND COATS BASED ON TITANIA AND ZIRCONIA, R.B. Heimann, H. Kurzweg, Dept. of Mineralogy, Freiberg University of Mining and Technology, 09596 Freiberg, Germamy; T. Troczynski, Dept. of Metals and Materials Engineering, University of British Columbia, Vancouver, B.C., V6T 1Z4, Canada; and M. L. Wayman, Dept. of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Canada

Bond coats for plasma-sprayed hydroxyapatite (HAp) coatings on Ti6A14V hip endoprostheses are being developed for improved in vivo performance. To deposit bond coats powders consisting of i) titania, ii) Ca-stabilized zirconia, and iii) a mechanical mixture of titania and (non-stabilized) zirconia corresponding to the eutectic composition were applied by atmospheric plasma spraying (APS) to coupons and 100 µm-thick Ti6A14V foils. Subsequently a 150-180 µm-thick layer of HAp (AMDRY™6021) was sprayed onto the thin (10-15 µm) bond coats.

Peel tests on Ti6A14V foil/bond coat/HAp top coat assemblies revealed that titania and titania/zirconia bond coats increased the peel adhesion strength in a statistically significant way from 22 N/m (HAp without bond coat) to >42 and >32 N/m respectively. Microstructural investigations by SEM, TEM and 2D-SIMS imaging on cross-seclions of as-sprayed coatings and coatings leached in simulated body fluid for up to 28 days led to the conclusion that the chemically very stable bond coats act as a natural extension of the native oxide layer of titanium metal and thus provide an improved chemical barrier against in vivo relase of metal ions from the implant as well as an improved adhesive bond by development of very thin well-adhering reaction layers, presumably composed of perovskite, calcium dititanate and/or calcium zirconate.

12:30-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Session III - Biomaterials for soft tissues

G-III.1 - invited - 14:00-14:30

THE WAR AGAINST JUNK SCIENCE: USE OF EXPERT PANELS IN COMPLEX MEDICAL-LEGAL SCIENTIFIC LITIGATION, **J.M. Price**, E.S. Rosenberg, Faegre & Benson, LLP, Attorneys at Law, 2200 Norwest Center, Minneapolis Minnesota 55402, USA

In the legal context, junk science is defined as evidence that is outside of mainstream scientific or medical views. Junk science does not have indicia of reliability and is not generally accepted. Despite the lack of scientific reliability, U.S. courts, expert witnesses and juries are increasingly reliant on junk science in making causation decisions in complex medical liability cases. Courts have accepted junk science even were reliable scientific evidence is available.

The United States silicone gel breast implant litigation is a prime example of this phenomenon. The issue of whether silicone breast implants are associated with disease has been a controversial subject for scientists and physicians, an emotional issue for women who have breast implants, and a lucrative business for the lawyers and expert witnesses who are the proponents of Junk science. Junk science has provided to juries a quick and convenient explanation for claimed diseases or syndromes which have requiree years for reliable scientists to conclude are not related to breast implants. The breast implant litigation highlights the often dramatic difference between decisions based upon junk science and decisions grounded in scientific method, fact and reality.

Recently, judges involved in the breast implant litigation have become concerned about the use of junk science in light of the growing body of legitimate scientific evidence that breast implants do not cause disease. Several judges have been motivated to take the unique and novel approach of convening scientific panels of independent experts to study the scientific issues and make findings to the court. Through the use of independant scientific experts, several judges have meaningfully assessed the evidence that the litigants present and have prevented or strictly limited the use of junk science in the courtroom. Using this procedure, other judges are weighing the evidence for future cases.

This paper will briefly explore the background of mass tort medical products litigation and the development of junk science. The paper will then focus on the history of the breast implant litigation and the steps that the courts have already taken to combat junk science, including the use of scientific panels.

G-III.2 14:30-14:45

BIORESORBABLE POLYMERS FOR THE USE AS BIOMATERIALS, G. Jakse, Interdisciplinary Centre of Clinical Research «BIOMAT», Pauwelsstr. 30, 52057 Aachen, Germany

Biodegradable polymers are used or tested in an increasing number of medical applications. The applications are as diverse as ureteric stents of membranes for guided tissue regeneration in the treatment of periodontitis. With regard to the desired function of these implant materials, modified surface characteristics like e.g. protein adsorption and cell adhesion are often needed. Also, a need for the covalent attachment of bioactive compounds (drugs) to the polymer surface may exist. Our approach to these surface modifications was the graft polymerization of suitable monomers. Additionally, the polymers can be used for drug delivery at the implantation site for a predicted period of time. We were able to incorporate different antibiotics and proteins, e.g. growth factors without loss of biological activity using the gassing process technology. All materials and modifications used in our studies were tested for their in vitro biocompatibility.

G-III.3 14:45-15:00

ARTERIAL PUNCTURE SITE CLOSURE BY MICROCRYSTALLINE CHITOSAN, A. Hoekstra(1), H. Struszczyk(2), O. Kivekas(3), (1)Biomedical Technology Center, University of Groningen, The Netherlands, (2)Institute of Chemical Fibres, Lodz, Poland, (3)Novasso Oy, Tampere, Finland

Arterial catheterization is one of the most frequently performed inpatient diagnostic and therapeutic procedures in the development countries. Complications may occur after any catheterization from inadequate hemostasis, particularly in the setting of aggressive anticoagulation. This study suggests that microcrystalline chitosan (MCCh) sealant installation via an arterial sheath at the completion of catheterization may improve hemostasis. Results using MCCh in 8 heparinized dogs documented significant reductions in manual compression time (>50%) of the artery after withdrawal of both the sheath introducer and catheter. Comparative results were found in rats, wherein a created wound in the aorta could be sealed relatively quickly and easily. The biodegradability and optimalization of this potential hemostatic agent require further consideration.

G-III.4 15:00-15:15

ARE LONGITUDINAL RUPTURES OF KNITTED POLESTER VASCULAR PROSTHESES AVOIDABLE? N. Chakfe, G. Riepe, E. Urban, J.L. Le Magnen, S. Cottin Bizonne, J.G. Kretz, B. Durand, Groupe Européen de Recherche sur les Prothèses appliquées à la Chirurgie Vasculaire, Faculty of Medecine, Strasbourg University, 11, rue Humann, 67085 Strasbourg, France

Late degradation of polyester vascular prostheses still remain a dreaded complication for vascular surgeons. One kind of delayed degradation is the occurence of longitudinal ruptures of the prostheses.

We analysed 14 knitted polyester vascular prostheses explanted from humans as a part of our european retrieval program, and demonstrating a longitudinal rupture.

The prostheses were implanted for a mean duration of 13.7 ± 3.0 years (range: 6 to 17 years). They were implanted for surgery of the abdominal aorta in 11 cases, as an axillo-femoral bypass in 1 case, the site of implantation being unknown in 2 cases. The main reason leading to the observation of the rupture was a false aneurysm requiring reoperation for the patient. The longitudinal ruptures accured on the remeshing line in 9 cases and on the black line in 1 cases, both sites being observed in 1 case.

The knowledge and the characterization of such areas of weakness is very important to propose a research program in order to help manufacturers to optimize their manufacturing process of polyester vascular prostheses. The remeshing line is a performed by a yarn that joins both textile surfaces carried out by each needle bed in order to obtain a cylinder. Manufacturers have to avoid to undersize this yarn and have also to be sure to apply the same absorbed lenght in order to avoid an impairment of its mechanichal strenght. The blue line is performed by incorporating a black or blue dyed yarn. This yarn must have the same size and have not be chemically changed during the dying process which could allow faster degradation after implantation.

G-III.5 15:15-15:30

EFFECTS ON NEUTROPHIL ADHESION AND COMPLEMENT CASCADE WITH HEPARIN-COATED CARDIOPULMONARY BYPASS, P. Dhôte-Burger, A. Gozin, M.-P. Carreno, C. Pasquier, C. Latremouille, N. d'Attellis, J.-N. Fabiani, Hop. Broussais - Dpt Chir. CardioVasc., 75014 Paris, France

Background: Cardiopulmonary bypass (CPB) is responsible for systemic inflammatory response syndrome, which may lead to organ dysfunction.The present study was performed to compare complement activation and neutrophil adhesion with heparin-coated and uncoated CPB circuits during coronary artery bypass grafting or valvular surgery.

Patients and methods: 21 patients ranging from 27 to 78 years (mean 60 years) were included in a prospective study, and randomly perfused with a heparin-coated circuit (HC Duraflo), or with a similar noncoated circuit (UC control). Neutrophil count, elastase and lactoferrin concentrations, C5a desarg and sE-Selectin were measured in all patients between myocardial venous blood and myocardial arterial blood before, during (before and after aortic cross clamping) and after surgery.

Results: A significant increase in neutrophil count during CPB, with a lower neutrophil count in myocardial venous blood as compared to arterial blood was observed. No difference between the two groups was apparent. Elastase concentrations significantly increased during the myocardial ischemia-reperfusion sequence (HC $p<0,05$; UC $p<0,01$), but not during earlier reperfusion for the HC group. C5a desarg significantly increased during CPB ($p<0,05$) at reperfusion, and postoperatively ($p<0,05$) for the UC group. sE-Selectin concentrations and tendency was similar for the two groups, with a significant decrease between the onset of CPB and before surgery ($p<0,05$); with a peak value 24 hours after CPB ($p<0,05$).

Conclusions. The loss of a significant difference during earlier reperfusion of elastase concentrations in venous myocardial blood for the HC group seems to indicate a real but non lasting limitation of neutrophil activation. In addition, the reduction in complement activation in the heparin-coated group suggests that biocompatibility is enhanced. Heparin-coating does not appear to change the kinetic process of sE-Selectin concentrations.

G-III.6 15:30-15:45

EVOLUTION OF RESEARCH IN THE AREA OF CARDIOVASCULAR BIOMATERIALS, E. Le Borgne, G.I.S., Rennes, France and J.-N. Fabiani, Hop. Broussais - Dpt Chir. CardioVasc., 75014 Paris, France

G-III.7 15:45-16:00

A SECOND GENERATION OF ARTIFICIAL CORNEA, J.-M. Legeais, Department of Ophthalmology, Hôtel-Dieu Hospital, 1 Place du Parvis Notre-Dame, 75004 Paris, France.

A first generation of biointegrable keratoprosthesis was evaluated between 1991 and 1996 on 79 patients with corneal inflammatory disease and we obtained 47 % of visual rehabilitation. The device consists of a flange using a 9 mm porous PTFE and a 5 mm PMMA optical system. (Arch. Ophthalmol. 1995, 113:757-763). To increase the biointegration of the skirt we evaluated a transparent PTFE and a 7 mm soft optical system mimicking the cornea. We now investigated the second generation in a human prospective study.

We obtained the authorization of the Ethics committee and the study is conducted under French FDA regulation (loi Huriet). We presented the first 8 consecutive implanted cases. Only bilaterally blind patients with untreatable inflammatory corneal diseases were included in the study. 7 patients were phakic and 1 were pseudophakic.

None anatomic failures or retroprosthetic membranes occurred in the first 5 months. 7 of 8 patients had visual acuity improvements (20/400 to 20/60). The Goldmann visual field is 120° to 130°. BioKpro II can be implanted succesfully but we are able to present only preliminary results. A long term evaluation is needed. Supported by la délégation de la Recherche Clinique AP-HP, INSERM. None.

G-III.8 16:00-16:15

AN OVERVIEW OF THE BIOMATERIALS USED IN OPHTALMOLOGY, A. Catros, J.F. Charlin, C. Nsabimana, Rennes and Vannes, France

16:15-16:45

BREAK - VISIT OF THE POSTERS

See programme of the poster session p. G-9 to G-12.

Session IV - Dental Biomaterials

G-IV.1 - invited - 16:45-17:15

A CONCRETE MODEL OF SCIENTIFIC WINNING COOPERATION: CONCERTED ACTION BE 7317, **P. Cavaliere**, Brindisi, Italy

G-IV.2 17:15-17:30

BIOLOGICAL BEHAVIOUR OF MATERIALS FOR IMPLANT SURGERY AND DENTURES, M. Mattioli Belmonte, A. De Benedittis, G. Biagini Inst. Normal Human Morphology, Via Tronto 10, 60020 Torrette (AN), Italy; and P. Mengucci, G. Majni, Dept. Materials Science, via Brecce Bianche, 60131 Ancona, Italy.

Much work has been carried out on the cyto-toxicity and bio-compatibility of materials used in dentistry but there has been relatively little investigation correlating the actual composition of these materials and their interaction with «in vitro» cells. Scanning electron microscopy and EDS were used to study the ultrastructural aspects and surface composition of materials commonly used for dental implants and prostheses. Moreover, gum tissue fibroblasts were cultivated on samples of each of these materials. Our observations confirm the biocompatibility of some Titanium alloys and also demonstrate how noble alloys are able to encourage cell growth. The lack of cell growth sometimes observed could be ascribed almost in part to the relative instability of the material and consequent liberation of toxic ions. Our study shows that in some cases the surface composition did not agree with that of the bulk provided by the manufacturer.

G-IV.3 17:30-17:45

IN-VITRO CORROSION OF TITANIUM, R. Strietzel, Free University Berlin, Dept. Dental Materials, Assmannshauser Str. 4-6, 14197 Berlin, Germany

Titanium is used in dentistry for implants and frame work because of it's sufficient chemical, physical and biological properties. The corrosion behaviour is from high interest to value biocompatibility.

A static immersion test was undertaken with titanium test specimen (30 mm •10 mm • 1 mm, immersion time = 4 • 1 w, n = 3 for each serie). Investigated parameters were:

specimen preparation	influence of:
grinding	pH-value
different casting systems	chloride, thiocyanate, fluoride
comparison with CAD/CAM	lactate, citrate, oxalate, acetate

Atomic absorption spectroscopy was used to analyse the solutions weekly. The course of corrosion was investigated photometrically.

Titanium reveals ion releases {(0,01 - 0,1) μg/{cm^2 • d)} in the magnitude of gold alloys. There is little influence of grinding and casting systems in comparison with organic acids or pH value. The ion releas increases extrem {up to 500 μg/{cm^2 • d)} in the presence of fluoride. Low pH values accelerate this effect even more. Clinical no corrosion effects were observed.

Nevertheless it is recommended to avoid the presence of fluoride or reduce contact time. By prophylacitc fluoridation of teeth a varnish should be used.

G-IV.4 17:45-18:00

SURFACE ANALYSIS OF GALLIUM ALLOY RESTORATIVE MATERIALS, B. Reusch, Ch. Ziegler, Institute of Physical and Theoretical Chemistry, J. Geis-Gerstorfer, Department of Prosthodontics, School of Dentistry, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

The clinical application of mercury-free restorative material would be desirable. Several analytical methods may be used to give relevant data of amalgam substitutes before clinical studies.

We here repon on surface analytical methods such as scanning electron microscopy (SEM), scanning force microscopy (SFM), electron dispersive X- ray analysis (EDX), and X-ray photoelectron spectroscopy (XPS) which were used to study the surface properties of two gallium restorative materials (Gallium Alloy GF II, Tokuriki Honten Co. and Galloy, Southern Dental Industries Limited) and one amalgam (Amalcap Plus, Vivadent) comparatively. To give relevant practical data, these measurements were performed before and after storing the alloys in artificial saliva (0.1 M NaC1/0.1 M lactic acid, DIN EN ISO 1562) to simulate physiological oral conditions. Large differences in the corrosion resistance of the different materials, but also the different phases in these heterogeneous materials could be established.

Subsequently an analysis of the artificial saliva was carried out with atomic emission spectroscopy with inductively coupled plasma (AES/ICP). Mean ions released in case of amalgam were tin and copper. For gallium alloys mainly gallium and only low concentrations of other metal ions were detected. Different storage times in artificial saliva point at a lower passivation of the gallium alloy surfaces if compared to the amalgam. In this context the specific physiological effect if the dissolved metal ions must be taken into consideration.

G-IV.5 18:00-18:15

STUDY OF DENTAL MATERIALS BY LASER BEAM SCANNING, V. Fano, W.Y. Ma, I. Ortalli, K. Pozela, Istituto Scienze Fisiche, via M. D'Azeglio 85, 43100 Parma, Italy

Several properties of dental materials (dimensional variation, thermal expansion/contraction, inhibition, evaporation of components, wear, elastic recovery, etc.) can be studied by measuring the change of specimen dimensions. We describe a new method, the laser beam scanning, that is suitable for these measurements. The advantages of the method are: no mechanical or chemical contact with dental material, high accuracy (±1 μm), possibility to analyze small specimens, easy to use. Representative characteristics (shrinkage, thermal expansion/contraction, oral fluid absorption) of some materials (polymeric impression materials, restorative composite resins, glass-ionomer materials) as a function of time are shown in detail.

Wednesday June 18, 1997 Mercredi 18 juin 1997

Morning Matin

Session V - From Research to Industry for the Patient Benefit, Part 1

G-V.1 - invited - 8:30-9:00

ION BEAM PROCESSING OF MEDICAL DEVICES, **P. Sioshansi**, SPIRE Corp., One Patriats Park, Bedford MA 01730-2396, USA

Ion beam-based processing is an effective method for improving performance, longevity, and biocompatibility of medical devices. Techniques such as ion implantation and ion beam assisted deposition (IBAD) offer the ability to beneficially modify a wide array of surface properties at low temperature. Ion implantation has been used for more than a decade to improve durability and extend the lifetime of orthopedic prostheses. It is also used in many other application, such as reducing friction and minimizing biofouling an catheters and lowering friction on orthodontic appliances. IBAD is used to deposit antimicrobial coatings on surfaces of catheters and other medical devices, to reduce oxygen and water vapor permeation, and to deposit hard, wear resistant coatings. Established and emerging applications of ion beam processing will be reviewed in this paper.

G-V.2 - invited - 9:00-9:30

HIGHLY FLUORINATED MATERIALS FOR IN VIVO OXYGEN TRANSPORT (BLOOD SUBSTITUTES) AND DRUG DELIVERY, **J. Riess**, Univ. of Nice, France and Alliance Pharmaceutical Corp., San Diego, USA

Fluorocarbons are characterized by exceptional chemical and biological inertness, extreme hydrophobicity, lipophobicity, high gas-dissolving capacities, low surface tensions, high fluidity and spreading coefficients, high density, absence of protons, and magnetic susceptibilities comparable to that of water. These unique properties are the foundation for a range of biomedical applications.

An injectable oxygen-carrying fluorocarbon emulsion has completed Phase II clinical trials as a temporary substitute for blood for use in conjunction with normovolemic hemodilution. The objective is to reduce or eliminate the need for donor blood transfusions during elective surgery. A liquid fluorocarbon is in Phase II/III clinical trials for treatment of acute respiratory failure through liquid ventilation. Other fluorocarbon-based products are in various stages of development as contrast agents for diagnosis of perfusion defects by ultra-sound imaging.

Numerous families of well-defined pure fluorinated surfactants have recently been synthesized. These surfactants are significantly more surface-active than their hydrocarbon analogs and they display a greater tendency to self-assemble, thus forming well-ordered stable supramolecular assemblies such as vesicles, tubules, fibers, ribbons, etc. Fluorinated amphiphiles also allowed the obtaining of a variety of stable reverse and multiple emulsions and gels. These systems are being investigated as drug delivery devices.

G-V.3 - invited - 9:30-10:00

THE FRENCH APPROACH OF BIOMATERIALS EVALUATION AND REGULATION: THE NATIONAL GROUP OF SCIENTIFIC INTEREST ON BIOMATERIALS, **E. Le Borgne**, G.I.S., Rennes, France

10:00-10:45

BREAK - VISIT OF THE POSTERS
FINAL DISCUSSION AND CONCLUSIONS OF THE POSTER SESSION
See programme of the poster session p. G-9 to G-12.

Session VI - From Research to Industry for the Patient Benefit, Part 2

G-VI.1 10:45-11:00

LACE OF BIOMATERIALS IN THE EC RESEARCH PROGRAMMES, U. Faure, E.C. DG XII, Brussels, Belgium and D. Muster, Univ. of Strasbourg, France

G-VI.2 - invited - 11:00-11:30

SMEs/SCIENCE COMMON RESEARCH ON DESIGN OF NEW/MATERIALS AND NEW STRUCTURES TO OBTAIN A LTS (EUROPEAN NETWORK PROJECT), **R. Doddoli**, Eurobiomatex, Strasbourg, France

11:30-12:15

ROUND TABLE ON RESEARCH-INDUSTRY INTERACTIONS THE FIELD OF BIOMATERIALS AND BIODEVICES. HOW TO OPTIMIZE THEM ?
Moderators : F. Burny, D. Muster, J. Price, T. Yamamuro

12:15-12:30

Concluding Remarks

12:30

LUNCH

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SYMPOSIUM G

POSTER SESSIONS

Tuesday June 17, 1997 **Morning**
Mardi 17 juin 1997 Matin

10:15-10:45

Tuesday June 17, 1997 **Afternoon**
Mardi 17 juin 1997 Après-midi

16:15-16:45

Wednesday June 18, 1997 **Matin**
Mercredi 18 juin 1997 Matin

10:00-10:45

G/P1 THE IMPACT OF THE CRIMPING AND THE LONGITUDINAL TENSION OF A VASCULAR PROSTHESIS ON THE FLUID FLOW VELOCITY DISTRIBUTION, S. Ben Adessalem, B. Durand, N. Chakfe, S. Cottin Bizonne, E. Urban, J.F. Le Magnen, G. Riepe, J.G. Kretz, Groupe Européen de Recherche sur les Prothèses appliquées à la Chirurgie Vasculaire, Faculty of Medecine, Strasbourg University, 11, rue Humann, 67085 Strasbourg, France

We proposed to determine the impact of the crimping and the longitudinal tension of a vascular prosthesis on the distribution of the flow velocity.

We analysed two kind of polyester vascular prosthesis: a woven and a knitted structure. The prostheses were opened and fixed on a support placed in a flow field. The measure of flow velocities was performed by a Laser Doppler. The laser beam crossing was computer driven and sweeping was carried out from 2 mm to 50 mm from the prosthetic interface. We changed the crimp density by stretching the prostheses with 4 prescheduled stresses. Corresponding crimp velocities were taken for each crimp density. The velocity profile demonstrated a decrease in flow speed near the prosthesis compared to calibration flow. Graphic representation of the velocity difference (ΔV) showed that ΔV increased when we approached the prosthetic interface. Statistical study of the results shows that ΔV follows a decreasing exponential law given by:

$\Delta V = a.b^{-x}$

x was the distance between the measure point and the prosthesis

The terms a and b of the mathematical expression were calculated. For all experiments b was relatively constant, arount 1.4. Crimp density had no effect on b value. However, value decreased from 1.4 to 1.2 when viscosity went down from 45 to 37 mPa.s. a value was influenced by the crimp density since its value decreased from 4.14 to 1.41 when crimp density decreased from 4.2 to 1.4 crimp/cm.

G/P2 SINTERING OF TCP-TiO_2 BIOCOMPOSITES: INFLUENCE OF SECONDARY PHASES, F. Caroff, R. Famery, K.S. Oh, and P. Boch, Laboratory of Ceramics and Inorganic Materials, Ecole Supérieure de Physique et de Chimie Industrielles de Paris, 10, rue Vauquelin, 75231 Paris 05, France

Biocompatible titanium is used for making surgical or odontological prostheses. In normal oxidizing environments, the metal oxidizes to titania, which implies that titanium parts are covered with a thin TiO_2 layer. This demonstrates the biocompatibility of titania. Titania exhibits good mechanical properties but is bioinert, in contrast with tricalcium phosphate (TCP), which exhibits poor mechanical properties but is bioactive and, therefore, is expected to favour osteo-conduction. TiO_2-based graded parts with a TCP-rich surface were prepared in aiming at combining mechanical properties of TiO_2 with bioactivity of TCP. The present paper reports on the role of calcium and phosphorus on the sintering behaviour of composites.

99.9% pure TiO_2 titania powders were pre-sintered to prepare porous skeletons, which were subsequently impregnated with TCP precursors. Various precursors were used for making «A- TiO_2 materials» where A is Ca, Ca+P, Na, or Na+P, in various concentrations. Then, the impregnated materials were sintered, the shrinkage behaviour being controlled using dilatometry. Finally, the composites were characterized by X-ray diffraction, SEM, and microanalysis. Although TiO_2 is the main phase in the composites, the densification is very sensitive to the nature and concentration of secondary phases. All the dopants slow down the densification rate, the main effect being found for the Na+P grouping. In all cases, one detects the presence of crystallized secondary phases, located along the grain boundaries or segregated at the triple points. Grain size also depends on the nature of secondary phase.

TCP-TiO_2 materials with graded composition (core made of dense TiO_2 and surface made of TCP granules embedded in TiO_2) are expected to exhibit favourable osteoconduction properties. Preliminary experiments[1] have confirmed the potential of these new biocomposites.

[1] Preparation and cytocompatbility of TCP-TiO_2 biocomposites F. Caroff, R. Famery, K. S. Oh, and P. Boch European Ceramic Society Meeting, Versailles, France (June 22-26,1997)

G/P3 CASTED TITANIUM FOR DENTAL APPLICATION: AN XPS AND SEM INVESTIGATION, B. Demri, A.M. Ferenczi and D. Muster, LEED Biomatériaux, Institut d'Anatomie Normale, CHRU, BP 426, 67091 Strasbourg Cedex, France

Casted titanium for dental applications obtained with an OHARA equipment has been characterized by means of SEM, XPS and XRD SEM investigations revealed a regular surface improved by grit, blasting with alumina and polishing. XPS analysis of the Ti/investment inteerface performed on the investment side showed the presence of metallic carbide and the reduction of SiO_2 into SiO_x After 20 days immersion in artificial saliva, no significant amounts of calcium phospate species has been fixed on the surface. However, XPS analysis of the Ols and Cls lines showed the presence hydroxyl groups, hydrocarbons and carbonate species.

G/P4 ADHESION OF MAMMALIAN CELLS TO POLYMER SURFACES: FROM PHYSICAL CHEMISTRY OF SURFACES TO SELECTIVE ADHESION ON DEFINED PATTERNS, J.L. Dewez, J.B. Lhoest, E. Detrait, Ph. Van den Bosch de Aguilar, Y.J. Schneider, P. Bertrand, P.G. Rouxhet, Biomaterials Programme, Université Catholique de Louvain, Place Croix du Sud 2/18, 1348 Louvain-la-Neuve, Belgium

Radichemical and XPS studies of collagen adsorption and tests of epithelial (HeP G2) cell adhesion were performed on different commercial and surface modified polystyrene materials, pre-conditioned or not by extracellular matrix proteins (ECM) in presence or not of Pluronic F68, a PEO-PPO-PEO surfactant polymer. Cell spread provided that ECM proteins were present at the surface, brought either by pre-conditioning or through cell secretion. When ECM proteins and Pluronic F68 were present simultaneously in the solution, the latter adsorbed preferentially on very hydrophobic supports while the opposite occured on less hydrophobic supports.

This has been used to control the adhesion of different mammalian cell lines (MSC 80 mouse Schann, Rat adrenal pheochromocytoma PC 12) and primary cells (Hepatocytes) on tracks of a few tens of µm. Therefore polystyrene surface was modified by oxygen plasma treatment on tracks laid out by microlithography, and the substratum was conditioned by a solution containing an ECM protein and Pluronic F68.

G/P5 ELABORATION AND EVALUATION OF AN INTRA-ORAL COLLED RELEASE DELIVERING SYSTEM, M. Diarra(1),(2), G. Pourroy(2), D. Muster(1), M. Zingraf(3), C. Boymond(3), (1) LEED Biomatériaux, CHRU, BP 426, 67091 Strasbourg Cedex, France, (2)IPCMS, Groupe des Matériaux Inorganiques, UMR 046 du CNRS, 23 Rue du Loess, 67037 Strasbourg Cedex, France, (3) Laboratoire de Pharmacotechnie Faculté de Pharmacie 74, Route du Rhin, BP24, 67401 Illkirch Cedex, France

In order to improve the administration of drugs for all pathology of the oral cavity, we developpe an intra-oral controlled release delivery system, permetting to reach high enough local concentrations for desirable therapeutic effect. We have formulated tablets of 200 mg intended to be sealed on a tooth. Those tablets resist to foods and drinks attacks. The tablets we elabored have a granular matrix composed by hydroxyapatite, ethyl cellulose and Eudragit^{R}. Zinc sulfate is used as first model of active drug, it has therapeutic effect on buccal mucosa. Profiles of continous in-vitro drug release in distilled water and artificial saliva at 37°C follow the relation $q/q_0 = k\ t^{1/2}$.

G/P6 EVALUATION OF PET DEGRADATION OF VASCULAR PROSTHESES, F. Dieval, Laboratoire de Physique et,Mécanique Textile, Université de Haute Alsace, Mulhouse, B. Durand, J.L. Le Magnen, N. Chakfe, S. Cottin Bizonne, E. Urban, G. Riepe, J.G. Kretz, P. Viallier, Mulhouse and Strasbourg, France

Polyester yarns used for the construction of vascular prostheses may be damaged during the different steps Qf the process: i.e. thermal processing, chemical exposure, or mechanical stresses. These dammages may induce structural modifications of the yarns. Assessment of the degradation state of polyester filaments still remain difficult.

We tested monofilaments taken from polyester vascular prostheses and no processed monofilaments of polyester representing the reference state.

We used three methods to charactenze the state of the fibers:

Method of critical dissolution time: consisted in shaping a loop with the fiber to submit it to the action of a mass. The whole was dipped in a 100% phenol at 60°C which is a solvant for PET. We determine the time required to the mass to fall at the bottom.

Calculation of the activation energy obntained from measuring of the dissoluting at different temperatures Measure of the residual constraint characterizing the preconstrained state of monofilaments.

A classical dynamometry was undertaken on filaments before end after processing.

Classical dynamometry failed to demonstrate any difference before and after processing. On the other hand, the method of critical dissolution time demonstrated differences in the activation energy and time of dissolution between filament before and after processing. Filaments coming from the prosthesis dissolved faster than the non processed filaments. The method of residual constraint measure demonstrated an heterogeneous state within the prosthesis.

This promising approach of PET degradation will allow to study the dammages related to the manufacturing process and to the long term implantation in humans.

G/P7 CHEMICAL METHODS OF CONTROLLING HYDROXYAPATITE POWDERS PARTICLE SIZE, SHAPE AND SURFACE ACTIVITY FOR DIFFERENT APPLICATIONS IN SURGERY, V. Doubok, L. Ivanchenko, N. Ulyanchich, A. Zyrin, Institute of Material Problems; E. Buzaneva, T. Veblaya, N. Kharchenko, A. Gorchinsky, L. Ilchenko, E. Smirnov, V. Malyi, A. Ivanisik, D. Fedin, National T.Schevchenko University, Kiev, Ukraine

The Ukrainian osteotropic ceramics materials based on hydroxyapatite (CERHAP) were approved by Health Ministry and introduced into state medical practise at the middle of 1996. Since that time the CERHAP have been successfully used for hundreds of patients in surgery. This communication is devoted to results of controlling HAP powder particle size, morphology, and surface relief during synthesis. For this purpose after chemical deposition slurry were introduced solutions of starch or perhydrol or precipitates were washed with ethanol. The powders were calcined at 400-1200°C. Then particle size, morphology, surface relief as well as powder pressing ability, ceramics sintering and strength were studied (XRD, IR-, Raman-spectroscopy, Lasermicroscopy: Laser-emission spectrochemical analysis, XPS, AFM) were adopted for the powders. Treatments can produce very disperse soft powders (as with starch additions) with agglomerate size about l µm or powders with bigger but porous particles. Powders with perhydrol additions can produce microporous ceramics coralline-like ceramics structure. IR-spectra of the most of the powders are similar to human bone but in high-density ceramics exists some pecularity for inner $(P0_4)^{-3}$ oscillations.

G/P8 BONE IN GROWTH INTO POROUS CERAMICS WITH DIFFERENT PORE SIZES, L. Galois, D. Mainard, K. Bordji, D. Clement, J.P. Delagoutte, Institut Européen de Biomatériaux et de MicrochirurgieURA CNRS 1288, CHRU Nancy-Brabois, 6 allée du Morvan, 54511 Vandoeuvre les Nancy Cedex, France

Introduction:

Porous calcium phosphate ceramics, especially hydroxyapatite ceramics, are used as bone-filling biomaterials. Many properties of these materials have been described, but how pore size influence bony integration of various porous ceramics remain unclear.

Objectives:

This study was performed to quantify the bone ingrowth and biodegradability of two porous calcium phosphate ceramics according to four different pore size ranges (45-80 µm 80-140µm, 140-200 µm, and 200-250 µm). All biomaterials had a homogeneous pore distribution and a porosity of 45 %. Acomparative study was performed in vivo and in vitro.

Conclusion:

Our results suggest that apore size of over 80 µm is necessary for bony ingrowth for both HA and TCP ceramics. The amount of bone seems to be higher within the TCP implants No difference is noted between the three highest pore size ranges (80-140, 140-200, and 200 250 µm). Percentage of resorption is higher in the case of TCP implants. Biodegradability of the implants seems to reduce the pore see influence on bony in growth, so after six months, in the case of TCP, no difference was noted between all pore size ranges.

G/P9 SYNTHESIS AND SURFACE CHARACTERIZATION OF FUNCTIONALIZED POLYLACTIDE MICROPARTICLES, K. E. Gonsalves, S. Jin, Polymer Program at the Institute of Materials Science & Department of Chemistry, University of Connecticut, Storrs, CT 06269, USA and M.-I. Baraton, LMCTS ESA 6015 CNRS, Faculté des Sciences, 87060 Limoges, France

Microparticles of poly(lactide) (PLac), its graft copolymers with amino acids, serine (P(Lac-Ser)), and aspartic acid (P(Lac-Asp)), were synthesized respectively using solvent evaporation microemulsion technique. Poly(vinyl alcohol) (PVA) was added as non-ionic surfactant to stabilize the particles. The particle sizes are in the range of 200 nm. The surface of the particles were characterized by FT-IR transmission spectroscopy at room temperature under vacuum. Hydroxyl groups originating from PVA exist on the surface of the particles and they were observed at 3506 cm^{-1}. Free hydroxyl groups originating from serine residue were pendant to the copolymer P(Lac-Ser) backbone and were observed at 3476 cm^{-1}. Also, free carboxylic acid groups pendant to the polymer P(Las-Asp) backbone originating from aspartic acid residue were observed at 3387 cm^{-1}. These hydroxyl and carboxylic acid groups were not found by regular FT-IR transmission technique. The appearance of the free hydroxyl and carboxlic acid groups in our IR spectra also showed that these hydrophilic functional groups migrated to the surface of the particles in the process of microemulsion.

G/P10 UNDERSTANDING THE MECHANICAL LAW BEHAVIOR OF POLYESTER VASCULAR PROSTHESIS MAY IMPROVE ITS IMPLANTATION, J.L. Le Magnen, Groupe Européen de Recherche sur les Prothèses appliquées à la Chirurgie Vasculaire, Faculty of Medecine, Strasbourg University, 11, rue Humann, 67085 Strasbourg, France, B. Durand, E. Urban, S. Cottin Bizonne, F. Dieval, G. Riepe, J.G. Kretz, N. Chakfe, Strasbourg, France

Polyester vascular prostheses are constructed as knitted and woven textile structures The morphological characterization and the performance evaluatoin of these prosthese areconducted using european and international standardized tests (CEN, ISO). We studied a woven and a knitted structure in order to determine the impact of the knowledge of their mechanical law on its implantation in humans.

We compared both structures using the tests proposed by the standards but also using modified tests taking into account the spatial configuration of the prosthesis.

The prostheses demonstrated significantly differences in their results which were found to be largely satisfactory to resist to physiological stresses applied during implantation However, these tests are probably unsatisfactory to predict the long term behavior of vascular prostheses since dilatations or ruptures are still observed. In our observations maintening the prosthesis in shape in a system with adapted clamps during the increase of the longitudinal stress modified significantly the mechanical law of the prosthesis. This confirms the orthotropic behavior of textile structures and involves the stiffness moduli in the transverse and longitudinal direction as well as Poisson's coefficient in relation to the stresses related by the blood flow.

A better knowledge of the usuable lenght under multidirectional stesses will help surgeons to implant the prosthesis under optimal conditions in order to improve its mechanical stabity in humans. This optimal condition should allow to apply a preconstraint to the prosthesis that would be cancelled when the blood flows.

G/P11 A MURIN MODEL TO EVALUATE THE BIOCOMPATIBILITY AND THE HEALING SEQUENCE OF VASCULAR PROSTHESES, V. Lindner, Groupe Européen de Recherche sur les Prothèses appliquées à la Chirurgie Vasculaire, Faculty of Medecine, Strasbourg University, 11, rue Humann, 67085 Strasbourg, France, B. Gasser, N. Chakfe, C. Marin, J.G. Kretz, Strasbourg, France

We proposed a murin model to characterize the cellular reaction developped against a biomaterial in the peritoneal cavity of the mouse and to compare the healing sequence of 2 kinds of vascular prostheses (textile polyethylene terephthalate (PET) and expanded PTFE).

Five pieces of biomaterials were inserted in the peritoneal cavity of mouses which were sacrified 4 and 8 weeks after implantation. The pieces were fixed after explantation and we performed a quantitative evaluation of the cellular reaction (macrophages, polynuclear cells, lymphocytes).

Healing sequence according to time of implantation: the cellular infiltration of the periprosthetic tissue was the same at 4 and 8 weeks for both PET and PTFE. At 4 weeks, there was a majority of macrophagic and polynuclear cells. At 8 weeks, the polynuclear cells decreased and the lymphocytes increased, in a significant level. There was no significant difference for the macrophages at 4 and 8 weeks. In the inner part of PTFE prostheses, the polynuclear cells decreased as the macrophages increased. By contrast, in PET prostheses, no significant difference was noted.

Healing sequence according to biomaterials: there was no significant difference between the healing sequence in the contact of the two kinds of biomaterials. However, after 4 weeks, the porous structure of PTFE was infiltrated by more polynuclear cells and less macrophages than the textile structure of PET.

The cellular reactivity developed against PET and PTFE was similar in this model as showed by the histological study at the interface. However, the cellular components of the intra prosthetic infiltrate seems much more influenced by the geometry of the structure than the hiomaterials itself.

G/P12 R&D ON BIOMATERIALS AND RELATED TECHNOLOGIES CARRIED OUT IN NEW MATERIALS DIVISION, NEW TECHNOLOGIES DEPARTMENT, ENEA, C. Piconi, P. Delogu, R. Vatteroni, ENEA, New Technologies Dpt., 301 Anguillarese, 00060 Roma, Italy

The New Materials Division of the New Technogies Dpt (INN-NUMA) of ENEA, the Italian national Authority for New Technologiess, Energy and the Environment, is active in the field of biomedical technologies since 1987. INN-NUMA carries out R&D in partnership with many national and european partners, in the framework both of national funded research, both of CE sponsored Research programs. The exploitation of results typically consists in a Technology Transfer and Assistance to the Industry, with special attention ot SMEs.

The R&D projects now in progress are concerning ceramic coating on ceramics, diamond coating on metals, development of high purity ceramic powders for production of ceramic biomaterials (Hydroxyapatite and Yttria stabilized Tetragonal Zirconia Ceramics).

G/P13 THE RESEARCH OF CALCIUM STATE IN ULTRA DISPERE PHOSPHATE CLUSTER TYPE SYSTEMS, A. Shpak, V. Karbovskii, Institute of Metal Physics, 36 Vernadsky Str., Kiev 252142, Ukraine

We have studied the occupied valence states of calcium inmetallic calcium, CaO, $CaCO_3$, $Ca_3(PO_4)_2$, $Ca_{10}(PO_4)_6(OH)_2$, egg shell, gall-stones and hydroxyapatite of human bone. The distinct feature of hydroxyapatite of human bone is its ultra disperse structure. The size of the crystals of human bone do not exceed 500x100x100 Å. Such crystals have a specific surface of more than 400 m^2/g. More than 25% of atoms constituing the crystals are at the surface. These atoms are especially suitable for a chemical exchange. A transition of calcium compounds to the cluster state changes essentially their electronic structure. The X-ray emission spectra which represent the energetic distribution of the valence p electrons of oxygen, phosphorus and calcium as well as Ca d electrons have been plotted in the same energy scale using the binding energies of the core electrons obtained from XPS studies. We have established that the calcium K-bands in both ultra disperse hydroxyapatite of human bone and chemical hydroxyapatite are essentially similar. A rather strong covalent component of the chemical bond is observed in hydroxyapatite. In the ultra disperse hydroxyapatite we have observed a significant localization of calcium d-states, which have an atomic character. The fact is of particular importance for an explanation of abnormal physical and chemical properties of calcium based inorganic phosphate materials and of the bio-chemical processes of substance exchange in native human and animals bones.

G/P14 EYES REMEDY FILMS FOR TREATMENT OF GLAUCOMA, M. Umerzakova, Gh. Mustafina, G. Boiko, B. Zhubanov, Institute of Chemical Sciences NAS, 106 Valihanov 480100 Almaty, Kazakhstan; and Z. Dzhumabaeva, M. Kurmangalieva, G. Djakova, Gh. Mustafina, Kazakh Institute of Eyes Deseases, 95a Tole bi, 480012 Almaty, Kazakhstan

Some nature and synthetic high molecular compounds for producing of polymer forms of liothics have been investigated. Immobilization was conducted by chemical interaction of functional groups of polymer with remedy and by compositional inclusion of remedy into the polymer. Pilocarpine, pyridoxine (B_6), ascorbinicum acid, rutinum were used as remedy additions. For imparting of elasticity to the eyes remedy films there was added glycerine.Cinetics of the release of pilocarpine and vita-mins from the remedy films was studied in theartificial medium which modeled biological conditions. It was shown that release of the remedy substance had gradual character and mainly depended on the functional activity of the polymer matrix.

Combined application of pilocarpine with vitamin significantly rises effectivity of treatment.

G/P15 POLYMER PHARMS FOR OPHTALMOLOGY ON THE BASIS OF DERIVATIVES OF GLYCYRHETINIC ACID, M. Umerzakova, Gh. Mustafina, M. Irismetov, B. Dzhienbaev, G. Boiko, B. Zhubanov, Institute of Chemical Sciences NAS, 106 Valihanov, 480100 Almaty, Kazakhstan; and A. Kairov, M. Kurmangalieva, Gh. Musta-Fina, Kazakh Institute of Eyes Deseases, 95aTole bi, 480012 Almaty, Kazakhstan

Glycyrhetinic acid and it's derivatives (glyde-rinine and it's Na salt) produced from liquorice were used as effective antiinflammatory, antiburning, antiulcer remedy preparation.

In order to prolong activity there were obtained their polymer forms. Conditions of immobilization of Na-glyderinine have been studied. Optimal polymer matrix for producing of eyes remedy films was determined. Release of Na-glyderinine from polymer matrix was studied. Cinetic parameters and coefficient of bonding were determined. Prolong effect was shown.

At present time the effectiveness of remedy eyes films at treatment in ophtalmology during postoperational period is studied.

G/P16 3D IMAGING OF VASCULAR PROSTHESES: MODELIZATION AND QUANTIFICATION OF MORPHOLOGICAL CHANGES, E. Urban, N. Chakfe, J.G. Kretz, B. Durand, GEPROVA, Faculté de Médecine, Strasbourg, France, M. Sadki, G. Zöllner, Dèpartement de Radiology, Hôpital Civil, Strasbourg, France

Introduction: Although aortic prostheses are considered to be relatively durable, late complications due to material degradation (thrombosis, leaks, dilation, fissuration, elongation, migration) still occur. Therefore, there is a need for a low invasive precise method to explore vascular grafts an to provide a geometrical model of vascular lumen. Computed Tomography Angiography (CTA) data are used for a precise follow-up of in vivo grafts and post-processed to generale mathematical representations.

Material and Methods: Spiral CTA was performed in 45 patients with aorto-aortic, aorto-iliac or aorto-femoral polyethylene terephtalate (PET) prosthesis for aortic and aortofemoral aneurysms. All patients underwent control examinations: post-op, after six months, one year and two years. We developed a software for 3D Visualization Slicing and Measurement (3D-VSM) to perform 3D reconstructions and mathematical representations. The algorithm allows to provide real size vascular measurements like volume, section area, surface area, diameters. Each of these models is archived, creating then a database that allows to analyse the evolution of the morphologie structure of the prosthesis by using different operators (addition, subtraction, etc.).

Conclusion : Modeling of the in vivo prosthesis was successful in all cases. The 3D-VSM method offers the possibility of precise measurement of morphological changes of prosthesis, especially in time series. This quantification will allow to analyze why and where vascular prostheses degrade and to improve their conception.

G/P17 IMAGE PROCESSING TECHNIQUES APPLIED TO THE STUDY OF THE MUSCOLOSKELETAL SYSTEM AND ITS INTERACTIONS WITH BIOMATERIALS, A. Merolli, P. Tranquilli Leali, Clinica Ortopedica dell'Universita' Cattolica largo Gemelli 8,1-00168 Roma, Italia

Image processing is basically a measurement technique and in this acception it has been introduced into morphometrical practice. The study of bony structures seems to be particularly well suited for image processing for two reasons: a) the structure can be easily identified from the background; b) the principal function of the structure (mechanics) can be adequately described in terms of morphology. Several kinds of interfaces for different materials are suitable for quantitative studies when surface-related parameters are measured; the most fruitful application is probably the long-term monitoring of bioactive coatings. Also striated muscle histomorphometry can fruit of image processing technology in speeding up its routine procedures and in evaluating a greater number of parameters in a less tedious way. Type-l, IIA and IIB fibers can be differentiated from the background and surface related parameters measured; this makes feasible routine measurement of large number of samples llke those required for industrial purposes and biomaterial research.

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM H

Biodegradable Polymers & Macromolecules

Symposium Organizers

A. STEINBÜCHEL, Westfälische Wilhelms-Universität Münster, Münster, Germany

R.J. MÜLLER, GBF, Braunschweig, Germany

H.G. RAST, Bayer AG, Leverkusen, Germany

Y. DOI, The Institute of Physical & Chemical Research (RIKEN), Saitama, Japan

The assistance provided by
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SYMPOSIUM H

Monday June 16, 1997 **Afternoon**
Lundi 16 juin 1997 Après-midi

13:45-14:00 OPENING OF SYMPOSIUM H, **A. Steinbüchel**

Session I - Achievements and Developments for Applications of New Polymeric, Biodegradable Materials According to the Field of Application

Chairperson: Y. Doi, The Institute of Physical and Chemical Research (RIKEN), Saitama, Japan

H-I.1 - invited - 14:00-14:30 ECOLOGICAL CONSIDERATIONS ON THE USE AND PRODUCTION OF BIOSYNTHETIC AND SYNTHETIC BIODEGRADABLE POLYMERS, **W. Holley**, Fraunhofer Soc. ILV, Giggenhauser Str. 35, 85354 Freising, Germany

By the use life cycle assessment (LCA) methodology this contribution will show the establishment of life cycle inventory and a basic impact analysis for biodegradable polymers of nativ and synthetic origin. These two different «feedstock strategies» will be compared using resource efilciencies, finale waste quantities and a set of emission borne environmental burdens as criteria.

In a second paragraph the «biodegradable material life cycle approach» including waste composting will be compared to synthetic polymer life cycles including selected waste recovery strategies.

H-I.2 - invited - 14:30-15:00 PREREQUISITES FOR BIODEGRADABLE PLASTIC MATERIALS FOR ACCEPTANCE IN REAL-LIFE COMPOSTING PLANTS AND TECHNICAL ASPECTS, **B. De Wilde** and J. Boelens, Organic Waste Systems n.v., Dok, Noord 4, 9000 Gent, Belgium

For bioplastic materials to be accepted in composting plants biodegradability alone is not sufficient. As important is the disintegration during composting. This is the physical falling apart of the bioplastic material or more precisely of the product which has been made from it into fine visually indistinguishable fragments at the end of a typical composting cycle. The property of disintegration is measured in a pilot-scale or full-scale composting test. The test substance is subjected to a spontaneous composting process for a duration of 12 weeks. At the end a sieving over 2 mm followed by a precise sorting analysis is executed. It can be that a bioplastic passes the test at a specific thickness but fails the test at a higher thickness..

It must also be demonstrated that the bioplastic materials have no negative effect on compost quality. This involves chemical analyses, e.g. heavy metals, required to evaluate conventional compost quality. In addition also ecotoxicity tests are advised, including plant germination tests as well as animal toxicity tests. The purpose af the tests is to make sure that small additives (e.g. in the <1% range) falling beyond the sensitivity of biodegradation tests as well as metabolites from biodegradation do not exert any negative biological effect.

Technical aspects include the compatibility of pre- and posttreatment in a compost plant to the inclusion of bioplastics in the compost feedstock. The most important aspect is to schedule sieving at the end of the composting cycle.

H-I.3 - invited - 15:00-15:45 CURRENT MEDICAL AND PHARMACEUTICAL APPLICATIONS OF BIODEGRADABLE POLYMERS AND THEIR PROBLEMS, **Y. Ikada**, Research Center for Biomedical Engineering, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606, Japan

Biodegradable materials used in medicine and pharmaceutics include natural and synthetic polymers. Among the natural biodegradable polymers are proteins, polysaccharides, and polyesters, while aliphatic polyesters, polyanhydrides, polyorthoesters, and polycyanoacrylates are well-known synthetic biodegradable polymers. Generally, natural biodegradable polymers are hydrophilic and poor in mechanical properties except for chitin and poly(3-hydroxybutyrate), while synthetic biodegradable polymers are hydrophobic and have high mechanical strength in comparison with the natural polymers.

Biodegradable polymers of high strength have been clinically used for suturing, internal fixation of fractured bones, and clipping, while hemostasis, tissue adhesion, adhesion prevention, and scaffolding have been offered mostly by natural polymers. Biodegradable polymers have also attracted much attention in the pharmaceutical field as drug carriers which generally do not require high strength. In any biomedical applications of these biodegradable polymers, highly important issues are the toxicity of biodegradation products and the balanced relationship between the biodegradation rate and the rate of wound healing (or bone reunion, tissue regeneration, drug release, and so on). Some current applications of these biodegradable polymers in medicine and their related problems will be briefly demonstrated in this presentation.

H-I.4 - invited - 15:45-16:15 REQUIREMENTS FOR BIODEGRADABLE, WATER SOLUBLE POLYMERS **G. Swift**, Rohm and Haas Company, Norristown Road, Spring House PA 19477, USA

Water-soluble polymers are widely used in a variety of industrial and consumer products. After use, depending on their characteristics and the particular application, they are generally discarded as dilute aqueous solutions. These aqueous wastewater streams may go directly into the environment or more often, and preferably, they pass through a wastewater treatment facility for remediation. Currently, for water-soluble polymers remediation generally implies adsorption on sewage sludge and removal for landfilling or burning. In the future, it is anticipated that water-soluble polymers will be designed to be either completely biodegradable in the wastewater treatment facility or on the sewage sludge in a subsequent environmental compartment of choice. The rationale for this requirement and the synthetic approaches to polymers meeting this objective will be explored.

16:15-16:30 **BREAK**

Session II - Polyamides
Chairperson: A. Steinbüchel, Westfälische Wilhelms-Universität Münster, Münster, Germany

H-II.1 - invited - 16:30-17:00

SYNTHESIS AND CHARACTERIZATION OF HYDROGELS PREPARED FROM MICROBIAL POLY(γ-GLUTAMIC ACID) AND POLY(ε-LYSINE), **M. Kunioka**, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

Biodegradable and pH-sensitive hydrogels have been prepared from microbial poly(γ-glutamic acid) (PGA) produced by Bacillus subtilis and poly(ε-lysine) (PL) produced by Streptomyces albulus using γ-irradiation. When a dosage of γ-irradiation was 20 kGy or more for PGA aqueous solutions, transparent PGA hydrogels could be produced. It was found that PGA hydrogels had a high water sorption capability (200 - 3500 times). Under acid conditions, the PGA hydrogel deswelled due to the lack of -COO-'s ionic repulsion. These PGA hydrogels were degraded by heating over 60 °C in a deionized water.
When the dosage of γ-irradiation was 70 kGy or more, transparent and opaque hydrogels could be produced. Specific water content (wt. of absorbed water/wt. of dry gel) ranged from 20 to 160 g/g. Under acid conditions, the PL hydrogel swelled due to the ionic repulsion of the protonated amino groups in the PL molecules. The PL hydrogel was biodegraded by a Protease A from Asperigillus oryzae.
In addition, PGA hydrogels have been prepared by adding water soluble carbodiimide and alkanediamine such as 1,3-propanediamine, 1,4- butanediamine or 1,6-hexanediamine in an aqueous medium. Specific water content ranged from 300 to 1993 g/g.

H-II.2 - invited - 17:00-17:30

CHEMICAL SYNTHESIS OF POLYASPARTATES, **M. Schwamborn**, BAYER AG, OC Research & Product Development, Kaiser-Wilhelm-Allee, 51368 Leverkusen, Germany

In order to improve the environmental acceptability of water-soluble sequestrants and dispersants which can end up in the surface water, new alternatives to the currently used polycarboxylate homo- and copolymers are needed. One alternative might be «Polyaspartates», a group of acidic polyamides. These polymers which are functional equivalents of existing products are biodegradable. They can be used in many different applications such as home laundry detergents, automatic dishwasher detergents, water treatment chemicals, oil filed treatment additives, or dispersants for a variety of organic and inorganic solids and scales.
Synthetic approaches to «Polyaspartates» will be described. The resulting polymers are characterized by different analytical methods (i.e. ^{15}N-Solid Phase NMR) and evaluated in relation to their performance and biodegradability.

Session III - Lignin
Chairperson: A. Steinbüchel, Westfälische Wilhelms-Universität Münster, Münster, Germany

H-III.1 - invited - 17:30-18:00

APPLICATIONS OF MOLECULAR GENETICS FOR BIOSYNTHESIS OF NOVEL LIGNINS, **W. Boerjan**, J. Van Doorsselaere, M. Baucher, M. Van Montagu, Laboratorium voor Genetica, Universteit Gent, K.L. Ledeganckstraat 35, 9000 Gent, Belgium ; J.-C. Leplé, Station pour l'Amélioration des Arbres Forestiers, INRA, 45160 Ardon, France ; M. Petit-Conil, Centre Technique de Papier, 38004 Grenoble, France ; L. Jouanin, Laboratoire de Biologie Cellulaire, INRA, 78026 Versailles Cedex, France ; B. Monties, Laboratoire de Chimie Biologique, INRA, 78850 Thiverval-Grignon, France

Lignin is an abundant aromatic polymer deposited in the cell walls of mainly xylem cells. The removal of lignin during chemical pulping is a toxic and energy-consuming process. For the pulp industry it would be beneficial to process trees with either less lignin or a modified lignin that is more easily extracted. To achieve this goal, we have cloned several cDNAs encoding enzymes that play crucial roles in lignin biosynthesis in poplar. Antisense inhibition of caffeic acid/5-OH ferulic acid-O-methyltransferase activity in transgenic plants results in a dramatic change in the composition of lignin with the simultaneous appearance of a novel lignin unit, 5-hydroxyguaiacyl. Inhibition of cinnamyl alcohol dehydrogenase activity in poplar results in an increased lignin extractability during chemical pulping, i.e. a similar amount of lignin can be removed from the wood using less chemicals.
This work was carried out in the framework of EU Research Programmes-AGRE-0021-C, FAIR-PL 95424 and AIR2-CT93-1661.

H-III.2 - invited - 18:00-18:30

NOVEL STRUCTURE AND PROPERTIES OF LIGNINS, IN RELATION TO THEIR VARIABILITY, **B. Monties**, INRA, Laboratoire de Biochimie, Centre de Recherche Agronomique, 51686 Reims, France

As main component of woods and forages, the plant cell walls can be shown as a composite of cellulosic fibers embeded by hemicelluloses and lignins : lignocellulose. Recently, new possibilities for changing the properties of lignocellulose by genetic manipulation of the lignin monomers biosynthesis has been demonstrated. Even when the novelty of the genotype of these transformant is beyond doubt, their phenotype can be compared to natural mutants or ecotypes as biosynthesis of lignin monomers only appeared to be changed. It seems not trivial to discuss these changes of phenotypes in relation to lignin polymerization which occurs according a non enzymatic radical polymerization process, allowing the formation of networks, whose characteristics are correlated with mechanical properties and alcaline delignification of woods, with adhesion properties of lignocellulose components and even biodegradability. These points will be emphasized in relation to posters presented

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session IV - Polyesters, Part 1
Chairperson: M. Kunioka, Institute of Materials and Chemical Research, Ibaraki, Japan

H-IV.1 - invited - 8:30-9:00

CHEMICAL SYNTHESIS OF POLYLACTIDES AND ITS COPOLYMERS FOR MEDICAL APPLICATIONS, **D.R. Bendix**, Boehringer Ingelheim KG, PO Box 200, 55216 Ingelheim, Germany

Resorbable polyesters based on lactide are used as raw materials in the manufacturing of implantable medical devices and as excipients in the production of pharmaceutical dosage forms. In copolymers mainly glycolide is used as comonomer, but some polymers with trimethylene carbonate (TMC), dioxanone and ε-caprolactone are also available.

To produce resorbable polyesters different synthetic routes are known. The direct polycondensations of the corresponding α-hydroxy-acids with or without a catalysts leads only to relatively low molecular weight compounds, which are used exclusively in controlled release applications. To produce polymers with higher molecular weight averages the corresponding cyclic diesters or lactones are synthesized and polymerized by ring opening reactions using a catalyst/moderator system. Although solvent, emulsion and suspension polymerization have been reported, the bulk polymerization either in the melt or in the solid phase is the most commonly used process. By using the different stereo isomers of the lactide and the above mentioned comonomers, by controlling the molecular weight and/or the comonomer sequence tailor made polyesters are accessible. For the use of these polymers in medical applications a high purity of the starting materials and normally a purification of the crude polymer is required. Additionally, the production has to comply to cGMP and EC regulations and the products should be covered by master files.

H-IV.2 - invited - 9:00-9:30

ALIPHATIC POLYESTERS AND ITS COPOLYMERS SYNTHESIZED THROUGH THE DIRECT CONDENSATION POLYMERIZATION, **M. Ajioka**, H. Suizu, C. Higuchi, T. Kashima, Central Research Institute, Mitsui Toatsu Chemicals Inc., 1190, Kasama-cho, Sakae-ku, Yokohama 247, Japan

Polylactic acid(PLA) has been recognized as one of the promising biodegradable polymers because of its good mechanical properties, good compostability, and raw material position, renewable resources. We have studied the direct condensation polymerization of lactic acid and obtained PLA with a high molecular weight. Various aliphatic polyesters, such as copolymers of lactic acid and the other hydroxy acids, and polyesters of diols and dicarboxylic acids, were synthesized using the same polymerization method. Reactions of PLA and the other synthetic polymers or natural polymers were also studied.

H-IV.3 - invited - 9:30-10:00

LARGE SCALE PRODUCTION, PROPERTIES AND COMMERCIAL APPLICATIONS OF POLYMERS & MACROMOLECULES, **J. Lunt**, Cargill Inc., EcoPLA Business Unit, 2301 Crosby Road, Minneapolis, Minnesota, USA

Poly lactic acid polymers possess many of the properties of conventional petro chemical based plastics such as Polystyrene and Polyethylene Terepthalate. However, Polylactic acid is produced from a renewable resource monomer, lactic acid, which is derived from corn. Continuing improvements in economics of monomer supply, manufacturing technology, product development and marketing activities are demonstrating the potential for these polymers in the commodity plastics market.

The specific properties of poly lactic acid polymers, in many applications are equivalent or superior to other plastics. In addition, these new products are truly biodegradable. This total property spectrum indicates a promising future for these unique materials.

10:00-10:30 **BREAK**

Session IV - Polyesters, Part 1 (continued)
Chairperson: M. Kunioka, Institute of Materials and Chemical Research, Ibaraki, Japan

H-IV.4 - invited - 10:30-11:00

POLYESTERS FROM LACTIDES AND ε-CAPROLOACTONE. DISPERSION POLYMERIZATION VERSUS POLYMERIZATION IN SOLUTION, **S. Slomkowski**, S. Sosnowski, and M. Gadzinowski, Center of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Lodz, Poland

Polymerizations of cyclic esters are usually carried out in bulk and/or in solution. Recently, we began studies directed towards development of synthetic methods allowing to obtain polyesters by controlled dispersion polymerizations of cyclic monomers. During these studies we intend also to establish basic properties of dispersion ring-opening polymerizations. In this paper we will discuss the most important differences between the dispersion polymerizations and polymerizations in solution of lactides and ε-caprolactone, with special emphasis on advantages of the former processes.

The most important and characteristic features of the investigated dispersion polymerizations are: fast monomer conversions (faster than in solution due to the high local concentrations of active centers and monomer in growing particles) and reduction of transesterification reactions. With appropriate thermal post synthesis treatment it is possible to control the degree of crystallinity and surface properties of polymer particles. The latter is due to the thermally induced conformational rearrangement of surface active agent in the surface layer. Moreover, dispersion polymerizations offer the possibility of simple and convenient ways of polymer isolation.

H-IV.5 - invited - 11:00-11:30 BIODEGRADABLE POLYMERS: RECENT ADVANCES IN REACTIVE PROCESSING, BLENDS, AND COMPOSITES, **S.P. McCarthy**, NSF Center for Biodegradable Polymer Research, University of Massachusetts Lowell, Lowell, MA 01854, USA

The development of biodegradable polymers and materials has recently increased considerably. The use of blends and composites based on biodegradable plastics can be used to improve the mechanical properties and reduce the cost and in certain cases increase the biodegradation rate. Over the past five years, research in the Center has focused on miscible and compatible blends utilizing the commercially available polymers such as poly hydroxy butyrate-valerate, poly- caprolactone, polylactic acid, poly ethylene glycol and cellulose acetate. Recent work has included reactive processing on a number of these blends to obtain synergistic properties or compatibilization. The addition of a cellulosic component to PLA may be used to reduce the cost of the material, increase the biodegradation rate, and improve its mechanical properties. The composites chosen for this study utilize cellulose and a biodegradable resin in the form of laminates, paper coating, and reinforcing fibrous cellulosics. The cellulosics fibrous materials chosen for this study were paper waste fibers, paper, rayon nonwoven fabric.

Session V - Polysaccharides
Chairperson: H.G. Rast, Bayer AG, Leverkusen, Germany

H-V.1 - invited - 11:30-12:00 PRODUCTION AND APPLICATIONS OF XANTHAN GUM, **B. Katzbauer**, Jungbunzlauer International AG, St. Alban-Vorstadt, Postfach, 4002 Basel, Switzerland

XANTHAN GUM is a natural high molecular weight polysaccharide produced by a fermentation process.

The initial research publications on Xanthan Gum and its production came out in 1961. The research laboratories of the US Department of Agriculture had discovered that the bacterium Xanthomonas campestris found on cabbage plants produced an extracellular polysaccharide with exceptional rheological properties.

Since then a number of improvements in polysaccharide production and recovery have been made. Today Xanthan Gum is the commercially most important microbial polysaccharide.

Due to its exceptional rheological properties it is a very effective stabilizer for water-based systems. XANTHAN GUM is soluble in both cold and hot water and imparts high viscosity at low concentrations. The addition of XANTHAN GUM to water changes the rheological properties from Newtonian to pseudoplastic thus exhibiting high viscosity at rest but thinning under shear stress.

The numerous areas of application cover a broad range from the food industry to oil drilling. Typical food applications of XANTHAN GUM are salad dressings, sauces, gravies, dairy products, desserts, low-calorie foods and convenience foods in general. XANTHAN GUM is also used in cleaners, coatings, polishes, agricultural flowables and in oil drilling.

H-V.2 - invited - 12:00-12:30 BIOSYNTHESIS AND APPLICATIONS OF ALGINATES, **H. Ertesvaag** and S. Valla, Unigen, Center for Molecular Biology, NTNU, 7005 Trondheim, Norway

Alginate is a family of linear polysaccharides composed of mannuronic acid (M) and guluronic acid (G). Alginates from brown algae are used as gelformers an viscosifiers in a wide range of industrial applications and for encapsulation of cells. The properties of alginate is mostly determined by the amount and distribution of G. Consecutive G's (G-blocks) are necessary for the formation of gels, while the stretches of consecutive M's (M-blocks) or alternating M and G (MG-blocks) determine the pore size and water-binding capacity of the gel. M-blocks are also highly immunogenic. The amount and distribution of G varies in alginates isolated from different species or from different parts of the plant. Alginate is also made by some bacteria belonging to the genera Azotobacter and Pseudomonas. These alginates are partially O-acetylated. Alginates from Pseudomonas do not contain G-blocks, while Azotobacter is able to make all block-types.

The biosynthesis of alginate has mostly been studied in P. aeruginosa, where also many of the involved proteins have been identified. In both algae and bacteria the polymer is first produced as polymannuronan, which is then epimerized by the enzyme mannuronan C-5-epimerase. A gene encoding a periplasmic epimerase have been identified in the alginate gene clusters of P. aeruginosa and A. vinelandii. The A. vinelandii genome also encodes a family of at least five secreted epimerases, some of which make G-blocks, others MG-blocks, or a mixture of both types. It is probable that A. vinelandii uses different alginates at different stages of its life cycle.

12:30-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Poster Session I

14:00-16:00 See programme of this poster session p. H-16 to H-19.

16:00-16:30 **BREAK**

Session V - Polysaccharides (continued)
Chairperson: H.G. Rast, Bayer AG, Leverkusen, Germany

H-V.3 - invited - 16:30-17:00

IMPROVED PRODUCTION OF BACTERIAL CELLULOSE AND ITS APPLICATION POTENTIAL, **E. Vandamme**, S. de Baets and P. de Wulf, Laboratory of Industrial Microbiology and Biocatalysis, University of Gent, Coupure links, 653, 9000 Gent, Belgium

Bacterial cellulose, produced by Acetobacter species, displays unique physical properties, including high mechanical strength, high water absorption capacity, high crystallinity, ultra-fine and highly pure fiber network structure. It is expected to be a new commodity bio-chemical with diverse applications, if its mass production process could be improved especially via submerged fermentation methodology. It finds already application as food matrix (nata de coco) and as dietary fiber, as temporary dressing to heal skin burns, as acoustic or filter membrane, as ultra strength paper and as a reticulated fine fiber network with coating, binding, thickening and suspending characteristics; a wet spinning process for bacterial cellulose into textile fibers has also been developed, and applications as superconducting and optical fiber matrix are under study. We have been able to improve bacterial cellulose production in surface culture (up to 28 g/l), as well as in submerged culture (up to 9 g/l) via strain selection, mutation, medium composition optimization and physicochemical fermentation parameter control; glucose and fructose as carbon source, acetic acid as an energy source, combined with a precise control of pH and dissolved oxygen levels resulted in highly improved cellulose yields. An internal pH control in stationary surface cultures was achieved by a proper choice of the ratio of fructose/glucose/acetic acid. It was also demonstrated that cellulose formation could be enhanced by adding insoluble micro-particles such as diatomaeceous earth, silica, small glass beads, loam particles to submerged, agitated/aerated Acetobacter cultures. This microcarrier-enhanced cellulose synthesis could be the result of the formation of micro-environments with locally lowered dissolved oxygen levels because of the attachment of Acetobacter cells as a biofilm on the particles. As such, less glucose is lost as gluconate, saving it for cellulose formation and keeping the pH profile within the desirable range. We also developed a UV-mutation and proton suicide enrichment strategy, which allowed the selection of A. xylinum mutants, which are highly restricted in (keto)gluconate synthesis and produce cellulose more efficiently, even under oxidative culture conditions. Combining these nutritional, genetical and bioprocesstechnological improvements, very high levels of bacterial cellulose have been attained. Further improvements are needed to arrive at an economical fermentation process for mass production of bacterial cellulose.

De Wulf, P. et al. (1996). Improved cellulose formation by an Acetobacter xylinum mutant limited in (keto)gluconate synthesis. Joumal of Chemical Technology and Biotechnology, 67, 376-380.

H-V.4 - invited - 17:00-17:30

PRODUCTION AND APPLICATION OF MICROBIAL CELLULOSE, **R. Jonas**, Centro de Desenvolvimento Biotecnologico, PO Box 7151, 89239-970 Joinville, Brazil/ GBF, Mascheroder Weg 1, 38124 Braunschweig, Germany, and L.F. Farah, Rua Mateus Leme 2418, 80530-010 Curitiba, Brazil

Cellulose, the basic material of all plant substance, is also being produced by green algae (Valonia) and some bacteria, principally of the genera Acetobacter, Sarcina and Agrobacterium. Special attention has been given to strains from Acetobacter, specially Acetobacter xylinum. Acetobacter strains are wellknown for oxidizing alcohols to acids and ketones, specially for the production of vinegars using ethanol,wine or cider as carbonsources. The formation of the cellulose pellicle is ocurring on the upper surface of the supernatant film.The cellulose production was reported to be stimulated by addition of lactic acid, methionine, tea infusion, oligosaccharides and cellulase. For the production process new non conventional bioreactors have been developed. Low weight cellulose may be produced by a mixture of glucose with 2-deoxyglucose.

Bacterial cellulose can be applied in areas where plant cellulose can hardly be used. New applications were described as thickener to maintain viscosity in food, cosmetics, etc, as nonwoven fabric or paper for old document repair as food additive,and others.We could make use of cellulose films as a temporary substitute of human skin in the cases of burns,ulcers,decubitus and others. Biofill^R, Bioprocess^R, Gengiflex^R are products of microbial cellulose which have got now wide applications in surgery and dental implants.

H-V.5 - invited - 17:30-18:00

THERMOPLASTIC AND BIODEGRADABLE POLYMERS OF CELLULOSE, **J. Simon**, H.P. Müller, R. Koch, Zentrale Forschung, ZF-MFF, Q18, Bayer AG, 51368 Leverkusen and V. Müller, Wolff Walsrode AG, 29655 Walsrode, Germany

Polymers which are biodegradable currently achieve high interest in materials science since they offer reductions of landfill space during waste management as well as new end-user benefits in various fields of applications. Among these materials, those from renewable resources such as polysaccharides additionally offer CO_2-neutrality, partial independence from petrochemistry-based products and the exploitation of natures synthesis-capabilities via photosynthesis.

Cellulose, being a constituent of wood, is regenerated in much larger quantities than starch by natural photosynthesis from CO_2 and water.

The very substantial, but so far little exploited category of cellulose-based materials, which has lead to some of the very first industrial polymer-products such as celluloid, cellophane still offers numerous new possibilities for polymeric materials.

Basically two main groups of cellulose-materials can be distinguished: Regenerated celluloses are suitable only for fiber and film production from conventional and new processes. Thermoplastically processable cellulose derivatives such as esters can be used for extrusion and moulding. Based on general considerations on the correlation between biodegradability and molecular structure, cellulose derivatives allow both, thermoplastic processing and post-consumer waste management via biological decompostion. Ways to realize this demanding new mix of properties considering biodegradability, thermoplastic behaviour and material-properties as well as possible synthetic strategies and their realization are presented.

H-V.6 - invited - 18:00-18:30

CHEMISTRY AND APPLICATION OF CHITIN AND CHITOSAN, **K. Kurita**, Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino-shi, Tokyo 180, Japan

Chitin, as well as cellulose, ranks among the most abundant biomass resources, but it remains almost unutilized primarily owing to its intractable nature. Though structurally similar to cellulose, it is an amino polysaccharide with distinctive biological activities and, moreover, can be transformed into chitosan having free amino groups. Chitin is thus considered to have quite high potential as a biodegradable specialty biopolymer for developing advanced functions.

Chemical modifications of chitin are, however, generally difficult due to lack of solubility, and our attention has been focused on the facile modifications of chitin to explore its full potential. Recently, for example, some soluble precursors such as N-phthaloyl-chitosan have made possible efficient modifications useful for regioselective and quantitative introduction of substituents. Here, a recent trend of chitin chemistry will be discussed with emphasis on novel modifications, lysozyme susceptibility of the derivatives, and possible application.

H-V.7 - invited - 18:30-19:00

USE OF BIOPOLYMERS AS AN ALTERNATIVE TO AGAR FOR THE CULTIVATION OF MICROORGANISMS ON SOLID MEDIA, **E.C. Hill**, ECHA Microbiology Ltd, Unit M210, Cardiff Workshops, Cardiff, CF1 5EJ, UK

The biopolymer agar, is the common gelling agent for solid microbiological growth media. The property of a 1.5% aqueous solution of agar to «melt» at c.85°C and set at c.39°C has controlled the technologies available for viable counts both in the laboratory and on-site. Traditional methods are shake plates in molten agar which is then allowed to solidify or surface spreading samples onto solid agar plates. The former is unsuitable for on-site use but is regarded as an accurate reference method. The latter can be adapted for semi-quantitative on-site use, for example as a Dip-slide The use of a gelling agent with thixotropic and/or pseudo plastic properties allows the «shake»plate concept to be used to test samples in the laboratory or on-site. A sample is delivered onto the gel in a 65ml container which is then shaken vigorously to liquefy the gel and disperse the sample. The fluidised gel is allowed to re-set as a thick horizontal film. During incubation a sensitive redox indicator gives an early indication of colony formation or very large numbers of organisms.

The technology is suitable for quantitative «viable counts» on-site or in the laboratory and also gives a real time indication of heavy contamination. Gels can be formulated so that non-aqueous samples emulsify and completely disperse and have been used to test diesel and aviation kerosene; the results are comparable to the ret`erence method IP385/95.

Wednesday June 18, 1997
Mercredi 18 juin 1997

Morning
Matin

Session VI - Polyesters, Part 2
Chairperson: B. Witholt, ETH Hönggerberg, Zürich, Switzerland

H-VI.1 - invited - 8:30-9:00

CHEMICAL ROUTES TO POLY(ß-MALIC ACID) AND POTENTIAL APPLICATIONS OF THIS WATER SOLUBLE BIORESORBABLE POLYESTER, **M. Vert**, CRBA, Faculty of Pharmacy, 34060 Montpellier, France

The first attempt to synthesize a PMLA by step-growth polymerization of malic acid failed in the absence of protection of one of the two carboxylic groups. Step growth polymerization of a mono malic acid benzyl ester using dicyclohexylcarbodiimide (DCC) also failed. It is the first synthesis of malolactonic acid benzyl ester in 1979 which opened the route to high molecular weight PMLA. Since then, other routes have been prospected, starting from aspartic acid and malic acid, most of them being based on the same monomer. The key step of the synthesis is the use of hydrogen and palladium charcoal to deprotect the carboxylic pendent groups by selective cleavage of the benzyl ester groups without affecting the aliphatic ester bonds present in main chains. Investigation of the potential of poly(ß-malic acid) as attractive drug carrier will be presented together with the potential of initially water-insoluble derivatives such as benzyl ester polymers and copolymers to be used as solid bioresorbable materials. The effects of degradation on chain structures will be discussed in order to exemplify the complexity of the hydrolytic degradation of malic acid-derived polyesters.

H-VI.2 - invited - 9:00-9:30

BIOSYNTHESIS OF POLYESTERS IN BACTERIA AND RECOMBINANT ORGANISMS, **A. Steinbüchel**, Institut für Mikrobiologie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 3, 48149 Münster, Germany

Many bacteria are able to synthesize polyesters of hydroxyalkanoic acids (PHA) which occur as insoluble cytoplasmic inclusions in the cell and can contribute significantly to the cellular dry matter. More than 100 different hydroxyalkanoic acids have been detected as constituents in PHA. This contribution summarizes strategies and possibilities to obtain these biodegradable and thermoplastic/elastomeric polymers by fermentation of wild type bacteria as well as of mutants and recombinant strains from renewable resources, waste substrates or special precursor substrates. In addition, in vitro biosynthesis of PHA employing the purified polymerizing enzyme (PHA synthase) is described. Throughout analysis and cloning of the bacterial PHA biosynthesis genes enabled scientists to establish this pathway in non-PHA producing eukaryotic organisms such as yeast, plants and animals. This will allow new processes for cheap and economic production of PHA.

H-VI.3 - invited - 9:30-10:00

IN VITRO BIOSYNTHESIS OF POLYESTERS WITH ISOLATED ENZYMES IN AQUEOUS SYSTEMS AND ORGANIC SOLVENTS, **S. Kobayashi**, H. Uyama and S. Namekawa, Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, Sendai 980-77, Japan

In vitro synthesis of aliphatic polyesters was achieved by lipase-catalyzed polymerization. Lipase catalyzed a polycondensation of a dicarboxylic acid and a glycol in an aqueous medium, in which dehydration took place in water. This is a new aspect in organic chemistry. From a combination of sebacic acid and 1,8-octanediol, the corresponding polyester with molecular weight of 1600 was obtained.

Ring-opening polymerization of lactones with different ring-sizes proceeded through lipase catalysis. The polymerization behaviors depended on the lipase origin and monomer structure. Macrolides (12-, 13-, and 16-membered) showing much lower anionic polymerizability were enzymatically polymerized faster than ε-caprolactone. The lipase-catalyzed polymerizability of these lactones was evaluated by Michaelis-Menten kinetics of the polymerization. Single-step synthesis of end-functional polymers, methacryl-type macromonomer and a telechelic polyester having a carboxylic acid group at both ends, was achieved by the polymerization in the presence of vinyl methacrylate and divinyl sebacate, respectively. The lipase-catalyzed copolymerization of lactones, dicarboxylic acid divinyl esters, and glycols proceeded in organic solvents to give the corresponding copolyesters. In the copolymerization, two different types of polymerization, ring-opening polymerization and polycondensation, simultaneously occurred via the same acyl-lipase intermediate.

10:00-10:30 **BREAK**

Session VII - Polyesters, Part 3
Chairperson: S. Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

H-VII.1 - invited - 10:30-11:00

ARCHITECTURE OF BIODEGRADABLE COPOLYESTERS CONTAINING AROMATIC CONSTITUENTS, **R.J. Müller**, U. Witt, E. Rantze, W.-D. Deckwer, GBF, Mascheroder Weg 1, 38124 Braunschweig, Germany

Copolyesters, containing aliphatic and aromatic components, have been shown to be very promising biodegradable materials with good use properties and commercial importance.

While aliphatic polyesters exhibit in many cases good to moderate biodegradability, pure aromatic polyesters, like PET, are microbial resistant. Generally, degradation rate of the copolyesters decreases with increasing content of aromatic monomers. For a safe environmental degradation, especially attention must be payed to the degradation of aromatic components, which may remain as resistant intermediates during the copolymer degradation.

Different degradation experiments, including degradation of the copolyesters with whole microorganisms and enzymes as well as experiments with especially synthesized model oligomers and model substances, representing distinct structure elements of the copolyesters, help to understand, how the architecture of such complex aliphatic/aromatic copolyesters influences their biological degradability.

H-VII.2 - invited - 11:00-11:30

BIOLOGICALLY DEGRADING COPOLYESTERS OF BASF, **U. Witt**, BASF AG, ZKT-B1, Kunststofflaboratorium, 67056 Ludwigshafen, Germany

Due to increasing problems in waste management, biodegradable polymers have attracted enormous interest in public discussions and in science as well. As a result, a number of products have appeared on the market in the last few years. However, these materials - mainly based on renewable raw materials - were only launched in fairly small quantities. For optimum commercial success, a biodegradable polymer has to exhibit several features: reproducible properties, material properties which can be adjusted, immediate raw material availability, and a competitive price.

By carefully selecting a specific monomer and a tailor-made polymer structure, BASF has found a compromise that provides satisfactory use properties, along with low manufacturing costs and controlled biodegradability.

The basic structure is made up of aliphatic/aromatic copolyesters consisting of familiar monomers. An additional modification to this basic structure constitutes a crucial aspect when it comes to practical use. As in a modular system, for example, the incorporation af hydrophilic components, of monomers with a branching effect and/or of compounds that lead to a chain lengthening and thus to an increase in the molecular weight gives tailor-made products with totally different material properties such as, for instance, biodegradable copolyesters for film applications with an interesting combination of properties.

H-VII.3 - invited - 11:30-12:00

PROCESSABILITY AND PROPERTY OF ALIPHATIC POLYESTERS "BIONOLLE", **T. Fujimaki**, Showa High Polymer CO., Ltd., 3-20, Kanda Nishiki-cho, Chiyoda-ku, Tokyo 101, Japan

Biodegradable aliphatic polyesters such as polybutylene succinate (coded #1000 series) and polybutylene succinate adipate copolymer (coded #3000 series) with high molecular weight ranging from several tens of thousands to several hundreds of thousand were developed successfully through polycondensation reaction and coupling reaction and named «BIONOLLE».

A pilot plant with capacity of 10 tons/year was built on 1991, and a semicommercial plant with capacity of 3,000 tons/year was constructed on 1993. BIONOLLE is a white crystalline thermoplastics, has melting point ranging 96- 114 °C, Tg ranging -45~ -28 °C and density of ca. 1.25 g/cm^3.

BIONOLLE has excellent processability of, so can be processed on conventional equipments commonly used in polyolefin at the temp. of 160~ 200 °C into various molded products such as blown, extruded and injected products. Recently special grade of BIONOLLE (coded #1900 series), which has long chain branch and high melt tension, is developed, and consequently stretched blow bottle and highly expanded foam can be processed easily.

H-VII.4 - invited - 12:00-12:30

STATISTICAL AND BLOCK COPOLYMERS OF ε-CAPROLACTONE, **A. Duda**, S. Penczek, Polish Academy of Sciences, Centre of Molecular Studies, Department of Polymer Chemistry, Sienkiewicza 112, 90-363 Lodz, Poland; P. Dubois, R. Jérôme, University of Liège, Centre for Education and Research and Macromolecules, Sart-Tilman, B6, 4000 Liège, Belgium

Conditions of the living polymerization of ε-caprolactone (εCL), lactides (LA), and oligomerization of γ-butyrolactone (γBL) initiated with aluminium alkoxides will be briefly described and a microstructure of the resulting polyesters discussed.

It will be shown, that the otherwise «non-polymerizable» γBL does form high-molecular-weight copolymers with εCL, containing up to 50 mol-% repeating units derived from γBL. Their molecular weight is controlled by the concentrations of the consumed comonomers and the starting concentration of initiator. NMR and DSC data indicate the pseudoperiodic or statistical copolymers structure. TGA traces of the γBL/εCL copolymers show that presence of the γBL derived units (below 10 mol-%) statistially distributed within the poly(εCL) chain improves thermal stability of the latter.

H-VII.5 - invited - 12:30-13:00

BAK 1095 AND BAK 2195: COMPLETELY BIODEGRADABLE SYNTHETIC THERMOPLASTICS, **E. Grigat**, BAYER AG, Werk Uerdingen, Bldg. R33, Kunststoffe F+E, 47812 Krefeld, Germany

BAK 1095 was introduced to the market at the «K'95»-fair in Oct. '95 and BAK 2195 at an injection moulding symposium in Nov. '96. Both resins are copolyesteramides; BAK 1095 is based on PA 6 and BAK 2195 on PA 66.

BAK 1095 is a film grade, melting at 125°C, and is suitable for film blowing, film casting, fiber manufacturing, extrusion and even, but not optimized, for injection moulding. The biodegradability of BAK 1095 is tested according to German DIN 54900. The final reports are in print and all tests show positive results.

BAK 2195 is an injection moulding grade, melting at 175°C, which is also suitable for film and fiber manufacturing. The biodegradability of BAK 2195 is now in different tests according to German DIN 54900. Pretests show positive results.

The field of applications for the pure BAK-grades can be expanded by blending both grades and/or filling or reinforcing them with fillers «e.g. minerals, natural fibers, cellulose or starch». Additive masterbatches are available «e.g. with lubricants or colors».

13:00-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session II

14:00-15:00 See programme of this poster session p. H-20 to H-23.

Session VIII - Complex Polymeric Materials
Chairperson: R.J. Müller, GBF, Braunschweig, Germany

H-VIII.1 - invited - 15:00-15:30 POTATO PULP: PROPERTIES, PHYSICAL MODIFICATION AND APPLICATIONS, **F. Mayer**, Institut für Mikrobiologie, Grisebachstrasse 8, 37077 Göttingen, Germany

Production of starch from potato has, as an undesired side effect, the generation of huge amounts of a mass consisting of water, cell debris and intact starch cells («pulp»). Chemical analyses revealed the presence of starch, cellulose, hemi-cellulose, pectin, free amino acids, oligopeptides, polypeptides and ashes. Part of the pulp can be used up as cattle feed. Most of it has to be considered as an agricultural waste.

Besides studies on identification and activities of bacteria and fungi contaminating the pulp, we developed an approach for a technical use of this waste material as a glue. The pulp is first autoklaved, then treated by pressure release, and finally dried into a fine-grain powder which can be stored at room temperature. Tests of applications as the sole glue, omitting any other glue such as glue based on formaldehyde-urea, for the production of particle and fibre boards, small containers etc. have been successful.

H-VIII.2 - invited - 15:30-16:00 POLYPHENOLES FOR COMPOUNDED MATERIALS, A. Kharazipour, Pfleiderer Industrie, 59759 Arnsberg, Germany, C. Mai and **A. Hüttermann**, Universität Göttingen, Büsgenweg 2, 37077 Göttingen, Germany

The cell walls of woody plants are compounded materials made by an in situ polymerisation of a polyphenolic matrix (lignin) into a web of fibres (cellulose) catalysed by polyphenoloxidases (laccases) or peroxidases. The transfer of this construction strategy to the actual production of compounded materials required the adaptation of a process which takes weeks in nature to technical conditions where reaction times of only few minutes are allowed.

Several strategies have been developed to find conditions under which lignin becomes so active that the reaction may be feasable for technical purposes. Thus the following industrial processes for the production of compounded materials are now available:

- wood composites either by the addition of adhesives composed of lignin and phenoloxidases or activation of the wood fibres by these enzymes
- Compound materials made from lignin and carbohydrates, and
- Duroplasts from lignin and other monomers.

The main advantage of all these substances is that they are totally compatible with the terrestrial carbon cycle.

16:00-16:30 **BREAK**

Session VIII - Complex Polymeric Materials (continued)
Chairperson: R.J. Müller, GBF, Braunschweig, Germany

H-VIII.3 - invited - 16:30-17:00 PROPERTIES AND APPLICATIONS OF COMPOSTABLE, STARCH BASED PLASTIC MATERIALS, **J. Lörcks**, BIOTEC©, Blinder Weg 30, 46446 Emmerich, Germany

Biodegradable and compostable plastics especially those based on renewable ressources from the agricultural industry are an essential innovation. This innovation offers substantial impulses for the future technologies. A lot of jobs and a potential market of > 1 mio t /a for biodegradable plastics in Europe is proposed by the EU Comission Directorate General XII. Bioplastics based on starch are using the benefits of natural polymerisation and the availability of raw material and process technology. Thermoplastic starch TPS° and blends of TPS° with hydrophobic biodegradable polymers are in the BIOTEC° research and production program. Latest development results are reaction-compounding-process-technologies to produce TPS° derivates and starchesters in a continuous extrusion process.

Applications for TPS° bioplastic granules BIOPLAST° are film extrusion and injection molding. The BIOFLEX° film has mechanical properties like PE films is opaque to transparent, printable, sealable, shrinkable and can be colourized. BIOFLEX° is permeable to vapor and has good barrier properties to oxigen. BIOFLEX° can be used in the same way like conventional foils for instance for garbage sacks, shopping bags, packing up, nets for food packaging, diapers, agricultural or technical uses. According to DIN 54900 TPS° bioplastics are completely biodegradable and compostable.

The innovation of the bioplastic technology is an excellent example for a sustainable development, which means the responsible use of available natural resources and production processes that take environmental aspects and natural circulations into consideration.

H-VIII.4 - invited - 17:00-17:30

CONSTRUCTION MATERIALS BASED UPON BIOLOGICALLY RENEWABLE RESOURCES-FROM COMPONENTS TO FINISHED PARTS, **A.S. Herrmann**, J. Nickel and U. Riedel, DLR Institut für Strukturmechanik, Postfach 3267, 38022 Braunschweig, Germany

By embedding natural fibres e. g. flax, hemp, ramie etc. into a bio-polymeric matrix made of derivatives from cellulose, starch, lactic acid etc., new fibre reinforced materials, the so-called bio-composites, were created at the DLR Institute of Structural Mechanics in 1990 and are still being developed.

As far as the mechanical properties are concerned, bio-composites are comparable to the well-known glass fibre reinforced compounds. Therefore the new construction materials are very well suited to be used for anisotropic and specially tailored lightweight structural parts making use of the DLR know how in fibre reinforced technology. Some samples and structures will be shown in the presentation.

Whereas traditional compounds consist of very stable components being very difficult to decompose, bio-composites are made completely from biologically renewable resources. This offers additional possibilities of a convenient removal after the end of lifetime, i. e. biodegration, composting or carbon dioxide neutral combustion. Thus bio-composites can also meet the steadily increasing environmental demands of legislative authorities.

H-VIII.5 - invited - 17:30-18:00

PROPERTIES AND APPLICATIONS OF MATER-BI STARCH-BASED MATERIALS, **C. Bastioli**, Novamont S.p.A., Via G. Fauser 8, 28100 Novara, Italy

Starch is an abundant, inexpensive, natural raw material, suitable for the development of biodegradable products able to recycle atmospheric CO_2 when composted or incenerated. Such reasons excited the renewed interest for starch plastics testified by an impressive production of literature in the last years.

Novamont is generally recognized as a pioneer in the sector of starch-based biodegradable materials. It started its research activity on 1989, and is now on the market with 4 classes of materials, A, Z, V, and Y, sold under Mater-Bi trademark, containing starch and differing for the synthetic components.

This paper revises the main results obtained by Novamont in the field of thermoplastic and complexed starch in presence of specific synthetic polymers, and aspects such as processability physico-chemical and physico-mechanical properties, composting behaviour and future market perspectives of Mater-Bi products.

Moreover the paper considers aspects such as in-use performances and biodegradation behaviour of Mater-Bi bags for the separate collection of organic and yard waste, the first real industrial product in the sector of biodegradable materials introduced on the market by Novamont since 1992.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session IX - Degradation of Polymers by Microorganisms
Chairperson: U. Pagga, BASF Ecology, Ludwigshafen, Germany

H-IX.1 - invited - 8:30-9:00

THE EFFECTS OF PRIMARY STRUCTURE ON THE DEGRADATION OF COPOLYMERS, **S.J. Huang**, Polymers and Biosystems Group, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, USA

Biological systems degrade large molecules by hydrolysis and oxidation. The presence of hydrolyzable and/or oxidizable linkages along the main chain is the most important requirement for biodegradation of polymers. The rates of hydrolysis and biodegradation are greatly affected by the morphology of the polymer objects, with crystallinity and orientation generally retarding the rates of degradations. The degradations of copolymers are greatly affected by the composition, sequences (random, block, alternating, etc.) and geometry (branch, network, etc.). These ultimately determine tbe morphology of the copolymers and thus have a large effect on the rates of degradation. Some results on poly(amide-ester)s and copolyesters will be discussed.

H-IX.2 - invited - 9:00-9:30

RELEVANCE OF BIOFILMS FOR THE BIODETERIORATION OF SURFACES OF POLYMERIC MATERIALS, **H.-C. Flemming,** University of Duisburg, Dep. Aquat. Microb., IWW, Moritzstr. 26, 45476 Mülheim, Germany

Biofilms consist of microorganisms embedded in a polymer matrix, adhering to surfaces. They can deteriorate polymeric materials in various ways, among these: i) by enzymatical degradation of the polymer or of biodegradable constituents which migrate to the surface. In that case, the integrity of the material can be seriously damaged; ii) by penetration of the polymer matrix by filaments, as it is the case with fungi, in which case the structural integrity can be damaged and, if the material is used for insulation, unwanted conductivity is provided; and, iii) by excretion of pigments which diffuse into the material and cause unwanted colouring. Biofilms can be very effective in all three ways because they are located directly on the surface in question. In complex technical systems, they can usually not be detected easily: microbial data from the water phase, e.g., give no information about location, composition and extent of biofilms. In this form of life, the organisms exhibit an increased tolerance against biocides.

H-IX.3 - invited - 9:30-10:00

BIOCHEMISTRY OF MICROBIAL BIODEGRADATION OF WATER INSOLUBLE POLYESTERS, **D. Jendrossek**, Universität Göttingen, Grisebachstraße 8, 37077 Göttingen, Germany

Biopolyesters such as poly(3-hydroxybutyrate) [PHB], which is the most prominent member within the family of polyhydroxyalkanoates (PHA), are widespread compounds in the biosphere. Aerobic and anaerobic microorganisms, which decompose PHA and utilize the degradation products for growth, have been found in many ecosystems. Research on the enzymatic hydrolysis of polyesters by microbial extracellular PHA depolymerases has led to a brief understanding of the basic biological mechanisms of hydrolysis of water-insoluble polyesters and has been reviewed, recently (1).

All microbial extracellular PHA depolymerases analyzed so far are very stable, highly active proteins. They resemble serine-hydrolases and are similar to lipases, esterases or serine-proteases with respect to their catalytic active amino acids. In additon to the catalytic domain PHA depolymerases consist of a substrate-binding domain which enables them to bind specifically to the polymeric water-insoluble substrate. An overview on the biochemical principles of biopolymer degradation will be provided.

(l) Jendrossek, D. et al. 1996. Appl. Microbiol. Biotechnol. 46:451-463

10:00-10:30 **BREAK**

Session IX - Degradation of Polymers by Microorganisms (continued)
Chairperson: U. Pagga, BASF Ecology, Ludwigshafen, Germany

H-IX.4 - invited - 10:30-11:00

PROPERTIES AND BIODEGRADABILITY OF POLY(HYDROXYALKANOIC ACIDS), **Y. Doi**, Polymer Chemistry Laboratory, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-01, Japan

Various types of poly(hydroxyalkanoic acids) (PHA) were prepared by both biosynthetic and chemosynthetic methods, and their biodegradation tests were carried out at 25°C under aerobic conditions in fresh and sea waters. Biodegradabilities of PHA films were evaluated by monitoring the time-dependent changes in the biochemical oxygen demand (BOD), weight loss (erosion) of PHA film, and dissolved organic carbon concentration (DOC) of test solution. The microbial PHAs were degraded in the fresh and sea waters at a rapid rate, and the weight-loss- and BOD-biodegradabilities of the majority of biosynthetic polyesters were 100% and 80~5% for 28 days, respectively. In contrast, the biodegradabilities of chemosynthetic polyesters were strongly dependent of the chemical structure of monomeric units.

In addition, the effects of solid-state structures on the rate of emzymatic erosion for melt-crystallized PHA films have been studied at 37° and pH7.4 in the aqueous solution of an extracellular PHB depolymerase from Alcaligenes faecalis. The rates of enzymatic erosion decreased with an increase in crystallinity. The erosion rates for PHA copolymer films were several times higher than the rates of P(3HB) homopolymer films with the same degree of crystallinity. It has been suggested that the rate of enzymatic erosion on PHA films is influenced not only by the degree of crystallinity but also by the structure of thin PHA lamellar crystals.

H-IX.5 - invited - 11:00-11:30

BIODEGRADATION OF POLYAMIDES, **F.B. Oppermann**, S. Pickartz and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität, Corrensstraße 3, 48149 Münster, Germany

Naturally occurring homopolyamides are linear polyamino acids consisting either of glutamate (poly-γ–glutamic acid, γ-PGA [1]), lysine (poly-ε–lysine, PL [2]) or arginyl aspartate (poly-α–[arginyl aspartate], cyanophycin [3]), of which the first, γ-PGA, offers possible technical applications (e. g. as carrier molecule for medical and cosmetic drugs or thickener in food [1]). γ-PGA is synthesised as the major component of capsules and slimes of several Gram-positive bacteria (Bacillus licheniformis, B. subtilis natto, B. megaterium, B anthracis Sporosarcina halophila, Planococcus halophila [1, 4]). Purified γ-PGA produced from B. licheniformis ATCC9945 is a high molecular (Mr 1 x 10^5 to 1 x 10^6) water-soluble white powder leading to highly viscous solutions at low concentrations and is resistant to proteolytic attacks [1]. While the synthesis of γ-PGA has been investigated intensively since its discovery in 1937 not much work has been done on the biodegradation of the polymer [1,4]. A screening for γ-PGA-degrading microorganisms led to the identification and characterisation of 12 Gram positive and negative bacteria species. Current biochemical studies focus on the purification and characterisation of the γ-PGA-degrading enzyme(s). For this reason methods for detecting γ-PGA-depolymerase are developed.

[1] Troy, F. A. 1985. Methods Enzymol. 113: 146-168
[2] Shima, S., and H. Sakai. 1977. Agric. Biol. Chem. 41: 1807-1809
[3] Allen, M. M. 1988. Methods Enzymol. 167: 207-214.
[4] Birrer, G. A., A.-M. Cromwick, and R A. Gross. 1994 Int J. Biol. Macromol. 16: 265-275.

H-IX.6 - invited - 11:30-12:00

STRUCTURE-TO-FUNCTION RELATION SHIPS IN THE BIODEGRADATION OF POLY(AMINO ACID)S, **F. Rypacek**, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Synthetic poly(amino acid)s are polymers with a polypeptide backbone. While peptide bonds are resistant to a spontaneous hydrolysis under mild conditions of biological systems, their enzymatically catalysed degradation can be very efficient. The degrading enzymes, proteinases and peptidases, exhibit various specificities and are localized in different biological environments. A rational synthesis of poly(amino acid)s thus makes it possible to design polymer materials with engineered biodegradation patterns. Depending on the function for which the material was designed, the type, the rate and extent of its degradation in certain biological environment can be controlled through modifications of polymer structure. Structural variations controlling the biodegradability of poly(amino acid)s can be produced either by copolymerization or via polymer modification reactions. The relationships between the structure of some poly(glutamic acid) and poly(aspartic acid) derivatives and their biodegradation profiles will be presented, and their significance for using synthetic poly(amino acid)s as biomedical materials will be discussed.

H-IX.7 - invited - 12:00-12:30

RUBBERCYCLE© A BIOPROCESS FOR SURFACE MODIFICATION OF WASTE TIRE RUBBER, **R.A. Romine** and M. F. Romine, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

Microorganisms exhibiting biological activity towards sulfur were screened for use in producing surface-modified ground tire rubber (GTR) that exhibits improved compounding characteristics with virgin rubber stocks. The degradation of dibenzothiophene (DBT) was used as a model compound to screen strains of Thiobacillus, Rhodococcus, and Sulfolobus. The strains which were capable of degrading DBT were studied in more detail in small bench-scale degradation experiments, where the source of organically bound sulfur was finely ground waste tire rubber (74-micron particle diameter). Ion chromatography (IC), fourier transform infrared spectroscopy (FT-IR) and X-ray analysis of near edge surfaces (XANES) were used to chemically characterize process effluents and products of these bioprocess. IC was used to characterize spent processing media and showed that bound sulfur was released as sulfate ions when the bioreaction was allowed to run to completion, which agrees with the proposed progressive sulfur oxidation degradation model. The surface chemistry of biotreated GTR was characterized by infrared spectroscopy FT-IR and XANES. These analyses revealed that sulfur present in the GTR was oxidized, which corroborates the proposed biodegradative pathway.

Physical properties were determined on rubber samples compounded with various loadings of the surface-modified GTR. Results showed significant increases in the tensile strength and elongation properties for compounds containing up to 15% GTR processed with S. acidocaldarius. The results of the screening experiments, bench-scale process optimization studies and physical properties characterization identified Sulfolobus acidocaldarius as the best microorganism to use in developing a commercially viable bioprocess.

12:30-14:30 **LUNCH**

Thursday June 19, 1997 — Afternoon
Jeudi 19 juin 1997 — Après-midi

Session X - Presentation of Organizations dealing with Biodegradable Materials and of their Activities
Chairperson: R.J. Müller, GBF, Braunschweig, Germany

H-X.1 - invited - 14:30-15:00

ISO STANDARD ACTIVITIES IN STANDARDIZATION OF BIODEGRADABLE AND/OR COMPOSTABLE POLYMERS; DEVELOPMENTS OF TEST METHODS, DEFINITIONS, **H. Sawada**, Biodegradable Plastics Society, 3-2534 Sayama , Osaka-Sayama, Osaka 589, Japan

In 1993 a new working group(WG22) of Subcommittee(SC5) on biodegradability was created by ISO Technical Committee on Plastics(TC61).

The following three test methods have recently advanced to DIS (Draft of International Standard) stage.

1) Evaluation of ultimate aerobic biodegradability in aqueous medium - Method by determining the oxygen demand in a closed respirometer
2) Evaluation of ultimate aerobic biodegradability in aqueous medium - Method by analysis of released carbon dioxide
3) Evaluation of the ultimate aerobic biodegradability and disintegration of plastics under controlled composting conditions - Method by analysis of released carbon dioxide

Furthermore, WG22 plans to develop two test methods for anaerobic biodegradability. As far as definitions are concerned, ultimate aerobic biodegradation and composting were defined in connection with these test methods.

H-X.2 - invited - 15:00-15:30

BIODEGRADABILITY AND COMPOSTABILITY OF POLYMERIC MATERIALS IN THE CONTEXT OF THE EUROPEAN PACKAGING REGULATION, **U. Pagga**, BASF Ecology, 67056 Ludwigshafen, Germany

The treatment of compostable packaging, made from natural and synthetic polymeric materials, in controlled composting facilities can be an important possibility for reducing garbage. A prerequisite for official regulations and the decision as to which materials may be composted is investigations on their biodegradability and the quality of the compost produced. A standardization group at CEN has developed definitions, test methods and suggested a classification systems for differentiating compostable from non-compostable materials. After characterization of the test material biodegradability is determined in laboratory tests such as a controlled aerobic composting test or aquatic batch tests. The test methods are based on the evolution of carbon dioxide or oxygen demand. The composting test is different from other biodegradation tests because of the elevated temperature representative for real composting conditions and also because of enhanced fungal degradation activities. The laboratory tests are followed by investigations of the disintegration of the material in composting facilities and an analysis of the compost produced.

H-X.3 - invited - 15:30-16:00

CREATING THE FRAMEWORK FOR A WIDESPREAD USE OF BIODEGRADABLE POLYMERS (STANDARDIZATION, LABELLING, LEGISLATION, BIOWASTE MANAGEMENT), **J. Schroeter**, FH Rosenheim, Marienberger Str. 26, 83024 Rosenheim, Germany

During the last decade, various biodegradable polymers were developed to solve severe waste management problems. Only small quantities are used up to now. Paradoxically, waste management regulations revealed to form a bottleneck. Products from biodegradable polymers are often not accepted for biowaste collection.

Obviously, more than technical and scientific progress is necessary to establish the new technology. Thus, in 1993 biopolymer producers joined to organize the non-technical progress required. The result is IBAW, an association creating the framework for a widespread use of biodegradable polymers. The report describes recent results in the fields of standartization, labelling, legislation, and waste management.

16:00-16:30 **BREAK**

Session XI - Closing Session
Chairperson: D. Kaplan, Tufts University, Medford, MA, USA

H-XI.1 - invited - 16:30-17:00

PRODUCTION OF NOVEL POLYMERS IN TRANSGENIC PLANTS, **J. Riesmeier(1)**, J. Koßmann(2), R. Trethewey(2), A. Heyer(2), V. Landschütze(1) and L. Willmitzer(2), (1)PlantTec Biotechnologie GmbH, Hermannswerder 14, 14473 Potsdam, Germany, (2) Max-Planck-Institut of Molecular Plant Physiology, Karl-Liebknechtstr. 25, 14476 Golm, Germany

Transgenic plants will play a crucial role in modern agriculture. Crops displaying herbicide or insect resistance were grown world-wide on several billion acres in 1996. This first generation of transgenic crops will be complemented by the introduction of characteristics like increased yield, altered oil composition and novel or modified polymers. The production of novel or modified polymers in transgenic plants can be divided into the manipulation of plant metabolism and the introduction of new pathways into crop species. Polymers of interest are starch, fructans, PHB and cell wall polysaccharides.

During the last years several genes involved in starch biosynthesis were isolated. Following the antisense or the overexpression approach transgenic plants were created which produce starches with changed physical and chemical properties. The isolation of genes necessary for the synthesis of fructans from agronomically unfavourable plant species will allow the production of this polymer in a set of transgenic crops on a reduced cost level. Less information is available about the synthesis of cell wall polysaccharides. First attempts to manipulate the synthesis of precursors of cell wall biosynthesis are ongoing. The production of small amounts of PHB in transgenic plants was demonstrated some years ago. For a commercial production of PHB it is necessary to further increase the capacity of transgenic plants to synthesise and store PHB.

H-XI.2 - invited - 17:00-17:30

PROCESS ANALYSIS AND ECONOMIC EVALUATION FOR THE PRODUCTION OF PHA BY BACTERIA, **S.Y. Lee**, Dept. Chemical Eng., KAIST, Taejon 305-701, Korea

Polyhydroxyalkanoates (PHAs) are accumulated by numerous micro-organisms as an energy storage material under unfavorable condition in the presence of excess carbon source. Several processes for the production and recovery of PHAs by employing four best PHA accumulating bacteria, Alcaligenes eutrophus, Alcaligenes latus, Methylobacterium organophilum, and recombinant Escherichia coli were designed and analyzed by computer-aided bioprocess design software. It was demonstrated that PHA productivity, PHA content, and PHA yield significantly affected the overall economics of PHA production. With optimal design of fermentation and recovery process, the price of PHA can be lowered to US$ 3- 5 at large production scale. The cost of carbon substrate significantly affected the overall economics when the production scale increased. Details of fixed and operating cost analyses for several processes will be discussed.

H-XI.3 - invited - 17:30-18:00

CONSIDERATIONS ON THE ECONOMY OF PHA PRODUCTION BY FERMENTATION OR BY TRANSGENIC PLANTS, **B. Witholt**, Institute of Biotechnology, ETH Hönggerberg, 8093 Zürich, Switzerland

PHAs will become important industrial materials early in the next century as biodegradables with specialized medical and engineering applications and as bulk materials in biodegradable and durable consumer products. In this scenario, very large amounts of material will be produced. With bacteria, feedstocks will be bulk petrochemicals, sucrose, starch, or vegetable oils or agro-waste products such as whey or cellulose. Total costs will depend on fermentation costs (medium salts, substrates, energy input), down stream processing (chemicals, materials, energy), waste treatment (waste water/medium, processing wastes), capital costs (land, buildings, equipment depreciation, maintenance) and labor. We consider a price of US$ 5 per kg bioplastic as a practical lower limit, and achieving this will require considerable development of fermentation and downstream processing technologies for the production of PHAs.

An attractive alternative to fermentation is to produce PHAs in plants. The cost of producing PHA in plants will depend on plant yields per hectare, PHA content of the plants, cost of fertilizers, pest control agents, and irrigation, while costs for downstream processing include harvesting, transport, chemicals, energy, waste treatment, labor and capital costs for machinery. If transgenic plants can be developed which produce PHAs as a large-scale agro-plastic, comparable to starch, then prices similar to those of high grade potato starch, in the order of US$ 0.50-1.00 per kg, should be attainable.

Bioplastics produced in plants will ultimately compete effectively with petroplastics as oil sources dwindle and disposal of petroplastics and consequent CO_2 production cause increasing societal concerns. This bodes well for the development of PHAs both as a major bioplastic, and as a sustainable agrochemical source of hydrocarbons for the chemical industry.

H-XI.4 - invited - 18:00-18:30

DEVELOPMENTS AND ACHIEVEMENTS IN BIODEGRADABILITY AS SEEN WITH THE EYES OF A POLYMER CHEMIST, **G. Wegner**, Max-Planck-Institut für Polymerforschung, PO Box 3148, 55021 Mainz, Germany

Biodegradability of polymer materials has been a political and scientific issue for many years. Environmental concerns with regard to waste and waste management have been a driving force for research and development both in industry and in academia. The political and economical conditions in Europe have led to a situation in which the removal of polymers from the waste stream by uncontrolled biodegradation is the least desired possibility. Thus, replacement of otherwise optimized polymer materials by biodegradable products is not emphasized in technical or household applications. At the other hand, biodegradability is highly emphasized in speciality products to be used in agriculture, personal care products and in medicine.

In all cases biodegradability is an additional advantage which contributes to an existing spectrum of properties which has to be optimized in terms of structure-properties correlations. This is particularly true for polymers produced by biotechnology processes.

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SYMPOSIUM H
POSTER SESSIONS

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Poster Session I
14:00-16:00

H-I/P1 APPROACHES TO INCREASE THE ECONOMY OF THE PHB-PRODUCTION, J.-U. Ackermann, Univ. Leipzig, W. Babel, Umweltforschungszentrum Leipzig-Halle, Permoserstr. 15, 04318 Leipzig, Germany
The economic viability of the PHB production is determined by the efficiency and velocity of growth and product formation, and the intracellular content. The possible content is determined genotypically and the real one by the duration of the process. Efficiency and velocity are genotype- and substrate-related parameters. The theoretically possible yield coefficient of a certain substrate is not reached experimentally. By mixing substrates the carbon conversion efficiency can be increased. This will be shown with the help of the combinations of acetate/glucose and methanol/formate. The components of the mixture must be utilized simultaneously. There are several methods to realize simultaneous utilization. One of them is the (carbon-)substrate-limited chemostat technique. Chemostatic production requires growth coupling, which ought to occur if the PHB formation supports the energy budget for growth. We observed such a phenomenon with Methylobacterium rhodesianum growing on fructose. Growth-associated PHB accumulation seems to be the exception rather than the rule. Nevertheless, we should look further for such suitable systems. Continuous production is the method of choice, since it helps towards a constant product quality, too.

H-I/P2 BIODEGRADABLE PLASTICS BASED ON PROTEINS, M. Fossen, M.F.M. Engel, G.E.T. van Vilsteren and T. Jongsma, Agricultural Research Institute (ATO-DLO), PO Box 17, 6700AA Wageningen, The Netherlands
Proteins belong to the range of interesting renewable resources that can be used for the development of biodegradable plastics. Both animal and plant proteins can be processed by means of (sheet) extrusion, injection moulding and film blowing. Principles of polymer science can be applied to these systems such as mechanical and thermal properties in relation to structure and the influence of additives and processing on these properties. Research is done in the area of casted films as well as thermoplastics made by extrusion and moulding techniques.
Mechanical properties can vary from soft and flexible to stiff and hard. Natural fibres can be added to obtain reinforced composites. Some proteins are thermally stable up to 100°C.
Protein films have an extremely low O_2 and CO_2 permeability, so they can be used as an alternative for EVOH or aluminum in packaging. Water vapor permeabilities (WVP) are intrinsically high which may be an advantage for packaging of certain products. Nevertheless, WVP's can be lowered by adding suitable additives.
Applications of proteins can be found in disposables, packaging films, composites, foams, etc.

H-I/P3 BIODEGRADABLE POLYMERS AS CARRIER OF ANTITUBERCULOUS DRUG, R.M. Iskakov, E.O. Batyrbekov, L.B. Rukhina and B.A. Zhubanov, Institute of Chemical Sciences, 106 Valikhanov Street, Almaty, Kazakstan
Biodegradable polymers for the delivery of drugs received increasing attention during last few decades. In the present work a number of synthetic and natural biodegradable polymers have been studied as carriers of antituberculous drugs for controlled delivery application. Drugs, such as isoniasid, ethionamid, kanamicin, were physically incorporated into carrier (segmented polyurethanes, crosslinked dextran, hydroxyethylmetacrylate hydrogels and films of polyvynil alcohol) and chemically bound with the polymer chain by covalent or electrostatic forces (aldehyde- and carboxymethilderivatives of polysaccharides).
Biodegradation of polymeric systems and release of drugs have been studied by various physico-chemical methods. It was shown that the release of drugs depends of following factors; method of immobilization, character of the drug-polymer system bonding and their structure, drug loading. The tuberculostatic activity of biodegradable polymer systems was determined. The principal possibility of tuberculosis treatment was proved in experiments on animals.

H-I/P4 BIODEGRADABLE POLYMERS FROM CROPS-RESEARCH FUNDING IN GERMANY, S. Mann, B. Herrmann, Fachagentur Nachwachsende Rohstoffe e.V., Hofplatz 1, 18276 Gülzow, Germany
Germany's Fachagentur Nachwachsende Rohstoffe e.V. is an agency for renewable agricultural resources and coordinates research and development in this sector. The budget of annually ca. 50 Mill. DM by the Federal Ministry of Food, Agriculture and Forestry is to a considerable part spent on the further development of biodegradeble polymers. An overview over the most important progresses and barriers is given.

H-I/P5 BIODEGRADABLE POLYURETHANES IN THE CONTROLLED ADMINISTRATION OF ANTITUMOUR DRUGS, E.O. Batyrbekov, R.M. Iskakov, B.A. Zhubanov, Institute of Chemical Sciences, 106 Valikhanov Street, 480100 Almaty, Kazakstan, T.S. Teleuova, M.A. Volkova, Institute of Eye Dieseases, 95a Tole bi Str., 480012 Almaty, Kazakstan
Biodegradable polyurethanes as diffusion-controlled materials for the administration of antitumour drugs have been studied. Drug delivery systems consists of dispersion or dissolution of drugs in microporous polymeric matrix. Biodegradable polyurethanes were obtained by means a two step procedure using different oligoetherglycoles, diisocyanates and branching agents. Drugs were added in polymer at the stage of synthesis in liquid polyurethane prepolymer. The drugs used in the investigation were cyclophosphan, prospidin and vincristin. The biodegradation period and release profiles of antitumour drugs in model media and animal organism were studied. The rate of drug release from polymeric matrix can be controlled by manipulating of the percentage drug content in systems. The cytotoxicity was tested against leucemia cells in vitro experiments.

H-I/P6 BIODEGRADATION BEHAVIOUR OF NOVEL BLOCK COPOLYMERS OF [R,S]-ß-BUTYROLACTONE AND PIVALOLACTONE, M. Scandola and M.L. Focarete, Dipartimento di Chimica " G. Ciamician ", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy; Z. Jedlinski and M. Kowalczuk, Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland

Novel block copolymers of [R,S] ß-butyrolactone (BL) with pivalolactone (PVL) were obtained through the «living» polymerization of atactic poly(ß-butyrolactone) from racemic monomer, in the presence of potassium alkoxide/18crown6 complex; such a prepolymer was applied for polymerization of pivalolactone, yielding block copolymers of expected molecular weight and compositions. Block copolymers containing 5, 17, 23 mol% PVL were exposed in film form to a buffered solution of PHB-depolymerase A from Pseudomonas lemoignei (Tris-HCl buffer, pH=8, 37°C). The biodegradation rate of the copolymers increased with PVL content. In the block copolymers only the P([R,S]-BL) block was attacked by the enzyme. In the same experimental conditions the homopolymer of [R,S]-BL did not biodegrade. Enzymatic hydrolysis of the P([R,S]-BL) block in the presence of the partially crystalline P(PVL) block, confirmed earlier suggestions that the enzyme might require a crystalline phase for binding.

H-I/P7 BIODEGRADATION OF POLY(L-LACTIC ACID) OLIGOMERS, S. Karjomaa(1), J.-F. Selin(2), T. Suortti(1) and M. Itävaara(1), (1)VTT Biotechnology and Food Research, PO Box 1500, Tietotie 2, 02044 VTT, Finland, (2) Neste Oy Chemicals, Technology Centre, PO Box 310, 06101 Porvoo, Finland

Poly-L-lactide (PLLA) is an attractive material for environmental and packaging material applications. In compost at high temperatures, polylactide is rapidly biodegraded, but at mesophilic temperatures the process is slower. The degradation mechanism of PLLA is supposed to include chemical hydrolysis and enzymatic degradation. Yet the starting point of biodegradation after chemical hydrolysis has been unclear.

We have studied the degradation of poly-(L-lactic acid) oligomers of molecular weight range 260...2880 g/mol in the head space-biodegradation test. The experiments were run at +25°C and +58°C in biotic and abiotic environments. The water soluble poly-(L-lactic acid) oligomers of molecular weight less than 550 g/mol biodegraded readily at +25°C and +58°C. Larger, non-water soluble oligomers, having solubility properties similar to poly-L-lactide, biodegraded faster at +58°C than at +25°C. HPLC-results showed, that chemical hydrolysis did not produce as much water soluble degradation products as detected in biotic environments.

H-I/P8 CHARACTERIZATION OF THE STRUCTURE-PROPERTY-RELATIONSHIP OF BIOTECHNOLOGICALLY PRODUCED BIODEGRADABLE ALIPHATIC COPOLYESTERS AND INVESTIGATIONS OF THERMOPLASTIC PROCESSING PERFORMANCE, G. Schmack, G. Schauer, R. Vogel, D. Voigt, L. Häußler, Institut für Polymerforschung, PO Box 120411, 01005 Dresden, Germany, A. Steinbüchel, V. Gorenflo, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität, Corrensstraße 3, 48149 Münster, Germany

Employing genetically engineered bacteria allows the production of new polyesters. The thermoplastic processing performance of small batches of biotechnologically produced biodegradable aliphatic copolyesters containing 4-hydroxyvaleric acid and other medium-chain-length monomeric units in low concentrations in the spinning process is discussed. The thermal, rheological and mechanical properties of the basic samples and of the fibres are characterized. The results are compared with those which were determined for poly(3-hydroxyvaleric acid) homopolyester. The characteristical properties of the investigated copolyesters are the high elasticity, the low crystallinity, the low of melting temperature and the low velocity of crystallisation. These properties result from the structure of the polyester.

H-I/P9 COMPOSITION AND STRUCTURE OF ISOLATED POLY(L-MALIC ACID) FROM MYXOMYCETES AND FUNGI, B. Gaßlmaier, E. Holler, Institute of Biophysics and Physical Biochemistry, University, 93040 Regensburg Germany

Biogenic poly(L-malic acid) (PMA) is a natural product, synthesized by myxomycetes and several fungal strains, Physarum polycephalum and Aureobasidium pullulans, respectively, have been identified as the best producers (1 g and 15 g PMA per one liter of culture). We found that the composition and molecular mass of isolated PMA were grossly different between these representative sources, varying strongly with the time of harvest of the A. pullulans cultures. In a comparative investigation, the polymer was purified by the same standard method that also achieved the highest yields. For P. polycephalum, yields increased until day 4, when growth and PMA production ceased. The polymer was chemically pure and of molecular mass 2 kDa - > 300 kDa, $M_w = 50$ kDa, polydispersity (P) of 1.82. Amounts of PMA declined thereafter due to hydrolysis by a specific hydrolase. For A. pullulans the polymer was composed of PMA oligomers of $M_w = 3.7$ kDa, P = 1.05, covalently bound to neutral polysaccharides. Oligomer acid with few attached saccharide residues was extractable into dry acetone. The amount of secreted copolymer increased throughout day 20, degrading slowly into PMA oligomers. At day 13, isolated material consisted of polysaccharide/PMA copolymer, $M_w = 33$ kDa, P = 1.64, and free oligo-PMA. At day 20, nearly all PMA was in the free oligomeric form. Evidence exists indicating that the two forms of PMA are representatives of two main types of natural PMA.

H-I/P10 CONTROLLED LIVING POLYMERISATION OF α-AMINO ACID N-CARBOXYANHYDRIDES IN THE SYNTHESIS OF BLOCK COPOLYMERS, L. Machova, D. Kubies, M. Dvorak and F. Rypacek, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

A controlled living polymerisation of N-carboxyanhydrides of α-amino acids (NCA) was recently developed in our laboratory. The method is based on using various N-acyl-NCAs as co-itiators with diisopropylamine as a base catalyst. The co-initiator provides for a defined concentration of polymer growing centres, from which the polymer molecules grow solely by the activated monomer mechanism. The degree of polymerisation increases proportionally to the monomer conversion and the resulting polymers have the M_w/M_n, ratio between 1.1 - 1.3 . The chain propagating N-acyl-NCA end group can be subsequently modified or used directly for the synthesis of block copolymers. Block copolymers composed from two different poly(amino acid) segments were prepared by a stepwise polymerisation of diffferent NCA monomers. Copolymers containing poly(γ-benzyl L-glutamate) (PBLG) and poly(lactic acid) (PLA) blocks were prepared by using a telechelic PBLC, prepared by the living process and the end-group modification, as an initiator in the subsequent ring opening polymerisation of lactide.

H-I/P11 CRYSTALLINITY IN STARCH-BASED PLASTICS, S.D.H. Hulleman, J.J.G. van Soest and H. Feil, ATO-DLO, PO Box 17, 6700AA Wageningen, The Netherlands

In biodegradable plastics based on starch, several types of crystallinity can be observed, such as residual, double helical crystallinity, e.g. A-, B- and C-type crystallinity, B-type crystallinity originating from recrystallisation of amylose and/or amylopectin, and processing-induced, single helical crystallinity, e.g. V_H, V_A and E_H-type crystallinity.

The variables affecting the relative abundance of the various lattices, e.g. starch source, processing temperature and water content, and the relation between crystallinity and the mechanical properties of the thermoplast will be discussed.

H-I/P12 DEGRADATION BEHAVIOUR OF BIODEGRADABLE POLYMERIC MATERIALS IN COMPOSTING-PLANTS, M. Jungeilges, L. Streff, W. Bidlingmaier, Universität GH Essen, FB 10 Abfallwirtschaft, Universitätsstr. 15, 45141 Essen, Germany

According to DIN-Draft 54 900 (German Standardization Organisation) from January 1997 the compostability of polymeric materials is to prove in four steps. The last step is the testing under practical conditions in composting plants with different technical standards. In several test series polymeric materials have been examined in composting plants with low and high technical standard. The tests have been evaluated under the following aspects:

- Degradation-behaviour during a composting cycle.
- Degradation-rates in the whole composting procedure.
- Influence of occuring ranges in values of compost parameters on the degradation-behaviour and -rate.

The testseries showed clear differences in the velocity and rate of degradation of various materials. They also showed circumstances under which results become comparable and meaningful. These are the bases which enable us to evaluate the compostability of polymeric materials under practical conditions.

H-I/P13 ENGINEERING THE COMPOSITION OF CO-POLYESTERS SYNTHESIZED BY A. EUTROPHUS, A.S. Kelley, T.A. Leaf, K. Jackson and F. Srienc, Dept. Chem. Eng. & Matl. Sci. and BioProcess Technol. Inst., Univ. of Minnesota, Minneapolis/St.Paul, USA

The polymerization of poly-ß-hydroxyalkanoic acids (PHA) is catalyzed by relatively unspecific polymerase enzymes. Different monomers may be incorporated into the growing polymer chain, the primary sequence of the polymer being determined, therefore, by the reactions leading to the precursor pool of the polymerization step. To quantitatively predict PHA synthesis kinetics and the structure of the formed polymer we have developed a detailed model based on the reaction mechanisms leading to PHA formation. The model is useful as it predicts rate limiting and rate controlling steps in the PHA pathway and it suggests manipulations of the metabolism to obtain polymers of desired structure. To test the model predictions we have constructed several recombinant strains of Alcaligenes eutrophus that vary the levels of enzymes in the PHA pathway resulting in modulated PHA synthesis kinetics. In A. eutrophus, the flux through pathways leading into the PHA precursor pool can be modulated using molecular hydrogen. We pursue this strategy, supported by model predictions, to obtain via biosynthesis defined PHA co-polymers and block co-polymers.

H-I/P14 EVALUATION OF THE REPRODUCIBILITY OF THE SYNTHESES OF LIGNIN DEHYDROPOLYMER MODELS, B. Cathala(1), B. Monties(1), B. Saake(2), O. Faix(2), (1)INRA, UPBP, Equipe de Biochimie des Macromolécules Végétales, CRA2 Esp. R. Garros, 51686 Reims Cedex 2, France, (2)Institut für Holzchemie und chemische Technologie des Holzes, BFH, Leuschnerstrasse 91, 21031 Hamburg, Germany

Lignin is a complex polymer occuring in plant cell walls. In vivo, the polymerisation of lignin is a chemical process involving radicals. In vitro, in presence of peroxydase and hydrogene peroxyde, the three lignin precursors (p-coumaryl, coniferyl and sinapyl alcohol) are able to form dehydropolymers (DHP) that are relevant model compounds for lignin. The dehydrogenation of the precursors lead to an aroxyl radical, which is also present as four mesomeric forms. The reaction between this radical forms lead to polymeric structure where the frequency and the nature of the intermonomeric linkages change and also the molecular weight, the solubility etc... This pathway is very sensitive to the conditions of the reaction (pH, concentration, temperature, etc...), however the reproducibility of such systems has seldom be investigated. Two type of DHP were synthesised on several attempt. The molecular composition of each samples was determined by NMR, IR, but also by chemical degradation method. Polymeric features were also taken into account by studying the GPC elution curves.

H-I/P15 HYDROLYTIC DEGRADATION (IN VITRO) OF RACEMIC POLY-D,L-LACTIC ACID, M. Pickard and G. Rafler, Fraunhofer Institute of Applied Polymer Research, Kantstraße 55, 14513 Teltow, Germany

The degradation of parallelepipedic specimen (10mmx10mmx 1 mm) of poly-D,L-lactic acid was investigated in 0,4 molar aqueous NaCl solution and phosphat buffer solution of the same ionic strength at 37 °C. The polymer degradation is influenced by the dimensions of the specimen because of diffusion effects of water soluble products of the polymer degradation. Degradation products are able to diffuse out of the outer parts of the specimen into the surrounding solution. This diffusion process is hindered in the inner part of the specimen because there exists a maximum concentration in the aqueous phase present in the cavities. But all water soluble degradation products accelerate the degradation process with their carboxyl end groups. So the inner part of the specimen degrades faster than the outer part and a hollow shell remains. The hydrolytic degradation reaction is homogeneous and reflects statistical chain cleavage in the range of a molecular weight higher than 5000 g/mol.
Homogenous reactions in solution were done with lactide, lactoyllactic acid and low molecular weight polylactic acid under different conditions and observed by 'H-NMR-spectroscopy to estimate a time law and velocity constants. These time laws were used to model the degradation process.

H-I/P16 IMPROVEMENT OF STARCHY BIOMATERIALS BY BLENDING WITH LIGNINS PREPARATIONS, S. Baumberger, C. Lapierre, B. Monties*, INRA, Lab. de Chimie Biologique, INA-PG, 78850 Thiverval Grignon, France and P. Colonna, INRA, Lab. de Technologie des Glucides, BP 1627, 44316 Nantes Cedex, France
(* also Lab. Biochimie INRAA CRA 51686 Reims, France)

Starchs have been used for several years to produce plastic films at the laboratory and pilot scale. They have the main advantage over synthetic wraps of biodegradability but their industrial developement is restricted by their poor water resistance. Lignins obtained as by-product of pulp and paper industry are usually used as fuel. Preparation of polymeric materials from industrial lignins alone or blended with cellulosic materials have been however reported at laboratory scale.The goal of our studies was to blend lignin with starch in order to obtain starchy materials with improved water resistance. Lignin-starch films were obtained (both) by casting. Correlations between film performances (mechanical properties, thermal behaviour, wettability) and lignins structure will be reported, with emphasis on organosolv lignin preparations.

H-I/P17 INFLUENCE OF PREPARATION METHODS ON MICROPARTICLE'S SURFACE PROPERTIES, M. Jobmann and G. Rafler, Fraunhofer Institute of Applied Polymer Research, Kantstraße 55, 14513 Teltow, Germany

We used three types of poly-L-lactides characterized by different surface properties: poly-L-lactide (PLA), by use of stearyl alcohol end group modified hydrophobic poly-L-lactide (PLA/St) and hydrophilic poly-L-lactide, modified by copolymerization of L-lactide or alcoholysis of poly-L-lactide with polyethylene glycol (PLA/PEG) to prepare microparticles in the 1 µm-range by: a) spray drying process, b) salting-out process, c) «spontaneous emulsification solvent evaporation» method and d) solvent evaporation method (particle size control by type of homogenization or viscosity in the water/ solvent system). The surface properties of the microparticles were estimated by contact angle measurements. In dependence on the applicated microparticle preparation method there was a more or less intensive change in surface properties compared to the initial polymer characteristics. Microparticles from the spray drying process are only in the case of PLA/PEG able to adsorb water. Microparticles from the other processes were well wettable because of the used tensio-active agent (polyvinyl alcohol) during microparticle preparation.

H-I/P18 INNOVATIVE BIODEGRADABLE MATERIALS BASED UPON STARCH AND TPU, T. Seidenstücker and H.G. Fritz, Institut für Kunststofftechnologie, Universität Stuttgart, Böblinger Straße 70, 70199 Stuttgart, Germany

Proneness to hydrolysis in TPU can be achieved by synthesising thermoplastic poly(ester-urethanes) that contain as many ester-bonds as possible along the backbone. The degradability of different types of these TPU was tested under various conditions and environments applying different methods. All experiments have shown that a significant rate of degradation occurs, the speed of which can be significantly increased to meet the criteria set out by the latest DIN-proposal by incorporating starch.

The incorporation of native starch not only increases the rate of degradation but alters the material properties. This alteration of properties varies according to the filler content and type of starch incorporated. It is possible to incorporate up to 70 wt. % of starch using a co-rotating closely intermeshing twin screw extruder. The material properties of blends using thermoplastic starch (TPS) and TPU are much superior to the properties of the materials that are filled with native starch. The production of good sheets is possible with various compounds as well as further applications of these novel materials are conceivable.

H-I/P19 INVESTIGATION OF LIGNINS STRUCTURE IN CEREAL CROPS BY CHEMICAL DEGRADATION METHODS, E. Billa, E.G. Koukios, Bioresource Technology Unit, Dept Chemical Engineering, Div. IV, National Technical University of Athens, 15700 Athens, Greece and B. Monties, INRA, Laboratoire de Chimie Biologique, 78850 Thiverval-Grignon, France

The monomeric composition of in situ lignins in sorghum, maize and wheat straw stems is investigating by two chemical degradation methods, the thioacidolysis and the alkaline nitrobenzene oxidation. It is showed that the structural information obtained in the case of lignin chararacterisation by alkaline nitrobenzene oxidation is strongly dependent on the reaction conditions, namely the temperature and the reaction time; this is due to significant variations in the yields of aromatic aldehydes which correspond to the three main constitutive lignin units, p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S). Moreover, the complementary character of the two methods which stems from their different specificities is discussed in view of the molecular heterogeneity of lignins. Finally, the results obtained showed a significant structural variability of the lignins of the three crops examined.

H-I/P20 LDPE/STARCH BLENDS CONTAINING ETHYLENE-g-MALEIC ANHYDRIDE AS COMPATIBILIZER, N. Frangis(1), D. Bikiaris(2), J. Prinos(2) and C. Panayiotou(2), (1) Physics Department, (2)Department of Chemical Engineering, University of Thessaloniki, 54006 Thessaloniki, Greece

In the present study, LDPE/starch blends containing 5, 10, 15, 20 and 30 wt% starch were prepared. Native corn starch was plastisized with 25 wt% glycerine in a Haake-Buchler Reomixer at 180°C for 15 min. Three different Polyethylene-g-maleic anhydride copolymers containing 0.39, 1.07 and 1.94 mol % maleic anhydride groups were used as compatibilazers. Each copolymer was used in the blends at an amount of 10 wt% based on starch.

The blends after preparation were characterized by FTIR, Differential Scanning Calorimetry, Thermogravimetry and water absorption. Mechanical properties such as tensile strength and elongation at break were also measured. Biodegradation was realized by immersing the samples for eight weeks into activated sludge from a waste water treatment facility. The extend of biodegradation was followed by mechanical properties, weight loss and scanning electron microscopy.

H-I/P21 MOLECULAR TAILORING OF RESORBABLE POLYMERS, G. Rafler and M. Jobman, Fraunhofer Institute of Applied Polymer Research, Kantstraße 55, 14513 Teltow, Germany

Resorbable homo- and copolyesters of lactic acid can be modified by ring-opening polymerization in presence of different modifying components or ester interchange reaction of structure-different polyesters in the melt phase. Suitable modifying components are fatty alcohols and acid for producing of hydrophobic and polyethylene glycols for more hydrophilic polyesters, respectively. The ester interchange reaction is carried out by means of apparatus with high mixing effectiveness, such as twin-screw extruder or kneating machine. In this way it is possible to synthesize non-random polyesters with different microstructure of the copolyester chain. In addition to monomer composition and molecular weight the block length and is distribution and the end groups can be used for tailoring aliphatic polyesters. The material properties and the biodegradation of the modified polyesters can be varied in an extensive range. Hydrophobic polyesters of lactic acid are more slowly degradated than polyethylene-modified and unmodified polymers of this hydrocarboxylic acid. Also block copolyesters show another degradation rate than the random copolyester with the same monomer composition.

H-I/P22 OPTIMIZATION STUDIES IN THE RING-OPENING POLYMERIZATION (ROP) OF LACTONES, A.C. Albertsson, Department of Polymer Technology, The Royal Institute of Technology (KTH), 100 44 Stockholm, Sweden

Ring-opening polymerization (ROP) constitutes a unique reaction type in polymer chemistry. The ease of the reaction depends in principle on two factors; the ring strain of the monomer and the basicity of the monomer. The ROP of lactones has been a successful route to the preparation of degradable polymers with a controllable molecular weight and degradation time. The simplest member of the class lactones is the 4-membered ring ß-propiolactone. In several works we describe the polymerization of the lactone 1,5-dioxepan-2-one (DXO) by the ring-opening mechanism. The optimization of a ROP is based on the proper choice of e.g. initiator, temperature, reaction time etc. High monomer conversions and molecular weights will reached only by conducting the reactions as bulk polymerization using complex coordination initiators. The far most effective catalysts are tin compounds. Bulk polymerization of DXO with transesterification catalysts is discussed and the evaluation of optimal polymerization conditions based on multivariate statistics is described.

References: T. Mathisen and A-C. Albertsson, Macromolecules, 22, 3838 (1989); T. Mathisen, K. Masus and A-C. Albertsson, Macromolecules, 22, 3842 (1989).

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session II
14:00-15:00

H-II/P1 PLA/PEO/PLA BLOCK-COPOLYMERS: SURFACE PROPERTIES AND PROTEIN ADSORPTION, D. Kubies, J. Lukas and F. Rypacek, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic, and M. Jirouskova, Institute of Haematology and Blood Transfusion, 120 00 Prague 2, Czech Republic

Aliphatic polyesters, such as poly(lactic acid) (PLA) and block copolymers of PLA with poly(ethylene oxide) (PEO), are studied as biodegradable materials for tissue engineering. Films containing block copolymers with hydrophobic (PLA) and hydrophilic (PEO) domains exhibit a structured surface which can influence the adsorption of proteins and cells on such films. Triblock copolymers (PLA/PEO/PLA) were prepared by a ring-opening polymerisation of lactide using poly(ethylene glycol) as an initiator and Sn(II)-octanoate as a catalyst. Surface properties of cast films of PLA and PLA/PEO/PLA copolymers were characterized by measuring the water/air interface contact angle. The adsorption of human serum albumin and human fibrinogen on films was investigated using immunoassay and radioactive labelling. The changes in the contact angle and the protein adsorption are related to the molecular characteristics of copolymers and composition of films.

H-II/P2 POLYLACTIC ACID-A POTENTIAL SUTURE MATERIAL?, H. Hierlemann, H. Planck, Institute of Textile and Process Engineering, Koerschtalstrasse 26, 73770 Denkendorf, Germany

Sutures are very important from medical as well as economical point of view therefore the development of new resorbable materials are pushed ahead in the last few years. In this study monofilaments, multifilaments and braids of pure P-L-LA are tested comparative with commercial available sutures.

P-L-LA has been synthesized in-house and melt-extruded to mono- and multi-filaments in different titer sizes. The as-spun yarns are drawn and partly posttreated. The multifilaments has been braided to different constructions corresponding USP sizes 4/0, 2/0 and 0. P-L-LA devices and commercial available monofilament and multifilament sutures (all in USP size 2/0) are tested under the same conditions.

High-drawn P-L-LA monofilaments are produced in different sizes (0.1 to 0.4 in diameter), tensile strengths of 600-1200N/mm^2 and Youngs moduli of 7-12 GPa. Multifilaments of P-L-LA are braided according USP. It could be noticed that P-L-LA braids are much more influenced by braiding then comparable constructions of PGA. Mono- and multifilament systems of P-L-LA showed without exception a knot pull strength retention of only 50±5% of linear strength compared to PGA systems of 62+3%.

No P-L-LA braiding construction with different USP sizes could realize the USP limits (about 300 N/mm^2), monofilaments however fulfill the requirements. But the flexural stiffness of P-L-LA-monofilaments is higher compared to commercial available monofilaments and may suppose a problem when PLLA shall be used in sutures or ligament augmentation devices.

H-II/P3 PROCESS DEVELOPMENT OF PRODUCTION OF POLY-(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) BY METHYLOBACTERIUM SPEC., C. Wulfes, A. Christner, M. Hilliger, D. Driesch, Hans-Knöll-Institut für Naturstoff-Forschung e.V., Beutenbergstr. 11, 07745 Jena, Germany

The bioplastic poly-ß-hydroxybutyric acid (PHB) was produced by Methylobacterium rhodesianum from methanol. Some physical properties of the linear homopolymer PHB (such as brittleness, low tensile strength etc.) restricted the field of application. A small amount of 3-hydroxyvalerate in the polymers modifies their physical properties and extends the application field. In this work we report at process development of production of poly-ß-alkanoate (PHA) by Methylobacterium rhodesianum.

The aim was to be achieved by simultaneous feeding of the cosubstrates glycerol, succinic acid, n-amyl alcohol or valeric acid and the main substrate methanol. The testing of feeding parameters formed a major part of the process development. The impulse feeding of cosubstrates inhibited the cell growth and resulted in process instabilities. Continuous feeding at a constant feeding rate resulted in a stable process with high PHA yield and a high percentage of copolymers. The results indicate, that using cosubstrates in a poly-ß-alkanoate producing process would be economically interesting.

H-II/P4 PROCESSING AND CHARACTERIZATION OF BIODEGRADABLE PRODUCTS BASED ON STARCH, U. Funke, W. Bergthaller, and M.G. Lindhauer, Federal Centre for Grain, Potato and Lipid Research, PO Box 1354, 32703 Detmold, Germany

Different types of starches, native and chemically modified ones, were processed in blend systems with natural plastisizers and commercial fibres by conventional extrusion and injection molding techniques. Processing conditions and product qualities differed widely according to the kind of starches and additives used.

Starch polymer characteristics, i.e. amylose/amylopectin ratio and molecular mass distribution, were studied in native and extruded samples in order to reveal structural effects on product quality. As a result it could be shown that each thermomechanical treatment caused depolymerisation of starch, especially of the amylopektin fraction, resulting in a decrease of tensile strength and a loss of product quality, while the amylose fraction remained stable.

Considerable improvements in product properties were achieved by adding small amounts of fibres to the starch systems. Blending starch with 2-4 % fibres resulted in an increase in tensile strenghts and water resistances of these products

H-II/P5 PRODUCTION AND USE OF THERMAL POLYASPARTATES, R.J. Ross, L.P. Koskan, Donlar Corporation, 6502 South Archer Road, Bedford Park, Illinois 60501, USA

Thermal Polyaspartate (TPA) is a biodegradable, water soluble polypeptide obtained via the thermal polymerization of aspartic acid. TPA has a variety of uses as a mineral scale inhibitor, corrosion inhibitor, dispersant, humectant, and as a nutrient absorption enhancer in agriculture. The chemistry of manufacture of TPA and its use in agriculture will be discussed. Also known as poly-α,ß-D,L-aspartate, TPA has been found to enhance the absorption of nutrients by plants (US 5,350,735). Enhanced nutrient absorption can result in both increased nutrient levels in plant tissues (increased nutritional value), greater disease and stress resistance, and increased crop yields. Dramatic increases in tillering rates and root developement have been observed in hydroponically grown wheat. In the field, yield increases of 20 to 30% have been observed in winter wheat, along with up to a 20% increase in protein content. Similar yield increases have been observed in corn, tomatoes, and peppers. An over view of the manufacture, use and biodegradability of thermal polyaspartates will be presented.

H-II/P6 PRODUCTION OF HIGH MOLECULAR MASS PHB FROM METHANE, K.-D. Wendlandt, M. Jechorek, J. Helm and U. Stottmeister, UFZ Centre for Environmental Research Leipzig-Halle, PO Box 2, 04301 Leipzig, Germany

Poly-ß-hydroxybutyrate (PHB) and other polyesters can be produced by various species of bacteria and substrates. The known processes bear the disadvantages of sterile fermentation, the need of long cultivation time, and ignorance about the quality of the produced PHB.

The substitution of nonbiodegradable convential plastics by PHB and similar polyesters fails because of their high production costs. Therefore it's necessary to use new cheap substrates, to find efficient process strategies, and to produce PHB with high molecular mass.

Our strain of Methylocystis sp. GB 25 DSM 7674 is able to accumulate PHB under nonsterile conditions in a short time process with a high PHB-yield (0.4- 0.5 g PHB/g CH_4) and a PHB molecular mass of PHB above 1 MDa. The time course of PHB production shows that the highest effectivity of the accumulation process occurs during the first 8 h of reaction time.

Methane can be used as natural gas but also as biogas. The experiments were carried out using either 81 or 701 pressure fermenters ($P \leq 0.6$ MPa), the fermenters are coupled with a quadrupol process mass spectrometer.

H-II/P7 PROPERTIES OF MODELS COMPOUNDS OF LIGNIN (DEHYDROPOLYMERS = DHP), AT THE AIR/WATER INTERFACE, B. Cathala, V. Aguié-Béghin, R. Douillard and B. Monties, INRA UPBP, Equipe de Biochimie des Macromolécules Végétales, CRA 2 Esp. R. Garros, 51686 Reims Cedex, France

Lignin is, after cellulose, the second most abondant chemical component of plant tissues. The basic structure of lignin consists of C_6-C_3 units linked together by ether and carbon-carbon bonds. The macromolecular structure and properties of lignin are not, presently, clearly known. In the field of the design of new materials, the interfacial phenomenon which take place in the association between components having different chemical natures (for example: hydrophobic and hydrophilic) have to be considered.

The behaviour of two types of dehydropolymers (DHP) acting as lignin models have been studied at the air/water interface. The films of DHP spread on water were characterised by surface tension dynamical and static measurements. They show strong rheological properties characterised by long relaxation times (more than several hours). The dilational moduli measured at several surface concentrations are different for the two DHP types. The surface concentrations at which the films start to develop a significant pressure are different indicating that the surface area per monomer is related to the nature of the DHP.

These results are discussed according to the chemical and macromolecular structure of the DHP and compared to data obtained on lignin.

H-II/P8 RING-OPENING POLYMERIZATION OF LACTIDES USING YTTRIUM ETHOXYISOPROPOXIDE AS INITIATOR SYSTEM, V. Simic, N. Spassky, Laboratoire de Chimie Macromoléculaire, Université P. et M. Curie, Paris, France, L. Hubert-Pfalzgraf, Laboratoire de Chimie Moléculaire, Université de Nice Sophia-Antipolis, France, A. Duda, Centre of Macromolecular Studies, Lodz, Poland

Polymerization of (D,L)-lactide (DLLA) was carried out at room temperature in dichloromethane solution ([DLLA] = 1 M) using $[Y(OCH_2CH_2OiPr)_3]_n$ as initiator system. The polymerization is fast at the beginning, e.g., 60% of conversion in 2 min for a ratio (DLLA)/(Y) = 63 and 140 min for a ratio of 250. Then the polymerization slows down and 95% of conversion are obtained after 60 min for a ratio of 63. Narrow molecular weight distributions (Mw/Mn) of approximatively 1.15 are observed during all the reaction. If prolonging the time of reaction during several hours after completion of polymerization, an increase in Mw/Mn is observed. End-group analysis by ^{1}H NMR indicates that the polymerization proceeds by acyl-oxygen bond cleavage. Block copolymers between ε-caprolactone and (DLLA) or (LLA) were prepared.

H-II/P9 SPECIFIC DEGRADATION OF HYALURONIC ACID AND ITS RHEOLOGICAL PROPERTIES, M. Hückel, P.-J. Müller and E. Gura, Hans-Knöll-Institut für Naturstoff-Forschung e.V., Beutenbergstr. 11, 07745 Jena, Germany

Hyaluronic acid is a naturally occuring polysaccharide, which consists of alternating units of glucuronic acid and N-acetyl-D-glucosamine. The macromolecule has found application in several diverse areas due to its viscoelastic behaviour. It is biodegradable by hyaluronidases; the resulting oligosaccharides with a molecular weight of 140 000 - 160 000 g/mol contribute to healing of wounds by inducing angiogenesis.

Hyaluronic acid shows a high sensibility to shear stress. Therefore degradation can also be easily achieved by treatment with ultrasonication or with a high pressure homogenizer equipped with a cell rupture valve. The molecular weight of the fragments have been determined precisely by multi-angle-laser-light-scattering (MALLS), but not by size exclusion chromatography (SEC), because the molecule shows a very high molecular rotation radius in comparison with standards like dextran or pullulan with the same molecular weight.

Based on these examinations rheological investigations could be proceeded with definite molecular weight fractions in any solvent. Measurements at very low shear rates had to be performed to calculate the Mark-Houwink parameter. This was achieved with a Zimm-Crothers viscosimeter.

H-II/P10 STRUCTURAL FEATURES OF LIGNIN DETERMINING ITS BIODEGRADATION BY OXIDATIVE ENZYMES, B. Kurek(1), M.J. Martinez-Inigo(1), B.R. Hames(2), I. Artaud(3) and B. Monties(1), INRA, Laboratoire de Chimie Biologique, Centre de Grignon, 78850 Thiverval-Grignon, France; (2) N.R.E.L., Center for Renewable Chemical Technologies and Materials, 1617 Cole Boulevard, Golden, CO 80401-3393, USA; (3)CNRS, URA400, Rue des Saint-Pères, 75270 Paris, France

Peroxidases and laccases are key enzymes in the lignin biodegradation process. They oxidize phenolic and non-phenolic lignin model compounds into their phenoxy and cation radicals, respectively. Further non-enzymatic evolution lead then to various C-C and ether bond cleavages. Nevertheless, almost no information on the structural alterations undergone in vitro or in situ by lignin after enzymatic catalysis is available. We report here on the molecular structure of lignin oxidized by various (per)oxidasic systems. The oxidizability of phenolic and non-phenolic structures of the guaiacyl and syringyl type in the lignin network will be discussed as well as the modification of the macromolecular properties of the polymer oxidized in situ or in isolated state.

H-II/P11 STRUCTURAL STUDY OF BONE AND TOOTH TISSUES, N. Melnikova, V.V. Petrova, Petrozavodsk State University (PSU), Lenin st. 33, 185640 Petrozavodsk, Russia

The structural state and the phase composition of bone and tooth tissues have studied by X-ray diffraction methods.

Investigated samples are cuts of radioulnar bones and different tooth parts of European mooses living in the normal (Ml) or ecological unfavourable (M2) conditions. X-ray scattering patterns are obtained with the help of apparatus DRON-2.0 in monochromatic CuKα - radiation.

Analysis of X-ray diffraction spectra of Ml bones showed that their unorganical component are the complex of calcium salts $Ca_5(PO_4)_3(OH)$, $(Ca, Mg, Na)_{10}((P,C)O_4)_6$. Radioulnar bones of M2 contain three phases: Hydroxylapatite, Carbonat - Apatite and Chlorapatite ($Ca_5Cl(PO_4)_3$).

Diffractograms of tooth tissues differ from bone X-ray patterns essentially. Besides there are differences in the phase compound of a root of the teeth and their external parts. In present X-ray phase analysis of these spectra has been carried out.

H-II/P12 SUITABILITY OF FULLSCALE TESTS TO EVALUATE COMPOSTABILITY; OPTIMIZATION ATTEMPTS, C.P. Breustedt, L. Streff, W. Bidlingmaier, Universität GH Essen, FB 10 Abfallwirtschaft, Universitätsstr. 15, 45141 Essen, Germany

The German Standardization Organization (DIN) has developed the standard DIN-Draft 54.900 for testing the biodegradability and compostability of polymeric materials. The first step of the test scheme is to show toxic nonrelevance in the chemical analysis, the second step is to prove the biodegradability of polymeric material in lab scale tests. The last step is to show compostability in a full scale test in composting plants. To prove suitability and practicability of the fullscale test the University of Essen, Institute of Environmental Engeneering, Waste Management, has carried out testseries in high standard and in low-standard composting plants as demanded in DIN 54.900. Biowaste is mixed with biodegradable polymeric materials in a defined mixing ratio and put in special sample bags. These bags are following the whole composting process and get analysed at defined periods. The tests showed good practicability of standard DIN-Draft 54900-3. Optimizations made from experience with the fullscale test have been adapted to the testmethod.

H-II/P13 SYNTHESIS AND PROPERTIES OF ESTER-AMIDE COPOLYMERS OF L-LACTIC ACID WITH α-AMINO ACIDS, I. Stefko, D. Kubies, L. Machova and F. Rypacek, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Due to their low immunogenicity and good biocompatibility, polymers of α-hydroxyalkanoic acids, such as poly(lactic acid) and poly(glycolic acid), are used as biodegradable medical and pharmaceutical materials. Because such polymers have no functionalised pendant groups, the possibilily to modify their properties is limited. The introduction of L,α-amino acids into polyester molecules opens up opportunities for further structural modifications and controlling their biodegradation pattern.

Copolymers of L-lactic acid and α-amino acids, such as L-glutamic acid, L-aspartic acid and L-phenylalanine, were prepared in our laboratory by a ring opening polymerisation of L-lactide and N-carboxyanhydrides of respective amino acids, or their protected derivatives, and subsequent deprotection of protecting groups. The effect of reaction conditions during the polymerisation and deprotection precesses on the composition and molecular properties of copolymers was investigated.

H-II/P14 THE MORPHOLOGY AND ENZYMATIC DEGRADATION OF THERMOPLASTIC STARCH/POLYCAPROLACTONE BLENDS, M. Vikman(1), S. Hulleman(2), M. van der Zee(2), H. Feil(2) and M. Itävaara(1), (1)VTT Biotechnology and Food Research, PO Box 1500, Tietotie 2, 02044 VTT, Finland, (2)Agrotechnological Research Institute, PO Box 17, 6700AA Wageningen, The Netherlands

Starch can be processed under the influence of heat and mechanical energy to produce plastic-like, thermoplastic material. Polycaprolactone (PCL) is a synthetic polyester which can be blended with thermoplastic starch (TPS) to improve its material properties e.g. water resistance. The aim of this study was to examine the influence of the processing conditions on the morphology and enzymatic degradation of TPS/PCL blends. The enzymatic hydrolysis was performed using Bacillus licheniformis alpha-amylase and Aspergillus niger glucoamylase. According to scanning electron microscopy the removal of starch by enzymatic hydrolysis resulted in a porous structure. The enzymatic hydrolysis of the blends proceeded from the surface of the material inwards and intact area was very distinct. When the mixing speed during the processing was kept constant, enzymatic hydrolysis was more rapid in higher blending temperature. One possible reason for this is the degradation of starch during processing in higher temperatures.

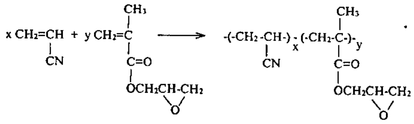
H-II/P15 THERMOPHILIC ACTINOMYCETES-USEFUL ORGANISMS FOR ACCELERATED BIODEGRADABILITY-TESTING OF POLYMERS?, I. Kleeberg(1), R.-J. Müller(1), R.M. Kroppenstedt(2), W.-D. Deckwer(1), (1) GBF, Mascheroder Weg 1, 38124 Braunschweig, Germany, (2)DSMZ, Mascheroder Weg 1b, 38124 Brauschweig, Germany

Detailed examinations of biodegradability and metabolites of polymers are necessary for their safe disposal in composting plants.

52 strains of thermophilic microorganisms i.e. 25 bacteria, 25 actinomycetes, 2 fungi isolated from composted green wastes were screened for their ability to degrade an aliphatic/aromatic copolyester. The group of actinomycetes revealed best degradation capabilities (100 μm polymer-films were degraded up to 90% in 7 days). Degradation rates obtained with pure cultures under defined laboratory conditions were tenfold higher as those of copolyester-films in composting-tests. The actinomycetes also exhibited depolymerizing activities for other polyesters and polyesteramides. Mechanistic aspects will be discussed. Our results showed that thermophilic actinomycetes play an active role in composting of polymers and can be useful as potential testorganisms in biodegradability-testing of polymers.

H-II/P16 PREPARATION OF COPOLYMER OF ACRYLONITRILE WITH GLYCIDYLMETHACRYLATE AND ULTRAFILTRATION MEMBRANE THEREOF, V. Konsulov(1), T. Godjevargova(2), A. Dimov(2), (1)Konstantin Preslavsky University, Shumen, Bulgaria, (2)University " Assen Zlatarov ", Bourgas, Bulgaria

Functional copolymer of acrylonitrile (AN) with glycidylmethacrylate (GMA) was obtained by radical copolymerization in DMF or benzene solution. The reaction was carried out at 60 °C for 5 h in the presence of initiator azoisobutyronitrile (0.75 mass%, vs monomers):



Copolymerization was studied gravimetrically in sealed glass ampules in inert medium The copolymer composition was determined by infrared spectroscopy and elemental analysis. Biodegradation of macromolecules was examined.

The copolymerization of AN and GMA in various proportions in solution DMF or benzene have been investigated. The rate of copolymerization, the composition and the properties of functional copolymer depends on the nature of the used solvent. Azeotropic proportions have been determined: x:y=1:2 in DMF and x:y=2:3 in benzene. Using the two parameter terminal model, reactivity ratios were calculated by the Kelen-Tudos method r,=0.23 and r,=0.65 (in benzene) and r,=0.27 and r,=0.58 (in DMF).

Membranes were cast from the copolymer obtained by the phase-inversion method. The porosity of the membranes was studied by mercury porosimetry. The average pore radius in the selective range of the membrane obtained was measured to be from 100 to 400 A.

The membrane has water content of 75% water permeability 0.6 m'/m h and it is selective for substances with molecular mass over 9xl0 . The membrane performance was stable at temperatures up to 90'C and pH interval 2-:12.

H-II/P17

INVESTIGATIONS ON FACTORS INVOLVED IN THE SOLUBILIZATION OF RUBBERS DURING CULTIVATION WITH GORDONA SPEC., A. Linos, C. Brämer and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität Münster, Corrensstr. 3, 48149 Münster, Germany

Solubilizing properties of strains of new isolated Gordona species towards rubbers indicate the presence of biosurfactants as special strategy for enhancing availability of such solid hydrophobic substrates and could be of great interest for the recovery of rubber raw material from used rubber products. Subject of this study was to examine the occurrence of factors being involved in the solubilization process. First hint was obtained by adding sterile supernatant of culture medium to natural rubber latex suspension resulting in prevention of normally ocurring coagulation during shaking. In another assay, partial solubilization of already coagulated latex material could be observed when concentrated sterile supernatant was added. This indicates that bacteria produce solubilizing agents which are excreted in the liquid environment. In both assays, the responsible factors did not pass 10 kDa pore size membranes and were heat sensitive suggesting proteins. Direct presence of solubilized rubber material led to loss of solubilizing properties assuming strong interaction between the factors and rubber. Separation of solubilized rubber by means of ultracentrifugation yielded solid material that was not soluble in water methanol, acetone or ether, but in chloroform, suggesting the occurrence of high molecular weight polyisoprene. Proteins and other low molecular weight molecules being involved in the degradative strategy of the bacteria on rubbers are under current investigation and results will be presented during the conference.

H-II/P18

BIOSYNTHESIS OF NOVEL POLYHYDROXYALKANOIC ACIDS CONTAINING CONSTITUENTS WITH METHYL-BRANCHES IN THE POLYESTER BACKBONE, B. Füchtenbusch, M. Wältermann, D. Fabritius and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität Münster, Corrensstr. 3, 48149 Münster, Germany

Since the discovery of poly(3-hydroxybutyric acid) (poly3HB) in 1926 over 100 other constituents of polyhydroxyalcanoic acids were found [1]. Alcaligenes eutrophus H16 and Burkholderia cepacia synthesized and accumulated a terpolyester containing 3-hydroxybutyric acid (3HB), 3-hydroxyvaleric acid (3HV) and 2-methyl-3-hydroxybutyric acid (2Me3HB), when 2Me3HB was fed as the sole carbon source under defined conditions. The presence of 1-2 mol% (2Me3HB) in the synthesized polyester was confirmed by nuclear magnetic resonance spectrometry and by gas chromatography/mass spectroscopy, respectivly [2]. An other new terpolyester, synthesized by Rhodococcus ruber, contained 2,2-dimethyl-3- hydroxypropionic acid (3-hydroxypivalic acid, 3HP) beside 3HB and 3HV. When R. ruber was cultivated on mineral salts medium with 3HP and yeast extract as sole carbon sources, an incorporation of nearly 50 mol% 3HP was determinated in the isolated and purified polyester. For the first time these compounds were identified as constituents of a bacterial polyesters The cultivation experiments are currently upscaled in order to obtain lager quantities of the biotechnologically produced ne polyesters and to analysis its material properties.

[1] Steinbüchel, A.& Valentin, H.E. (1995), FEMS Microbiol; Lett., 219-228.
[2]Füchtenbusch, B.; Fabritius, D. & Steinbüchel, A. (1996), FEMS Microbiol; Lett., 138, 156-160

H-II/P19

IN VITRO PHA BIOSYNTHESIS EMPLOYING THE PHA SYNTHASE OF CHROMATIUM VINOSUM, R. Jossek and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität Münster, Corrensstr. 3, 48149 Münster, Germany

A wide range of bacteria accumulate polyesters of hydroxyalkanoic acids (PHA) as a storage reserve in form of insoluble granules in cells. These polyesters have the properties of natural, biodegradable thermoplastics (Steinbüchel 1991). By controlled fermentation processes with wild type isolates as with recombinant strains more than 100 different hydroxyacids could be incorporated into these polymers in vivo (Steinbüchel and Valentin 1995). The usability of hydroxyacids as possible constituents of PHA is limited by the availability of appropriate substrates of PHA synthases that are the key enzymes of PHA- biosynthesis and which can be provided by the metabolism of the cell. This limitation can be overcome by in vitro synthesis of PHA with isolated PHA synthase which catalyzes the polymerisation reaction. In this work we studied the in vitro synthesis of PHB by using purified recombinant PHA synthase from Chromatium vinosum. The influence of various proteins, ions, detergents and coenzymes on synthase activity and substrat-turnover were examined. The formation of PHB granules in vitro was demonstrated

Steinbüchel, A. & Valentin, H.E. (1995), FEMS Microbiol; Lett. 128, 219-228.
Steinbüchel, A. (1991), Polyhydroxyalkanoic acids, in Biomaterials (Byrom, D., ed.) MacMillan, London, 123-213.

H-II/P20

ISOLATION OF NOVEL BACTERIA BELONGING TO THE GENUS GORDONA AND ABLE IN DEGRADING RUBBERS, A. Linos and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität Münster, Corrensstr. 3, 48149 Münster, Germany

Isolation procedures from various enrichment cultures adapted in scrap tire crumb material over several months and from soil of a Hevea brasiliensis (rubber tree) plantation led to axenic cultures of newly described nocardioform actinomycetes belonging to the genus Gordona. The isolates were able to alter during cultivation the properties of natural and synthetic cis-1,4-polyisoprene containing rubbers and rubber products and to use them as sole source of carbon and energy for growth. All strains were very similar in exhibiting coryneform morphology and adhesive growth behaviour. Colonies appeared smooth upon primary isolation, but subcultivation often yielded rough, flat colonies with extremely hydrophobic surfaces. In liquid culture they led to desintegration and solubilization of the rubber materials resulting in stabilization of the solid hydrophobic substrate in the aqueous phase. Evidence about the degradation of the polyisoprene chain could be achieved for all isolates by determination of the mineralization rate during biomass increase. Considering the fact that various Gordona strains could be isolated from different environmental sources, it has to be assumed that several species of this genus represent specialists being responsible for biodegradation of polyisoprenes and probably other isoprenoid compounds in nature. To our knowledge, this is the first time that species of this genus are referred to participate in the degradation of recalcitrant polymeric materials.

H-II/P21

ISOLATION AND CHARACTERIZATION OF POLYAMIDE-DEGRADING BACTERIA, S. Pickartz, T. Hai, F.B. Oppermann and A. Steinbüchel, Institut für Mikrobiologie der Westfälischen Wilhelms-Universität Münster, Corrensstr. 3, 48149 Münster, Germany

Poly-γ-glutamic acid (PGA) is a natural occuring homo-polyamide consisting of D-and L-glutamic acid monomers, which are connected by amide linkages involving the γ-carboxyl-moiety. PGA is the main component of the traditional japanese food «natto»(l) and can be found in capsules and slimes of different Gram-positive bacteria as well as in Hydra-nematocysts (2). While the synthesis of PGA has been investigated intensively since its discovery in 1937 not much work has been done on the biodegradation of the polymer (3). A screening for PGA-degrading microorganisms resulted in the isolation of different bacterial strains from various habitats (i.e. fresh water, activated sludge, sewage sludge and soil), which were able to grow with PGA as the only carbon-source. Belonging to the polyanionic water soluble polymers thermally synthesized poly-α,ß-D,L-aspartic acid (TPA) has been investigated as a substitute for non-biodegradable polycarboxylates [4]. From different habitats we have isolated bacteria capable to grow on mineral medium with TPA as sole carbon source added. Partial biodegradation of TPA was studied by us. Characterization of the isolated strains was performed with classical tests and with commercially available identification systems.

[l] T. Hara and U. Seinosuke. 1982. Agric. Biol. Chem. 46:2275-2281.
[2] J. Weber. 1990. J. Biol. Chem. 265:9664-9669.
[3] F. A. Troy . l985. Methods Enzymol. 113:146-168.
[4] D. D Alford, A. P. Wheeler, and A. A. Pettigrew. 1994. Environ. Pol. Degradation 2:225- 226

Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM I

Interrelation of Science Economy and Policy in Materials Research and Processing

Symposium Organizers

H.-U. HABERMEIER, Max-Planck-Institut für Festkörperforschung, Stuttgart,
Germany

M.J. LEDOUX, Université Louis Pasteur - EHICS, Strasbourg, France

N. YAMASAKI, Koichi University, Koichi, Japan

SYMPOSIUM I

Monday June 16, 1997 **Afternoon**
Lundi 16 juin 1997 Après-midi

Session I - R&D Policy

Chairperson: H.-U. Habermeier, Max-Planck-Institut für Festkörperphysik, Stuttgart, Germany

I-I.1 - invited - 14:30-15:15 COMPETITIVENESS, HIGH TECH ACTIVITIES AND R&D POLICIES, **A. Jacquemin**, Université Catholique de Louvain, Chief Advisor, European Commission, Belgium

I-I.2 - invited - 15:15-16:00 DEVELOPING ENTREPRENEURAL SPIRIT FOR EMERGING INDUSTRIES, **W. Low**, RACAH Institute, Hebrew University of Jerusalem, Jerusalem, Israel

16:00-16:30 **BREAK**

I-I.3 16:30-17:00 SYSTEM-RELATED ASPECTS OF CONVERSION OF SCIENTIFIC RESEARCH RESULTS INTO INDUSTRIAL TECHNOLOGICAL SOLUTIONS, A. Mazurkiewicz, Institute for Terotechnology, 26-600 Radom, ul. Pulaskiego 6/10, Poland

The «linear model» describing the process of the scientific research results flow to industry is ineffective and has been replaced in developed countries by the so-called «system model» taking into consideration many factors, including the principal one, that the market must influence research directions. In Poland, in the conditions of the economic system transformation towards market economy integrated with the EC countries, certain transitional models have been developed. In the paper these transitional models, as well as conditions of their functioning and examples of implementation into practice are presented. A detailed description of system-related conditions of research results transformation through so-called «high technology centres» is presented on the example of research work and application of plasma techniques in the field of the wear resistant coatings deposition.

I-I.4 17:00-17:30 ST.PETERSBURG MARKET OF COMMERCIAL R&D PROJECTS (RUSSIAN FEDERATION), N. Mourina, V. Krivobodrov, Research Center «Composite», P.O. Box 28, St.Petersburg 194017, Russia

The current transformation of Russian economy has created a new approach to research and development - commercial R&D projects commissioned by private companies. An analysis of this market in St.Petersburg is presented. The analysis is primarily focused on the two main players of this market - state-run R&D enterprises (Institutes) representing traditional scientific schools and new private companies. The analysis covers the following aspects:

- Characteristic features of commercial R&D projects (scope of analysis, time length, pricing, equipment requirements, research team)
- Identification of market segments for state R&D institutions and private R&D companies
- Potential customers of R&D companies
- Competition on R&D market
- Corporate strategy for a private company specializing on R&D with advanced materials and technologies
- The corporate financial management and taxation
- Interfacing Russian economy restructuring with new trends on the market of R&D projects

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session II - Strategies for Materials and Technology Development
Chairperson: M. Ledoux, Université Louis Pasteur - EHICS, Strasbourg, France

I-II.1 8:30-9:00

MaTech - A STRATEGIC PROGRAM FOR MATERIALS RESEARCH IN GERMANY, W. Faul, Project Management New Materials on Chemical Technologies NMT, Forschungszentrum Jülich, Box 1913, 52425 Jülich, Germany

The production and processing of high performance materials have taken a prominent role in the innovation process for many industrial sectors and technology fields. The incorporation of new materials offers a large range of benefits: from reducing the consumption of resources and energy through to the introduction of innovative products, which are competitive in international markets.

The materials research program MaTech of the German Ministry of Education, Science, Research and Technology (BMBF) successfully supports the efforts of industrial labs, universities and national research centers in the research and development process. The strategy, objectives and structure of this programme are the result of intensive discussions with both scientific and industrial communities.

The mission of the program is to promote rapid transfer of basic R+D-results in materials technology to market - competitive innovations.

The globalisation of the activities of maior companies is a challenge for national and international R+D-programs. By improving international cooperations, expensive research and development costs can be spread out and innovation processes can be accelerated.

I-II.2 9:00-9:30

UNITED KINGDOM TECHNOLOGY FORESIGHT IN MATERIALS, H.V. Atkinson, University of Sheffield, Department of Engineering Materials, Hadfield Building, Mappin St., Sheffield, Sl 3JD, UK

Technology Foresight is a systematic process to identify areas of research and technology to meet future perceived market requirements. The UK Government has recently conducted a Technology Foresight Programme with widespread consultation. The Programme had fifteen sector Panels, of which Materials was one.

In this paper, the aims of Foresight are identified and the process described. The findings of the Materials Panel are outlined, along with the steps now being taken in the implementation. The specific priorities of the Materials Panel are modelling, sensors, weight saving, biomaterials, higher temperature materials, efficient and green processing. Communication up and down the supply chain both about short term needs and the longer term are critical for future competitiveness. Industry/academic collaboration is essential for future exploitation of the knowledge base.

I-II.3 9:30-10:00

IMPORTANCE OF SOFT AND SOLUTION PROCESSING FOR ADVANCED INORGANIC MATERIALS, M. Yoshimura, Materials and Structures Laboratory (Formerly Research Laboratory of Engineering Materials), Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226, Japan

Inorganic materials such as ceramics have generally been prepared at high temperatures as far synthesis requires thermal agitation of raw materials. In addition, the formation of desired shapes, generally by sintering (or melting for glasses) requires high temperature too. Novel processing using a gaseous phase like CVD, MOCVD, etc., or vacuum systems such as sputtering, MBE, etc., requires and exhausts much higher energies than usual high temperature processing. Therefore, those processing methods have resulted in environmental problems.

In order to reduce the environmental loads on the earth, I believe that soft processing using solution systems [Soft and Solution Processing] must be developed. Since all living creatures: virus, microbe, plant, animal, etc. on earth consist of solution systems at ambient temperature and pressure, and all the materials, energies, entropies involved are cycled (or recycled) by water flows or circulation on the earth, the solution processing should be the most environmentally friendly one. We are requested to develop such processings even for fabrication of advanced materials.

When we choose particular materials systems and processings using the reactions between appropriate substrates/reactants and active solutions assisted by a minimum heat (hydrothermal) or by other energies (electrochemical, etc.), we can fabricate such advanced ceramics in desired shapes, sizes, structures, etc.

Thin films of $BaTiO_3$, $SrTiO_3$ 1) on Ti, $CaTiO_3$ coating 2) on TiAl, carbon coating 3) on SiC fibers, $CaWO_4$ 4) on W and hydroxyapatite whiskers 5), etc., have been fabricated in our laboratory.

1) J. Am. Ceram. Soc., 78, 1251 (1995) and 79, 613 (1996); 2) Intermetallics, 3, 125 (1995); 3) Nature (London), 367, 628 (1994); 4) Appl. Phys. Lett., 66, 1027 (1995); 5) J. Mater. Res., 10, 521(1995)

I-II.4	10:00-10:30	SILICON PRODUCTION IN RUSSIA: POLICY AND STRATEGY OF BILATERAL PROJECTS WITH FOREIGN COMPANIES, A. M. Prokhorov, General Physics Institute, Moscow, Russia, G.N. Petrov, T.M. Tkacheva, and G. K. Ippolitova, ELLINA-NT, Co. Ltd., Moscow, Russia As a result of the USSR decay all economic and industries alliances between the plants and studies institutes in the Republics of the former USSR were broken. So, at present there are two ways to recover silicon production in Russia: first way - to build all facilities on a new base - is uneconomic and unprofitable; the second one includes the «bridges» with old partners and simultaneously creation of new relationships with our colleagues from other countries. Russian scientist and engineers have successful experience in investigations of natural quartz with the history of its origin, analyze of carbon thermal reduction conditions and metallurgical silicon; the development of ecologically pure and reliable technology of polycrystalline silicon growth; development of new growth technology for 8’-12’ silicon single crystals based on the magnetic fields application and includes the design of new furnace; investigation of MCZ Si crystals properties including the properties of high resistivity MCZ Si after the neutron doping both by fast and by thermal neutrons irradiation; development of new ID slicing machine (for 8» Si ingots) with low vibration in the cut-area. This knowledge and «know-how» are the base of bilateral Russian-Kyrgyzian project one of the goal of which is the using of the plant build during USSR existence and cooperation with several European companies.
	10:30-11:00	**BREAK**
I-II.5	11:00-11:30	NN
I-II.6	11:30-12:00	NN
	12:00-14:00	**LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Session III - Aspects of Globalization
Chairperson: N. Yamasaki, Koichi University, Koichi, Japan

I-III.1	14:00-14:45	BASIC RESEARCH AND THE WEALTH OF NATIONS, D. Foray, University of Paris Dauphine, France
I-III.2	14:45-15:15	ROLE OF MATERIALS SCIENCE IN A GLOBALIZED TECHNOLOGY BASED FUTURE, H.U. Habermeier, Max-Planck-Institut für Festkörperforschung, Postfch 80 06 65, 70506 Stuttgart, Germany
I-III.3	15:00-15:30	NN
I-III.4	15:30-16:00	NN
	16:00-16:30	**BREAK**

Session IV - Round Table

16:30-18:00 **ROUND TABLE DISCUSSION**
Moderators: M. Ledoux, N. Yamasaki, H.-U. Habermeier

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Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM J

Light-Weight Materials for Transportation

Symposium Organizers

H. WALLENTOWITZ, Institut für Kraftfahrwesen, RWTH, Aachen, Germany

R. CIACH, Institute of Metallurgy and Materials Science, Krakow, Poland

C.G. LI, Chinese Materials Research Society, Beijing, P.R. China

J. LAWLER, FORBAIRT, Dublin, Ireland

P. RAMA RAO, Government of India, Ministry of Defence, New Dehli, India

SYMPOSIUM J

Monday June 16, 1997 **Afternoon**
Lundi 16 juin 1997 Après-midi

Session I

Chairperson: J. Baumeister, Fraunhofer Institute for Applied Materials Research, Bremen, Germany

J-I.1 - invited - 14:00-14:30 NEW CARS - NEW MATERIALS, **A. Jambor**, Mercedes-Benz AG EP/VF, Tilister Str. 1, 71059 Sindelfingen, Germany

Due to more demanding requirements of car ocupants in relation to comfort and safety enhancing measures, the weight of cars has been increasing, and as a result additional difficulties have been encountered in realizing lighter cars. In the development of every new car there is a search for new ways to combine the demands of the customers with reducing the weight of new cars.

Further progress in optimizing steel body design can only take place gradually. Reeinforced steel or tailored blanks are already in common use today. Even further reductions can be achieved by design in aluminium, magnesium or plastics. At Mercedes-Benz, for example, the hard-top of the SL-sports-car is made of aluminium and the petrol tank protection wall of the SLK-roadster is made of die-cast magnesium.

Lightweight design and consequence fuel saving will only be sucessfully realized, if proper materials are selected for appropriate part.

J-I.2 14:30-15:00 FRICTIONAL CHARACTERISTICS OF Al-SiC COMPOSITE BRAKE DISCS, K. Laden, J.D. Guérin, J.P. Bricout, J. Oudin, Laboratoire d'Automatique et de Mécanique Industrielles et Humaines, URA CNRS 1775, Université de Valenciennes et du Hainaut-Cambrésis, BP 311, 59304 Valenciennes Cedex, France

Reduction of non-suspended masses is one of the key objectives in transportation research. The braking device is most concerned and the use of aluminium discs reinforced by particular silicium carbide (SiC) is naturally envisaged. These particles greatly improve wear strength and delay the seizure occurrence. Moreover, the high thermal diffusivity of these materials reduces the occurrences of hot spots and crackings. 1/4 reduced scale discs have been considered for the study using two distinct elaboration processes: the vortex method and the centrifugation method. As regards the vortex method, SiC particles are incorporated by mechanical mixing in an aluminium bath heated to semi-liquid state. The centrifugation process induces a low porosity and gives much higher reinforcement rates.

A brake stand has been especially designed to analyze tribological behaviour of different friction materials in the continuous braking configuration. The Al-SiC discs have been tested against metallic, organic and ceramic pads in wet and dry environments. Friction performances are evaluated through the analysis of experimental and analytical results such as stability of the friction coefficient, surface temperature level and wear rate. The results show that the Al-SiC disk/organic pad system gives a very steady friction coefficient and low surface temperature. It therefore seems to be promising for braking applications.

J-I.3 15:00-15:30 COST-EFFECTIVE SYNTHESIS OF LIGHT-WEIGHT METALS FOR TRANSPORTATION, F.H.(Sam) Froes and Y.L. Wu, Institute for Materials and Advanced Processes (IMAP), University of Idaho, Moscow, Idaho 83844-3026, USA and C.G. Li, Chinese Materials Research Society, BIAM P.O. Box 81, Beijing 100095, China

The cost-effective synthesis of light-weight metals requires careful consideration of mechanical properties requirements, and a balance with the cost that can be afforded for a particular component. In this presentation developing ingot alloys will be discussed as well as products produced by «non-equilibrium» processes such as conventional powder metallurgy (P/M), rapid solidification, mechanical alloying, spray deposition and composite concepts. Attention will also be given to compaction processes and joining of components. Applications in a number of transportation industries will be presented including aerospace, automobiles, rolling stock (trains), bicycles and naval systems including submarines. The cost which can be afforded varies substantially with the particular transportation system being considered.

J-I.4 15:30-16:00 ALUMINIUM - GRAPHITE COMPOSITES USED FOR PRODUCTION OF SLIDING BEARINGS, A.P. Laskovnev, A.T. Volochko, Belarusssian Academy of Science, Physical - Technical Institute, 4 Zhodinskaya, Minsk 220141, Belarus

The use of aluminium alloys for production of sliding bearings is limited by a tendency of these materials to adhesion with a steel. Recently solid lubricants such as dispersed particles of graphite and MoS_2 are used as structure components of aluminium alloys to enhance their antifriction properties.

The authors have developed some materials having properties comparable to antifriction bronzes.These materials are produced using the technologies combining the operations of powder metallurgy and casting. The bearings produced from these materials have the required properties owing to a uniform distribution of graphite particles throughout the sample volume. The constructions which have bearings from of aluminium-graphite materials installed in friction units are more light-weight in addition to the required properties ensuring minimum losses on friction.

16:00-16:30 **BREAK**

Session II
Chairperson: H.Wallentowitz, Institut für Kraftfahrwesen, RWTH, Aachen, Germany

J-II.1 - invited - 16:30-17:00

ALUMINIUM FOAMS FOR TRANSPORT INDUSTRIES, **J. Baumeister**, J. Banhart, M. Weber, Fraunhofer Inst. for Applied Materials Research, Lesumer Heerstr. 36, 28717 Bremen, Germany

Foamed materials are widespread in transportation industry applications. While polymeric foams have been applied for many years foamed metals are now beginning to move into the focus of interest.

A powder metallurgical method which allows for the production of aluminium foams with porosity levels up to 90% is described. The foams typically have closed pores and densities ranging from 0.4 to 1 g/cm^3, so that this foamed metals float upon water. The unique mechanical properties of metal foams are described. The density dependence of metal foam properties is shown with the Young's modulus, flexural strength and compression strength as examples. A non-linear dependency of these properties on the density is found and discussed. The discussion then focuses on the energy absorption properties of aluminium foams and tools to select appropriate foams for a given energy absorption task.

J-II.2 17:00-17:30

INNOVATIVE LIGHT METALS: METAL MATRIX COMPOSITES AND FOAMED ALUMINIUMS, H.P. Degischer, Leichtmetall-Kompetenzzentrum, 5282 Ranshofen, Austria

Low weight is required especially for means of transport, for which material properties have to be validated with respect to their specific weight. Specific properties of recyclable light metals can be further increased by - reinforcement by ceramics or carbon - by reducing weight by foaming. Examples of particulate and continuous fibre reinforced aluminium and magnesium matrices, their production by extrusion, casting or gas pressure infiltration, respectively, are given together with their specific property profiles. The perspectives of selective reinforcements of components are discussed. The state of development of foamed metals by powder metallurgically produced precursor material is described and examples of processing shaped parts of aluminium foams lighter than water are presented together with some of their properties. Possible applications as stiff panels or crash absorbing elements are discussed.

J-II.3 17:30-18:00

MICROSTRUCTURAL OPTIMIZATION OF 2091 (Al-Li BASE) ALLOY SUBJECTED TO FUSION WELDING OPERATIONS, I.G. Solorzano, DCMM - PUC/Rio, C.P. 38008 - Gavea, 22452-900 - Rio de Janeiro, Brasil and M.G. Diniz, DEM-UERJ, Rio de Janeiro, Brasil

It is widely recognized that a number of application of light-weight materials in transportation systems are limited by its weldability and processing. The material chosen for this investigation was a 2091 Al-Li base alloy received in the T3 metallurgical condition in the form of a 2,5mm thick plate. Previous studies with this alloy developed in our laboratories have demonstrated the good weldability of this alloy by fusion welding processes leading, however, to the formation of brittle phases during solidification of the weld metal. These phases tend to segregate along grain boundaries and are considered responsible for the degradation in the mechanical properties of the as-welded joints. It has been also shown that a significant recovery of the mechanical performance can be achieved by subjecting the welded joints to adequately defined heat treatment schemes, which results in the dissolution of the intergranular phases and in finely dispersed re-precipitation distribution. The present contribution deals with studies of the sub-structure, in terms of dislocation arrangements, on the phase stability and precipitates microstructure, at the nanometric scale, developed upon welding and post-heat treatment operations. Detailed TEM microstructural observations have been conducted. These observations are correlated with the mechanical properties exhibited under identical microstructural conditions.

J-II.4 18:00-18:30

GRAIN GROWTH AND GRAIN ORIENTATION DISTRIBUTION OF Al-Mg ALLOYS, Y. Umakoshi, K. Matumoto, T. Shibayanagi and H. Morisada, Department of Materials Science & Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

The application of aluminum alloys to the body sheets for automobiles has been attempted because of their superior light-weight and recyclability. One of the major problems which must be overcome for industrial application is poor press-formability because of unfavourable crystallographic orientation distribution in recrystallized grains. Grain orientation distribution and grain growth behaviour of Al-Mg alloys were investigated focusing on effects of annealing temperature, initial grain orientation rolling direction and grain boundary character distribution. The texture change was divided into two stages during annealing; the cube texture primarily developed and then declined with the development of these grains accompanied by abnormal growth of no cube grains. This was more accelerated at low temperatures. The grain growth process was very sensitive to the local grain boundary character distribution. Orientation of recrystallized grains was influenced by the initial grain orientation before rolling. The effect of rolling direction on recrystallization and grain growth behaviour was also investigated using crystals with columnar grains.

Tuesday June 17, 1997 **Morning**
Mardi 17 juin 1997 Matin

Session III
Chairperson: Y. Umakoshi, Osaka University, Osaka, Japan

J-III.1 - invited - 8:30-9:00

LIGHT WEIGHT CARBONFIBER RODS AND TRUSS STRUCTURES, **R. Schütze**, DLR, PO Box 3267, 38022 Braunschweig, Germany

Lightweight carbonfiber rods and truss structures have recently found a lot of applications in modern transportation technologies. The struts of such frameworks are commonly designed as fiber-wound CFRP tubes. Here CFRP sandwich rods are an advantageous alternative. They have a lightweight foam core covered by a relative thin layer of composite material.

In many real applications, however, the superior mechanical properties of such struts can only be utilized with appropriate load transfer elements. A design of a special form locking load transfer element for high tensile and compressive loads with a simple screw connection will be described.

Apart from the form-locking clamp connectors fiber-reinforced struts can be combined with each other only by bonding. Therefore it is important to choose a connection design where the adhesive layer is always loaded in a right manner and with low stress only. The framework structures discussed in this paper refer to framework beams which have, in their simple version, cross-sections of a equilateral triangle. The presented structures are paradigmatic for connection designs without any metallic connection elements.

The structural mechanics aspects of the CFRP sandwich rods and of their connections as well as different frameworks are discussed. An outstanding application of CFRP-trusses, rod connectors and the mentioned form-locking load transmitting elements can be found in the advanced lightweight structure of a new rigid airship - the Zeppelin NT.

J-III.2 9:00-9:30

CHEMICAL VAPOR DEPOSITION OF TITANIUM NITRIDE ON CARBON FIBERS AS A PROTECTIVE LAYER IN METAL MATRIX COMPOSITES, N. Popovska(1), S. Poscher(2), H. Gerhard(1), D. Wurm(3), G. Emig(1) and R.F. Singer(3); (1) Lehrstuhl für Technische Chemie 1. Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany, (2)Fraunhofer Institut für Integrierte Schaltungen, Schottkystr. 10, 91058 Erlangen, Germany, (3)Lehrstuhl Werkstoffkunde und Technologie der Metalle, Universität Erlangen-Nürnberg, Martensstr. 5, 91058 Erlangen, Germany

The significance of carbon fibers for reinforcing metals has increased in the last years, because of their excellent mechanical properties However, to avoid the weakening reaction between the fiber and the liquid metal, a protective coating has to be applied.

Continuous carbon fibers with 6000 filaments were coated with TiN by chemical vapor deposition using a gas mixture of $TiCl_4$, N_2 and H_2 as a precursor. The deposition process in the reactor was simulated by a modified Phoenics-CVD software program using a 2D-axisymmetric model.

The mechanical properties can be used to demonstrate the efficacy of the coated fiber approach. For a pure magnesium matrix the bending strength was increased from 1180 MPa for the uncoated carbon fiber to 2130 MPa for the TiN-coated carbon fiber.

J-III.3 9:30-10:00

HOT ISOSTATIC PROCESSING OF METAL MATRIX COMPOSITES, H.V. Atkinson. A. Zulfia, A. Lima Filho and H. Jones, University of Sheffield, Department of Engineering Materials, Hadfield Building, Mappin St., Sheffield, Sl 3JD,UK

Metal Matrix Composites (MMCs) offer the prospect of improved specific stiffness and specific strength relative to unreinforced materials. However, the properties can be adversely affected by porosity present from stir-casting. The effect of Hot Isostatic Pressing (HIPping) on porosity in the aluminium casting alloy A357 and stir-cast A357/15 vol% SiC particulate MMC has been investigated. Four different HIPping treatments have been investigated and single notch four point bend tests carried out on the HIPped samples. The bending strength has increased significantly after HIPping relative to as-received. The optimum HIPing cycle has been identified.

Ceramic particle reinforced MMCs do not have adequate toughness for many commercial applications. Metal reinforced MMCs made by combining an aluminium alloy matrix with stainless steel reinforcing wire can provide a compromise between the requirements for weight saving and for toughness. The production by HIPping of such composites will be discussed along with the properties of the resulting specimens.

10:00-10:30 **BREAK**

Session IV
Chairperson: R. Schütze, DLR, Braunschweig, Germany

J-IV.1 - invited - 10:30-11:00

THE WAY TO COMPLEX CASTINGS, **R. Woltmann**, Bayerische Motoren Werke AG, Ohmstrasse 2, 84030 Landshut, Germany

The opening of the world market controls more and more our life and acting. That means for us, we have to differentiate our products from the competition, to highlight our competence for products of higher value and to dominate the whole process chain.

If we want to survive in this market, we have to change basically several parameters. We have to become faster, the co-ordination between the partners has to be made earlier and we have to use the most modern casting processes for the realisation of these tasks. The innovative lost foam casting process offers the best opportunities for complying with these requirements.

J-IV.2 11:00-11:30

STRUCTURE, TEXTURE AND MECHANICAL PROPERTIES OF AlZnMgCuTi ALLOY ROLLED AFTER HEAT TREATMENTS, J. Dutkiewicz, J. Bonarski, Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, 25 Reymonta St., 30-059 Krakow, Poland

The aluminium alloy containing 6.7 wt%Zn, 2.6 wt% Mg, 1.6 wt% Cu and 0.1 wt%Zr was continuously cast, then either quenched from 465°C, or furnace cooled down to 100°C to find the best ductility for further cold plastic deformation. The alloys were then cold rolled down to the highest possible degree of deformation (75% and 90% respectively) without formation of cracks. The initial texture in both alloys can be described by (112)[111], (213)[364) and (101)[121] ideal orientations. With increasing deformation other orientations like {110}<001> and cubic {100}<001> appear in both types of alloys.

Hardness increased during ageing at room temperature up to 150HV after 4 days, and then up to 160HV during two weeks. On ageing at 120°C for 24 hours the maximum hardness of 210HV was reached, similarly as for the alloy aged directly after quenching. The alloys deformed after quenching and aged at 120°C attained the hardness of 230HV.

The alloys in the quenched state showed already dispersed precipitates with size of several nm in addition to larger ones containing zirconium and copper. During ageing very small GP zones formed with increasing size up to a few nm after several days giving diffused diffraction effects. After ageing at 120°C for 1 day the precipitates grow and can be identified as η'.

J-IV.3 11:30-12:00

STRUCTURE AND HARDNESS CHANGES OF AlSiCuMg ALLOY DURING TWO STAGE AGEING, W. Reif, S. Yu, Technical University Berlin, Strasse des 17 Juni 135,1062 Berlin; J. Dutkiewicz, R. Ciach and J. Krol, Institute of Metallurgy and Materials Sci., Polish Acad. Sci., 25 Reymonta St., 30-059 Krakow, Poland

Aluminium-silicon base cast alloys containing 9 wt% Si, 3.5 wt% Cu and 0-1.5 wt% Mg were cast into an iron mould, then quenched and aged in two stages; first at room temperature (RT), then at 160°C. With increasing magnesium content RT ageing causes higher hardness increment, especially between 6 and 24 hours depending on the magnesium content. Second stage of ageing performed at 160°C causes additional hardening with a maximum observed after 30 and 100hrs, rising with magnesium content.

Structure changes during ageing were investigated using X-ray phase analysis, X-Ray Small Angle Scattering (XSAS) and transmission electron microscopy (TEM). Formation of fine G.P. zones of size of a few nm was found after RT ageing and their growth was registered using XSAS and TEM techniques.

Precipitation of plate like Θ' and rod like S' both following <100> directions was observed in the second stage of ageing at 160°C The increasing fraction of S' formed at higher magnesium content which formation is apparently responsible for the higher hardness of magnesium containing alloys. Following crystallographic relationship between the matrix and S' was observed: [100]S' || [210]Al and (010) S' || (120) Al.

J-IV.4 12:00-12:30

STRUCTURE AND MECHANICAL PROPERTIES OF Al-B COMPOSITE POWDER PRODUCT, F. Muktepavela and I. Manika, Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., LV 1063 Riga, and V. Mironovs, Technical University, 1 Kalku Str., 1658, Riga, Latvia

Al-B composite powder has been obtained by disintegrating pieces of composite material presenting industrial waste. Structural peculiarities and microhardness of separate powder particles (d~1 mm) have been investigated. Original design of high precision microhardness tester made it possible detect the properties of powder both in near-surface layer and in the depth. Aluminium powders after disintegration represent a new structurally non-homogenous material with the increased microhardness (1.5GPa) which grows up to 4GPa in near-surface layers. Except slight changes after annealing structural state and properties of powders are stable that evidently is due to forming of stable oxide compounds on internal surfaces and defects of the aluminium alloy during its disintegration. Powder compacts were obtained. Adhesion on Al-B and Al-Al interfaces at various temperatures and pressures were investigated. Properties of the powder compacts and their applications are considered.

12:30-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Session V
Chairperson: D. Brungs, Honsel AG, Meschede, Germany

J-V.1 - invited - 14:00-14:30 LASER BEAM WELDING OF LOW WEIGHT MATERIALS AND STRUCTURES, **K. Behler**, A. Ehrhardt, W. Frohn, Fraunhofer Institut für Lasertechnik, Steinbachstr. 15, 52074 Aachen, Germany

Increasing requirements on reduction of used resources, recycling of material and reduction of exhaust as well as contamination in transportation industry lead more and more to the application of aluminium alloys. These alloys are fulfilling all the different specifications for modern, light weight, stiff and high strength constructions.

Laser beam welding of aluminium alloys has been developed since laser power as well as beam quality allows to reach high process intensity by focusing the laser beam. Different investigations and research projects show the weldability by laser beams as well as the applicability of this technology on certain parts or structures. So laser beam welding of aluminium has been developed as a new technology for innovative light weight construction.

In this presentation special aspects of laser beam welding aluminium will be discussed, as microscopic structure of seam surfaces and solidificated material, element distribution in the weld metal and mechanical properties of weld seams will be discussed. In addition to that some examples of laser beam welding in the application field will show the technological potential in construction, manufacturing and systems engineering.

As a conclusion the presentation delivers some data and information which allow to compare the technological features of laser beam welding with other joining technologies.

J-V.2 14:30-15:00 LIKE ALL FRICTION WELDING VARIANTS THE FRICTION STIR WELDING (FSW) PROCESS IS CARRIED OUT IN THE SOLID-PHASE, W.M. Thomas, E.D. Nicholas, TWI, Friction-Forge Processes Dept., Abington Hall, Abington, Cambridge, UK

Friction stir welding is a process which produces low distortion, good appearance welds at relatively low cost. Essentially, a portion of a specially shaped rotating tool is plunged between the abutting faces of the joint. Once entered into the weld relative motion between the rotating tool and the substrate generates sufficient frictional heat to form a plasticised region around the immersed portion of the tool. The shouldered region provides additional friction treatment to the weld region as well as preventing plasticised material being expelled. The tool is then translated with respect to the workpiece along the joint line, while the plasticised material coalesces behind the tool to form a solid-phase joint.

Trials undertaken up to the present time show that a number of light weight materials suitable for the automotive, rail, marine and aerospace transportation industries can be fabricated by Friction Stir Welding.

Potential applications would include railway carriages, high speed ferries, small marine vessels, bus bar conductors, storage containers, and the fabrication of extrusion panels.

J-V.3 15:00-15:30 BEHAVIOUR OF BUBBLES IN WELDING FOR THE REPAIRMENT IN SPACE, K. Nogi, Joining and Welding Research Institute, Osaka University, Mihogaoka 11-1, Ibaraki 567, Japan and Y. Aoki, Faculty of Engineering, Graduate School, Osaka University, Yamadaoka 2-1, Suita 565, Japan

In order to investigate the behavior of bubbles under a microgravity condition, the gas tungsten arc (GTA) welding was carried out with a high quality microgravity condition. The microgravity condition was achieved using a drop shaft and an Al-Mg alloy was used as a sample. The welding was also performed under the lG conditions. Under the lG condition, pores are segregated in the upper part of the bead. In the microgravity environments, on the other hand, pores distribute uniformly in the bead and are smaller than those in the 1G environment.

J-V.4 15:30-16:00 SOME ASPECTS OF SOLIDIFICATION AND HOMOGENISATION OF Mg-Ag ALLOYS, A. Rakowska, Technical University of Mining and Metallurgy, 30 Mickiewicza Av., 30-059 Krakow, Poland, M. Podosek and R. Ciach, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Street, 30-059 Krakow, Poland

The model of nonequilibrium solidification based on assumption of full diffusion in liquid and its lack in the solid state has been adopted in Krupkowski's evaluation to Mg-Ag alloys to describe maximum microsegregation of components resulting in appearance of maximum amounts of nonequilibrium phases. The results were then compared with experimental results in alloys solidified at various rates and an optimal cooling rate at which the results coincide best has been established.

The influence of additions of zirconium and 2.5wt% neodymium (RE) on solidification of the binary MgAg2,5wt% alloy has been investigated by means of scanning and transmission electron microscopy with energy dispersive spectroscopy. It was found that zirconium entered the solid solution while neodymium appeared as a net of thernary eutectic Mg-Ag-Nd.

The homogenisation process has been studied based on hardness measurements and structure analysis. The times and temperatures of homogenisation to receive uniform distribution of components in the solid solution have been chosen neglecting the eutectic precipitates due to economica reasons.

16:00-16:30 **BREAK**

Session VI
Chairperson: K. Behler, Fraunhofer Institut für Lasertechnik, Aachen, Germany

J-VI.1 - invited - 16:30-17:00

LIGHT WEIGHT DESIGN WITH LIGHT METAL CASTING, **D. Brungs**, Honsel AG, Postfach 1364, 59870 Meschede, Germany.

New light-weight materials and advanced casting technologies are opening up new opportunities for weight reductions in vehicles. The key to intelligent light metal concepts is the design potential offered by

- new and improved alloys
- advanced production technologies
- tailored heat treatment and processing technologies.

The high perfection of the high-pressure die casting technology will be presented by demonstrating latest aluminium die casting designs for application in automobile engines, body structures and suspension components. Welded assemblies, combinins aluminium die catings with extreded and rolled products, respectively are opening new design opportunities.

Mechanical properties can be tailored to specifc requirements. Net shape or near net shape die castings reduce manufacturing cost.

For magnesium die castings, there are special opportunities in thin-wall body structure applictions. Higher material cost for magnesium alloys can be compensated by intelligent casting design with multiple integratet structrural functions.

Particle reinforced light metals lead to new alloy properties. Applications for best technical, economical and enviromental performance will be presented for silicon and siliconcarbide reinforced aluminium alloys.

J-VI.2 17:00-17:30

ABNORMAL GRAIN GROWTH IN Al OF DIFFERENT PURITY, B.B. Straumal and W. Gust, University of Stuttgart, Institut für Metalkunde, Seestr. 75, 70174 Stuttgart, Germany, L. Dardinier, S. Risser, J-L. Hoffmann, CRV PECHINEY, Parc Economique Centr'Alp, BP 27, 38340 Voreppe, France, V. G. Sursaeva and L.S. Shvindlerman, Institute of Solid State Physics, Chernogolovka, Moscow District, 142432 Russia

The onset of abnormal grain growth can disturb the grain structure of Al products and can reduce seriously their quality. It can be especially critical in case of light-weight products having low thickness. The influence of different factors like mechanical treatment, annealing temperature, geometry of the samples and content of impurities on the onset of the abnormal grain growth have been studied. It was shown that the larger is the initial grain size after homogenization annealing before cold rolling, the easier proceeds the transition from normal to abnormal grain growth during the annealing after cold rolling. For every alloy studied a temperature exists, below which the abnormal grain growth never proceeds. This temperature increases logarithmically with increasing impurity content in Al. Above this temperature, if the deformation grade is constant the onset time of the abnormal grain growth depends on the thickness of the sample. The higher is the thickness of the Al sheet, the later starts the abnormal growth. The influence of the grain boundary mobility, misorientation parameters and grain boundary phase transitions is discussed. The financial support from the TRANSFORM programme of the German Federal Ministry for Education, Science, Research and Technology and the Volkswagen Foundation under contract I/7 1 676 is acknowledged.

J-VI.3 17:30-18:00

THE DISPERSION MECHANISM OF TiB_2 CERAMIC PHASE IN MOLTEN ALUMINIUM AND ITS ALLOYS, A. Jha, The School of Materials, Clarendon Road, University of Leeds, Leeds LS2 9JT, UK

Titanium diboride (TiB_2) ceramic particulates are dispersed in molten aluminium and its alloys for grain refining and for making cast metal-matrix composites[1,2]. The dispersion of the ceramic phase is facilitated via aluminothermic reduction of K_2TiF_6 and KBF_4 with molten aluminium above 700°C. In this paper, the aspects of interfacial energy that govern the dispersion and agglomeration of TiB_2 particulates are examined. The importance of the Gibbs-adsorption interface equation for determining the surface adsorption characteristics of alloying elements is particularly discussed. The adsorption equation is also employed to quantify the change in the surface energy as a function of the alloying element concentration and, consequently the effect of interfacial energy on the nucleation rate and the size of the ceramic phase is also explained. The variation of interfacial energy of molten aluminium with various ceramic phases such as AlN, TiN and Al_2O_3 is also reviewed in the light of designing a strong interface metal-matrix composite materials.

[1] J. V. Wood, P. Davies and J. L. F. Kellie, Mater. Science. Tech., 1993, 9, pp. 830-840.

[2] A. Cibula: J. Inst. Met., 1949-50, 76, 321-360.

J-VI.4 18:00-18:30

INFLUENCE OF HEAT TREATMENT ON THE STRUCTURE AND MECHANICAL PROPERTIES OF THE AlZnMgLi ALLOY, A. Klyszewski, The Institute of Non-Ferrous Metals, Light Metals Division, ul. Pilsudskiego 19, 32-050 Skawina, Poland

The influence of lithium and silver additions on the properties of AlCuMg after heat treatment was determined. The heat treatment of AlCuMgLiAg alloy allows for obtaining high strength properties with respectively high elongation. These values are substantialy higher than those determined by domectic standard requirements. At the same time the AlCuMgLiAg alloy shows good thermal stability.

Wednesday June 18, 1997 — Morning
Mercredi 18 juin 1997 — Matin

Session VII
Chairperson: G. Hirt, EFUGmbH, Simmerath, Germany

J-VII.1 - invited - 8:30-9:00

MAGNESIUM LIGHTWEIGHT APPLICATIONS IN AUTOMOTIVE INDUSTRY REQUIREMENTS FOR MATERIAL AND DESIGN, **E. Hoffmann**, T. Hühnert, Adam Opel AG, TDCE Advanced Engineering, TEZ-Zentrallabor 85-70, 65423 Rüsselsheim, Germany

Magnesium has been a strategic material in automotive industry until the end of the 60ties. It has been used in transmission cases, engine blocks and ventilation cases with a yearly material consumption of more the 42,000 MT.

Due to increasing costs and technical requirements aluminium took over the lead as lightweight material in the recent 20 years.

At present, the development of new high purity magnesium alloys with better corrosion resistance and the increased need of weight reduction in the automotive industry has led to a renaissance of magnesium. Especially in North America, several applications i.e. instrument panel reinforcements, pedal brackets etc. has been successfully introduced into high volume automobil production.

In order to continue the positive way efforts both from the side of material development, advanced casting, machining and joining technology as well as from the side of design and computer based development tools are requested.

The paper will give an overview on the present status and on the trends in magnesium applications. It will highlight the future requirements with regard to material properties (e.g. improved creep resistance at elevated temperatures, enhanced wear resistance, data on fatigue as casted) as well as the needs for advanced technologies in rapid prototyping and joining magnesium parts.

J-VII.2 - invited - 9:00-9:30

A NEW CORROSION PROTECTION COATING SYSTEM FOR PRESSURE-CAST ALUMINIUM AUTOMOTIVE PARTS, **H. Schmidt**, R. Naß, G. Jonschker, S. Langenfeld, H. Schirra, Institut für Neue Materialien, Im Stadtwald, Geb. 43A, 66123 Saarbrücken, Germany

Pressure cast Al-alloys when used in corrosive and/or fuel containing environments have to be treated with several steps involving a pore sealing and a corrosion protection treatment. For pore sealing, polymer infiltration and for corrosion protection, anodizing is used as state-of-the-art technology. Apart from causing logistic problems these processes are rather costly.

Based on a newly developed coating material, a pore closing and corrosion protecting technique to be integrated into the part manufacturing line has been developed. The coating system is based on a chemically synthesized nano composite material made from Al_2O_3 nanoparticles, a silane-linked epoxide, tetraethylorthosilicate and aluminum alkoxides. The coating system shows a very good adhesion on Al and Al alloy surfaces and is perfectly stable against organic solvents and fuels. This is due to its high content of inorganic components. It is very scratch-resistant compared to organic coatings and can be employed in thicknesses of 5μm only. Standard salt spray and the cass test results are comparable to anodized Al surfaces or even better. These results are attributed to specific additives forming a stable interface between the metal surface and the coating. The coating system is employed by simple wet coating techniques followed by a curing process at 100 - 130°C. In the paper, the coating material, the coating process and the properties of the coating will be discussed.

J-VII.3 9:30-10:00

TECHNOLOGICAL ASPECTS OF PARTICLE REINFORCED COMPOSITES PRODUCTION, M. Cholewa, J. Gawronski, Silesian Technical University, Foundry Division, 7 Towarowa Street, 44-100 Gliwice, Poland and Z. Ignaszak, Poznan University of Technology, Foundry Division, 5 Piotrowo Street, 61-138 Poznan, Poland

The paper deals with crystallization and solidification of MMC (metallic matrix composite) with aluminium alloy matrix, reinforced with C-graphite, SiC and Al_2O_3 particles, in the amount up to 5% by weight.

It is aimed at defining the factors affecting the composite casting quality, namely: 1 - geometrical features of reinforcing particles, 2 - the kind of reinforcement in initial and final stages of crystallization, 3 - the way of preparation of the matrix alloy.

The possibilities of identification of shrinkage-gaseous porosity of the composite matrix are also presented on the ground of analysis of the phenomena accompanied by interpretation of thermal simulation results of solidification process. Usefulness of post-processing procedures, including so-called gradient criteria, was also evaluated.

The composites here investigated are designed as material for mechanical parts, which should be characterized by considerable wear resistance, low or high friction coefficient as well as erosion and corrosive wear resistance.

10:00-10:30 **BREAK**

Session VIII
Chairperson: E. Hoffmann, Adam Opel AG, Rüsselsheim, Germany

J-VIII.1 - invited - 10:30-11:00

LIGHTWEIGHT NEAR NET SHAPE COMPONENTS PRODUCED BY THIXOFORMING, **G. Hirt**, T. Witulski, R. Cremer, EFU GmbH, PO-Box 1180, 52147 Simmerath, Germany and H.C. Tinius, Krupp-Gerlach GmbH, PO-Box 1252, 66424 Homburg (Saar), Germany

Recent thixoforming development work at EFU has been concentrated on

- improved machine concepts for serial production
- die design and prototype manufacturing from various light metals including Magnesium and Metal Matrix Composits
- numerical simulation for process optimization
- accessing process benefits through the appropriate use of design options (specially designed steering knuckle demonstator)

The new modular heating system uses a proprietary inductive sensor for closed loop control of the billet's condition. A pilot system consisting of four heating modules, an ABB robot for billet handling and a Frech 5,8 MN real time controlled high pressure die casting machine is used to produce various prototype parts. Incomplete die filling experiments and numerical simulation could clearly demonstrate that the injection velocity profile significantly influences the die filling pattern.

To exploit the full potential of the thixoforming process a steering knuckle for a compact passenger car has been redesigned, thixoformed and tested. The weight of the new part is approx. 35% below that of a conventional forged steel design, despite identical functional capabilities.

J-VIII.2 11:00-11:30

HYPEREUTECTIC Al-Si ALLOYS WITH THIXOTROPIC STRUCTURE PRODUCED BY ULTRASONIC TREATMENT, V.O. Abramov and O.V. Abramov, Centre of Applied Acoustics, Leninsky prospect 31, Moscow, 117907 Russia, B.B. Straumal and W. Gust, University of Stuttgart, Institut für Metalkunde, Seestr. 75, 70174 Stuttgart, Germany

The quality of alloys can be improved by imposing ultrasound during the solidification process. This ultrasonic treatment of the solidifying melts refines the microstructure and improves the mechanical properties. The problem of thixotropic casting of hypereutectic AlSi alloys with ultrasonic is of special scientific interest and is very important for technological applications. In conventional casting solidified at moderate cooling rates primary silicon crystallizes as hexagonal plates joined together at a centre into star shaped particles, as they appear in cross-section. Most of the silicon plates were disassembled and broken during the ultrasonic treatment and forming spheroidized crystals. It was shown that ultrasonic treatment promotes Al diffusion into the primary Si crystals. The structure changes led to an improvement of the ductility of brittle hypereutectic Al-Si alloys. To study the thixotropic behaviour, the treated specimens were upset in an electro-hydraulic press under semi-solid conditions. Our data confirm great advantages of ultrasonically treated ingots of Al-Si alloys upon deformation in the semi-solid state. The influence of the grain boundary wetting transition on the formation of the microstructure in the semi-solid state is discussed. The financial support from the INCO-COPERNICUS programme under contract ERBIC15CT960740 and the Volkswagen Foundation under contract I/71 676 is acknowledged.

J-VIII.3 11:30-12:00

THE EFFECT OF SILVER ADDITION ON 7055 Al ALLOY, C.W. Lee, Y.H. Chung, K.K. Cho, M.C. Shin, Div. of Metals, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

There has been some controversy in the effect of silver addition on microstructures and mechanical properties of Al alloys. We investigated the effect of silver addition in 7055 Al alloy (7.73 wt% Zn-2.29 wt% Mg-2.60 wt% Cu-0.37 wt% Ag) which was fabricated by melting and casting procedure. Microstructure was observed and analyzed by transmission electron microscopy, scanning electron microscopy, secondary ion mass spectrometry, and electron probe micro-analyser. The constituent particles and fine precipitates consist in the matrix were analyzed. Tensile strength, hardness, and electrical conductivity were also measured. It was found that silver refined the η' precipitates in 7055 Al alloy. However, tensile strength of silver-bearing 7055 alloy was lower than that of commercial 7055 alloy due to the decreased number density of η' precipitates by consuming Mg and Zn with newly produced Mg-Zn-Ag constituent particles in the silver-bearing alloy.

J-VIII.4 12:00-12:30

FORMATION AND RELATIVE STABILITY OF INTERSTITIAL SOLID SOLUTIONS AT INTERFACES IN METAL MATRIX COMPOSITES, S. Dorfman, Dept. of Phys., Technion, 32000 Haifa, Israel, and D. Fuks, Mat. Eng. Dept, Ben-Gurion Univ. of the Negev, P.O.B. 653, 84105 Beer Sheva, Israel

Formation of the metal matrix composite is linked to the formation of the interstitial solid solutions at the matrix-fibre interface. These solutions are of extremely small concentration and the solubility process is usually diffusion-controled. To regulate this process the appropriate alloying of the matrix may be used. This allows to change the height of the diffusion barrier which leads to stimulating or suppressing the diffusion.

To calculate this effect the model of the interstitial solid solution has to be used which gives a possibility to choose whether octahedral or tetrahedral interstitial positions are occupied by the fibre atoms dissolved in the matrix. On the example of Cu-C composite material we show the way to calculate the occupancy of the interstitial positions and its temperature dependence. The results obtained on the basis of non-empirical calculations predict the preferable occupation of octahedral positions till T ~1200K. This confirms the structure of the interstitial solid solution. In the framework of this model we calculate also the influence of the alloying on the height of diffusion barrier and on the temperature dependence of carbon diffusion in copper.

12:30-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session

14:00-16:00 See programme of this poster session p.J-16.

16:00-16:30 **BREAK**

Session IX
Chairperson: J. Lawler, FORBAIRT, Dublin, Ireland

J-IX.1 - invited - 16:30-17:00 DEVELOPMENT OF ADVANCED MAGNESIUM ALLOYS, **K.U. Kainer**, Technische Universität Clausthal, Agricolastr.10, 38670 Clausthal-Zellenfeld, Germany

The driving force for an expected growth in magnesium production recently has been the inceeasing demand for magnesium alloys by the automobile industrial as a result of political pressure and public opinion to use natural resources wisely and sparingly and to reduce vehicle emissions and environ- mental contamination. Attention is being devoted to a save in weight of passenger cars and commercial vehicles. Magnesium alloys fulfill the requirements of low density, good forming and machining properties and high recycling potential. Nevertheless, applications are still well behind those of competing aluminium and polymeric materials. The reasons for this lie in the high cost of the primary material, the limited choice of tailored made alloys and sometimes the unsufficient propeproperty profile low creep resistance, low ductility and low toughness. There are also knowledge gaps in the user-industries, which prevent a substitution of conventional materials by magnesium alloys.

In the paper the trends in the development of new magnesium alloys and magnesium matrix composites are discussed. Also included is a summery of the process development of advanced production of these materials, eg spray forming, comporting thixo casting and squeeze casting. A comparison of the microstructure and properties with those of conventional cast and wrought magnesium alloys shows the potential of the new materials.

J-IX.2 17:00-17:30 ALUMINIUM INFILTRATION PROCESSING, A. Mortensen, C.S. Marchi, V.J. Michaud, Swiss Federal Polytchn. Inst. of Lausanne EPFL, 1015 Lausanne, Switzerland

Weight reduction combined with decreasing fuel consumption is a very important target of the industry, which is working on new transportation systems for the future.

Metal Matrix Composites contribute to achieving weight-saving and improved properties. Furthermore, the advantages of MMC, such as improved static and fatigue strength, high stiffness, low therm expansion coefficient and good wear resistance can provide additional benefits and open up new potentiai fields of application.

Long-fibre-reinforced materials exhibit excellent stiffness and strength values In fibre direction which are higher than with stell and titanium. Nevertheless, possible applicatlons are still limited due to cost aspects, but local reinforcement seems to be able to avoid this disadvantage,

Particulate and short-fibre-reinforced Al and Mg materials exhibit high stiffness and excellent wear behaviour. They are very costly, and are made by different production routes.

Several parts made from MMC are close to application and a few have already been realized for series production. Examples of applications are fittings and stringers for aircraft due to the higher stiffness and strength. Brake disks for automotive application, will be produced from MMC due to their improved wear resistance, and the advantage of good fatigue behaviour is exploited for the control ring of helicopters.

The overview concerning the potential of Metal Matrix Composites will Composites will be rounded off with an outlook concerning the necessary development work.

J-IX.3 17:30-18:00 MICROCRACKING AT THE CHANGE OF THE DEFORMATION PATH OF AL RODS, M. Kurowski, J. Kusnierz, A. Grabianowski, E. Bielanska, Institute of Metallurgy and Materials Science, Reymonta 25, 30-059 Krakow, Poland

In most metals the change in the deformation path of rods of circular cross-section results in the reduction of the work of plastic deformation. The additional negative phenomenon is the occurrence of microcracks. The above problem has been considered on Al rods of Al 99.8 grade, which were deformed using the drawing technologies (A), rolled in the mode «circle-oval-circle» (B) and in the combined mode (C), and next subjected to torsion. A small range of work softening (I) was observed, which was followed by a considerably greater range of strain hardening (II). The mode of technology of predeformation affected the generation of microcracks in the I range, as well as the appearance of areas of markedly deformed metal with numerous cracks, in the form of folds in the II range of work hardening. The investigations have shown that microcracks occurring at the change in the gradient of layered work hardening are greater than in the case when the character of work hardening is changed from an «island-like» into a layered one. It appears that the phenomenon of the folded external surface of the rods is associated with poor work hardening of Al in comparison with other metals, and as a result of the deformation geometry assumed by most researchers to accompany torsion, does not occur. The phenomenon of microcracks should be each time taken into consideration when combining various modes of the technologies of Al deformation, especially those inducing work softening in view of the possibility of reducing the fatigue strength.

J-IX.4 18:00-18:15

STRUCTURE AND MECHANICAL PROPERTIES OF AGE-HARDENED DIRECTIONALLY SOLIDIFIED AlSiCu ALLOYS, J. Krol, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Reymonta 25, 30 059 Krakow, Poland

The precipitation effect of copper addition in AlSi alloys on the mechanical properties was investigated. Directionally solidified Al10wt.%Si alloys with additions of 2 and 4 wt% copper were homogenised at 530°C, quenched in water and aged at 200°C. The precipitation kinetics of Θ' phase was studied using texture and lattice parameter measurements, X-ray small angle scaterring, scanning microscopy and transmission electron microscopy methods. The mechanical properties were investigated in hardness and tensile tests. The increase of mechanical properties was influenced by the formation of Θ' precipitates. The highest values of these properties were obtained after ageing between 10 to 20 hours. The highest precipitate formation velocity measured according to lattice parameter changes and XSAS results was observed up to about 15 hours of ageing. The coarsening of the precipitates diminished the mechanical properties of the investigated alloys above 30 hours of ageing. Alloys with higher copper content attained much higher amount of precipitates (measured as the integral intensity) and higher mechanical properties. The precipitates of slightly larger size formed in the alloy with smaller copper addition, which gave decrease of hardness after about 20 hours of ageing.The changes of mechanical properties were in good agreement with the results of structural investigations.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session X
Chairperson: R. Ciach, Institute of Metallurgy and Materials Science, Krakow, Poland

J-X.1 - invited - 8:30-9:00

CARBON FIBRE IN AUTOMOTIVE APPLICATION, **H. Adam**, Forschungsgesellschaft Kraftfahrwesen mbH Aachen, Steinbachstrasse 10, 52074 Aachen, Germany

Short fiber reinforced composites have proven their substantial potential for automotive application and are state-of-art technology for volume production of non-structural vehicle components. Examples for these components are spread over the vehicle from frontend-reinforcement member made by GMT stamping to intake manifold made by injection moulded thermoplastics.

Based on the high potential of advanced composites for both, structural lightweight design and material lightweight design, research and development focussing on innovative engineering solutions is an ongoing process within the automotive industry and related institutions.

In this paper, different automotive components made out of advanced composites are presented and discussed with reference to their chances and risks for automotive realization. Furthermore, main restrictions and restraints for the use of advanced composites, e.g. load applications, damage tolerance and high volume production technologies, are explained. Technical solutions as key enablers for industrial realization are shown.

J-X.2 9:00-9:30

PROCESSING AND CHARACTERIZATION OF TiPd SMA FIBER REINFORCED Ti COMPOSITE, K. Mizuuchi(1), K. Hamada(2), K. Yamauchi(3), K. Okanda(1), K. Enami(4), M. Taya(2), K. Inoue(2); (1)Osaka Municipal Research Institute, Osaka, Japan; (2)University of Washington, Seattle, Washington 98195-2120, USA; (3) Tokin Corporation, Sendai, Japan; (4) Ryukoku University, Seta, Otsu, Japan.

Shape memory alloy fiber-reinforced metal- and polymer-matrix composites have recently been receiving strong attention because fo their unique mechanical properties associated with internal stress due to shape memory (SM) effects of the fiber. Composites fabricated and characterized include Al- and polymer-matrix composite reinforced with NiTiSM alloy fiber for aerospace structure materials that are required to have good mechanical properties such as high specific strength.

In the present study, we have fabricated Ti-matrix composite containing continuous TiPd-based high-temperatures SMA fiber by means of sheath rolling in an attempt to fabricate smart composite for high temperature applications. The fabricated Ti-matrix composite has been observed to show interfacial reaction layer with a uniform thickness of about 30μm between fiber and matrix. This reaction layer consists of three intermetallic compounds. Yield strength of the composite increases with increasing temperatue at temperatures higher than the martensite transformation finish temperature. The fracture surface of composite samples fractured in tension at room temperature has shown typical ductile fracture mode, indicating good interfacial strength between the Ti matrix and TiPd-based SMA fiber. The mechanical properties obtained are being analyzed based on a micromechanics-based model.

J-X.3 9:30-10:00

TENSILE PROPERTIES AND MICROSTRUCTURE OF NiAl-20TiB$_2$ AND NiAl-20TiC IN-SITU COMPOSITES, J.T. Guo, D.T. Jiang, Z.P. Xing, G.S. Li, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, P.R. China

A hot-pressing aided exothermic synthesis (HPES) techique was developed to fabricate NiAl matrix composites reinforced with TiB$_2$ and TiC particles which were in situ reaction synthesized from their elemental powders. These particles were uniformly dispersed in the matrix. The resulting products were HIPed to nearly complete densification. High temperature tensile properties were tested. It was found that the tensile yield strength at 900°C were about two times stronger than that of unreinforced NiAl and were approximately three times stronger at 980°C. The strength of NiA1-20TiC showed a little bit stronger than that of NiAl-20TiB$_2$, however its ductility decreased comparatively. The fracture surfaces of the tensile samples were analyzed using SEM. The microstructure and interfaces between the matrix and particles of the two composites were observed by TEM and HREM. The interfaces between NiAl and TiC or TiB$_2$ were atomically flat, sharp and free from any interfacial phases in most cases, however, thin interfacial amorphous layers were observed at the interfaces in some cases. This type of interfacial structure may be beneficial to the strength of the composites.

10:00-10:30 **BREAK**

Session XI
Chairperson: H. Adam, Forschungsgesellschaft Kraftfahrwesen, Aachen, Germany

J-XI.1 10:30-11:00

GROWTH CHARACTERIZATION AND DEFORMATION OF A DS GAMMA TITANIUM ALUMINIDE ALLOY, Y.G. Zhang, Y.H. Lu and C.Q. Chen, Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, P.R. China and V. Ji, LM3, EMSAM, 75013 Paris, France

The mechanical properties of gamma titanium aluminide alloys depend strongly on their $(\gamma+\alpha)$ two-phase microstructures. Among the microstructures, the lamellar microstructure is of special interest not only because it is so common and persistent but also its mechanical properties are quite anisotropy with respect to lamellar orientation. The particular features of the lamellar microstructure have attracted considerable attention and interest in the directional solidification (DS) processing of the alloys more recently. The attempts have been made in the DS processing of Ti-48Al alloy in laboratory scale and some of the results are reported in this paper. The microstructure of the DS alloy was controlled both during solidification and by post-solidification heat treatments. The alloy has been tested at room temperature and deformation and fracture behavior have been examined in details, with particular attention focusing on $\gamma/\alpha_2/\gamma$ interfaces and grain boundaries. The prospects of the DS alloys are discussed on the basis of the present results.

J-XI.2 11:00-11:30

THE EFFECT OF MICROSTRUCTURE ON MECHANICAL PROPERTIES OF THE TWO-PHASE TITANIUM ALLOYS, J. Sieniawski, R. Filip and W. Ziaja, Rzeszow University of Technology, W. Pola 2, 35-959 Rzeszow, Poland

The wide range of two - phase titanium alloys makes it possible to use them as a high strength structural material or in conditions requiring certain special properties like corrosion resistance or paramagnetizm. Operational characteristics of these materials are determined by diffusionless and diffusion transformations and decomposition both of the α and ß phases.

The materials tested were two - phase α + ß titanium alloys with different volume fraction of the ß phase. Different kinds of microstructure parameters were obtained by controlled cooling rates selection. Microstructure of the specimens was examined using optical microscope. Fracture surfaces were observed by SEM technique. The influence of the microstructure and phase composition on the mechanical properties of the alloys have been studied. Static tensile tests, hardness tests and fatigue investigations were performed. It has been noticed that the volume fraction and chemical composition of the ß phase has a significant effect on mechanical properties and cracking process during fatigue failure.

J-XI.3 11:30-12:00

EFFECT OF FORGING CONDITIONS AND ANNEALLING TEMPERATURE ON THE FATIGUE STRENGTH OF TWO PHASE TITANIUM ALLOYS, K. Kubiak and J. Sieniawski, Rzeszow University of Technology, W. Pola 2, 35 959 Rzeszow, Poland

In the paper the influence of deformation degree and temperature and annealing temperature on the fatigue strength of forgings made of two phase martensitic titanium alloys Ti-6A1-4V and Ti-6A1-2Mo-2Cr was characterised.

Dilatometric examination and X-ray phase analysis of the alloys was applied to determine the start and finish temperature of the α+ß ⇔ ß phase transformation during heating and cooling and phase composition of the alloys after continuous cooling from the ß-range with rate in the range of 0.004-48 K s^{-1}. Forgings were annealed at 950, 1060 and 1250 K for 1 and 3 hours and air-cooled. Wöhlers diagrams were worked out for specimens of both alloys heat treated according to all schemes. Microstructure of the specimens was examined using optical microscope and TEM.

The maximum fatigue strength was obtained by forging in α+ß-range (1170K). Forging in ß-range (1320K) led to 20% decrease in fatigue strength Ti-6A1-4V alloy and 13% for Ti-6A1-2Mo-2Cr alloy. Increase in deformation degree resulted in lower fatigue strength.

J-XI.4 12:00-12:30

ADVANTAGES AND OBSTACLES IN THE APPLICATION OF LIGHT WEIGHT MATERIALS IN A CAR'S BODY IN WHITE, A. Poth, A. Kahle, A. Weichenrieder, C. Buro, BMW AG, Research and Engineering Center, Petuelring 130, 80788 Munich, Germany

Fuel efficency and ecological compatibility are some oft the key phrases in discussions on automobiles. On the other hand customers are demanding better performance, comfort, safety, quality and visual appeal at lowered costs. These requirements are compounded by public opinion and legislation with respect to the reduction of emissions and resource consumption. The car manufacturers are competeing in a race to reach these higher goals at lower costs.

Today's body in-white accounts for about 20 to 25 % of a cars total weight. In addition to this decreasing weight percentage the functional capability has increased greatly. The energy absorption potential has been increased by 270 %, and the body stiffness doubled. Yet we still see potential in the development of steel body-in-white. A conventional main-stream body-in-white can be divided into three major structural areas:

- Beam-structure,
- Shell-elements
- Hang on parts.

Each of these three areas asks for different material properties and capabilities. For example stell is a superior material for frameworks in the body structure. In future such materials will compete for their share and place in a car body. It is therefore necessary to compare the properties, the production processes and the costs of each available solution. The final decision, of which material and design solution is the appropriate one, can only be made if the customer is clear about how much he is prepared to pay for a light weight solution which can pay back in terms of fun, performance of fuel efficency.

The goal for the future is to better understand and develop the advantages of materials, to learn the efficient manufacturing processes and to reduce costs in order to build a lighter body-in-white with better performance.

12:30-14:00 **LUNCH**

Thursday June 19, 1997 Afternoon

Jeudi 19 juin 1997 Après-midi

Session XII

Chairperson: H.Wallentowitz, Institut für Kraftfahrwesen, RWTH, Aachen, Germany

J-XII.1 - invited - 14:00-14:30

METALLURGICAL PROBLEMS ASSOCIATED WITH THE PRODUCTION OF ALUMINIUM - TIN ALLOYS, **T. Stuczynski,** Institute Non-Ferrous Metals, Light Metals Division, ul. Pilsudskiego 19, 32-050 Skawina, Poland

Of all the plain bearing alloys available, aluminium alloys have a better combination of ideal bearing characteristics than any other single materials. Conventional Babbit alloys, especialy the leaded bronzes are increasingly being replaced by aluminium alloys, particulary in the automobile industry. It has been know, that the addition of elements like tin or lead improves the antiscoring and antifrictional properties of aluminium. Alumimnium and tin have a wide miscibility gap in the molten state and are virtually insoluble in each other during solidification. Further difficulties arise from the large freezing range of their alloys and the wide density difference between the two componentas greatly increases tin segregation during alloy preparation. It has therefore been difficult to introduce and disperse tin unformly in aluminium to the desired extent by conventional melting and casting techniques The present autors have developed a simple foundry technique which has been used successfully to disperse and retain tin at contents up 20 wt % in aluminium ingots. This results form the subject of the present paper.

J-XII.2 14:30-15:00

INVESTIGATION ON ANNEALING BEHAVIOUR OF NANOCRYSTALLINE NiAl, L.Z. Zhou, J.T. Guo, G.S. Li, L.Y. Xiong and S.H. Wang, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, P.R. China

A nanocrystalline NiAl prepared by mechanical alloying and vacuum heat pressing at 900°C /62.5MPa for lh has been studied to investigate its stability with annealing time. Isothermal annealing was conducted at 1000°C for different time on the nanocrystalline NiAl. The grain sizes of the annealing specimens are measured from x-ray line broading. The results show that a significant grain growth takes place from 30nm at the initial stage to 56nm by annealing for l0h, then maintains this value regardless of annealing time up to l00h. Microhardness test results show that the microhardness of the annealing specimens reduces obviously with annealing time up to 5h and then increases slightly with further annealing due to off-stoichiometry.

In addition, positron annihilation microscopy has been used to investigate the interfacial defects in the nanocrystalline NiAl specimens with annealing time. The results show that there are three kinds of defects in the interfacial region of the nano-NiAl alloy. They are monovacancy-sized free volumes, microvoids and large voids. During the present annealing process, the sizes of the three defects have no significant change, but amount of the defects, especially for monovacancy-sized free volumes and microvoids varies clearly with annealing time, and that has been associated with crystallite rotation, structure relaxation and atoms rearrangement. The relationship between the microhardness properties and the positron annihilation parameters is discussed.

J-XII.3 15:00-15:30

CRITICAL PHENOMENA AND NON-LINEAR EFFECTS AT FeB MECHANICAL ALLOYING, V.A. Tsurin, V.A. Barinov, Institute of Metal Physics, Ural Branch of RAS, 620219 Ekaterinburg, Russia

Mechanically alloyed mixture of powders is an open system and MA takes place under conditions far from equilibrium. The behaviour of such systems is determined by training dissipative structures resulting in non-equilibrium phase transitions. The nuclear γ-resonance spectroscopy method is used in studying microscopic processes during FeB solid solution synthesizing in a centrifugal-planetary ball mill. Dispersion of powder particles, absorbed energy increase under conditions when the speed of defect formation is greater than that of diffusion result in both lattice defects accumulation up to critical concentration and unstable structure formation. The increase of treatment time above a certain critical value leads to the space-time oscillations of boron concentration in synthesized FeB solid solution. At the critical point the system loses its stability and the steady regime turns out to be oscillating regime, i.e. a succession of concentration maxima takes place. The mentioned process is the result of synergism in quasi-static dissipative structures and is analogous to the self-oscillating regime of the Belousov-Zhabotinski reactions for solids.

J-XII.4 15:30-16:00

SIMULTANEOUS DEPOSITION OF COVERINGS AND HIGH-DOSE ION IMPLANTATION ON METAL SURFACE FOR IMPROVEMENT OF SERVICING CHARACTERISTICS, A.D. Pogrebnjak(1), V.I. Lavrentiev(1), B.P. Gritsenko(2), S.M. Duvanov(3), A.V. Kamko(4), Y.M. Ageev(4), N. Karataeva(1), (1)Sumy Institute for Surface Modification, P.O.Box 163, Av.Shevchenko 17, 244030 Sumy, Ukraine, (2)Institute of Strength Physics and Material Science, RAS 634021 Tomsk, Russia; (3)Dubna, JINK Moskovskaia Reg., Russia, (4)Institute of Applied Material Science, NAS, Kiev, Ukraine

Ti samples have been subjected to Cu ion deposition and simultaneous ion implantation. Ti-V-Al (alloy) samples have been subjected to double implantation of Fe ions (10^{16} to 10^{18}) cm^2 plus Zr ions (5 x 10^{16}) cm^2 and Cu ions (10^{16} to 10^{18}) cm^2 plus Ni ions (5 x 10^{16}) cm^2. Implantation has been performed using the implanters “Diana” and “Impulse-4” with the following beam parameters: the accelerating voltage of about 60kV, pulse duration of a hundred of microseconds, current density of several milliamps. Deposition has been performed using the pulsed source having about 1 millisecond pulse duration, 5 to 50 Hz frequency and about 50 to 100 eV energy. RBS, AES, TEM, SEM, measurements of microhardness, wear, internal friction, friction coefficient as a result of loading have been used for our investigations.

16:00-16:30 **BREAK**

Session XIII
Chairperson: C.G. Li, Institute of Metal Research, Shenyang, P.R.China

J-XIII.1 - invited - 16:30-17:15 DEPOSITION OF COVERINGS AND FILMS MADE OF CERAMICS, SEMICONDUCTORS, METALS AND METALLIC TARGETS, **A.D. Pogrebnjak**, Sumy Institute for Surface Modification, P.O. Box 163, Av. Shevchenko 17, 244030 Sumy, Ukraine

J-XIII.2 17:15-17:45 CHARACTERISTIC FEATURES OF SILUMIN ALLOYS CRYSTALLIZATION, S. Pietrowski, Inst. Mat. Eng. Technical University of Lodz, ul. Stefanowskiego 1, 90-924 Lodz, Poland

The results differential thermal analysis (DTA) of crystallization of multicomponend silumin alloys with 8÷22 wt % Si and Mg, Cu, Ni and Fe minoz admixtures are presented in the paper. It has been proved that to any one of the solidphases crystallizing from the liquid (α, ß, Mg_2Si, Al_6Cu_3Ni, A_2Cu, Al_9Fe_2Si) a particular thermal effect can be deduced and identified. A new hypothesis concerning hypereutectic silumin alloys crystallization has been proposed in the work.

J-XIII.2 17:45-18:15 RAPID SOLIDIFICTON PROCESSED ALUMINIUM ALLOYS IN AUTOMOTIVE APPLICATIONS, W.H. Kool, H. Kleinjan, L. Katgerman, F.J. Dom*, Lab. of Materials Science and Technology, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands; *RSP Products B.V., Bierstraat 15, 3011 XA Rotterdam, The Netherlands.

High cooling rates applied to aluminium alloys provide a structural refinement which leads to an improvement of various properties such as ductility, formability, strength, corrosion resistance, mechinability etc. Studies have shown that, using meltspinning as the rapid cooling technique, cost effective processing can be possible for e.g. automotive applications.

The paper will focus on the application of hypereutectic alloys for pistons. Prototype pistons of diameter of 50 mm were made by meltspinning, followed by extrusion and forging. These pistons are now tested in high-performance engines, used for kart-racing. Preliminary results show that weight reductions of the piston of 10-15% are obtained. Further, the lower CTE gives the possibility of a 20-30% lower clearance resulting in better performance after a cold-start.

Potential exists for other types of piston as well. High temperature performance is improved which might benefit pistons used for Diesel engines and pistons used in combination with direct fuel injection into the cylinder. At the moment work is performed for the set-up of a full continuous process for regular production.

☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ **END OF SYMPOSIUM J** ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆ ☆

SYMPOSIUM J
POSTER SESSION

Wednesday June 18, 1997 — **Afternoon**
Mercredi 18 juin 1997 — Après-midi

14:00-16:00

J/P.1 THE EFFECT OF COPPER ADDITION ON THE STRUCTURE AND STRENGTH OF AN Al-Li ALLOY, O. Kabisch, W. Gille, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany, and J. Krol, Institute of Metallurgy and Materials Science of the Polish Academy of Sciences Krakow, Reymonta 25, 30-059 Krakow, Poland

In the present study the effect of copper addition on the kinetics of precipitation and the development of hardness of the AlLi alloy after treatment at 200°C was investigated. The hardness changes distinctly for the AlLi and AlLiCu alloys. The formation and geometrical arrangement of all precipitates was studied using XSAS and TEM methods. The structure parameters R_g and Q of both alloys after ageing were investigated. Two methods, the Guinier approximation and the calculation of the correlation function $\gamma(r)$, were applied. From correlation function analyses structure parameters of SAS were studied. By use of a plot of $r.\gamma(r)$ the distribution law of the thickness of the T_1-discs was obtained. Two types of δ' precipitates of size about R_g=2nm and about R_g=8nm were inspected. In the AlLiCu alloy, due to more numerous nucleation sites and a small amount of lithium which appears in the T_1-phase, the R_g value was distinctly smaller than in the AlLi alloy. This decreases the lithium- amount precipitated in δ' phase. The hardness of the AlLiCu alloy is significantly higher due to disc like T_1-precipitates.

J/P.2 EROSIVE WEAR BEHAVIOUR OF ALUMINIUM BASED COMPOSITES, Qi Fang(1), P. Sidky(1), M.G. Hocking(1) and Jun-Ying Zhang(2), (1) Department of Materials, Imperial College, London SW7 2BP, UK. (2)Department of Electronics & Electrical Engineering, University College London, Torrington Place, London WClE 7JE, UK

Al-MMCs reinforced with short fibres or particles of ceramics such as alumina, TiB_2 and silicon carbide result in composites of high specific strength and stiffness, suitable for advanced engineering applications such as in the aerospace and automotive industries. It is generally accepted that reinforced Al-MMCs exhibit higher tensile strengths and elastic modulus than unreinforced Al-alloys, but have lower ductility. However, there are few published data on the resistance of Al-MMCs to solid particle erosion. This paper studies the erosion wear behaviour of alumina-fibre and in-situ TiB_2 particles reinforced Al-alloy matrix composites using a water/SiC particles slurry jet. From the results of our experiment, the erosion resistance of reinforced Al-MMCs depends on that of Al-alloy and reinforced ceramics, as well on the interface between the matrix and ceramic fibres or particles.

Some design strategies to enhance the erosion resistance of Al-MMCs reinforced with short fibres and particles have been discussed.

J/P.3 SYNTHESIS AND CHARACTERISATION OF Me-HTSC COMPOSITE, Z.D. Stankovic, University of Belgrade, Technical Faculty in Bor, 19 210 Bor, Yugoslavia and L.T. Mancic, Institute of Technical Sciences of Serbian Academy of Sciences and Arts, K.Mihailova 35/1V, Belgrade, Yugoslavia

This study has demonstrated that homogeneous composite compacts with improved superconducting and mechanical properties can be successfully prepared from pure Me-HTSC powders (Me=Ag, Cu, Al; HTSC=$YBa_2Cu_3O_{7-x}$). The composites were produced under following conditions: mass fraction of metal phase in the range of 2.5 to 40%wt., compacting pressure from 15 to 30kN/cm^2, sintering temperature from 543 to 1223K and cooling rate of 50K/h and 220K/min. Beside T_c value determination, microstructure and X-ray diffraction analysis have been done.

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM K

Coatings and Surface Modifications for Surface Protection and Tribological Applications

Symposium Organizers

J.P. RIVIÈRE, Université de Poitiers, Futuroscope, France

J.-M. MARTINEZ-DUART, Universidad Autonoma de Madrid-Cantoblanco, Madrid, Spain

A. GRILL, IBM Research Division, Yorktown Heights, USA

L. PRANEVICIUS, Vytautas Magnus University, Kaunas, Lithuania

SYMPOSIUM K

Monday June 16, 1997
Lundi 16 juin 1997

Afternoon
Après-midi

Session I -Tribological Coatings
Chairperson: J.M. Martinez-Duart, Universidad Autonoma, Madrid, Spain

K-I.1 - invited - 14:00-14:30 DESIGN ASPECTS FOR ADVANCED TRIBOLOGICAL SURFACE COATINGS, **A. Matthews** and A. Leyland, RCSE, The University of Hull, Hull, HU6 7RX, UK, and K. Holmberg and H. Ronkainen, VTT Manufacturing Technology, 02044 VTT, Finland.

The paper introduces a holistic approach to the description of contact mechanisms, which is especially pertinent to coated surfaces. This classifies the tribological contact effects in terms of macromechanical, micromechanical, nanomechanical, tribochemical and material transfer mechanisms. This approach allows the identification of optimum coating characteristics to resist specific wear phenomena. In particular we discuss the use of duplex combinations of processes and multi-layered or multi-phased coatings as having characteristics suitable to meet these needs. The reasons for the beneficial properties of such coatings are discussed with regard to their load response behaviour, and this allows the identification of suitable applications for different duplex and hybrid combinations of coatings and treatments. Information is presented on specific applications-related test results and the likely uses of these coatings in the future.

K-I.2 14:30-14:50 INFLUENCE OF THE MICROSTRUCTURE OF PLASMA DEPOSITED MCrAlY COATINGS ON THEIR TRIBOLOGICAL BEHAVIOUR, S. Li, C. Langlade, S. Fayeulle, D. Tréheux, Laboratoire Ingénierie et Fonctionnalisation des Surfaces, UMR 5621, Ecole Centrale de Lyon, 69130 Ecully, France.

MCrAlY coatings (CoNiCrAlY and NiCrAlY bentonite) have been plasma sprayed under various atmospheres (air, argon, vacuum) on a nickel based superalloy (Hastelloy X). Their microstructures (porosity, presence of oxides, phase composition) and mechanical properties (hardness, Young modulus) have been characterized. The friction behaviour of these coatings sliding against a vacuum plasma sprayed NiCoCrAlYTa coating has been evaluated under two different tribological conditions:

- fretting test: The study has mainly been focussed on the different degradation mechanisms which may occur under fretting conditions. Depending on the coating microstructure, two kinds of damage are observed: particle detachment or microstructural transformation (tribologicaly transformed structure).
- cylinder/flat friction test at speed up to 5m/s where high temperatures are obtained in the contact. This allows to study the role of transfer and oxidation.

These complementary testing conditions allow to identify clearly the influence of three important parameters: speed, load and temperature.

K-I.3 14:50-15:10 LASER SURFACE MODIFICATION: STRUCTURAL AND TRIBOLOGICAL STUDIES OF AlN COATINGS. C. Meneau, P. Andreazza, C. Andreazza-Vignolle, C.R.M.D.Université d'Orléans-CNRS, BP 6759 Rue de Chartres, 45067 Orléans Cedex 2, France; P. Goudeau, J.P. Villain, L.M.P., Université de Poitiers-CNRS, BP 179, 86960 Futuroscope Cedex, France; C. Boulmer-Leborgne, G.R.E.M.I., Université d'Orléans-CNRS, BP 6759, Rue de Chartres, 45067 Orléans Cedex 2, France.

In order to improve the superficial wear resistance and hardness of aluminum substrates, aluminum nitride AlN coatings have been elaborated by laser induced plasma surface processing. The effect of excimer laser irradiation under nitrogen atmosphere allows, thanks to plasma formation on the Al surface, nitrogen diffusion and then AlN growth in the Al matrix. To understand mechanisms which govern this surface transformation, chemical and microstructural investigations have been correlated with processing conditions. Influence of significant parameters such as laser pulses number and laser spots overlapping mode from step by step to quasi continuous scan, have been studied by several analysis methods: Grazing Incidence X-ray Diffraction, Transmission and Scanning Electron Microscopy coupled with EDX analysis have emphasized in-depth and in-plane evolution of the main microstructural characteristics. Moreover low microstrains rate and residual stresses have been evidenced by X-Ray diffraction measurements (integral breadth and $\sin^2\psi$ methods) performed at LURE, the french synchrotron radiation facility. These results have been correlated with microhardness and wear resistance estimated by a pin-on-disc machine.

K-I.4 15:10-15:30 MICROSTRUCTURAL, MECHANICAL AND TRIBOLOGICAL PROPERTIES OF PA-CVD TiN COATINGS, K.S. Mogensen, J. Bottiger, Aarhus University, 8000 Aarhus C, Denmark; N.B. Thomsen, A. Horsewell, Riso National Laboratory, 4000 Roskilde, Denmark; S.S. Eskildsen, C.Mathiasen, Danish Technological Institute, 8000 Aarhus C, Denmark

Titanium nitride coatings (TiN) on tool steel were investigated. The coatings were made using pulsed-DC plasma-assisted chemical vapour deposition (PA-CVD). A parametric study of the deposition parameters was performed. The process pressure, bias voltage and partial gas flows were varied. Information on coating properties as a function of deposition parameters is essential to the design of a coating system which exhibits optimal wear performance. The coatings were characterized in terms of microstructure and mechanical and tribological properties using SEM, RBS, X-ray diffraction, nanoindentation as well as pin-on-disc. The performed variation of deposition parameters showed a significant effect on the residual stress levels and hardness of the coatings whereas the tribological properties displayed minor variations.

K-I.5 15:30-15:50 INFLUENCE OF LASER PRODUCED MICROSTRUCTURES ON THE TRIBOLOGICAL BEHAVIOUR OF CERAMICS, M. Geiger, S. Roth, W. Becker, Chair of Manufacturing Technology, University Erlangen-Nuremberg, Egerlandstrasse 11, 91058 Erlangen, Germany.

For less friction and wear in lubricated sliding applications a full lubricant film separation of the contact bodies is necessary. Microstructuring of the surface by laser radiation has a positiv influence on the tribological behaviour of bearing components.

Because of its beam properties excimer laser radiation is qualified for producing microstructures in many materials. Especially ceramics are very sensitive to thermal shock which is avoided by using excimer laser radiation. Therefore excellent treatment results (e.g. accuracy, reproducibility) are possible.

By using a mask projection technique lubricant pockets with almost any geometry and a structure size of a few micrometers can be produced. By a controlled motion between workpiece and laser defined depth profiles are also possible. The potential of excimer laser structuring of ceramic surfaces can be shown by some working examples.

The aim of the structuring is an improvement of the tribological properties of hydrodynamic respectively elastohydrodynamic sliding applications. The laser produced lubricant pockets generate local pressure increases and thus cause a higher lubricant film thickness and allow an optimal separation of the contact surfaces even at lower sliding velocities. Wear-intensive boundary lubrication at frequent starting and running-out procedures can be minimized.

First studies about the influence of different geometries of lubricant pockets on the film thickness were practiced on a block-on-ring-tribometer. The results for alumina and silicon carbide show that the structuring results in a significant improvement of the lubricant film thickness compared to untreated surfaces.

15:50-16:20 **BREAK**

Session II - Plasma Assisted Coatings
Chairperson: P.B. Barna, RITP, Budapest, Hungary

K-II.1 - invited - 16:20-16:50 FAR REMOTE NITROGEN PLASMAS FOR MATERIAL FONCTIONALIZATION AND THIN FILM ELABORATION, O. Dessaux and P. Goudmand, LPCEP/LEFEMO, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France.

Remote nitrogen plasma presents two distinct non equilibrium thermodynamic zones : the first, called FRNP, exempt from any electrons or ions; its main reactive species are nitrogen atoms $N(^4S)$, electronically and vibrationally excited N_2. The translation temperature of FRNP is about 300 K. The second is ionized by a thermal convective process in the FRNP its temperature is about 600 K. These plasmas are used in :

1 - Fonctionalization of polymers, and metallic materials for hardening or increasing of surface free energy and adhesion properties.

2 - Deposition of thin films such as :

* metal-metal or metal-insulating materials,

* polymer with many outstanding and attractive properties, low friction coefficient, good dielectric, or barrier effects,

* hard or superhard materials : (Si,N, O, H) complex with low Young modulus, CNx with carbon atoms in tetrahedral environment (β-C_3N_4).

K-II.2 16:50-17:10 SCRATCH RESISTANT TRANSPARENT BORON-NITRIDE FILMS, E.H.A. Dekempeneer, S. Kuypers, K. Vercammen, J. Meneve, J. Smeets, Vlaamse Instelling voor Technologisch Onderzoek, Boeretang 200, 2400 Mol, Belgium, and P.N. Gibson, W. Gissler, Institute for Advanced Materials, Joined Research Centre of the Commission of the European Communities, Ispra (Va), Italy.

Transparent BN coatings were deposited in a conventional capacitively coupled r.f. PACVD system starting from diborane (diluted in helium) and nitrogen. By varying the plasmaconditions (biasvoltage, ion current density), coatings were prepared with hardness values ranging from 2 to 12 GPa (measured with nano-indenter). Infrared absorption measurements indicate that the BN is of the hexagonal type. GAXRD measurements show that the material is nanocrystalline. Good agreement could be found between the measured diffraction spectra and simulated spectra assuming a disordered hexagonal type BN phase (turbostratic material). Some of these films were alo analysed with HRTEM. Preliminary results indicate that there is a correlation between hardness and the degree of disorder, the hardest films being obtained for maximum disorder in the c-direction. In addition to these structural investigations, the wear and friction behaviour of these films was tested using ball-on-disc tests using a range of different counterbody materials.

K-II.3 17:10-17:30 ETCHING OF BORON NITRIDE IN R.F. PLASMAS, C. Schaffnit, F. Rossi, European Commission, Joint Research Centre, Institute for Advanced Materials, TP 750, 21020 Ispra (VA), Italy, and L. Thomas, I.M.P. CNRS, Université de Perpignan, Av. de Villeneuve, 66025 Perpignan Cedex, France.

The attempts to deposit cubic boron nitride from Physical Vapour Deposition or Plasma Assisted Chemical Vapour Deposition have all demonstrated the role of ion bombardment on the formation of the cubic phase. However, the films obtained have high residual stresses which limit their applicability. In the present work, we have tried to evaluate the possibilities offered by competitive deposition/etching mechanisms. In order to study the occurrence of possible physical and chemical phenomena, post-treatments of boron nitride coatings have been performed using respectively pure argon, Ar/H_2 and Ar/Cl_2 plasma mixtures. The study reveals the effects of ion bombardment, H/H_2 atoms, and Cl/Cl_2 on h-BN content in the films. It has been found that, in addition to ion bombardment, hydrogen atoms and more efficiently Cl and/or Cl_2 can be considered as chemical etchant of sp^2 bonded boron nitride, therefore opening a new possible route for c-BN deposition of films with low residual stress.

K-II.4 17:30 -17:50

PLASMA-ASSISTED CHEMICAL VAPOUR DEPOSITION OF CUBIC BORON NITRIDE THIN FILMS, I. Konyashin, B. Inkson, J.Bill and F. Aldinger, Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium und Universität Stuttgart, Institut für Nichtmetallische Anorganische Materialen, Heisenbergstr.5, Stuttgart 70569, Germany.

This paper reviews recent work on plasma-assisted chemical vapour deposition (PACVD) of cubic boron nitride (c-BN) and presents some new experimental results on c-BN deposition. Deposition procedures precursors, deposition parameters, substrates and characterisation techniques employed in PACVD of c-BN are reviewed. Mechanisms of the formation of sp^3 hybridised boron nitride during PACVD by use of either high-energy nitrogen and argon ions or hydrogen plasmas are discussed. Etching rates of amorphous or cubic boron nitride in the hydrogen plasma are found to be noticeably different. Experimental evidence is obtained that BNH_X metastable species formed in the gas phase as a result of interaction between a BNH precursor and atomic or ionised hydrogen play an essential role in the c-BN synthesis. Thus, c-BN PACVD by using BNH-precursors added to the hydrogen plasma is thought to occur in much the same way as diamond deposition from the hydrocarbon-hydrogen gas mixture. Thin c-BN based films, that are free of any «non-cubic modifications» of boron nitride, are obtained for the first time in the present study by using PACVD.

K-II.5 17:50-18:10

NANOPOWDER OF SiN PRODUCED IN RADIO FREQUENCY MODULATED GLOW DISCHARGES FROM SiH_4 and NH_3, G. Viera, S.N. Sharma, J.L. Andujar and E. Bertran, LFCF, Departament de Fisica Aplicada i Electronica, Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain.

Square-wave modulated rf plasmas have been revealed as a suitable source of nanopowder, of high purity and controllable structure. Here, we report the production of SiN nanopowder, which could be a promising raw material for tribological applications, ductile ceramics, nanoscale filters, or for supporting catalytic surfaces. The powder was obtained at room temperature by glow discharge descomposition of SiH_4 and NH_3 at 40 Pa. The rf power was modulated at 200 mHz and the power absorbed in the discharge was 30W. Transmission electron microscopy showed that the particles are amorphous and had a size distribution between 20 and 100 nm. The chemical composition was analyzed by X-ray photoelectron spectroscopy and elemental analysis. In addition, Fourier transform infrared spectroscopy and Raman spectroscopy revealed the presence of SiN, NH and SiH bonds.

K-II.6 18:10-18:30

EFFECT OF DEPOSITION PARAMETERS ON THE PROPERTIES OF ION PLATED TiN FILMS, C. Sravani[1], K.R. Gunasekhar[1], T.V. Balasubramanyam[2], K.N. Krishna[1] and S. Mohan[1], [1]Department of Instrumentation, Indian Institute of Science, 560012 Bangalore, India, [2]DMRL, Hyderabad-58, India.

Titanium Nitride films are being widely used in decorative and functional applications. It is also being used as diffusion barriers in electronic applications. These coatings are synthesised by both CVD as well as PAPVD techniques. In PAPVD it is possible to deposit coatings at temperatures much lower than that of CVD. Low temperature synthesis retains the mechanical and metallurgical properties of the work piece.

In the present work TiN coatings have been deposited by triode ion plating using electron beam evaporation. These coatings have been chacterised for their composition, structure, electrical and mechanical properties. The properties of these coatings have been found to be strongly dependent on the deposition parameters such as substrate bias voltage, nitrogen content etc. The effect of these parameters on the properties of the coatings are discussed.

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session III - Structure and Properties Relationship
Chairperson: F. Rossi, JCR, Petten, The Netherlands

K-III.1 - invited - 8:30-9:00

SYNTHESIS OF AMORPHOUS AND NANOCRYSTALLINE METALLIC ALLOY THIN FILMS, **J. Dudonis**, Kaunas University of Technology, 3000 Kaunas, Lithuania, and L. Pranevicius, Vytautas Magnus University, 3000 Kaunas, Lithuania.

Over the past decade significant progress has been achieved in the understanding of the amorphous thin film formation processes by physical vapour deposition methods such as codeposition from the multicomponent targets or sequential deposition from separate targets employing thermal evaporation, ion and magnetron sputtering and arc deposition techniques. This paper describes the dependence of the growing film structure on the process parameters, substrate temperature and film composition with respect to the different above mentioned deposition modes. Emphasis is made on the analysis of the role of the mean energy of arriving atoms and the influence of the ion irradiation effects on the microstructure of thin film.

In this paper it is focused on the deposition of two-component materials with negativ (Zr-Cu, Ti-Cu) and positive (Mo-Cu) heat of mixing. The glass forming ranges are presented and complementary the electrical and optical properties are studied. High resolution TEM, SEM and AFM techniques are used to support theoretical concepts explaining the behavior of the metallic two-component system with respect to the phase and roughness evolution. The emphasis on the kinetics of surface diffusion in the resulting phase distribution is made. A thermodynamic model based on the minimization of the surface free energy of the actual uppermost island-forming layer is considered. The phase distribution and micostructure in the resulting films is highly sensitive to the diffusion and attachment behavior of components in the growth zone and can be influenced independence of the mean energy of arriving atoms. The phase distribution can be described by a dynamic model of structural evolution based on the far from equilibrium process of diffusion limited aggregation.

K-III.2 9:00-9:20

STRUCTURE RELATED OPTICAL AND MECHANICAL PROPERTIES OF OXYGEN DOPED Al FILMS, P.B. Barna, M. Adamik, Research Institute for Technical Physics, P.O. Box 76, 1325 Budapest, Hungary, U. Kaiser, Friedrich-Schiller Universität Jena, Institute für Festkörperphysik, Max-Wien-Platz 1, 07743 Jena, Germany, S. Laux, Fraunhofer Institut Angewandte Optik und Feinmechanik, Schillerstrasse 1, 7745 Jena, Germany, and K.A. Pischow, Surfcoat Oy, Insinöörinkatu 8, 50100 Mikkeli, Finland, M. Pulliainen, Savcor-Consulting Oy, Insinöörinkatu 8, 50100 Mikkeli, Finland.

Recent investigations of nanocrystalline structures have revealed that these materials can be produced by the application of additives to the matrix material of the film. By the introduction of oxygen into the deposition chamber during the deposition of Al film the structure of the film can be varied from large crystalline columnar to nanocrystalline and eventually to amorphous Al_2O_3 structure. Through the whole scale of oxygen content related to these structures, the structural changes are accompanied by remarkable changes of optical and mechanical properties. The aim of the present work was to investigate in details of the effect of oxygen on the structure evolution of Al films in the whole scale of oxygen contamination levels and relate the structural changes with the optical and mechanical properties. The investigations were carried out by transmission electron microscopy, optical spectroscopy in the visible range, and nanoindentation measurements. The optical properties vary from pure metallic to pure dielectric behaviour.

K-III.3 9:20-9:40

SURFACE AND INTERFACE MORPHOLOGY OF THIN OXIDE FILMS INVESTIGATED BY X-RAY REFLECTIVITY AND ATOMIC FORCE MICROSCOPY, M. Alvisi and L. Vasanelli, INFM c/o Dip. Scienza dei Materiali, Universita' di Lecce, 73100 Lecce, Italy, and L. Tapfer, Centro Nazionale Ricerca e Sviluppo Materiali (PA.S.T.I.S.-C.N.R.S.M.), 72100 Brindisi, Italy.

High performance laser optic devices can be realized by thin films made of HfO_2/SiO_2 or ZrO_2/SiO_2 multilayers. The mechanical stability (adhesion) as well as the device performance is strongly influenced by the structural properties, in particular the surface and interface morphology of the films. In this work, we investigate in detail the air/film and film substrate interface morphology of single HfO_2 and ZrO_2 and SiO_2 films by means of x-ray reflectivity and atomic force microscopy measurements. The thin films were deposited on silicon substrates by dual ion beam sputtering technique. The experimental x-ray reflectivity and x-ray diffuse scattering measurements as well as reciprocal space maps close to the (000) relp were analyzed and simulated by using kinematical x-ray scattering models. The structural parameters (roughness) obtained from the x-ray scattering experiments were compared with the atomic force microscopy data. The combination of both techniques yield accurate information on the interface and surface roughness and in particular, a better understanding of the correlation between the interface and surface roughness can be obtained. We also show, that the x-ray reflectivity and AFM measurements may provide a deeper insight in the deposition process of thin oxide films.

K-III.4 9:40-10:00 FORMATION OF PORE-FREE NITRIDE LAYERS IN IRON AT T ≤ 300°C, D.K. Inia, W.M. Arnoldbik, A.M. Vredenberg, and D.O. Boerma, Department of Atomic and Interface Physics, Debye Institute, Utrecht University, P.O.Box 80.000, 3508 TA Utrecht, The Netherlands.

A new method for gaseous nitriding of iron at temperatures below 300°C in NH_3/H_2 mixtures has been developed. In this method, the iron layer is coated with a thin nickel layer, which protects the iron from oxidation and serves as a catalytic surface for the decomposition of NH_3. After decomposition, the atomic N diffuses through the Ni layer into the underlying Fe, where a γ'-Fe_4N or ε-$Fe_{3-x}N$ layer is formed. Due to the low process temperature the nitride layer is pore-free, in contrast with nitride layers formed at normal process temperatures (500 - 600°C). Micrometer thick layers are obtained. Moreover, this low temperature gaseous nitriding method can serve as an alternative for plasma nitriding, deposition or Ion implantation techniques.

The relevant steps leading to the formation of the layer (NH_3 decomposition, N transport, nucleation and growth of a nitride phase) were studied. By using this new method it was for the first time possible to directly measure the Fe-N phase diagram and to study the stability of iron nitrides at temperatures below 300°C.

10:00-10:30 **BREAK**

Session IV - Mechanical Characterization
Chairperson: L. Pranevicius, Vytautas Magnus University, Lithuania

K-IV.1 - invited - 10:30-11:00 A NEW TECHNOLOGY FOR NANOHARDNESS MEASUREMENTS : PRINCIPLE AND APPLICATIONS, J.C. Dargenton and **J. Woirgard**, Laboratoire de Métallurgie Physique, Université de Poitiers, UMR CNRS 6630, SP2MI.Bd 3, Téléport 2, BP 179, 86960 Futuroscope Cedex, France.

Nanoindentations tests are widely used for the mechanical characterization of very small volumes of materials. The method being of special interest for thin coatings or fine grained materials. Existing apparatus are presented, including a novel one allowing very low depth indents. The advantages and drawbacks of the different techniques are pointed out. The main methods proposed for the quantitative exploitation of the results are then detailed. It is shown that most methods are essentially empirical since a satisfactory modelization of the whole indentation process is not yet available, despite the intensive work devoted to the subject. It is however shown that sound values of the hardness and the elastic modulus can be derived from a close examination of the unloading portion of the indentation curves. Results obtained in various materials are then presented to point out the possibilities and limitations of the technique.

K-IV.2 11:00-11:20 PHYSICAL AND MECHANICAL PROPERTIES OF $Ti_{1-x}Si_xN$ FILMS, F. Vaz(1), L. Rebouta(1), S. Ramos(2), M.F. da Silva(3) and J.C. Soares(3), (1)Dept. Fisica, Universidade do Minho, Azurém, 4800 Guimaraes, Portugal, (2)Dept. Eng. Mecânica, Universidade de Coimbra, 2030 Coimbra, Portugal, (3)ITN, Dept. Fisica, EN 10, 2685 Sacavém, Portugal.

For several applications of a film, its hardness and adhesion are of primary importance. To improve its performance, adjustments in the microstructure, developing nanocrystalline materials, are known to be a promising field of investigation in hard systems. The scratch and the ultramicrohardness tests have been used as two of the most generally accepted methods of assessing adhesion and hardness. The present study can be considered as a contribute for the adhesion failure mechanisms as well as for the hardness of hard TiN based coatings, based on a comprehensive compilation of results obtained for $Ti_{1-x}Si_xN$ samples. $Ti_{1-x}Si_xN$ coatings with $0 \leq x \leq 0.3$ and thicknesses ranging from 1.4 to 1.8 µm, were deposited on polished high-speed steel substrates by DC and RF reactive magnetron sputtering. The atomic composition of the samples were measured by RBS. The structure and grain size were determined by XRD. Maximum hardness and higher critical loads were obtained for $x = 0.15$. The discussion of hardness and failure mechanisms as a function of the x value, will be shown and discussed in some detail. An attempt to establish relations between hardness and Adhesion results will also be made.

K-IV.3 11:20-11:40 INFLUENCE OF DEPOSITION RATE AND Al CONCENTRATION ON THE STRUCTURES AND MECHANICAL PROPERTIES OF $(Ti_{1-x}Al_x)N$ FILMS PREPARED BY ION PLATING METHOD, Jung-Joong Lee, In-Haeng Lee, Department of Material Science and Engineering, Seoul National University, San56-1, Kwanak-Ku, Shinrim-Dong, 151-742 Seoul, Korea.

$(Ti_{1-x}Al_x)N$ films ($0<X_{Al}<0.9$) could be formed on high speed steel by ion plating method in which Ti and Al were evaporated independently by different energy source, and the structures and mechanical properties of films were investigated. Ti was evaporated by electron beam while resistance heating was needed for Al evaporation and NH_3 was used as reactive gas. The Al concentration of the film, X_{Al}, could be controlled by changing Al resistance heating current at constant Ti evaporation rate. From structural investigation, it has been found out that when Ti evaporation rate was high, the $(Ti_{1-x}Al_x)N$ films showed (111) preferred orientation and had a columnar structure at low X_{Al}, which changed to a dense one at higher X_{Al}. When the evaporation rate of Ti was low, however, a strong (200) preferred orientation was built up and dense films could be formed regardless of X_{Al} The knoop hardness of the deposited $(Ti_{1-x}Al_x)N$ films exhibited the hardness values between 2000kg/mm^2 and 4000kg/mm^2 according to film structures. The adhesion strength of deposited film was good at low X_{Al} but decreased at high X_{Al}. The adhesion strength which was low could be improved by introducing thin Ti layer between the film and the substrate.

K-IV.4 11:40-12:00 MECHANICAL AND STRUCTURAL PROPERTIES OF Ni-C FILMS OBTAINED BY R. F. SPUTTERING, N. Laidani(1), L. Calliari(1), and E. Galvanetto(2), (1)Centro Materiali e Biofisica Medica (I.T.C.), Via Sommarive, 38050 Povo (Trento), Italy, (2)Dipartimento di Meccanica e Tecnologia Industriali, Universita di Firenze, via Santa Marta 3, Firenze, Italy.

Metal containing carbon films represent a promising class of materials as they exhibit good wear properties and a good friction behaviour against metals. This work reports on the structural and mechanical properties of nickel-carbon films. These materials consisted of a mixture of about 50 at.% Ni in carbon, deposited on silicon substrates by r. f. plwanar magnetron sputtering of a Ni-C alloy target. The latter was prepared by plasma-spray of nickel and graphite powders. The morfology andw stwructure ofw the sputtered films were studied as a function of the power density to the cathode, at a constant sputtering gas pressure. The Knoop hardness has been determined and the scratch resistance has been investigated for the various power densities and compared to those of sputtered amorphous carbon films.

K-IV.5 12:00-12:20 THE MICROHARDNESS ANALYSIS OF THE Ti(OCN) SURFACE LAYERS, K. Rozniatowski, K.J. Kurzydlowski, Department of Materials Science and Engineering, Warsaw University of Technology, Narbutta 85, 02-524 Warsaw, Poland.

The work concerns the microstructure and properties of the Ti(OCN) films produced by a PACVD method. The paper provides basic definitions and procedures which can be used to quantitatively characterize microgeometrical features of surface layers.

The size of near spherical grains characteristic for PACVD structure have been studied for a series of specimens of Ti(OCN) obtained by a PACVD process on the different base materials: pure iron, pure iron prenitrided by a plasma nitriding method at 520°C and nickel. The Ti(OCN) layers were produced at 550°C employing two deposition times: 0.5 and 2h in thetraisopropoksytitanium atmosphere.

The microstructure of the surface layers influence their properties. This effect of the microstructure have been illustrated by the results of microhardness tests performed on Ti(OCN) layers produced on a various materials with different time of the deposition process.

Additionally, the surface friction effect has been studied using the different environment of the microhardness measurements. The result of the measurements have been discussed in terms of the relationship between the thickness and grain size of thin Ti (OCN) films and their properties. The «surface effect» of microhardness is also discussed.

12:20-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-Midi

Session V - CVD Coatings
Chairperson: A. Figueras, CSIC, UAB, Barcelona, Spain

K-V.1 - invited - 14:00-14:30

CVD PROCESSES FOR COATINGS AND SURFACE MODIFICATIONS, **G. Wahl**, M. Pulver, Institut für Oberflächentechnik und Plasmatechnische Werkstoffentwicklung, TU Braunschweig, Bienroder Weg 53, 38108 Braunschweig, Germany.

Chemical Vapor Deposition (CVD) has a number of important properties which are described in detail by examples:
I) Similar layer structures can be realized in CVD and vacuum processes as is demonstrated in the case of Y stabilized ZrO2 coatings.
2) Internal surfaces can be deposited. This is demonstrated for the aluminizing of tubes.
3) Continuous deposition processes are possible. This is demonstrated for the deposition of high temperature superconductors on tapes.
4) Functional gradient materials and composite materials can be deposited. The different mechanisms to produce such coatings are discussed. As an example the composite TiN -MoS2 is described.
5) CVD processes can be carried out at low temperatures. First results of the deposition of SiO2 layers on polymers are described.

K-V.2 14:30-14:50

PREPARATION AND CHARACTERIZATION OF LAYERS OF Al-Ti MIXED OXIDES, A. Stabel, A. Caballero, J.P. Espinos, F. Yubero, A.R. Gonzalez-Elipe, Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Avda. Américo Vespucio s/n, 41092 Sevilla, Spain.

Layers of $Al_xTi_yO_z$ mixed oxides of variable composition have been prepared by Ion Beam Induced Chemical Vapor Deposition (IBICVD). By this method, two flows of volatile precursors of titanium ($TiCl_4$) and aluminum ($Al(CH_3)_3$) are directed onto the surface of a suitable substrate while it is bombarded with accelerated O_2^+ ions (400 eV). This leads to the formation of very compact layers where the composition (i.e. Al/Ti ratio) can be controlled by changing the partial pressure of the precursors. This procedure permits an intimate mixture of the cation components and leads to a homogeneous composition through the layer thickness. TiO_2-Al_2O_3 bilayers or layers of variable composition can also be prepared by this method. The obtained films have been characterized by SEM/EDAX, XPS, XAS and UV-vis spectroscopy. A correlation is found between the refraction index of the layers and its composition in terms of the Al/Ti ratio.

K-V.3 14:50-15:10

COMPOSITION AND TRIBOLOGICAL CHARACTERISATION OF CHEMICAL VAPOUR DEPOSITED TiN LAYER, L. Fouilland, L. Imhoff, A. Bouteville and J.C. Remy, Laboratoire de Physico-Chimie des Surfaces-E.N.S.A.M.-C.E.R d'Angers-2 Bd du Ronceray 49035 Angers, France and J. Perrière and M. Morcrette, Groupe de Physique du Solide-Tour 23, 2 Place Jussieu, 75251 Paris, France.

Titanium nitride is a well known material for various applications such as mechanic, microelectronic or jewelry. Physical vapour deposited TiN films are widely studied but very little data is available about Chemical Vapour Deposited thin films.

In the present paper, TiN films of less than one micron thick are deposited by Low Pressure C.V.D. from the $TiCl_4$-NH_3-H_2 gaseous phase on silicon substrate. R.B.S. analyses show that TiN films are always close to the stoechiometry. The contamination levels are very low: less than 3,5% for oxygen and less than 0,1 % for chlorine. In conjunction with thickness measurements through a stylus profilometer, the density is determined. Its value lies in the range 3,5-4 g/cm3. Deposited films are very adherent to the substrate as confirmed by microscratch tests. Friction and wear are studied through a pin-on-disk tribometer in air and at room temperature. The common value of 0,2 for friction coefficient is obtained even for films as thin as 150 nm.

K-V.4 15:10-15:30

YSZ PROTECTIVE COATINGS ELABORATED BY MOCVD ON METALLIC SUBSTRATES, J. Esteve and E. Martinez, Departament de Fisica Aplicada y Electronica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, G. Garcia and A. Figueras, ICMAB/CSIC, Campus U.A.B., 08193 Bellaterra, Spain.

The aim of this work is to study both the mechanical and the protective properties of Yttria Stabilized Zirconia (YSZ) coatings prepared on metallic substrates. YSZ films were obtained in a hot wall MOCVD reactor using $Zr(thd)_4$ and $Y(thd)_3$ as organometallic precursors. The evaporation and the deposition temperatures were chose in order to stabilize the cubic phase of the zirconia. The coatings were obtained on different substrates such as 304 and 309 stainless steel and on nickel alloys.

X-ray diffraction, SEM and SIMS techniques were used to characterize the influence of different experimental parameters, such as substrate nature, deposition temperature and thermal treatment, on the structure and composition of the YSZ film and the interface film/substrate.

Mechanical properties of the coatings were also determined, before and after heat treatment, by the methods of nanoindentation and microscratch tests.

K-V.5 15:30-15:50 CHEMICALLY VAPOR DEPOSITED SILICON CARBIDE FILMS FOR SURFACE PROTECTION, A. Hoerner, J. Vierhaus and E.P. Burte, Fraunhofer IIS-B, Schottkystrasse 10, 91058 Erlangen, Germany.

Silicon carbide (SiC) films offer excellent chemical and mechanical properties and are, therefore, well suited for protection against corrosion and abrasion. SiC films in the thickness range from 100 nm to 300 nm were chemically vapor deposited in a hot wall, low pressure reactor at temperatures between 800°C and 900°C. As precursor material hexamethylendisilacan (HMDS) was used. The substrates used for the deposition were single crystalline silicon and quartz glass wafers with a diameter of 100 mm. In order to influence the mechanical stress, different intermediate layers were used.

Intrinsic and extrinsic mechanical stress of the films was determined in dependence on measuring temperature with and without intermediate layers between the substrate and the SiC film grown at various temperatures. Surface investigations were performed by means of atomic force microscopy and by tribological abrasion experiments. The tightness against corrosive liquids and the homogeneous coverage of the surface was proved by exposing the films to hydrofluoric acid and a mixture of nitric and hydrofluoric acid.

15:50-16:20 **BREAK**

Poster Session I

16:20-18:30 See programme of this poster session p. K-23 to K-29.

Wednesday June 18, 1997
Mercredi 18 juin 1997

Morning
Matin

Session VI - Carbon Based Coatings
Chairperson: A.R. Gonzales-Elipe, CSIC-Univ. Sevilla, Spain

K-VI.1 - invited - 8:30-9:00

RECENT PROGRESS ON THE TRIBOLOGY OF DOPED DIAMOND-LIKE AND CARBON ALLOY COATINGS, **C. Donnet**, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes UMR 5513, B.P. 163, 69131 Ecully Cedex, France.

Diamond-like carbon (DLC) coatings have been widely recognized as being a wear resistant solid lubricant with low friction coefficient. Its tribological behavior strongly depends both on the tribotesting conditions and the nature of the coating, which in turn depends on the technique used for film deposition. Recently there have been attempts to improve the tribological behavior of DLC coatings by the addition of elements, such as silicon, nitrogen, fluorine and various metals. The paper will present an updated review of the tribological properties of doped DLC, in comparison with the conventional hydrogenated and non hydrogenated carbonaceous films.

K-VI.2 9:00-9:20

ENGINEERED INTERFACES FOR ADHERENT DIAMOND COATINGS ON THERMAL EXPANSION COEFFICIENT MISMATCHED SUBSTRATES, R.K. Singh, University of Florida, Department of Materials Science and Engineering, Gainesville FL 32611-2066, USA.

Adhesion of thin of thick films on substrates is a critical issue in systems where the linear thermal expansion coefficients of the coating and bulk material significatly different from each other. The large thermal expansion coefficient mimatch results in generation of very high stresses in coating which may lead to delamination, cracking or other deleterious effects. The high compressive stresses in the diamond film coupled with the large diffusion coefficient of carbon in iron and the catalytic graphitization of carbon by iron and/or cobalt prevents formation of adherent diamond coating on these substrates. In this talk we report a nobel method to increase the adherence of coatings on high thermal expansion mismatched substrates. This method is based on morphological surface modification of the substrate, which results in the creation of a three-dimensional thermal and composition graded interface. The increase in interfacial area, and the modification of interfacial stress significantly improves the intrefacial adherence of the film. Results of diamond films grown on 418 steel and tungsten carbide (with 10% Co) substrates have been presented. Scratch and indentation tests on diamond coated samles on steel and tungsten carbide donot exhibit film fracture at the interface and concomitant catastrophic propagation of the interfacial crack.

K-VI.3 9:20-9:40

WEAR RESISTANT FLUORINATED DIAMONDLIKE CARBON FILMS, A. Grill, V. Patel, and C. Jahnes, IBM Research Division, T.J. Watson Research Center, P.O.Box 218, Yorktown Heights, NY10598, USA., J. Fontaine, C. Donnet, and M. Belin, Ecole Centrale de Lyon, Laboratoire de Tribologie et Dynamique des Systèmes, UMR 5513, B.P. 163, 69131 Ecully Cedex, France.

Fluorinated diamondlike carbon (FDLC) films have been prepared by RF plasma assisted chemical vapor deposition from mixtures of fluorocarbon vapors and hydrogen. The films have been deposited on Si wafers using a variety of deposition conditions. The films have been characterized using FTIR, index of refraction measurements, and RBS combined with FRES for determination of film composition. The stresses in the films were determined by measurement of wafer bowing caused by the deposited films. Tribological characterization was performed in a pin-on-disk apparatus for wear measurements and a reciprocating pin-on-flat arrangement for determination of friction coefficient. It was found that, by adjusting the deposition parameters, the properties of the FDLC films could be changed from soft films, with no significant wear resistance, to films having wear resistance comparable to unfluorinated DLC while still containing more then 20 % fluorine and less then 10% hydrogen. The tribological properties of the FDLC films will be discussed in relation to their physical properties, as influenced by the deposition conditions. Possible mechanisms explaining the tribological behavior of the films will be presented.

K-VI.4 9:40-10:00

TRIBOLOGICAL PROPERTIES OF LOW FRICTION CARBON COATINGS PRODUCED BY LOW TEMPERATURE PVD METHODS, W. Precht, M. Pancielejko, W. Walkowiak, Technical University of Koszalin, Institute of Materials Science and Technology, P. Myslinski, A. Czazniewski, Technology Transfer Centre, Raclawicka 15-17, 75-620 Koszalin, Poland.

Using unbalanced magnetron sputtering and cathodic arc plasma deposition, DLC, CN_x and Me-C:H thin films on bearing steel substrates are produced by varying bias voltage vand gas mixture composition at temp. below 200° C. The micro-hardness, adhesion, friction coefficient, wear rate, film composition and structure of the coatings were investigated. The CN_X, DLC and W-C:H films having the best tribological properties were used for ball bearings coatings, which are friction and fatigue strength tested under hard exploitation conditions without lubrication. The highest abrasive wear resistance were revealed by the bearings coated with W-C:H films (ca 300x more as uncoated), resulting in the lowest friction coefficient f=0,06 (in air). The influence of film structure and composition (mainly hydrogen) on the tribo-properties of coatings were discussed. Also the possibility of introducing developed technologies to the bearings Industry for application of coated bearings for space and UHV attachments were considered.

10:00-10:30 **BREAK**

Session VII-Surface Protection Coatings
Chairperson: W. Ensinger, Universität Augsburg, Germany

K-VII.1 - invited - 10:30-11:00

ION IMPLANTATION FOR HIGH TEMPERATURE CORROSION PROTECTION, **M.F. Stroosnijder**, Institute for Advanced Materials of the Joint Research Centre-European Commission, 21020 Ispra (VA), Italy

A great deal of research work is undertaken to improve the high temperature corrosion behaviour of materials by alloying additions. These published corrosion data show a large scatter and even lead to contradicting conclusions. This is possibly partially caused by differences in alloy purity, because several elements have been demonstrated to possess a significant effect on the corrosion properties even if they are present in small quantities. Ion implantation offers the advantage of adding an element to the alloy in a surface layer in a well controlled and reproducible manner. Ion implantation has been used successfully for studying the mechanisms underlying the crucial and dominating role of specific elements upon the corrosion behaviour of metals and alloys.

The presentation will show the use of ion implantation for screening purposes to develop more corrosion resistant materials and as a research tool to obtain a better understanding of underlying corrosion mechanisms.

K-VII.2 11:00-11:20

CORROSION RESISTANCE OF (TiAl)N AND CrN HARD COATINGS AT ELEVATED TEMPERATURES IN Cl CONTAINING ATMOSPHERES, L. Cunha and M. Andritschky, Departamento de Fisica, Universidade do Minho, Largo do Paço, 4719 Braga Codex, Portugal.

TiAl-nitride and Cr-nitride hard coatings were deposited on stainless steel substrates by Reactive Magnetron Sputtering technique. The corrosion behaviour, at room temperature, was studied by electrochemical measurements (Open Circuit Potential and Potentiodynamic measurements) in aqueous solution containing chloride ions (HCl 3.3% and NaCl 9%). The same samples were then tested at elevated temperatures (300°C < T < 400°C) atmospheres containing gaseous HCl.

The corrosion mechanism of the coating during these aggressive tests was by X-Ray Photoelectron spectroscopy (XPS). Best results were obtained for samples with metallic interlayers between substrate and the nitride hard coating. Denser structures also increase the performance of these coatings in aggressive environments.

K-VII.3 11:20-11:40

ANTI OXIDATION PROTECTION OF STAINLESS STEEL BY LANTHANUM DEPOSITION : ADVANTAGES OF THE SYNCHROTRON X-RAYS DIFFRACTION FOR STRUCTURAL STUDIES, J.M. Capitan, ESRF, BP 220, 38042 Grenoble Cedex, France, J.P. Dallas, CECM, 15 rue G. Urbain, 94400 Vitry/Seine, France, M. Paul, Departement de Quimica Inorganica Universidad de Seville-CSIC, Apdo 874, 41071 Sevilla, Spain, S. Lefebvre, LURE, Université Paris Sud, 91405 Orsay, France

The beneficial effect of active element additions (as for example rare earth) on the oxidation resistance of many heat resistant alloys is still difficult to explain. We present a comparative structural study of the oxide layers formed during the oxidation process of a conventional stainless steel (AISI 304) protected by a lanthane deposition obtained by a pyrosol process

The components of the oxide layer belong to three structural families. For each one, several compounds with different Fe/Cr composition ratio are known:
- Family of rhombohedral structure: Fe_2O_3, $Cr_{1.3}Fe_{0.7}O_3$, Cr_2O_3. O
- Family of Cubic manganese rich compounds with spinel structure: $Mn_{1.5}Cr_{1.5}O_4$, Mn_2CrO_4, $MnFe_20_4$.
- Perowskite family of Lanthanum oxides: $FeLaO_3$ and $CrLaO_3$.

Owing to the similarity of the lattice parameters of the compounds belonging to the same family and the atomic diffusion factors of the three elements Cr, Fe and Mn, the structural analysis is difficult and has been resolved by high resolution powder diffraction and anomalous diffraction using synchrotron beam line.

K-VII.4 11:40-12:00

THE REE : A WAY TO IMPROVE THE HIGH TEMPERATURE BEHAVIOUR OF STAINLESS STEELS? S. Chevalier, G. Bonnet, and J.C. Colson, LRRS, UMR 5613 CNRS, BP 400, 21011 Dijon Cedex, France

The effects of small quantities of so called «reactive elements» on the high temperature oxidation behaviour of stainless steels have been claimed in many studies : they generally decrease the oxidation rate and prevent the spallation phenomena occuring under thermal shocks.

The aim of this work was to deposit a rare-earth element oxide (Nd_2O_3) mixed or not with chromia and to study the influence of such coatings on the high temperature oxidation of a chromia-former alloy (F17Ti).The MOCVD process appeared to be a convenient way to produce this kind of coatings, which permitted to drastically improve the F17Ti isothermal oxidation behaviour and to inhibit the decohesion of the scale under cooling. Long oxidation tests (336 h) are in agreement with these results.

The usual analysis techniques, SEM, EDAX, X-Ray diffraction, TEM, yielded informations about the spectacular influence of surface-applied RE.

K-VII.5 12:00-12:20

THE INFLUENCE OF Nb ION IMPLANTATION UPON HARDNESS AND OXIDATION BEHAVIOUR OF A Ti-48at.%Al ALLOY, Y.G. Zhang, X.Y. Li, W. Wang and C.Q. Chen, Department of Material Science and Engineering, Beijing, University of Aeronautics and Astronautics, Beijing 100083, P.R. China and V. Ji, LM3, EMSAM, 75013 Paris, France

A Ti-48at.%Al alloy was implanted with Nb ion with a dose of $3\mathrm{x}10^{17}$ions/cm^2. The implanted layer has been examined by AES, XPS and TEM. It was found that the distribution of Nb in the layer followed near gaussion curve and the valence state of Nb atoms changed from the outer surface to the internal region. Both hardness and isothermal oxidation resistance in an atmospheric environment were tested in comparison with the alloy without the ion implantation. It was found that the implantation remarkably increased the surface hardness and improved the isothermal oxidation resistance of the alloy at 900°C. It is also found that post-implantation annealing at a proper temperature in vacuum could further improve the oxidation resistance, but decrease the hardness a little, and the annealing temperature is a key parameter in such a treatment. The effect is suggested to be due both to the redistribution of the implanted Nb and to annihilation of the defects induced by the implantation in the implantation affected zone, which has been confirmed by AES and TEM examination.

12:20-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-Midi

Session VIII - Industrial Applications of Coatings
Chairperson: J.C. Rostaing, Air Liquide, France

K-VIII.1 - invited - 14:00-14:30

PLASMA TREATMENT OF COLD ROLLED STEEL : ACTUAL STATE, PROBLEMS TO OVERCOME AND FUTURE, **S. Lucas**, P. Vanden Brande, A. Weymeersch, Research Center of Cockerill Sambre, P 57, Bld de Colonster, 4000 Liège, Belgique.

The corrosion protection of steel substrates is an important industrial process for many industries like automotive industry, packaging industry etc... The most common methods of corrosion protection of steel surfaces are actually hot-dipping and electrogalvanizing. However, these methods suffer from several drawbacks: weak variety of coatings, multilayer deposition difficult to produce, important disposal costs, health and safety risks. It is known that plasma deposition of thin films (including sputtering) can give very dense structure with uniform deposition, a low amount of pin holes and adequate long term corrosion performances. Unfortunately, most of the work has been restricted to small objects except for plastic and glass substrates. Plasma processing of large metallic substrates has been rarely reported. In this paper, we will try to remedy that by presenting some of the literature and personal work related to surface cleaning and corrosion prevention of steel sheets, but also related to interface engineering for the improvement of paint adhesion. Surface cleaning and nature of coatings will be discussed bearing in mind the industrial application and market requirements. In addition some technological aspects of a continuous invacuum coating line will also be addressed. Finally, a few guidelines will be drawn for the implementation of vacuum technology in steel industry.

K-VIII.2 14:30-14:50

IMPROVEMENT OF TRIBOLOGICAL PROPERTIES OF HUREAULITE COATING ON STEEL BY ANNEALING, Ph. Hivart, B. Hauw, and J.P. Bricout, LAMIH, Groupe de Recherche en Génie Mécanique, B.P. 311, 59304 Valenciennes Cedex, France.

Hureaulite $(Mn,Fe)_5H_2(P0_4)_2$, $4H_2O$ is a manganese phosphate often used as an anti-friction coating on steel parts in relative motion. The authors have studied the tribological behaviour of hureaulite coating first modified by annealing.

After phosphatation (treatment by dipping), the part is dried then heated during 15 min at constant temperature. Once cooled, it is oiled as usual. Using a friction test allowing the determination of the resistance to seizure and of the duration of the hydrodynamic lubrication step, it is shown that the modifications of the coating (dehydration, appearance of new phases and new compounds) lead to the improvement of the friction properties particularly of the resistance to seizure which value is multiplied by 5 to 10 according to the heating temperature.

The micrographies show that the modifications generate cracks through the crystals; these cracks are perpendicular to the surface and do not lead to scaling phenomenon. They act like lubricant traps and so delay the seizure.

Annealing temperatures from 100 to 700 °C and treatment time from 1 to 100 min for chosen temperatures are studied. The possibility of reducing temperature while reasonably increasing time is shown so the heat treatment does not affect the steel substrate and could be industrialised.

K-VIII.3 14:50-15:10

TRACTION CONTROL OF FRICTION SLIDER PAIR UNDER A BOUNDARY LUBRICATION CONDITION, K. Tanahashi, Yamato Laboratory, IBM Japan, Ltd., 1623-14, Shimotsuruma, Yamato-shi, Kanagawa-ken 242, Japan, T. Yamamoto, Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology, 24-16, Naka-cho 2-chome Koganei, Tokyo 184, Japan.

We conducted a research on the traction control technology for rotating axis-sliding supporting bearing system where torque stability maintains for a long life time under atmospheric and boundary lubrication conditions. Its technology will be applied to hinges of the mobile PC since the hinges may improve torque functional specifications.

The hinges' mechanism is of a mechanical friction type. It has double friction plates on the shaft axis. The hinges have tribologically conflicting problems in friction and lubrication technology for realization of a sufficient torque stability until PC life end. This study is a new trial in tribology not only to reduce friction, but also to control traction itself.

We will present a paper to define the hinges' characteristics and to optimize the design based on a tribological point of view.

K-VIII.4 15:10-15:30

NITROGEN CONTRIBUTION TO TRIBOLOGICAL BEHAVIOUR IMPROVEMENT OF TITANIUM ALLOYS, Y. Corre, NITRUVID, 42490 Fraisses, France.

Titanium and titanium alloys are being used more and more frequently as materials in mechanical applications. A low density and very interesting mechanical properties put these materials as a first choice in many fields (aeronautics, automobile precision mechanics, biomedical, etc...) Nevertheless, their poor tribological qualities often negate them as a friction surface.

Modifying their surface properties is thus a real concern. The introduction of nitrogen on the surface improves significantly the tribological behaviour of these materials.

Nitrogen ion implantation is a technique largely used in titanium alloy surface treatment. Industrial applications of this process are numerous (biomedical, aeronautics, ...) but the limitations of this technique (essentially treatment depth) prevent its use in certain case. The increase in treatment temperature can overcome these limitations. Thus, the analysis of the properties obtained after treatment at various temperatures (20°C to 1000°C) enables us to find the best compromise between metallurgic, geometrical properties (surface condition, deformation) and friction properties. This compromise enables us to solve a majority of tribological problems of titanium alloys.

K-VIII.5 15:30-15:50 CRACKING BEHAVIOUR AND RESIDUAL STRESSES OF CARBON-COATING ON SiC-FIBRE IN Ti/SiC MMCs, Qi Fang(1), P. Sidky(1), M.G. Hocking(1) and Jun-Ying Zhang(2), (1)Department of Materials, Imperial College, London SW7 2BP, U.K., (2)Department of Electronics & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K.

Continuously reinforced SiC /Ti -MMCs are potential materials for use in aerospace industry and other high-technology fields due to their low density, high performance and high specific strength at room and elevated temperatures. However, the full potential of Ti-based / SiC composites has not been fully realised to date, primarily owing to problem of thermal expansion mismatch between Ti and SiC fibres. To solve this problem and to improve the thermomechanical properties of the interface between the matrix and fibres, a carbon-coating (5-10μm) was usually deposited on the SiC-fibres. The main purpose of the present work was to study the cracking behaviour and residual stresses of carbon-coating on SiC-fibre in Ti/SiC MMCs by SEM, acoustic emission(AE) and thermomechanical cycling testing to get more information of Ti-MMC damages.

The Ti-6A1-4V/ SiC(sigma fibre 1140 plus) composite was used. The AE peaks reveal that the AE signals come mainly from SiC-fibre crack and debonding of interface between C-coating and Ti-matrix. The SEM results was identical with the acoustic emission data. Coating layer cracking and interface debonding were found after testing. This means that the stresses caused by the thermomechanical loading is released mainly by interfaces of matrix, coating layer and fibres.

15:50-16:20 **BREAK**

Poster Session II

16:20-18:30 See programme of this poster session p. K-30 to K-35.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session IX - Magnetron Sputtering Technology
Chairperson: A. Grill, IBM Research, Yorktown Heights, USA

K-IX.1 - invited - 8:30-9:00

RECENT ADVANCES IN MAGNETRON SPUTTERING TECHNOLOGY, **J. Musil**, Department of Physics, University of West Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic.

The paper gives a short survey of milestones in development of sputtering systems and sputtering process. It shows that all major advances in sputtering technology are stimulated by the industry and its urgent need to produce new thin films and coatings with prescribed physical and functional properties. Some recent advances in the sputtering process, such as pulsed sputtering, low-pressure sputtering, high-rate sputtering and self-sputtering are discussed in detail.

A special attention is devoted to properties of sputtered films. The film microstructure, phase and chemical composition can be controlled by two fundamental processes:(i) the particle bombardment of the film during growth and (ii) the «mixing effect», i.e. an incorporation of one or several additional elements into a base material. Both methods are analysed. Present trends in sputtering development are also outlined.

K-IX.2 9:00-9:20

CHARACTERISATION OF CARBON NITRIDE THIN FILMS DEPOSITED BY REACTIVE DC MAGNETRON SPUTTERING ON VARIOUS SUBSTRATE MATERIALS, N. Hellgren, W.T. Zheng, H. Sjöström, and J.-E. Sundgren, Department of Physics, Linköping University, 58183 Linköping, Sweden.

The effect of substrate material on structure, composition and mechanical properties of carbon nitride thin films, deposited by reactive dc magnetron sputtering in N_2 discharge, have been studied. CNx films, having nitrogen concentrations between 15 and 30 at~%, were deposited onto a number of different substrate materials, SiO_2, Si_3N_4, TiN, Ni and high speed steel, kept at temperatures between ambient and 500 °C. The films were deposited to a total thickness of approximately 400 nm using nitrogen partial pressures of either 2.5 or 10 mTorr directly on substrates cleaned using sputter etching and thermal annealing. No intermediate buffer layers were used. The results show that the adhesion of the CN films to Ni and steel substrates was very poor, especially at elevated temperatures, while in the case of SiO_2, Si_3N_4 and TiN substrates the adhesion was generally good. Atomic Force Microscopy (AFM) revealed that the films grown at the lower pressure were very smooth with rms roughnesses between 0.2 and 0.3 nm while the roughness was more than one order of magnitude higher (2 - 10 nm) for films grown at 10 mTorr. Nanoindentation measurments showed that the films grown at the low pressure and at temperatures above 200 °C were both hard (30-50 Gpa) and elastic as expected based on previous results. The films grown at temperatures < 200 °C were much softer (5-15 Gpa) and less elastic. The results obtained are discussed in terms of the film structure and interface characteristics. For example, the films exhibiting a high hardness and high elasticity were, in agreement with previous results, shown to have a fullerene-like structure.

K-IX.3 9:20-9:40

GROWTH CHARACTERISTICS OF TUNGSTEN-CARBON FILMS DEPOSITED BY MAGNETRON SPUTTERING, E. Harry, Y. Pauleau, CEA- Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France, and P.B. Barna, M. Adamik, Research Institute for Technical Physics, P.O. Box 76, 1325 Budapest, Hungary.

Tungsten-carbon protective coatings proved to have remarkable wear properties, making them suitable for industrial applications. In the present work tungsten and tungsten-carbon films have been deposited by direct and reactive magnetron sputtering in pure Ar and Ar-CH_4 mixtures respectively. The structural properties have been investigated and related to the mechanical behaviour of the films. Both the pure tungsten and the tungsten-carbon films show a regular columnar structure. however in case of carbon doped films the growth starts by the formation of a nanocrystalline structure. At a certain thickness, depending on the amount of the incorporated carbon, the growth of the film changes to the formation of polycrystalline columnar structure. The investigations have been carried out by transmission electron microscopy, Auger-spectroscopy, nuclear reaction analysis and microhardness measurements. The presence of the nanocrystalline structure at the film-substrate interface is an important finding which can have influence on the adhesion properties of the films. Possible interpretation of this phenomenon will be presented. The work was partially supported by NATO Scientific Affairs Division, High Technology Research Grant.

K-IX.4 9:40-10:00

OXIDATION AND STRUCTURAL CHANGES IN FCC TiN_xTHIN FILMS STUDIED WITH X-RAY REFLECTOMETRY, S. Logothetidis, G. Stergioudis and P. Patsalas, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

The evolution of oxidation process at room temperature of thin fcc titanium nitride (TiN_x) films, grown by DC reactive magnetron sputtering was studied by X-ray Reflectometry (XRR) measurements and supported with in-situ spectroscopic ellipsometry (SE) and stress measurements. Precise thin film thickness and density as well as surface roughness were determined from the X-ray specular reflectivity data analysis. The XRR measurements were conducted with a conventional powder diffractometer equipped with a Goebel mirror and a special reflectometry sample stage. The XRR results obtained from the TiN film during exposure to air show an exponential increase in density and thickness and a decrease in the value of rms surface roughness. Analysis of the SE results shows that oxidation takes place in the bulk of the TiN_x film transforming it to titanium oxide. The percentage of transformation and the type of the oxide depend on the TiN_x film stoichiometry. The above structural and compositional changes are in consistent with the evolution of compressive stress measured in the TiN_x films during exposure to air by cantilever technique.

10:00-10:30 **BREAK**

Session X - Gradient and Multilayered Coatings
Chairperson: M.F. Stroosnijder, Institute for Advanced Materials, Italy

K-X.1 - invited - 10:30-11:00

GRADIENT PROTECTIVE COATINGS OF DIFFERENT APPLICATION PRODUCED BY EB-PVD, B.A. Movchan, **G.S. Marinski**, International Centre for Electron Beam Technologies of E.O. Paton Electric Welding Institute, 68 Gorky Street, Kyiv 252005 Ukraine.

The report deals with the results of experimental studies of structure and some properties of gradient coatings deposited with Electron-Beam Physical Vapour Deposition method from one source of metals and oxides mixtures.

The most attention is focussed on Heat Resistant and Wear Resistant Coatings of Al-Metall-Al_2O_3 and Al-Metall-Al_2O_3-MgO grade as well as to Thermal-Barrier Coatings of Al-Al_2O_3-ZrO_2 grade. Potential fields for the application of Heat Resistant and Wear Resistant Coatings are analysed. Brief description of laboratory, pilot and commercial EBPVD equipment for the deposition of all mentioned above grades of coatings is presented.

K-X.2 11:00-11:20

VACUUM ARC DEPOSITION OF Ni-Ti GRADIENT COATINGS, B.B. Straumal and W. Gust, University of Stuttgart, Institut für Metallkunde, Seestr. 75, 70174 Stuttgart, Germany, N.F. Vershinin, Institute for Vacuum Technology, Chajanov str. 8/26,125047 Moscow, Russia, M. Friesel and M. Willander, SIMS Laboratory, Chalmers University of Technology, Dept. of Physics, Physikgränd 3, Gothenburg 41296, Sweden.

The so-called vacuum arc burns in the vapour of the cathode material. In case that several cathodes are used, the possibility exists to control each discharge independently from the others because no reactive gas is needed which can lead to interrelation among the discharges of individual cathodes. This feature permits an easy fabrication of the multicomponent coatings with the aid of vacuum arc deposition. And more, the deposition rate of each component can be changed during the deposition process in situ. It permits to produce gradient coatings. In this work, Ti and Ni were deposited onto silica glass substrates in a chamber having two separated vacuum arc sources. The discharge power for both cathodes was gradually changed during the deposition process. Deep-profiling of the produced coatings was made with the aid of secondary ion mass spectroscopy. The concentration of Ni is maximal close to the substrate and gradually decreases with increasing thickness of the coating. The concentration of Ti is minimal close to the substrate and maximal on the surface of the coating. The slope of the concentration profiles depends on the distance between the substrate and cathodes. Therefore, it is possible to influence the concentration gradient in a coating not only by changing the discharge power but also varying the position of the substrate relative to the cathodes. The financial support from the INTAS programme under contract 93-1451 and the Volkswagen Foundation under contract 1/71 676 is acknowledged.

K-X.3 11:20-11:40

SIALON CERAMICS WITH GRADIENT MICROSTRUCTURE, L. Chen, E. Kny and G. Groboth, Division of Engineering, Austrian Research Center Seibersdorf, 2444 Seibersdorf, Austria.

Silicon nitride based Sialon ceramics have been successfully used in high temperature and wear applications. α-Sialon has a high hardness but a low toughness and β–Sialon has a high toughness but a low hardness. The interlocking elongated grains of the β-Sialon ceramics are responsible for the high fracture toughness of these materials.

In order to combine the high hardness of the α-Sialon with the high toughness of the, β–Sialon together, gradient Sialon ceramic has been developed in this work. The microstructures and the properties of the gradient Sialon ceramic vary gradually inwards from the spherical α–Sialon grains on surface (HV10=19GPa, HV0.1=34GPa, and K_{1c}=4.3MPam$^{1/2}$) to the elongated, β-Sialon grains in inner core (HV10=15.7GPa, HV0.1=24GPa and K_{1c}=7.3MPam$^{1/2}$). Mixtures of the α-Sialon grains and the β-Sialon grains were observed in the transitional zone (HV0.1=24~30GPa). The gradient Sialon ceramic was in-situ produced with a green compact starting from a homogeneously mixed powder mixture.

K-X.4 11:40-12:00

ANALYSIS OF SURFACE AND INTERFACE MODIFICATIONS OF THIN MULTILAYERED FILMS, M.G. Beghi, C.E. Bottani, P.M. Ossi, Dip. di Ingegneria Nucleare, Politecnico di Milano, via Ponzio 34/3, 20133 Milano, Italy, M. Poli, Bede Scientific, UK, B.K. Tanner, Univ. of Durham, UK, B-X. Liu, Tsinghua Univ., China.

An important requirement in film deposition is assessing the characteristics of its surface and interfaces, both with the substrate and, in multilayered films, between adjacent layers. Low angle, high resolution X-ray diffraction, X-ray reflectivity and surface Brillouin scattering are used to determine structure, layer thickness and roughness as well as film acoustic properties, thus providing a detailed, non destructive structural and mechanical characterization of the film. Multilayered Au-Ta thin films, with nominal thickness of 50 nm, consisting of six couples of Ta (4.4 nm) and Au (2.7 nm) alternating layers, corresponding to a designed composition $Ta_{62}Au_{38}$, have been evaporated onto oxidized Si substrates, then bombarded at room temperature with 190 keV Xe^+ at different doses, to induce in a clean way progressive atomic mixing and subsequent structure vitrification. X-ray measurements allowed us to determine film thickness, density, structure and microstructure. By Brillouin scattering local acoustic properties of the samples were tested and from these the elastic constants were deduced. The presence of a critical softening trend of the phase velocity of surface waves (Rayleigh and Sezawa) with increasing irradiation dose is correlated with film alloying and subsequent amorphization.

K-X.5 12:00-12:20 MULTILAYER COATINGS ON CFC-COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS, V. Wunder(1), N. Popovska(1), A. Wegner(2), G. Emig(1), and W. Arnold(2), (1)Lehrstuhl für Technische Chemie I, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany, (2)Fraunhofer Institut für zerstörungsfreie Prüfverfahren, 66123 Saarbrücken, Germany.

The interest in carbon fiber reinforced carbon (CFC) composites has increased in recent years, because of their excellent performance for high-temperature applications. However, a protective coating is necessary to avoid the oxidation of the carbon. Multilayer coatings on CFC composites consist of pyro carbon, hafnium carbide and silicon carbide as a ground layer, diffusion barrier and oxidation protection respectively. The hafnium carbide coating was deposed by thermally induced CVD using a gas mixture of hafnium tetrachloride, methane and hydrogen as precursor. The silicon carbide was deposited from methyltrichlorosilane and hydrogen.

The multilayer coatings was characterized by TEM, SEM, AES and XRD. The quality of the adhesion of the coatings was measured using a new ultrasonic technique. It is based on the generation of harmonics at the interface of the adhering coating. A corresponding evaluation procedure is used in order to distinguish between various states of adhesion.

12:20-14:00 **LUNCH**

Thursday June 19, 1997 — Afternoon
Jeudi 19 juin 1997 — Après-Midi

Session XI - Ion Beam Treatment
Chairperson: E. Richter, FZR, Rossendorf, Germany

K-XI.1 - invited - 14:00-14:30

MODIFICATION OF MECHANICAL AND CHEMICAL SURFACE PROPERTIES OF METALS BY PLASMA IMMERSION ION IMPLANTATION, **W. Ensinger**, Universität Augsburg, Institut für Physik, 86135 Augsburg, Germany.

Plasma immersion (ion) implantation PII has been developed almost a decade ago for modifying mechanical and chemical surface properties of metals. In analogy to conventional ion implantation, it uses energetic ions, mostly nitrogen, which are implanted in the near-surface region of a material. A sample is wrapped by a plasma and subjected to negative high-voltage pulses. In the electrical field, the ions are accelerated to high energies and incorporated into the sample. This process takes place at all sides of the samples simultaneously without requiring ion beam and sample manipulation, by contrast to conventional ion implantation.

The present review discusses the fundamentals of PII including plasma generation and high voltage pulse generation. The influence of the process parameters such as ionic species, ion density, pulse repetition rate, and sample temperature on mechanical features such as hardness and wear resistance and the chemical properties such as corrosion resistance of metals and alloys such as mild steel, stainless steel, nickel-, aluminum- and titanium-alloys are discussed. Examples of results of field tests and of industrial applications are given.

K-XI.2 14:30-14:50

MEDIUM ENERGY ION BEAM NITRIDING OF STAINLESS STEELS AT ELEVATED TEMPERATURES AND THEIR CORROSION AND HARDNESS BEHAVIOR, G.K. Wolf, Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 500, 69120 Heidelberg, Germany, and S. Schell, Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 500, 69120 Heidelberg, Germany.

This work presents the results of medium energy Ion Beam Implantation of X2CrNil8-9 and X6CrNil7-12 Stainless Steels with nitrogen. At elevated temperatures (about 400°C) of the specimens, ion energys from l0keV to 25keV, ion fluxes from 0,2mA/cm^2 to 1,5mA/cm^2 and ion doses from 0,8*10^{18}N/cm^2 to 8*10^{18}N/cm^2 phase formation of the so called S-Phase (γ_N-Fe) occurs wich should combine high hardness with good corrosion resistance. Also phase transformations of α'-Fe into γ-Fe, α-(Fe,Ni) and Fe_xN takes place. This was examined through Conversion Electron Mössbauer Spectroscopy (CEMS) and Grazing Incidence X-Ray Diffraction (GXRD) with incidence angle α of 1°.

The Corrosion behavior was studied in 5N H_2S0_4 with Cyclo Voltametric measurements and shows improved corrosion resistance for all implanted specimens.

Hardness measurements with an microindenter show increasing and also decreasing hardness compared with the untreated Stainless Steels depending on the bombardment parameters for X2CrNi18-9. No significant differences have been seen yet for the X6CrNi17-12 Stainless Steels.

K-XI.3 14:50-15:10

SUB-SURFACE MODIFICATIONS INDUCED BY NITROGEN ION IMPLANTATION IN STAINLESS STEEL (SS316L). CORRELATION BETWEEN MICROSTRUCTURE AND NANOINDENTATION RESULTS, M. Guemmaz(1), A. Mosser(1), J. Hommet(1), J-J. Grob(2) and R. Stuck(2), (1)IPCMS-GSI, (2)CNRS-PHASE, 23 rue du Loess 67037 Strasbourg Cedex 2, France.

The surface of SS316L was modified through nitrogen ion implantation at high fluences. Multiple energy ion implantations at decreasing energy (180, 100, 50 and 20 KeV) were performed on the same samples in order to obtain nearly flat depth-profiles over a thickness of about 300 nm. The doses were chosen with help of a Monte Carlo simulation method (TRIM90) in order to obtain three different nitrogen atomic concentrations: 20%, 30% and 40%.

The SIMS measurements show that the nitrogen profiles are nearly flat with an important nitrogen diffusion toward the bulk in case of high fluences, which increases the thickness of the nitrided layers and limits the concentration to a saturation value. The grazing angle X-ray diffraction experiments show that for the 20%N sample the austenitic unit cells are strongly expanded and form a nitrogen solid solution of ψ-structure. For the 30% and 40% samples, besides the solid solution, one part of the austenite is transformed in iron nitride ε-$Fe_{2-3}N$ and an other part in an α-Fe phase. Moreover, the samples were analyzed by XPS in order to precise the chemical bonds.

The nanoindentation study shows that the formation of the solid solution induces an important hardness increase, from 2.0 GPa for the non-implanted sample to 15 GPa for the 20%N implanted one. In case of 30% and 40% N samples, the hardness remains about the same as for the 20% N implanted sample, but over higher thicknesses which confirms the nitrogen diffusion towards the bulk.

K-XI.4 15:10-15:30

INFRARED AND ION BEAM ANALYSIS OF BORON NITRIDE COATINGS, M.F. Plass, W. Fukarek, A. Kolitsch and W. Möller, Forschungszentrum Rossendorf, Institut für Ionenstrahlphysik und Materialforschung, Postfach 510119, 01314 Dresden, Germany

The layered structure of c-BN containing films has been investigated with films deposited by ion beam assisted deposition. The layer sequence of nanocrystalline c-BN on top of an h-BN interlayer can also be resolved using the two non-destructive techniques, i.e. polarised infrared reflection (PIRR) spectroscopy and Rutherford backscattering spectroscopy. The c-BN fraction of the toplayer (approximately 90 %) is independent of the ion energy in the range of 0.5 to 1.5 keV. The hexagonal BN interlayer thickness is decreasing with increasing ion to atom ratio during deposition. The established IR peak ratio is mainly determined by the thicknesses of both layers with nearly pure phase composition and can not be related to a spatial mixing of trigonally and tetragonally coordinated BN throughout the whole film. The findings will be discussed with regard to the common c-BN growth models. In particular, the transition of the two phases will be emphasised.

K-XI.5 15:30-15:50

AR$^+$-IMPLANTATION EFFECTS ON THE INTERFACIAL PROPERTIES OF THE WC / Ti-6A1-4V SYSTEM, C. Dorigoni$^{(1)}$, N. Laidani$^{(2)}$, A. Miotello$^{(1,3)}$ and L. Calliari$^{(2)}$, $^{(1)}$Dipartimento di Fisica, Universita degli Studi di Trento, via Sommarive 14, 38050 Povo (Trento), Italy, $^{(2)}$Centro Materiali e Biofisica Medica (I.T.C.), via Sommarive, 38050 Povo (Trento), Italy, $^{(3)}$INFM-Istituto Nazionale per la Fisica della Materia

This work reports on the Ar$^+$-implantation effects on the mechanical, compositional and structure properties of the WC/Ti-6Al-4V system interface. The WC films were deposited by r. f. magnetron sputtering on Ti-6A1-4V substrates and then implanted at the film/substrate interface with Ar$^+$ ions at 160 keV. Two parameters have been varied in the implantations: the ion dose Φ (Φ varying in the 1x10^{16} - 2x10^{17} atoms/cm^2 range) and the sample temperature, T_i (less than 323K and the range 393-453K). Scratch hardness was measured on the unimplanted and the implanted films, using a scratch tester and scanning electron microscopy (SEM). Compositional and chemical structure of the WC/Ti-6A1-4V system was obtained by Auger electron spectroscopy (AES). New phase formation was investigated by X-ray diffraction (XRD). Significant differences between the scratch hardness behaviour as a function of ϕ were observed for the two implantation temperatures, while the evolution of the interfacial composition resulted independent of T_i. These findings are discussed in terms of thermodynamical effects which conditioned new phase formation at the film/substrate interface during the ion-beam mixing.

15:50-16:20 **BREAK**

Session XII - Laser assisted treatments
Chairperson: L. Lelait, EDF-Research Center, France

K-XII.1 - invited - 16:20-16:50

SURFACE MODIFICATION OF METALS BY HIGH POWER LASER, **J.de Damborenea**, Dpt de Corrosion y Protection, Centro de Investigaciones Metalurgicas, CSIC, Avda Gregorio del Amo n° 8, 28040 Madrid, Spain.

Lasers are a powerful tool for surface modification of metals in order to improve their corrosion and triboligical properties. Due to its intrinsic characteristics, lasers can be focussed on a metallic surface producing a broad range of treatments from heating to melting depending on the input energy. So, phase transformation to increase the surface hardness or cladding or alloying to obtain new materials can be done on the surface of a base metal . Other applications such as laser physical deposition (LPVD) or laser chemical deposition (LCVD) are being currently done.

In the present paper, a review of different treatments on several materials are discussed focussing on the modification of the corrosion properties of metals and alloys for applications at low temperatures (electrochemical corrosion) and high temperatures (oxidation procces).

K-XII.2 16:50-17:10

SURFACE MODIFICATION AND TRIBOLOGICAL BEHAVIOUR OF TITANIUM AND TITANIUM ALLOYS AFTER YAG-LASER TREATMENTS, C. Langlade, A.B. Vannes, J.M. Krafft and J.R. Martin, IFoS Laboratory, Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France.

Commercially pure Ti and Ti alloys substrates have been treated using a YAG-Nd laser radiation (1,06 µm). A large range of laser parameters have been tested resulting in very different colored layers. X ray diffraction and Raman spectroscopy have been performed in order to characterize the composition and crystalline structure of the coatings. Their roughness and thickness were also measured.

Their tribological properties have been evaluated under reciprocating friction and fretting conditions against 100Cr6 spheres. The value of the resulting coefficient of friction and endurance life are discussed. Evolution of the composition and structure of the coating during friction has been followed.

K-XII.3 17:10-17:30

PROPERTIES OF C-BN THIN FILMS DEPOSITED BY A HYBRID RF-PLD-TECHNIQUE, T. Klotzbücher$^{(1)}$, M. Mergens$^{(1)}$, D.A. Wesner$^{(2)}$, E.W. Kreutz$^{(1)}$, and R. Poprawe$^{(1, 2)}$, $^{(1)}$RWTH Aachen, Germany, Lehrstuhl für Lasertechnik, $^{(2)}$Fraunhofer Institut für Lasertechnik, Steinbachstrasse 15, 52074 Aachen, Germany.

In the hybrid RF-PLD-technique Pulsed Laser Deposition is combined with an additional RF-discharge resulting in ion bombardment of the growing film due to DC-self-biasing of the substrate electrode. In regions of the film where a certain ion-to-atom arrival ratio is present the cubic phase was formed as measured by FTIR spectroscopy. The typical ion-to-atom arrival ratios achievable with this technique are in the order of 1, so that ion energies of some hundred eV are necessary for the formation of the cubic phase. Maximum c-BN contents of about 60 % have achieved so far and the layered sequence (h-BN interlayer between substrate and c-BN film), typical for c-BN film deposition, was observed. XPS analysis revealed that the films are nearly stoichiometric with little boron enrichment. Using pure argon discharges without any molecular nitrogen leads to boron rich films and the formation of c-BN is therefore suppressed. From strong peak shifts in the FTIR spectra it can be concluded that high compressive stress is present in regions of c-BN formation, leading to partial delamination and cracking of the films. Micro Raman analysis showed only peaks characteristic for h-BN from which is concluded together with the fact that c-BN has a relatively low Raman scattering efficiency, that the c-BN is nanocrystalline.

K-XII.4 17:30-17:50

COMPARISON OF MODIFICATIONS INDUCED BY ArF EXCIMER LASER IRRADIATION ON SILICON NITRIDE FILMS DEPOSITED BY DIFFERENT LCVD METHODS, N.Banerji, J. Serra, C. Serra, F. Lusquinos, B. Leon and M. Pérez-Amor, Dpto. Fisica Aplicada, Univ. de Vigo, Lagoas-Marcosende 9, 36200 Vigo, Galicia, Spain.

A comparative study of the post-deposition modifications induced by ArF excimer laser irradiation on amorphous silicon nitride films deposited by different LCVD processes, (CO_2 and ArF laser-induced CVD) and gas mixtures (silane/ammonia or disilane/ammonia) has been carried out. The UV irradiations were performed at room temperature and in inert gas atmospheres on films deposited at 350°C. Characterisation was done by Fourier-transform infrared spectroscopy (FTIR), energy dispersive x-ray spectroscopy (EDX), atomic force microscopy and single wavelength ellipsometry. The observed film evolution in all cases indicated an initial elimination of bonded hydrogen (Si-H and N-H) followed by oxidation to oxynitrides resulting from reactions with adsorbed water in the films. However, a comparison among the different films indicated that the films deposited with disilane/ammonia gas mixtures using ArF laser were much more resistant to oxidation than the silane/ammonia films deposited with CO^2 or ArF laser. We attribute this variation in the oxidation resistance to the morphological and compositional differences among films which in turn affect the nearest-neighbour environment of the Si-N bonds.

K-XII.5 17:50-18:10

XPS INVESTIGATION OF $B_xN_yC_z$ COATINGS DEPOSITED BY LCVD, M.N. Oliveira, Departamento de Fisica, Universidade de Lisboa, Campo Grande, Ed. C1, 1700 Lisboa, Portugal, A.M. Rego, CQFM-Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa, Portugal and O. Conde, Departamento de Fisica, Universidade de Lisboa, Campo Grande, Ed. C1, 1700 Lisboa, Portugal.

Some of the most interesting novel materials are located in the boron-carbon-nitrogen composition triangle. Laser assisted Chemical Vapour Deposition (LCVD) using different gas phase precursors and processing conditions yields $B_xN_yC_z$ coatings with varying crystallographic structure and stoichiometry.

In this work we investigate the capabilities of the X-ray photoelectron spectroscopy (XPS) technique for the characterisation of $B_xN_yC_z$ films produced by LCVD from diborane, ethane and ammonia or diborane and dimethylamine reactive atmospheres, using a continuous wave CO_2 laser. The XPS results are interpreted together with those obtained by glancing incidence X-ray diffraction, micro-Raman and electron micro-probe analyses in order to study the chemical bonds present in the coatings.

We found that the films produced with dimethylamine, which is a simultaneous precursor for carbon and nitrogen, display tetragonal and/or rhombohedric structures with well defined crystalline planes. Conversely, those grown from the other gaseous mixture consist of both hexagonal and rhombohedric phases having poor long range order.

K-XII.6 18:10-18:30

CORRELATION OF THE MICROHARDNESS WITH THE NITROGEN PROFILES AND THE PHASE COMPOSITION IN THE SURFACE OF LASER-NITRIDED STEEL, P. Schaaf, C. Illgner, F. Landry, K.-P. Lieb Universität Göttingen, Zweites Physikalisches Institut, Bunsenstrasse 7/9, 37073 Göttingen, Germany.

The effect of the nitrogen take-up upon irradiation of iron or steel with excimer laser pulses in air or nitrogen atmosphere is well established. The resulting nitrogen depth profiles and phase compositions were measured by a combination of Rutherford Backscattering Spectrometry (RBS), Resonant Nuclear Reaction Analysis (RNRA) and Conversion Electron Mössbauer Spectroscopy (CEMS) as a function of the laser parameters (energy density, number of pulses, atmosphere). The accuracy of the nitrogen profiling via the $^{15}N(p,\alpha\gamma)^{12}C$ reaction - the laser irradiation was carried out in a $^{15}N_2$ enriched atmosphere - allowed us to detect very low nitrogen concentrations and also to resolve them laterally across the laser spot. The laser induced changes in surface topography were observed with optical and Scanning Electron Microscopy (SEM+EDX) and surface profilometry. The microhardness across the laser spot and as a function of the depth is compared with the nitrogen depth and lateral profiles and the phase composition. Thus the mechanical and tribological properties can be related to the microstructure and phase composition in the laser modified surface layer.

Friday June 20, 1997 **Morning**
Vendredi 20 juin 1997 Matin

Session XIII - Polymers Coatings and Surface Modifications
Chairperson: G.K.Wolf, University of Heidelberg, Germany

K-XIII.1 9:00-9:20 STUDY OF THE INFLUENCE OF SURFACE FRACTALITY ON TRANSPARENT GAS BARRIER COATINGS PERMEABILITY, G. Garcia-Ayuso and J. Martinez-Duart, Dpto. Fisica Aplicada, C-XII (UAM), Cantoblanco, 28049 Madrid, Spain; O. Sanchez and L. Vazquez, Instituto de Ciencia de Materiales de Madrid, Cantoblanco, 28049 Madrid, Spain and R. Salvarezza, Visiting Researcher from INIFTA, La Plata, Argentina.

The surface morphology of silica/alumina coatings on polymer (PET) substrates for transparent gas barrier films has been characterized by Atomic Force Microscopy (AFM). From the AFM images the surface pore fractal dimension has been determined. From these results, it has been found that the water vapor permeability of the silica/alumina coatings increases as the pore surface fractality, D, decreases (i.e. the pore becomes more regular). However, it has been observed that the oxygen permeability does not change appreciably with the surface pore fractal dimension. This difference is explained on the base of the different transport mechanisms for water vapor (a surface diffusion mechanism) and oxygen (gas diffusion through the pore volume network, i.e. Knudsen flow). The former one, which is surface-mediated, is affected by the degree of surface pore irregularity (i.e. D), whereas the latter one is insensitive to the surface pore morphology. Thus, the surface pore fractal characterization from AFM images constitutes a suitable way to quantify the pore surface contribution to the surface-mediated permeability of diffusion barrier coatings.

K-XIII.2 9:20-9:40 SURFACE AND STRUCTURAL CHARACTERIZATION OF POLYPYRROLE LAYERS ON ALUMINIUM, A. Yfantis, G. Appel, D. Schmeisser, Technical University of Cottbus, Department of Physics, P.O. Box 101344, 03013 Cottbus, Germany, D. Yfantis, National Technical University of Athens, Department of Chemical Engineering, Iroon Polytechniou 9, 15780 Athens, Greece.

Among the conductive organic materials, poly(pyrrole) (Ppy) films are of special interest due to their high conductivity as well as their improved chemical stability. In our study poly(pyrrole) layers doped with PTS and AlF_6^{3-} were prepared electrochemically on aluminium foils from aqueous solutions. Smooth films were obtained by varying synthesis conditions such as current density and dopant's concentration. The films were characterised by using XPS, AFM and FTIR.

Moreover adhesion measurements and accelerated corrosion tests were performed. An effort to correlate the above mentioned results was attempted. The results indicate a good prospective on applying a polypyrrole coatings on Aluminium surfaces for protection against corrosion.

K-XIII.3 9:40-10:00 SURFACE MODIFICATIONS OF NI SUBSTRATES WITH SELF-ASSEMBLED MONOLAYERS OF ALCANETHIOLS FOR TRIBOLOGICAL APPLICATIONS, Z. Mekhalif(1), J. Delhalle(2), J-J. Pireaux(1), S. Noël(3) F. Houzé(3), and L. Boyer(3), (1)L.I.S.E., (2)L.C.T.S.I., FUNDP, 5000 Namur, Belgium, (3)L.G.E.P., Plateau du Moulon, 91192 Gif sur Yvette Cedex, France.

In the past few years, an increasing number of studies have been devoted to n-alkanethiols adsorbed from aqueous solutions on solid surfaces like gold. Adsorbed alkanethiols. CH_3-$(CH_2)_n$-SH easily, form oriented and ordered structures ($n>9$), often referred to as 'self-assembled' monolayers or SAMs. These SAMs have been used to model and to investigate interfacial properties of biological membranes and organic materials in processes and phenomena such as molecular recognition, ion transport, adhesion, friction and others. Other metals such nickel and iron have received very little attention because of the complexity of the preparation of alcanethiol SAMs on such oxidisable metals.

The new approach we have been working on is the adsorption of alcanethiols on nickel polycristalline surfaces. To obtain a chemically adsorbed molecules and a well organised monolayer, an electrochemical pretreatment prior the adsorption of the alcanethiol is necessary in order to reduce the oxide layer. Our study is motivated by the the utility of nickel as final coating for separable electrical contacts in various types of application: batteries, automotive connectors, etc.

In this contribution, we present first a brief description of the substrate preparation and modification, the type of molecules and substrates used. Then, we report the main physicochemical characterizations. The electrical and tribological properties of the monolayers formed on nickel slabs are investigated in a ball/plane configuration simulating a real contact element. The influence of an electrochemical pretreatment of the nickel surface prior to the layer assembly is shown. Excellent tribological behaviours can already be obtained with corresponding values of the contact resistance varying between 1 Ω and 10 mΩ. The results show that building organised monolayers acting as protective coatings is of high interest for electrical contacts.

10:00-10:30 **BREAK**

Session XIV - Process Control
Chairperson: J.P. Rivière, University of Poitiers, France

K-XIV.1 - invited - 10:30-11:00

REAL TIME CONTROL BY ELLIPSOMETRY OF THE GROWTH OF OPTICAL COATINGS, **B. Drévillon**, LPICM (UPR 258 du CNRS), Ecole Polytechnique, 91128 Palaiseau, France.

The deposition of high performance optical coatings requires the presence of an accurate process control system. Such coatings can consist of multilayer or gradient index structures. Real time control, by multiwavelength Phase Modulated Ellipsometry (PME), of the growth of plasma deposited structures is described here. The structures consist of SiO_2 and SiN_y stacks or SiO_xN_y films with variable composition. The accuracy of a control method of multilayers growth, based on the comparison between real time PME measurements and pre-computed target trajectories, is emphasised. In particular, this feedback method, incorporating the incoherent modelling of the transparent substrate, is applied to the growth of Fabry perot and Quaterwave filters. The resulting optical coatings show a reproducible accuracy, with less than 1% error between target and measured optical responses. In case of gradient index structures, an efficient method for estimating the optical parameters of the outermost layer based on a non linear least square fitting is described. Furthermore, an integral expansion of the reflection coefficient is implemented in the real time inversion algorithms[1]. As an exemple of application, the successfull real time control of the growth of a linear gradient index structure is demonstrated.

[1] M. Kildemo, O. Hunderi and B. Drévillon, J. Opt. Soc. Am. A14, 1(1997)

K-XIV.2 11:00-11:20

STUDIES WITH NON-DESTRUCTIVE TECHNIQUES OF THE COMPOSITION, INITIAL STAGES OF GROWTH AND SURFACE TOPOGRAPHY OF THIN AMORPHOUS CARBON FILMS, S. Logothetidis, G. Stergioudis and N. Vouroutzis, Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece.

Amorphous carbon (a-C) films, free of hydrogen, were prepared by magnetron sputtering. The thin films composition during deposition was analysed by in-situ spectroscopic ellipsometry (SE), a non-destructive technique, in the energy region 1.5-5.5eV. The films were deposited either under positive or negative bias voltages at the substrate and from a few monolayers to 400Å thick. It was found that films deposited under negative bias are rich in sp^3 C-C bonds from their initial stages of growth to the final thickness of the film. All films, even those of few monolayers, were also examined by X-ray Reflectometry and Atomic Force Microscopy in order to study the surface topography versus the film thicknesses, calculated by SE, and other preparation conditions, e.g. the bias voltage and the Argon partial pressure in the vacuum chamber. The results show that the films deposited under negative bias are atomically smooth and independent on their thickness whereas those films deposited under positive bias exhibit surface roughness depending on their thickness. Their rms surface roughness are about 5Å at the first 4-5 monolayers and increases to 10Å when the film is about 400Å thick. These results support that two different type of growth are taken place in a-C films deposited by sputtering and are discussed in comparison with the subplantation model for the development of rich in sp^3 C-C bonds films.

K-XIV.3 11:20-11:40

IN-SITU AND EX-SITU CHARACTERIZATION OF Ti/TiN AND Al/AlO_x MULTILAYERS FOR HARD COATING APPLICATIONS, P. Boher and J.-L. Stehle, SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France; Ph. Houdy, S. Labdi, Université d'Evry Val d'Essonne, Boulevard des Coquibus, 91025 Evry Cedex, France.

Multilayered Ti/TiN and Al/AlOx thin films have been deposited by reactive rf-sputtering with in-situ control by spectroscopic ellipsometry. The thickness of each component was varied from 1 to 10nm and the total thickness of the stacks was fixed around 200nm. After deposition, the multilayers were characterized by grazing x-ray reflectance (thickness and roughness) and spectroscopic ellipsometry (layer interdiffusion). For Ti/TiN samples sliding wear tests were made to evaluate the wear lifetime of the samples For Al/AlOx samples conductivity was measured by four probes technique. The proposed paper will focused on the influence of the interfacial properties on the tribological or electrical properties of the multilayer films. For this purpose, in-situ spectroscopic ellipsometry is a technique of choice since the optical contrast between the metallic layer (Ti or Al) and the insulating layer (TiN or AlOx) is very high. Different examples of such investigations will be given changing the deposition conditions and in particular the sample temperature during deposition.

K-XIV.4 11:40-12:00

EXCIMER LAMP-INDUCED DECOMPOSITION OF PALLADIUM METALORGANIC FILMS FOR ELECTROLESS COPPER PLATING, J-Y Zhang and I.W. Boyd, Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K., S. Draper, Department of Chemistry, Trinity College, Dublin, Ireland.

Photo-induced decomposition of palladium metalorganic films was performed using a novel excimer UV source with 222 nm wavelength radiation. Palladium deposition on arbitrary substrate materials from a palladium compound using excimer lamps for subsequent electroless copper plating is described. This palladium compound is an ideal metalorganic precursor for photo-induced metallization process since it has sufficient optical absorbance at the lamp wavelength to initiate reaction, has weak bonding but is sufficiently stable at room temperature, is readily soluble in common organic solvents and easily produces homogeneous films.

The palladium films formed and the palladium metalorganic layers used were characterised using ultraviolet spectrophotometry UV) and Fourier transform infrared (FTIR) spectroscopy. The photo-decomposition of palladium compounds was shown to be a function of both the UV intensity and chamber pressure during irradiation. The exposure conditions were found to affect the density of the palladium catalyst. The morphology of the metal layers was investigated with a scanning electron microscope (SEM). The selectivity of the metal electroless plating using a commercial copper bath was demonstrated by irradiating the surfaces through a quartz contact mask. Since larger lamps can in principle be obtained by scaling up the geometry, this large area and low cost UV-induced metal deposition can become readily available to provide an interesting alternative for the manufacture of thin film microcircuits in ultra-large scale integrated (ULSI) devices.

K-XIV.5 12:00-12:20 CARBON ION CHARGE STATES AND ENERGY DISTRIBUTIONS FOR DLC ABLATION PLUMES FROM 100 FEMTOSECOND 800 NM LASER PULSES, P.P. Pronko, P.A. VanRompay and M. Nantel, Center for Ultrafast Optical Science and Dept. of Electrical Engineering, University of Michigan, 48129 Ann Arbor, MI, USA.

A time of flight, sector field, electrostatic analyzer has been used to obtain detailed information about the ionic charge states of carbon and their associated energy distributions for ablation plumes typical of those used for depositing DLC diamond-like carbon films .Time resolved spectra of individual mass/charge peaks are used to construct the energy distributions. It is observed that, for 100 fs laser pulses in the lE14 to lE16 watts/sq. cm intensity range, the characteristics of these distributions are highly dependent on the peak to background contrast ratio of the laser pulse. These in turn are dependent on the specific operational parameters of the laser. Likewise, deliberate introduction of a specified low intensity pre-pulse background that is capable of generating a pre-plasma, can have a drastic effect on the nature of the ion species and their energies. It is determined that absolute control of the pulse contrast and any low lying pre-pulse is essential for reproducible ablation plume generation. Ion energies are observed and examined in the kinetic energy range from a few hundred electron volts to 20 keV. Energy distributions are compared to numerical code results for hydrodynamic expansion and for effects of plasma double layers. Neutral species in the plume are also examined by way of a neutral pass filter in the ion spectrometer. Direct measurement of the neutral to charged ratios is thereby possible and its effect on film properties determinable.

12:20 **LUNCH**

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SYMPOSIUM K
POSTER SESSIONS

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Poster Session I
16:20-18:30

K-I/P1 POLYCARBOSILANE-BASED COATINGS BY LASER-INDUCED POLYMERIZATION OF SILENES IN THE GAS PHASE, J. Pola, Institute of Chemical Process Fundamentals, 165 02 Prague, Czech Republic.

CW $C0_2$ laser-induced homogeneous SF_6-photosensitized decomposition (LIHPD) of silacyclobutanes $R_1R_2SiCH_2CH_2CH_2$ ($R_{1.2}$ = e.g. H, CH_3, CH_2=CH, Cl) into very reactive silenes $R_1R_2Si{=}CH_2$ polymerizing in the gas phase affords polycarbosilane-based films which are deposited on the reactor surface. The transient silenes were identified via chemical trapping with alcohols. Despite that carbon analogues of silenes do not polymerize efficiently, reactive silenes containing C=C and C C bonds afford polymeric coatings in which these multiple bonds are lost. These results suggest that new types of saturated polycarbosilanes can be produced from unsaturated organic monomers containing a neighbouring Si=C bond. The LIHPD of silacyclobutanes can be carried out as an non-explosive or a faster explosive process; these different modes of the decomposition result in different composition of polycarbosilanes.

ArF laser and TEA $C0_2$ laser photolyses of silacyclobutane and disilacyclobutane in the gas phase is also dominated by the cleavage of the four membered ring, and it result in the deposition of polycarbosilanes composition of which depends on the irradiation parameters: the UV photolysis is controlled by silene polymerization, while the IR photolysis is dominated by silene dehydrogenation/polymerization.

All the processes contribute to the efficient chemical vapour deposition of Si/C/H phases.

K-I/P2 LASER ASSISTED PLASMA TREATMENTS OF a-Si:H AND a-SiC:H THIN FILMS, M. Balucani(1), G. de Cesare(1), S. La Monica(1), G. Maiello(1) and A. Ferrari(1), M. Dinescu(2), D. Ghica(3), C. Stanciu(2), G. Dinescu(2), (1)Rome University "La Sapienza", Electronics Eng. Dept., Via Eudossiana 18, 00184 Roma, Italy, (2)INFLPR, P.O.Box MG 16, 76900 Bucharest, Romania, (3)INOE, P.O.Box MG 22, 76000 Bucharest, Romania.

Amorphous hydrogenated silicon (a-Si:H) and silicon carbide (a-SiC:H) thin films were laser treated in the presence of a capacitively coupled RF expanding flowing plasma working in nitrogen, ammonia or oxygen. The films had been deposited onto Si (100) wafers or glass plates by PECVD. As laser source we used an Nd:YAG laser: I = 1.06 um, tFWHM = 12 ns, Emax/pulse = 0.015 J. The aim of this work was to study the effects of the interactions between the plasma activated species and the films, in the presence of laser irradiation. Different analysis techniques were used to detect any chemical, structural and optical transformations in the films: X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), Spectroscopic Ellipsometry (SE), Scanning Electron Microscopy (SEM). Depending on the irradiation parameters and plasma characteristics, various degrees of oxidation and nitrogen incorporation have been observed.

K-I/P3 PULSED LASER DEPOSITION OF CERAMIC THIN FILMS USING DIFFERENT LASER SOURCES, A. Husman, J. Schmidt, T. Klotzbücher, E.W. Kreutz, and R. Poprawe, RWTH Aachen, Lehrstuhl für Lasertechnik, Steinbachstrasse 15, 52074 Aachen, Germany.

Al_2O_3 thin films are deposited onto silicon and steel (1.3343) using a pulsed laser deposition (PLD) technique with Excimer (λ= 248 nm, τ= 25 ns) and CO_2-laser radiation (λ=10,6 µm, τ= 3 µs). The CO_2-laser is a common industrial fast axial gas flow laser with a cw-output- power of 5 kW. It is equipped with a mechanical chopper (Q-switch), yielding laser pulses with a pulse energy of 35 mJ, a peak power of 10 kW, and an average power of 300 W at a repetition rate of up to 15 kHz.

Different experimental setups concerning the arrangement of target and substrate are used and their effect on the film deposition is evaluated. The influence of setup and processing variables (gas pressure, laser fluence) on the kinetic energy of the particles in the plasma/vapour is discussed and correlated to the resulting film properties.

Film structural properties are characterised by micro Raman spectroscopy and ellipsometry. Film micro hardness is determined by a nano-indentation method, Young's modulus is measured using a laser-acoustic method.

K-I/P4 LASER TREATMENT OF STEELS-EXPERIMENT AND THERMAL MODEL, G.Buza, Z.Kálazi, R. Kohlhéb, I.Felde, B. Verõ, and J.Gyulai, Zoltán Bay Institute for Materials Science and Technology, Fehérvári 130, 1116 Budapest, Hungary.

Surface treatment of steels by energetic laser beams opens new possibilities to reach desired properties. The localised temperature rise using a $C0_2$ laser is one of the advantages.

Modelling of gamma-alpha allotropic phase transformation of steels can theoretically predict results of laser treatment. In this work, effect of different steel grades and technology parameters were investigated to change surface hardness and its distribution. Characterisation of the samples was made in the first hand by dilatometric measurements as the case of quick induction heating there is comparable to thermal processes during laser treatment. Dilatometric measurements were completed by metallographical and microhardness investigations. Energy distribution, absorption, duration, etc. of the laser beam was varied and the experimental results were compared with results of modelling.

The process and the model was tested and verified with treatment of the groove of a 1500 mm diameter ball bearing. The average temperature of the bearing never reached 65 °C, as compared to over 800°C in case of traditional treatment. Consequently, the uniform heat input during the treatment of 30 minutes duration did not accumulate any observable thermal stress in the bearing ring.

K-I/P5 TiN FILMS DEPOSITED BY LASER CVD : A CHEMICAL KINETICS STUDY, A.J. Silvestre, Instituto Superior de Transportes, R. Castilho n°3, 1250 Lisboa, Portugal, and O. Conde, Departamento de Fisica, Universidade de Lisboa, Ed. C1, Campo Grande, 1700 Lisboa, Portugal.

Results on the deposition of titanium nitride films on mild steel substrates by pyrolytic laser-induced chemical vapour deposition (LCVD) are presented. Golden coloured lines of TiN with a broad gaussian profile were deposited from a reactive gas mixture of $TiCl_4$, N_2 and H_2 using a continuous wave TEM_{00} CO_2 laser beam as heat source.

The chemical composition and structure of the films were determined by electron probe microanalysis (EPMA) and glancing incidence X-ray diffraction (GIXRD). The coatings are nearly stoichiometric and were deposited as polycristalline non-textured material with a lattice parameter close to the standard value for stoichiometric δ-TiN.

A non-contact laser profilometer was used to measure the thickness profiles of the films. Using the data obtained in the steady-state region of the TiN laser-written lines, growth rates in the range 3.5 to 7.0 $\mu m.s^{-1}$ were deduced. The Arrhenius relation between the deposition rate and the deposition temperature yield an apparent activation energy of 46.9 ± 3.8 $kJ.mol^{-1}$. This result allowed us to conclude that under our deposition conditions the LCVD of TiN is controlled by mass transport in the vapour phase. A reactive mechanism for the TiN formation based on three sequential elemental reactions is discussed.

K-I/P6 DEPENDENCE ON THE C_2H_4 AND SiH_4 GAS MIXTURE OF THE SiC FILM PROPERTIES OBTAINED BY EXCIMER LAMP-CVD, X. Redondas, P. Gonzalez, B. Leon and M. Pérez-Amor, Dpto. Fisica Aplicada, Univ. de Vigo, Lagoas-Marcosende 9, 36200 Vigo, Galicia, Spain.

Amorphous silicon-carbon alloy films were obtained by irradiating a gas mixture of ethylene and silane diluted in argon with a xenon excimer lamp (λ=172 nm). Films were deposited at low temperatures (T=200 °C) onto c-silicon and aluminium substrates.

The role of the gas phase parameters on the film properties is reported. Film characterization by EDS reveals that an increase of the ethylene/silane concentration ratio leads to important changes in film composition. The ellipsometric measurements indicate a logarithmic decrease of the refractive index from 1.9 to 1.3. Infrared spectroscopy shows the presence of Si-C bonds as well as hydrogen bonded in different configurations to silicon and carbon atoms, being the density of C-H bonds considerably larger than those of Si-H. Ethylene-rich gas mixtures produce a decrease of the number of Si-H bonds and a shift of their stretching frequencies towards higher wavenumbers as a consequence of the compositional variations.

K-I/P7 OPTICAL PROPERTIES OF ALUMINA AND ZIRCONIA THIN FILMS GROWN BY PULSED LASER DEPOSITION, J. Schmidt(1), A. Husmann(1), D.A. Wesner(2), E.W. Kreutz(1), R. Poprawe(1,2), (1)Lehrstuhl für Lasertechnik RWTH Aachen, Germany, (2)Fraunhofer Institut für Lasertechnik, Steinbachstrasse 15, 52074 Aachen, Germany.

Sintered targets of ZrO_2 and Al_2O_2 are ablated by KrF excimer laser radiation. The plasma/vapour expands into an ambient gas atmosphere consisting of O_2 at typical pressures of 10^{-3} to 0.5 mbar. The films are deposited on a Pt/Ti/Si multilayer substrate.

Analytical techniques used for the determination of chemical and structural characteristics of the films are X-ray photoemission spectroscopy, X-ray diffraction and electron microscopy. The thickness and the complex refractive index are determined by ellipsometry by fitting a model for the film geometry to the measured data. The optical film thickness at different wavelengths is determined using interference reflection photometry.

The investigations concentrate on the influence of the oxygen pressure the target-substrate distance and the laser fluence on the refractive index of the films, which is correlated with the film density. The densification of the films is achieved by kinetic energies above 30 eV of the ablated particles impinging on the growing surface. The kinetic energy of the particles depending on the process parameters is modelled and compared to the resulting film properties.

With pulsed laser deposition dense alumina (refractive index 1.72, packing density 94%) and zirconia thin films (refractive index 2.2, packing density equal to 100%) are achieved without ion- or heat treatment.

K-I/P8 MICROSTUCTURE OF CLAD LAYERS OF CHROMIUM ONTO MILD STEEL BY LOW PRESSURE LASER SPRAYING, Y. Isshiki(1), H. Nakai(2), and M. Hashimoto(2), (1)Tokyo Metropolitan Institute of Technology, Nishigaoka, Kita-ku, Tokyo 115, Japan, (2)University of Electro-Communications, 1-5-1, Chofugaoka, Chofu-si, Tokyo 182, Japan.

Clad layers of chromium onto a mild steel substrate are obtained by low pressure laser spraying(LPLS). Atomic composition of clad layers is studied by energy distributed X-ray spectroscopy(EDX). Structure of surface layer is confirmed by X-ray diffraction(XRD). Microstructure of clad layers is investigated by cross-sectional transmission electron microscopy (X-TEM). When impinged energy density E_i on the substrate is selected to be 64 Wmm^{-2}, obtained clad layer consists of $Cr_{30}Fe_{70}$ alloy with rapidly solidified structure. Single phase of chromium with columnar structure grows when Ei is selected to be smaller than 13 Wmm^{-2}. At intermediate energy density between them, graded composition of chromium-iron is obtained. The formation of Cr_xFe_{1-x} at various values of **x** is guaranteed by controlling energy density which impinges on the substrate surface.

K-I/P9 PREPARATION OF PZT THIN FILMS ON YBCO ELECTRODES BY KrF EXCIMER LASER ABLATION TECHNIQUE, H. Kurogi(1), Y. Yamagata(1), K. Ebihara(1), and N. Inoue(2), (1)Department of Electrical Engineering and Computer Science, Kumamoto University, Kurokami, 860 Kumamoto, Japan; (2)Kyushu Electric Power Co., Inc., Suizenji, 862 Kumamoto, Japan.

We prepared $Pb(Zr_xTi_{1-x})O_3$(PZT) ferroelectric thin film. A pulsed KrF excimer laser was used to ablate the bulk target $[Pb(Zr_{0.48}Ti_{0.52})O_3]$. YBCO was used as bottom electrode. An epitaxial PZT ferroelectric thin film can be grown on the YBCO bottom electrode because PZT has perovskite structure and similar lattice constant to YBCO. We investigated the PZT crystallization on YBCO/MgO substrate. The X-ray diffraction (XRD) patterns showed that the PZT films prepared on YBCO/MgO(100) substrate at 600-680°C and with a laser fluence of $2J/cm^2$ have a perovskite(001) structure. The temperature range for crystallization of perovskite structure on YBCO/MgO substrate were so wide compare with temperature range for crystallization on Pt/MgO substrate. The ferroelectric properties of the Au/PZT/YBCO/MgO structure were studied. The polarization-electric field (P-E) characteristics and fatigue properties of PZT thin films were measured by a Sawyer-Tower circuit at lkHz. The remnant polarization and coercive field were about 15 $\mu C/cm^2$, 150kV/cm, respectively. Remnant polarization of PZT films on a YBCO/MgO substrate was reduced to one-half after about 10^8 cycles of switching.

K-I/P10 MECHANICAL, STRUCTURAL AND TRIBOLOGICAL PROPERTIES OF TITANIUM NITRIDED BY PULSED LASER, S. Ettaqi(1), V. Hays(2), J.J. Hantzpergue(1), G. Saindrenan(2) and J.C. Remy(1), (1)Laboratoire de Physico-Chimie des Surfaces, ENSAM, 2 Bd du Ronceray, B.P. 3525, 49035 Angers Cedex, France. (2)Laboratoire de Génie des Matériaux, ISITEM, La Chantrerie rue Christian Pauc, CP 3023, 44087 Nantes Cedex 03, France.

Pure titanium and titanium alloys possess excellent properties such as corrosion resistance and high strength-to-weight ratio. Their lightness and their ability to resist to extreme temperatures make they suitable for aeronautic and space industry. However, the disadvantage is the high friction and the poor wear resistance exhibited by these materials.

This work presents three processes for the surface nitriding of commercial pure titanium by means of a pulsed laser Nd-YAG: gas nitriding, melting of pre-deposited TiN powder and nitriding by reaction between titanium, nitrogen gas and TiN powder. Depending on the laser nitriding process, X-ray diffraction analyses always indicate formation of two phases, i.e. either (TiN, TiN_{03}) or (Ti,TiN). In the laser melted zones, metallurgical analyses by optical and scanning electron microscopies reveal dendritic microstructures.Thickness of the nitrided coatings was in the range 30 to 200 µm, depending on the nitriding process and the laser irradiation parameters. In-depth microhardness of the nitrided zones varied between 550 and 1800 Vickers.The tribological behaviour of the laser nitrided titanium surfaces has been investigated in room air by means of a pin-on-disk system.

K-I/P11 LASER ABLATION AND DEPOSITION OF BORON NITRIDE IN VACUUM AND IN PRESENCE OF N_2 AND NH_3, R. Teghil, Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, Potenza, Italy; V. Marotta, A. Santagata, Istituto Materiali Speciali CNR, via S. Loja, Tito Scalo (Pz), Italy; T.M. Di Palma, Dipartimento di Chimica, Università di Roma «La Sapienza», P.le A. Moro 5, Roma, Italy.

Boron nitride is one of the most interesting materials between the III-V compounds. BN thin films are widely used as protective coatings against oxidation and to increase the hardness of various materials. Boron nitride pellets have been evaporated by a doubled Nd:YAG laser and the removed material has been deposited on Si (100) substrates. The laser ablation has been performed either in vacuum or in the presence of nitrogen and ammonia at different pressures. Laser fluence and substrate temperature have been varied to optimise the deposition conditions. The morphological and structural characteristics of the films deposited in different experimental conditions have been studied by Scanning Electron Microscopy and X Ray Diffraction. The effect of a post annealing treatment on the structure of the films has been also analysed.

K-I/P12 ANTICORROSION TITANIUM OXIDE COATINGS DEPOSITED BY PULSED LASER ABLATION, V. Marotta, S. Orlando, Istituto Materiali Speciali CNR, via S. Loja, Tito Scalo (Pz), Italy; R. Teghil, Dip. di Chimica, Università di Basilicata, via N. Sauro 85, Potenza, Italy; A.M. Beccaria, Istituto Corrosione Marina dei Metalli CNR, via dei Marini 8, Genova, Italy; A. Giardini Guidoni, Dip. di Chimica, Università «La Sapienza», Pl. A. Moro 5, Roma, Italy.

Titanium oxide coatings have been deposited on iron and steel substrates, by Pulsed Laser Ablation, to prevent corrosion from aliments. The films, deposited from the laser ablation of titanium target in a vacuum chamber containing oxygen at different pressures, have been characterised by X-ray Photoelectron Spectroscopy, to analyse their composition, and by electrochemical test, to study the homogeneity of the coating and its resistance to corrosion. X Ray Diffraction analysis has been so used to study film structure. Laser fluence, substrate temperature and oxygen pressure have been optimised to improve the technological characteristics of the deposits.

K-I/P13 EXCIMER LASER TREATMENT FOR ALUMINIUM ALLOY MECHANICAL PROPERTY ENHANCEMENT, E. Sicard, C. Boulmer-Leborgne, GREMI, CNRS-Université d'Orléans, BP 6752, 45067 Orléans Cedex 2, P. Andreazza, C. Andreazza-Vignolle, CRMD, CNRS-Université d'Orléans, BP 6752, 45067 Orléans Cedex 2, C. Langlade and B. Vannes, Ecole Centrale, IFOS, 36 avenue de Collongue, BP 163, 69131 Ecully Cedex, France.

An excimer laser beam is focused (1-3J/cm^2) onto an aluminium alloy (AlSiMg) surface target in a nitrogen atmosphere (lbar) containing cell. A nitride and oxynitride layer (2x1.5 mm^2 area) is obtained by N diffusion in the alloy bulk on several μm depth. For chemical, structural and tribological analysis, lxl cm^2 samples are processed by scanning step by step the laser beam on the surface and different material analysis (RBS, NRA, GIXD, SEM, TEM) are performed. It appears that the N concentration is not constant across a processed area. To avoid this layer depth N concentration inhomogeneity, the total surface sample treatment is achieved by overlapping the processed areas. Different experimental conditions are investigated (laser fluence, laser pulse number, processed area percentage overlapping). Tests are performed to characterize the friction behaviour of the treated surface under fretting condition. The tribological results clearly show the influence of the experimental conditions and are discussed in relation to the physico-chemical structure of the coating.

K-I/P14 LASER-INDUCED DECONTAMINATION OF POLYCRYSTALLINE W SURFACES : PHOTOLITHIC AND PHOTOTHERMAL EFFECTS, C. Beleznai(1), D. Vouagner(2), J.P. Girardeau-Montaut(2), (1)Dept. of Experimental Physics, Jozsef Attila University, Dom t. 9., 6720 Szeged, Hungary. (2)Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard-Lyon 1, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Polycrystalline photocathodes with a covering native oxide layer were exposed to several wavelengths (213 nm, 266 nm, 355nm) of a picosecond Nd-YAG laser. The 213 nm wavelength was used to induce a measurable one-photon photoelectric response and the change of this signal was monitored throughout the irradiation process. A second wavelength was applied simultaneously to enhance photothermal effects and surface phase transitions during illumination. The evolution of the photoelectric signal was investigated as a function of applied wavelength and interpreted in terms of possible surface structural changes.

K-I/P15 UV LASER-INDUCED CLEANING OF NATIVE OXIDE COVERED W PHOTOCATHODES : THE EFFECT OF RECONTAMINATION AT VARIOUS PRESSURES, C. Beleznai(1), D. Vouagner(2), J.P. Girardeau-Montaut(2), (1)Dept. of Experimental Physics, Jozsef Attila University, Dom t. 9., 6720 Szeged, Hungary. (2)Laboratoire de Sciences et Ingénierie des Surfaces (EA 1877), Université Claude Bernard-Lyon 1, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

The 5th harmonic (213 nm) of a picosecond Nd-YAG laser was used to remove small fraction of the covering oxide overlayer from polycrystalline photocathodes. The evolution of the photoemitted charge (high density electron pulses) was followed along with the surface reflectivity change and they were interpreted in terms of the work function change of the surface. The careful choice of the laser fluence enables us to investigate the cleaning kinetics within a relatively narrow coverage range. Upon change in the ambient pressure we observe a marked change in the decontamination rate. Moreover, after recontaminating the surface at different pressures, we observe distinct kinetics as well. This latter effect is explained by the various rates of oxygen incorporation into the oxide lattice, resulting a looser, rougher surface (lower work function) for high pressures and a more compact oxide for low pressures.

K-I/P16 INFLUENCE OF LASER SURFACE MELT HARDENING CONDITIONS ON RESIDUAL STRESS IN THIN PLATES, J. Grum and R. Sturm, Faculty of Mechanical Engineering, University of Ljubljana, Askerceva 6, 1000 Ljubljana, Slovenia.

Wear resistance of products made of gray cast iron having ferrite-pearlite microstructure of the matrix may considerably be increased by the process of laser remelting of the surface. Products with thin walls (up to relatively 5 mm), however, seem to be problematic since the stresses introduced during laser heat treatment may produce deformations of the product.

The paper presents the results of research of various methods of laser beam guidance along the workpiece surface with various degrees of overlapping of remelted traces, and the influence of various machining conditions in laser machining on through-thickness variations in residual stresses in the workpiece. Residual internal stresses were measured by means of the relaxation method where the stressed modified surface layer was electro-chemically removed. On the basis of measurements made by a strain gauge mounted at the opposite side of electro-chemical etching, residual stress intensity in the surface layer was calculated in accordance with the appropriate physical model. The size of deformations occurring during heat treatment of test pieces was assessed. On this basis internal-stress intensity was assessed. The efficiency of the process of laser remelting of gray cast iron to increase wear resistance in thoroughly described by an analysis of microstructure and confirmed by through-thickness microhardness measurement of the modified layer.

K-I/P17 PHOTO-ASSISTED METALLISATION : RESOLUTION AND RELIABILITY STUDIES, D.J. Maucauley, K.F. Mongey, E.J. Lafferty, P.V. Kelly and G.M. Crean, National Microelectronics Research Centre, Lee Maltings, Prospect Row, Cork, Ireland.

Photo-activation processes for electroless plating have the potential for linewidth resolution on a scale of order 10 µm or less, depending on substrate surface morphology and plating conditions. This work investigates the surface morphology of a photodefined activation layer and the subsequent nucleation and growth of the electroless metallisation achieved from the activation. The morphology is studied on a range of substrates including ceramics of various surface roughnesses and highly orientated pyrolytic graphite(HOPG) using atomic force microscopy. An evaluation of the performance and the minimum resolution of the subsequent electroless copper metallisations on alumina ceramic substrates is also investigated.

Adhesion, resistivity and solderability results for the electroless metallisations are presented. The sawability and the strength of the subseqent wirebonding is also examined.

K-I/P18 PULSED PHOTOELECTRON MICROSCOPE FOR TIME RESOLVED SURFACE INVESTIGATIONS, O. Bostanjoglo, M. Weingärtner, TU Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany.

A new photoelectron emission microscope with time resolution of 5 ns and spatial resolution of 1 µm is presented. The photoelectrons are released by a short excimer laser pulse. It is sensitive to surface parameters such as work function and allows to visualize their fast changes.

The instrument is used to investigate evaporated metal films on a Si substrate and bulk metals treated with a pulsed frequency doubled Nd:YAG laser. Melting, recrystallizition and removal of oxide layers can be observed on the nanosecond time scale.

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K-I/P19 YSZ PROTECTIVE COATINGS ELABORATED BY MOCVD ON METALLIC SUBSTRATES, J. Esteve and E. Martinez, Departament de Fisica Aplicada y Electronica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, G. Garcia and A. Figueras, ICMAB/CSIC, Campus U.A.B., 08193, Bellaterra, Spain, J. Llibre, S.E. de Carburos Metalicos S.A., P. Zona Franca 14-20, 08038 Barcelona, Spain.

The aim of this work is to study both the mechanical and the protective properties of Yttria Stabilized Zirconia (YSZ) coatings prepared on metallic substrates. YSZ films were obtained in a hot wall MOCVD reactor using $Zr(thd)_4$ and $Y(thd)_3$ as organometallic precursors. The evaporation and the deposition temperatures were chose in order to stabilize the cubic phase of the zirconia. The coatings were obtained on different substrates such as 304 and 309 stainless steel and on nickel alloys.

X-ray diffraction, SEM and SIMS techniques were used to characterize the influence of different experimental parameters, such as substrate nature, deposition temperature and thermal treatment, on the structure and composition of the YSZ film and the interface film/substrate.

Mechanical properties of the coatings were also determined, before and after heat treatment, by the methods of nanoindentation and microscratch tests.

K-I/P20 X-RAY PHOTOELECTRON SPECTROSCOPIC ANALYSIS ON PLASMA ETCHED POROUS SiO_2 WITH CHF_3 GAS, Seok-Joo Wang, Il-Sup Jin, and Hyung-Ho Park, Dept. of Ceramic Eng., Yonsei Univ., Seoul, Korea.

Porous SiO_2 has a great potential as a promising intermetal dielectric due to its low dielectric constant resulted from the structural property. But it shows large contents of C, H, and O forming hydroxyl groups and organic groups as surface terminal species of porous SiO_2. This derivative compositional property from normally densified SiO_2, dry etching of porous SiO_2 should be carefully investigated for its application to device process.

Film shaped xerogel or aerogel were prepared on silicon substrate as porous SiO_2 by sol-gel derived method and successive ambient pressure drying or supercritical drying, respectively. Inductively coupled plasma etching using CHF_3 gas was effectuated to investigate the effect of C and H as constitutive elements of porous SiO_2 on the etching behavior. Etching was performed over the condition that rf power was 400 W and bias voltage was 100 V. Pressure was 10 mTorr and substrate temperature was 25 °C. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface composition and chemical bonding state after partial etching or overetching of the samples. And the thermal stability of observed bonding states after overetching was monitored during in-situ heating in XPS chamber. The observed spectra were compared with the data obtained from the etched - thermally grown SiO_2. Through the above analyses, the etching behaviour of porous SiO_2 could be well explained.

K-I/P21 PROPERTIES OF OXIDE-CERAMIC COATINGS ON ALUMINIUM ALLOYS SYNTHESIZED IN ELECTROLYTE PLASMA, H.M. Nykyforchyn, M.D. Klapkiv, V.M. Posuvaylo, Department of Corrosion-Hydrogen Degradation and Material Protection, Karpenko Physico-Mechanical Institute of NAS of Ukraine, 5 Naukova St., 290601 Lviv, Ukraine.

The coatings were obtained by high-temperature synthesis in plasma of spark discharges in the metal-electrolyte system at the electric voltage of 10^7 V/m. The physical parameters of plasma were defined, especially: temperature, electron and atom density, ionization level. The effect of alloying of aluminium alloys by copper, magnesium, silicon, zinc and lithium on the phase contents, thickness and microhardness of oxide-ceramic coatings was investigated.

Coatings consist of α–, γ– and δ-phases of $AL_2 0_3$. In the case of alloying by silicon AL_2SiO_5 is formed as well. Maximum thickness of the coating reaches 500 µm. The coatings of the thickness of 150-220 µm and the microhardness of 15-36 GPa (depending on alloying type) were formed when the values of the cathodic and anodic current densities and treatment duration were respectively: 1.5 during 60 min or 0.9 during 120 min. The coatings obtained on the lithium-containing aluminium alloys have the highest microhardness. The total fraction of copper and magnesium must not be less than 3.5%. The oxide-ceramic coatings, synthesised in electrolyte plasma, are dielectric and have high resistance to wear and corrosion .

K-I/P22 STRUCTURAL STEELS SURFACE MODIFICATION BY MECHANICAL-PULSE TREATMENT FOR CORROSION PROTECTION AND WEAR RESISTANCE, H.M. Nykyforchyn, V.I. Kyryliv, Dz.V. Slobodjan, Ju.M. Kovalj, Department of Corrosion-Hydrogen Degradation and Material Protection, Karpenko Physico-Mechanical Institute of NAS of Ukraine, 5 Naukova St., 290601 Lviv, Ukraine.

The mechanical-pulse treatment is an advanced method for improving physical and mechanical properties of surface layers of machine elements This method is based on the use of high speed pulse heating to surface layers in the friction contact zone. The contact of a special instrument,which rotates at the speed of 70...90 m/s, with the treated component provides a fast heating rate of the order of $10^5...10^6$K/s to the temperature over Ac_3 as well as plastic deformation rate of $10^3...10^4 s^{-1}$. Duration of action of maximum temperatures is $(6...10)10^3$ s. A special liquid is supplied to the treatment zone. Under these conditions, the microstructures of surface layers of iron-carbon alloys has a microhardness of 6...8 GPa.

During the treatment it is possible to change the chemical composition of the surface layers in depth of 50...100 µm by saturation of alloy elements (carbon, nitrogen, copper, chromium, nickel, boron) from special technological media. In this conditions the strengthening layer becomes 50...500 µm in thick and it's microhardness and the surface roughness increase up to 8...14 GPa and 0.4...2.5 µm respectively. This mechanical-pulse treatment provides a significant improvement in the corrosion and wear resistance of machine components.

K-I/P23 EVALUATION OF THE WEAR RESISTANCE OF ZrN COATINGS USING THIN LAYER ACTIVATION, J. Vinhas, F. Lanza, C. Brugnoni and M.F. Stroosnijder, Institute for Advanced Materials of the Joint Research Centre-European Commission, 21020 Ispra (VA), Italy.

Zirconium has an excellent biocompatibility and could thus be used for biomedical applications. However, its tribological properties are rather poor. In order to overcome this drawback a ZrN coating was prepared by thermal nitruration of Zircalloy 2. Wear tests using a pin on disk tribometer in a Ringer solution were very promising. A test of 1000 meter with an applied weight of 10 N showed a material loss of less than 0.1 mg. In order to obtain reliable numerical data and avoiding very long tests, the Thin Layer Activation (TLA) method was used. The principle basis of TLA is the creation of radionuclides in a surface layer to a well defined depth of a selected area, by exposure to a high energy charged particle beam. Any loss of activated material due to a surface degradation process, like wear or corrosion, will result in a decrease in γ-activity of the component. TLA offers various advantages, which include high sensitivity. The results indicate that TLA can contribute significantly to monitor surface degradation of these very wear resistant coatings.

K-I/P24 EFFECT OF THERMAL CYCLING ON THE MICROSTRUCTURE OF HVOF SPRAYED WC-CrNi COATINGS, F. Mor, Politecnico di Milano, 20133 Milano,Italy, I. Natali-Sora, Università di Brescia, 25123 Brescia, Italy, G.M. La Vecchia, Università di Brescia, 25123 Brescia, Italy, D.Doni, Flame Spray, Roncello, Milano, Italy.

In order to increase the service life of the coating components is fundamental an appropriate choice of the chemical composition of the powders and the optimization of the coating microstructure in terms of porosity, oxide inclusions and percentage and distribution of carbides. Furthermore the life of the HVOF coated parts can be affected by the service thermal history (temperature, holding time, environment).

In the present work WC-CrNi coating prepared with High Pressure High Velocity Oxy-Fuel (HP-HVOF) thermal spray method, have been studied by X-ray diffraction and scanning electron microscope techniques. The effect of different thermal cycles executed in the range 300-1073 K on the coating microstructure have been investigated. Microstructural examinations have been carried out by SEM and EDS both on the starting powders and on the cross section of the coatings before and after the heat treatments.

K-I/P25 THE COMPARATIVE ANALYSES OF S OR Se PASSIVATED GaAs (100) SURFACES, Seung-Hoon Sa(1), Min-Gu Kang(1), Hyung-Ho Park(1), Kyung-Soo Suh(2), and Kyung-Hui Oh(3), (1)Dept. of Ceramic Eng., Yonsei Univ., 120-749, Seoul, Korea, (2)ETRI, Taejon, (3) National Institute of Tech. & Quality, Kwachon, Korea

The high surface density and surface recombination velocity of GaAs and other III-V compound semiconductors are major constraints in the development of high speed electrical and optical circuitry. To overcome the above limits, the passivation with sulfur or selenium has been studied and it is found to be effective in improving the surface properties.

In this study, we report the chemical bonding states and the stabilities of S or Se treated GaAs using aqueous S or Se solutions through air exposure and thermal treatment under ultra high vacuum condition. The changes of bonding characteristic and surface state density were observed using X-ray photoelectron spectroscopy and photoluminescence. It was observed that the content of passivated S or Se in GaAs surface mainly depends on the surface state of cleaned GaAs before the passivation and As-S or As-Se bonds were dominant. The Se-treated surface showed fast decomposition of passivation layer after the air exposure. And during the thermal treatment, As-S or As-Se bonds were converted to Ga-S or Ga-Se bonds. The difference in the passivation effect of S or Se was attributed to the differences of bond strength between S or Se and GaAs, electronegativity, and ionic size.

K-I/P26 ANISOTROPIC ETCHING BEHAVIOR AND SURFACE STATES IN REACTIVE ION ETCHING OF TiW DIFFUSION BARRIER WITH SF$_6$ AND Cl$_2$ PLASMA. Il-Sup Jin (1), Seok-Joo Wang (1), Hyung-Ho Park(1), Chang-Il Kim(2) and Sang-Gi Kim(3), (1)Dept. of Ceramic Eng., Yonsei Univ., 120-749, Seoul, Korea, (2)Dept. of Electrical Eng., Anyang Univ., (3)ETRI, Taejon, Korea.

TiW is used as a diffusion barrier between silicon and metal contact for preventing the interdiffusion. In the etching of TiW, selectivity and anisotropy are necessary to adapt TiW to integrated circuit. And these etching behavior could be obtained by using the mixture of halogen based gases such as SF$_6$ and BCl$_3$. In this work, the surface states of horizontally or vertically etched plane of patterned or unpatterned TiW film have been investigated after reactive ion etching using SF$_6$ gas. The chamber pressure was varied and additional Cl$_2$ gas was introduced to study the anisotropic etching behavior. Chemical bonding states and composition of the etched TiW surface including the sidewall were analyzed by X-ray photoelectron spectroscopy and Auger electron spectroscopy. Anisotropic behavior was measured by cross- sectional observation of patterned TiW film after etching using scanning electron microscopy. The composition of surface residue was changed with the etching condition. The degree of anisotropy was dependent on the content of the additional Cl$_2$ gas.

K-I/P27 INVESTIGATION ON THE STRUCTURAL DISTRIBUTION OF S OR Se PASSIVATED GaAs (100) SURFACES, Seung-Hoon Sa(1), Hyung-Ho Park(1), Kyung-Soo Suh(2) and Jong-Lam Lee(3), (1)Dept. of Ceramic Eng., Yonsei Univ., 120-749, Seoul, (2)ETRI, Taejon, (3)POSTECH, Pohang, Korea.

Passivation of surface for stabilizing it during device process is a crucial issue in the development of compound semiconductor technology. It has been announced that the improvement of electronic properties of GaAs device is obtained by passivating the surface with chalcogen atoms such as S or Se However the nature of S or Se passivated GaAs surfaces was not the same and the characterization of the terminated layer structure on an atomic scale was urgently needed. In this work, we performed a study on the structural distribution of S or Se passivated GaAs surfaces using angle resolved X-ray photoelectron spectroscopy (ARXPS), and Rutherford backscattering spectrometry (RBS). The passivation of GaAs with aqueous S ofrSe solutions have been carried out in a glove box system under controlled atmosphere with nitrogen. Layer attenuation model was adapted for the simulation of passivated GaAs surfaces using the variation of photoelectron intensities with take-off angle. ARXPS studies showed that the surface is terminated with about one monolayer of S or Se. Also diffraction effect from the S or Se passivated GaAs surfaces were discussed. RBS channeling spectra supported the results of photoemission studies by observing the adsorption sites of S or Se in the passivated GaAs surfaces.

K-I/P28 MECHANISMS OF TRANSFERING THE SUBSTANCE IN FRICTION PROCESS IN TRIBOLOGY SYSTEM : POLYMERIC COMPOSITE-METAL, L. Starczewski, J. Szumniak, Materials Engineering Laboratory WITPiS, PO Box 1, 05-070 Sulejowek, Poland.

Polymeric composites are used in brake pads, brake linnings, brake couplings etc. These elements work in variable environmental conditions. Sometimes, outside of tribology system the temperature is about 60°C below 0°C but inside of this area, the temperature attains often 700°C or more. It's demanded, that coefficient of friction in these circumstances must be stabile in spite of the wear resistance less than 10^{-7}m^3/MJ. How it was shown in works performed by the authors, the process of forming the structure and property of these layers depends on intensity of reduction and transfer of organic and nonorganic composite's components of the contacted metal. The kind of transfer and the quantity of substance transfered in friction process, determine the friction properties of tribology connections. Controlling of tribology properties of these kind of connections is possible by selecting suitable composition of its elements. This fact was confirmed by model scale laboratory experiments and experiments which were realized in close to real conditions The obtained results prove the reality of the advantageous or destructive influence of substance transfer in the friction process on tribology properties of the connection: metal-polymeric composite.

K-I/P29 MAKING OF SPECIFIC ELECTRODES BY C.V.D., M'Barek Amjoud and F. Maury, ENSCT, 118 Route de Narbonne, 31062 Toulouse, France, and S. Soukane and P. Duverneuil, ENSIGC, 18 chemin de la Loge, 31078 Toulouse, France.

To realize specific electrodes several techniques can be employed, but Chemical Vapor Deposition is a suitable technique to control the quality of the deposited layers. We have deposited layers of tin oxide on titanium substrates from an organometallic source ($(C_2H_5)_4Sn$) by CVD. The experimental study will be presented with the description of the reactor and the deposition results for different operating conditions (temperature and composition of the inlet gas). A model taking into account hydrodynamics and heterogeneous reaction has been built to predict the deposition rate distribution. After a procedure of identification between experimental results and modeling predictions, a kinetic law has been established to represent the deposition rates.

In a second step the SnO_2 layers realized by CVD have been used as specific electrodes to study electrosynthesis reactions. The performances of the electrodes have been related to the conditions of SnO_2 layer deposition.

K-I/P30 COMPARISON OF ELECTROLESS COPPER PLATED ON ALUMINA PHOTO-ACTIVATED FROM CHLORINATED AND NON-CHLORINATED PHOTOCHEMICAL COATINGS, D.J. Macauley, P.V. Kelly and G.M. Crean, National Microelectronics Research Centre, Lee Maltings, Prospect Row, Cork, Ireland.

Photo-activation processes using a wide variety of photochemical coatings as activation precursors have been reported in recent years. Halide impurities are known to impair the solderability performance of metallisations. This work presents a comparison of the performance of chloride-based and chloride-free electroless copper metallisations on alumina ceramic substrates, photo-activated using both a chlorinated photo-activated precursor and a non-chlorinated derivative of that precursor.

The chlorinated activation precursor is found to be less susceptible to photolysis under a 222 nm excimer lamp, compared to its non-chlorinated derivative. UV spectral studies are presented.

Adhesion, resistivity and solderability results for the metallisations are presented, comparing the chloride-based and chloride-free electroless copper solutions.

K-I/P31 COVERING FROM POLYIMEDES OF A VARNISH, V.D. Kravtsova, B.A. Zhubanov, Head of Lab. of Syntheses of Polyimers of ICS MS-AS RK., Valihanov Street 106, 480100 Almaty, Kazakhstan and K.K. Bekmagambetova, D.D. Akhmettaev, Almaty Power Institution, 480067 Almaty, Kazakhstan.

New PIS of alicyclic structure were obtained.They form thin elastic films which can be used for protection of surfaces (metallic, ceramic) from corrosion. There were investigated their physical-mechanical, electrical, chemical, heatphysycal properties. Effect of γ–irradiation on some properties of polymers is shown. Polyimides of alicyclic structure can form films of different thickness: from n- 10^{-5} till 10^{-2} m.

There PIS were obtained by the reaction of one-stage policondensation of alicyclic dianhydrides with different diamines in the amidic solvents at the temperature interval 80-120 C. Imidization degre can be regulated.

Areas of application of these polymers are not limited only defending of surfaces from different factors. Polyimides of alicyclic structure also can be recommended for membrane technology, electronics and electrotechnics.

K-I/P32 MEASUREMENT OF REFRACTIVE INDEX PROFILES OF INHOMOGENEOUS OPTICAL COATINGS BY ELLIPSOMETRY, D.A. Tonova and J.E. Karmakov, Department of Condensed Matter Physics, Sofia University, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria.

Ellipsometry is applied for measurement of refractive index profiles of some transparent optical coatings. The refractive index gradient reflect an inhomogeneity in the microstructure (presence of voids) or a variation of composition of codeposited coatings. A recently developed numerical procedure for ellipsometric data interpretation for inhomogeneous layers is used. It works directly with continuous functions and thus avoids a discrete multilayer representation of the gradient coating. It retrieves refractive index depth profiles from multiple angle of incidence ellipsometry data. Void distribution profiles or compositional profiles of gradient coatings are determined from variable angle of incidence spectroscopic ellipsometry data. Functional relationship between microstructure or composition and optical constants of the material is modelled via effective medium theory. An analysis of accuracy and reliability of ellipsometric measurements is performed.

K-I/P33 COMPARISON OF THE STRUCTURE AND PROPERTIES OF PVD COATINGS ON W-Mo-V-Co HIGH-SPEED STEELS, L.A. Dobrzanski and M. Adamiak, Silesian Technical University, Division of Tool Materials and Computer Techniques in Metal Science, ul. Konarskiego 18a, 44-100 Gliwice, Poland.

Wear protection using coatings consisting of thin layers of mechanically resistant materials (hard coatings) have proved very successful and now is well established. On the other side investigations concerned with a role of chemical composition and heat treatment on properties of high-speed steel s leaded to elaborate new type of W-Mo-V-Co high-speed steels with increased contents of Si. The aim of the work was to compare a structure and properties of anti-wear PVD hard coatings deposited on the new type of high speed steel as well as a conventional high speed steel. To find out the structure and a chemical composition of coatings and inter-layers, X-ray, SEM and GDOS respectively were used. Investigation of mechanical properties shown that coatings have high microhardness and good adherence to the substrate, moreover an erosion test using air jet machine shown that Ti(C,N) arc evaporation coatings ensure the best erosion resistance. Based on these findings it is concluded that PVD coatings deposited on the new type of high-speed steel have the same properties like for the conventional type.

K-I/P34 WORKING CHARACTERITICS OF TWO UB MAGNETRON SPUTTERING DEVICES OF TYPE II, S. Groudeva-Zotova, Institute of Electronics, BAS, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.

The unbalanced (UB) magnetron sputtering devices of type II offer the possibility for ion-assisted vapour deposition of films and coatings with higher density and improved mechanical and protective properties. The peculiarities of the magnetic systems used in such devices can be decisive for most of the operational characteristics of the magnetron discharge, as well as for the possibilities for directing part of the plasma towards the substrates and realizing of ion bombardement of the growing film.

The aim of this study is to compare the working characteristics of a planar circular d.c. magnetron sputtering device in which two magnetic systems with different degree of unbalancing of type II have been alternatively used. The experiments were carried out in the pressure range $p_{Ar} = 0.2 - 1$ Pa, the specific discharge power was varied in the interval n = 1 -10 W/cm^2 and the used targets were 52 mm discs of Cu, Cr and C.

The comparative analysis of the ability of the sputtering devices for ion-assisted deposition is made on the basis of the following experimental results: 1/ Discharge characteristics of the magnetrons at different p_{Ar} and for different target materials; 2/ Measurements of some basic parameters characterising the plasma in the area of the substrates made by a 10 cm Al disk as a probe of the average behaviour of the discharge, incl. the floating potential and the substrate current at grounded or biased substrates.

K-I/P35 STRUCTURE PHASE ANALYSIS AND CHANGES OF ELEMENT COMPOSITION IN SYSTEM Cr/Fe, Zn/Fe, Cr/Al/Fe, A.D. Pogrebnjak, N.I. Shumakova, V.V. Sushko, Sumy Institute for Surface Modification, 17 av. T. Shevchenko, P.O. Box 163, Sumy, Ukraine.

Recently new methods of production of modified layers and deposition of thin films on steels with the purpose to improve their operational characteristics have been developing. Using relatively simple system Cr/Fe, Zn/Fe, Al/Fe, Cr/Al/Fe, which had been obtained from a salting melt, high current electron beam mixing was realized in this works. Parameters of the beam were: E mean = 10 to 20 KeV, pulse duration of 0.8 to 2 μs, energy flow of 3 to 14J/cm^2. SIMS, TEM, diffraction x-ray techniques were applied for our investigations. A fraction of the samples was subjected to RBS as well as measurements of microhardness, friction coefficient and corrosion resistance. Preliminary covering deposition from a melt and further thermal annealing during 6 hours resulted in formation of Cr_2Al, $CrAl_5$, Cr_5Al_8, Fe_2al_5, $FeAl_3$. After HCEB treatment under melting regime (and partial evaporation) a spectrum of structures demonstrated more phases and nano-dispersed layers formed, amorphous layers were also possible.

K-I/P36 IN SITU INFRARED ELLIPSOMETRY STUDY OF SUBSTRATE PREPARATION, GROWTH AND PROPERTIES OF A-SiO_2 THIN FILMS, N. Bertrand, P. Bulkin and B. Drévillon, Laboratoire de Physique des Interfaces et des Couches Minces, UPR 258 du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Due to its sub-monolayer sensitivity, in situ infrared (IR) ellipsometry is excellent tool to monitor plasma-surface interactions. We have shown in real time the removal of native oxide from stainless steel surface by H_2 plasma produced in a novel high-density planar plasma reactor. This plasma treatment is also found to be effective in the elimination of hydrocarbon contaminations, as demonstrated by studying the CH_2 and CH_3 vibrational stretching modes. In situ IR ellipsometry is used to establish mechanism of the plasma enhanced deposition of a- SiO_2 films from SiH_4+O_2 mixture. Study Si-O and Si-OH bonds gives the information about the interface and surface properties, respectively. Growth rates exceeding 2 nm/sec for non-porous stoichiometric material are obtained using optimal gas flow ratios at room temperature and without external bias. The growth mechanism of SiO_2 films and the relevance of in-situ IR ellipsometry as a tool for the analysis of evolution of vibrational properties during the growth are discussed.

K-I/P37 APPLICATIONS OF DIAMOND-LIKE CARBON THIN FILMS, A.H. Lettington, JJ Thomson Physical Laboratory, The University of Reading, Whiteknights, PO Box 220, Reading RG6 6AF, U.K.

This paper reviews the current state of published work relating to the use of diamond-like carbon (DLC) coatings in a range of optical, mechanical, electronic and biomedical applications. DLC does not have a unique composition but consists of structure of amorphous and crystaline phases. Its properties vary considerably with deposition conditions but it can be deposited cheaply over large areas on a variety of substrates.

DLC films can be exceedingly hard. Values in excess of 3000 kg mm^{-2} have been reported for its knoop hardness. In addition the materials usually have a low coefficient of fruition and are chemically durable. This makes them excellent candidates for a variety of wear-resistant applications. The films are generally absorbing in the visible but have good transmission in the infrared region of the spectra and are used for a number of infrared application. There have been a number of electronic applications of DLC reported in the literature. These range from photoemissive to electron emissive devices as well as acting as a resist for high resolution photolithography of semiconductor surfaces. Preliminary tests with DLC have shown an encouraging degree of biocompatibility and trials are underway on coated prostheses.

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-Midi

Poster Session II
16:20-18:30

K-II/P1 NICKEL ALUMINIDE THIN FILM FABRICATION VIA ION BEAM SPUTTERING OF COMPOUND TARGETS, S.C. McGuire and J.D. Sulcer, Ward Laboratory, Cornell University, Ithaca, New York 14853, USA.

We report recent results from our use of Kaufman-type ion beam sputtering to fabricate boron-doped nickel aluminide thin films on substrates of Si, NaCl, alumina and polycarbonate resin plastic. Compound targets of Ni_3Al were bombarded with ~ 1 keV Ar ions to form films having thicknesses up to 1900Å and areas of approximately 2.5 cm x 2.5 cm. Nondestructive measurements of film and target composition have been performed using X-ray fluorescence (XRF) spectroscopy and instrumental neutron activation analysis (INAA) for determining major and trace elements. X-ray diffraction and interference microscopy are being employed to investigate crystal structure, grain sizes and residual film stress. Monte Carlo simulations of the compound target sputtering process, taking into account primary ion energy, target surface binding energy, beam-target angle and anisotropy of sputtered species, are compared with film composition as determined by INAA and XRF. Results from these measurements comprise complementary data for investigating boron distributions in the films via neutron depth profiling.

*Work supported in part by U.S. Department of Commerce, NIST, Chemical Sciences and Technology Laboratory, Gaithersburg, MD 20899.

K-II/P2 DETAILED MODEL ON AMORPHOUS Al-Pt PHASE GROWTH IN THIN FILM SYSTEMS, Zs. Radi, P.B. Barna, Research Institute for Technical Physics, P.O. Box 76, 1325 Budapest, Hungary.

We present amorphous phase growth model in Al-Pt thin film system prepared by high temperature successive deposition (HTSD) at various experimental conditions. Our theory is based on detailed TEM, XTEM and SAED investigations.

The model contains short explanation for quasi two-dimensional phase formation on the sample surface during Pt deposition, as well as describes the modes of diffusional Al transport in the newly developed Al-Pt phases. Theoretical calculations, according to the experimental results, prove the existence of critical thickness (L_{C1}) of the amorphous phase. Related phenomena of crystalline phase nucleation (Al_3Pt_2) and amorphous ⇒ polycrystalline phase transition are treated in separate part of the model. Additionally, the diffusional limitation of the growth of coexisting amorphous - polycrystalline phases could be explained and characterised by the second critical thickness (L_{C2}).

L_{C1} depends weakly on experimental parameters, why L_{C2} shows strong dependence on substrate temperature and Pt deposition rate. It will be shown, that various thin film structures - e.g. thick (250 nm) pure a-Al_2Pt surface coatings - can be tailored by using different parameter ranges. This work was partly supported by the Hungarian - German Intergovernmental S&T Cooperation Program under project number OMFB TÉT D-124.

K-II/P3 STUDY OF DIAMOND-LIKE CARBON FILMS FOR PROTECTIVE COATINGS, V.Kh. Kudoyarova,(1) A.V. Chernyshov(1), T.K. Zvonareva(1), N.B. Dzhelepova(1), M.B. Tsolov(2), (1)A.F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia, (2)Central Laboratory of the Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

Interest in investigaion thin films of diamond-like carbon (DLC, a-C:H) has been motivated by the unique properties of this material and the demand of modern technologies. Development of low-temperature methods ($T_s < 200$ °C) of producing DLC films used as protection cover layers is of practical interest. In this work a-C:H films were prepared by low- temperature deposition by using two methods: magnetron sputtering and rf decomposition of a mixtures of gases (10% CH_4+90%Ar).

A comprehensive investigation of the composition, structure, optical and electrical properties of a-C:H films was performed from the standpoint of the requirements which protective coatings for electrophotograhic information carriers and stable protector for Ag- based optics must meet. The investigation of the composition and structure was performed by elastic recoil detection (ERD), resonance nuclear reaction $^{16}O(\alpha, \alpha)\,^{16}O$ and Raman spectroscopy. The optical properties (the transparency over a wide spectral range and the refractive index) were determined by means of IR - spectroscopy and ellipsometric measurements. It was shown that solid, diamond-like a-C:H films (DLC) can be obtained with low-temperature deposition.

It was shown that a protective DLC coating incrcases the storage time in the air and the strength properties of the a-Se electrophotographic information carriers. It was determined that a protective DLC coating is an effective and stable protector for Ag-based optics from an attack of active sulfide .

K-II/P4 DEPOSITION OF COVERINGS AND FILMS MADE OF CERAMICS, SEMICONDUCTORS, METALS ON METALLIC TARGETS, A.D. Pogrebnjak (1,2), (1)Sumy Institute for Surface Modification, Av. Shevchenko 17, P.O. Box 163, 244030 Sumy, Ukraine, (2)Sumy State University, Department of Physics and Electronics, 244007 Sumy, Ukraine

A review of works investigating Al_2O_3, BrN, TiN, ZrO_2, ZnS covering deposition on metallic materials using ablation of surface layer with the aid of high power ion beams (HPIB) and low-energy high current electron beams (LEHCEB) on a cold and hot substrates of stainless steel, metals and single crystals is presented. Beams of nanosecond and microsecond duration having a high deposition rate from 0.1 to 1.5 μm per impulse over an area from 100 to 1000 cm^2 have been used. Regularities of formation of amorphous nano-crystallic and poly-crystallic films and coverings have been considered and a comparison with other methods of covering deposition is presented. A promising perspective of covering and film deposition using pulsed beams for technological purposes has been demonstrated and an effect of stoichiometry of films on changes of mechanical properties has been considered.

K-II/P5 PROCESS PARAMETER OPTIMIZATION FOR TiN AND TiC FORMATION USING REACTIVE ION BEAM ASSISTED DEPOSITION AND SOME APPLICATIONS, L. Guzman, CMBM, 38050 Povo (TN), Italy, M. Bonelli and A. Miotello, Dipartimento di Fisica, Universita' di Trento, 38050 Povo (Trento), Italy

Titanium was electron-beam evaporated in an atmosphere of nitrogen and/or acethylene onto various substrates at ambient temperature. During condensation it was irradiated with 30 keV energy N_2 ions. Process parameter optimization to obtain TiN and TiC of required stoichiometry was carried out. The composition of the films was studied using secondary neutral mass spectroscopy. Important result obtained was that TiN can be formed by deposition of Ti in reactive atmosphere of N_2 gas, even without ion bombardment. Whereas to form TiC, in reactive atmosphere of C_2H_2, ion bombardment is necessary. The role of ion bombardment in the mechanism of TiC formation is not yet understood. Indications are that it suppresses TiH formation and helps to remove oxygen from the film. Scratch tests and microhardness measurements were carried out on the specimens. The films were used in applications as barriers to hydrogen permeation in steels and as biocompatible coatings on dentist implants and orthopaedical prostheses.

K-II/P6 CORROSION PROTECTION OF AN AISI 321 STAINLESS STEEL BY SiC COATINGS, J.P. Rivière, J. Delafond, Laboratoire de Métallurgie Physique, UMR 6630 CNRS, Université de Poitiers, SP2MI, 86960 Futuroscope Cedex, France, and P. Misaelides, F. Noli, Department of Chemistry, Aristotle University, 54006 Thessaloniki, Greece

SiC coatings of various thicknesses (100 nm - 800 nm) were prepared at room temperature (RT) or at temperatures up to 750° C by ion beam sputtering of a SiC target. The growing films could be continuously bombarded with a 160 keV Ar$^+$ ion beam and the influence of this dynamic ion mixing on both the structure and corrosion resistance was investigated.

The chemical composition of the coatings was determined by Rutherford Backscattering and Nuclear Reaction Analysis. The microstructural state of the coatings was investigated by High Resolution Transmission Electron Observations whereas their density was obtained by X-Ray reflectometry. Passivation/corrosion tests of the coated and uncoated AISI 321 steel were performed in 1NH$_2$SO$_4$ solution. A considerable improvement of the corrosion resistance is observed particularly when the coatings are deposited with dynamic ion mixing.

These results are discussed in relation with the interface mixing and the densification effect produced by the high energy ion bombardment.

K-II/P7 NANOINDENTION CHARACTERIZATION OF SiC COATINGS PREPARED BY DYNAMIC ION MIXING, J. Woirgard, J.C. Dargenton, Th. Cabioch and J.P. Rivière, Laboratoire de Métallurgie Physique, Université de Poitiers, UMR CNRS 6630, SP2MI.Bd 3, Téléport 2, BP. 179, 86960 Futuroscope Cedex, France

We have studied the influence of deposition temperature and ion bombardment on the nanoscale properties of SiC coatings on (100) silicon wafers. A SiC target was sputtered by a Ar$^+$ ion beam delivered by a Kaufman type ion source. During deposition the film was bombared with Ar ions. Hardness and elastic modulus were measured, for penetration depths ranging between 4 nm and 400 nm. The coating appeared highly elastic and the highest hardness values were obtained in mixed specimens in accordance with structural observations.

K-II/P8 THE CUBIC BORON NITRIDE FILMS PREPARED BY THE DUAL ION BEAM DEPOSITION TECHNIQUE, D.A. Golosov, I.V. Svadkovski, A.P. Dostanko, S.M. Zavadski, Belarussian State University of Informatics and Radioelectronics, P. Brovka Street, 220027 Minsk, Belarus

Dual ion beam deposition method has been used to produce cubic boron nitride (c-BN) films by sputtering from a target of hexagonal boron nitride (h-BN). The method has been realized by the ion beam system consisted of two closed-drift ion sources of the anode-layer version. The sputter beam current was varied up to 180 mA at an average ion energy between 500 and 1500eV, the bombarding beam current was in the range 20 - 180 mA at an average ion energy between 400 and 1200 eV. The Ar/N$_2$ ratio in the bombarding beam was varied from 0 to 3. BN films have been deposited on heated (50-700° C) silicon surfaces.

Infrared (IR) absorption spectroscopy and transmission electron microscopy (TEM) were used to study the properties of the resulting films. The effects of varying ion current density, ion energy, Ar/N$_2$ ratio and substrate growth temperature have been investigated.

K-II/P9 MIXING PROCESSES IN SYSTEMS Ta/Fe AND Mo/Fe, V/Fe, Ni/Fe AS A RESULT OF PULSED HIGH CURRENT ELECTRON BEAM TREATMENT, A.D. Pogrebnjak(1), A.V. Valiaev(2), O.G. Bakharev(3), Yu.F. Ivanov(4), S.V. Plotnikov(2), V.V. Sushko(1), (1)Sumy Institute for Surface Modification, P.O. Box 163, Av. Shevchenko 17, 244030 Sumy, Ukraine, (2)East-Kazakhstan University, c.Ust-Kamenogorsk, Kazakhstan, (3)Hakasskiy State University, Physical Faculty, Russia (4)Academy of Engineers and Building, Tomsk, Russia

Using RBS, AES, SEM, RFM, CEMS and microanalysis, systems of refractory film-iron which had been subjected to low-energy high-current electron beam (HCEB) treatment were considered. These systems are strongly different in their thermal-physical and thermal-dynamical properties. Melting dynamics of these systems has been calculated, cooling rate and coefficient of mass-transfer (diffusion) have been determined after electron beam treatment. It has been found that an amorphous structure is formed in a surface together with an oxide film. Deeper one finds a nano-crystal structure and intermetallic phases, which are followed by a sublayer of high dislocation density of 6 to 8 x 10^{10} cm^{-2} and solid solutions. A thickness of hardened layer, which plays an important role in increasing corrosion resistance, decreasing brittle wear ability, increasing hardness and fatigue resistance, amounts from several microns to 15 µm depending on the energy flow.

K-II/P10 INFLUENCE OF ION TREATMENT OF THE SUBSTRATE ON THE PHYSICAL AND MECHANICAL PROPERTIES OF THE COATINGS, V.V. Khodasevich, L.A. Solodukhin, V.V. Uglov, B. Rauschenbach, Belorussian State University, pr. F. Scoriny 4, 220050 Minsk, Belarus.

In this paper, influence of substrate surface irradiation by argon ions on the physical and mechanical characteristics of titanium nitride coatings was investigated. Carbon steel plate were used as the substrates. Irradiation by Ar$^+$ ions was being realized with energy of 30 keV up to dose of 5.10^{16} ions/cm^2 . Coatings were deposited using cathodic are sources of plasma. Coating thickness did not exceed value of 0,3 µm. By means of Auger electron spectroscopy, composition profiles were analyzed after two successive stages of the coating deposition: surface cleaning by Ti ions (for transitional layer formation) and TiN coating formation. Influence of preliminary irradiation of the substrates by Ar$^+$ ion on concentration and redistribution of the elements near coating/substrate interface is considered. Tribology tests have shown that TiN coatings, formed on the preliminarily irradiated substrates, have improved mechanical properties as compared with coatings deposited on the unirradiated substrates.

K-II/P11 IRON MICRO/NANOHARDNESS AFTER SINGLE AND DOUBLE IMPLANTATION BY NITROGEN AND BORON IONS, V.V. Uglov(1), A.K. Kuleshov(1), J.A. Fedotova(1), V.V. Khodasevich(1), B. Rauschenbach(2), A. Koniger(2), C. Hammerl(2), (1)Belarussian State University, Department of Solid State Physics, 220080 Minsk, Belarus and (2)Universität Augsburg, Institut für Physik, 86135 Augsburg, Germany.

Modification of micro and nanohardness of iron after monoelemental and successive boron and nitrogen implantation at different iron sequences together with the influence of postimplantation annealing was investigated. Implantation energy was 30 keV and 40 keV for nitrogen and boron respectively. Dose and current density of implantation did not exceed the value of 1.2 *10^{17} ions/cm^2 and 3.5 mA/cm^2 correspondingly. It was established that successive implantation with subsequent annealing at 850 K leads to nanohardness increase by factor of two in the area of average projectile range of B and N ions in comparison with monoelemental implantation. Nanohardness increase is attributed to the formation of thermostable compound ε-Fe$_{2+x}$(B,N) with 0<X<l in 80 mn surface layer.

K-II/P12 COMBINED USE OF ION BEAM BASED TECHNIQUES FOR TiN THIN FILMS CHARACTERIZATION, M. Balaceanu, National Inst.for Laser, Plasma and Rad. Phys., D. Pantelica, P.M. Racolta, C.I. Muntele, L. Popa-Simil, Inst.of Ph.and Nucl.Eng.-H. Hulubei, P.O.Box MG-6, 76900 Bucharest, Romania.

The TiN thin films, are used in applications like growing up of wearing resistance, optical and decorative coverings and as a diffusion barrier in VLSI integrated circuits. This TiN layers were obtained by a hallow cathode discharge deposition method . To characterize the thickness and stoichiometry of the layer, we use Rutherford Backscattering Spectrometry (RBS) method. Some various depositions and heat treatment conditions have been determined aiming to obtain data concerning TiN coatings as a diffusion barrier on silicon samples. The Thin Layer Activation (TLA) and Recoil Implant Techniques was used to put radio-tracers in the surface of different samples covered with TiN.The experimental data concerning the wear level was obtained on a Timken testing stand and our nuclear method was compared with the conventional ones.

+Partially supported by The Dept.of Research and Isotopes, IAEA, Vienna, Austria.

K-II/P13 MICROSTRUCTURE AND COMPOSITION OF TITANIUM NITRIDE FILMS FORMED ON TiA16V4 BY NITROGEN PLASMA IMMERSION ION IMPLANTATION, M. Rinner, K. Volz, W. Ensinger, B. Stritzker, B. Rauschenbach, Universität Augsburg, Institut für Physik, 86135 Augsburg, Germany, W. Assmann, Sektion Physik, Universität München, 85748 Garching, Germany.

TiA16V4 is a material which is used in aerospace and in biomedical applicalions. For these applications, the tribological properties often are not sufficient. These can be improved by implanting energetic ions in the near-surface zone. They change the microstructure and may form ceramic films such as TiN. In order to form a protective film, TiA16V4 samples were treated by plasma immersion ion implantation in a nitrogen plasma formed by ECR microwave excitation. This treatment resulted in formation of a TiN film with light golden colour. Pin-on-disc measurements showed that wear resistance increased with the process time, indicating that the film offers tribological protection.

The TiN films were analyzed for their composition by elastic recoil detection analysis. Phase formation and structure were determined by X-ray diffraction and cross-sectional transmission electron microscopy. The results show the dependence of the nitrogen content on the number of high voltage pulses, correponding to process time. The nitride grows in small crystallites with preferential crystallographic orientation on the large substrate grains. The results are correlated with the process parameters and discussed in terms of interaction of the ions with the solid material.

K-II/P14 HIGH QUALITY CONDUCTIVE In_2O_3<Sn> and RuO_2 LAYERS GROWN BY MAGNETRON SPUTTERING, R. Butkute, V. Lisauskas, B. Vengalis, Semiconductor Physics Institute, Gostauto 11, 2600 Vilnius, Lithuania.

Thin (d =0.2-0.5 μm) In_2O_3 < Sn > (ITO) and RuO_2 layers of various crystalline quality were grown by DC magnetron sputtering on various crystalline substrates. Crystallinity of the films was investigated by XRD and reflected high energy electron diffraction (RHEED). It was found that the highest quality epitaxial ITO layers may be grown at 500-750°C on (l00) (110) and (211)-axis oriented YSZ and MgO(l00), meanwhile similar RuO_2(011) layers grow epitaxialy at 400-750°C on α-Al_3O_3(1102). Carrier density and their mobility for the films prepared at various deposition conditions were evaluated from electrical conductivity, Hall effect, optical reflectance and transmittance. The thermal stability of the layers (in air atmosphere) was investigated by high temperature XRD. Stoichiometry variation of the ITO layers occuring with their annealing at various temperatures and oxygen pressures was investigated from in-situ resistivity measurements. Two limiting processes, namely, diffusion of oxygen vacancies and oxygen adsorption by film surface have been taken into account to explain the observed resistivity kinetics.

K-II/P15 MICROHARDNESS AND ADHESION MEASUREMENTS OF REACTIVELLY SPUTTERED TiAlN MULTILAYER COATINGS DEPOSITED AS FUNCTION OF MASS-FLOW OF NITROGEN, I. Manika and F. Muktepavela, Institute of Solid State Physics, University of Latvia, Latvia; H. Jensen, J. Sobota and G. Sorensen, Institute of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark.

Multilayer coatings of TiAlN have been deposited by reactive sputtering on a rotating substrate by controlling the nitrogen flow. Both metal rich and almost stoichiometric coatings were deposited. The rotation of the substrate holder was varied from 2 to 16 rpm resulting in bilayer thicknesses in the range 0.8-8 nm. The Vickers microhardness on soft stainless steel and hard WC substrates were measured in load range 0.01-50 N. In order to obtain true hardness values an optimal ratio of indentation depth and coating thickness was determined. Depending upon the nitrogen flow rate and bilayer thickness, hardness values 11-23 GPa were obtained. Acoustic emission scratch test measurements for adhesion determination were performed and critical load values up to 100N were obtained. These will be compared with the delamination values obtained from hardness measurements. Deposition conditions yielding high toughness and excellent adhesion will be discussed, and there will be concluded on the future perspectives of TiAlN multilayer coatings .

K-II/P16 ULTRASHARP TEXTURES IN Al/Ti LAYERED STRUCTURES, M. Adamik, P.B. Barna, Research Institute for Technical Physics, P.O. Box 76, 1325 Budapest, Hungary, and I. Tomov, Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgarie.

The application of metal underlayers for Al films is proved to enhance remarkably the texture sharpness of the films. One possible cause for this phenomenon can be the reduction of impurity incorporation into the glowing film at the beginning of growth. In this case enhanced grain growth can take place in the stage of coalescence which results in enhanced texture. The other cause can be that the film growing on the underlayer nucleates preferentially with an orientation of the main texture component. In the first case relatively large grained films can be expected while in the second case the grain structure is expected to show small grained morphology. In case of multilayer films the enhancement of texture is further increased, which enables the preparation of Al films with ultrasharp texture. In the present work the detailed study of the structure evolution during growth of the Al/Ti stratified films has been carried out. For this purpose various techniques of conventional and high resolution transmission electron microscopy, and x-ray diffraction measurements have been applied. The films have been studied in the different growth stages. in order to reveal the characteristics of the growth process, and the films have been measured in case of different number of Ti interlayers. The investigations show that the Al grains grow epitaxially on the Ti grains, however the film as a whole is not epitaxial. but the orientation of the grains is rotationally symmetrical.

K-II/P17 THE MECHANICAL AND TRIBOLOGICAL PROPERTIES OF Ti-C:H COATINGS, V.Yu. Kulikovsky, Institute for Problems of Materials Science, 3 Krzhyzhanovsky st., 252142 Kiev, Ukraine; and F. Fendrych, L. Jastrabik, D. Chvostova, J. Pridal, F. Franc, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18040 Praha 8, Czech Republic.

The aim of this work is to determine a correlation between the growth parameters of diamond-like coatings, with small amount of titanium, prepared by sputtering of titanium target in CH_4 + Ar gas mixture and their mechanical and tribological properties.

The composition, microhardness, internal stress, friction coefficient, adhesion and evaluation of substrate temperature dependent on methane flow rate, substrate bias and interlayers formation were studied.

It was found that increase of negative substrate bias voltage to -100 V leads to considerable increasing of layers microhardness, which slightly decreases at further bias increase to -200 V. The intrinsic stresses decreased at the same conditions due to substrate temperature growth. The best coatings had friction coefficient 0.12-0.15, microhardness 13-15 kN/mm^2 and demonstrated elastic behaviour and good adhesion. The nature and correlation of these properties is discussed.

K-II/P18 CORROSION PERFOMANCE OF DUPLE TiN COATINGS DEPOSITED BY ARC PLATING, S. Rudenja, P. Kulu, Institute of Materials Technology, E. Talimets, Institute of Chemistry, V. Mikli, Centre of Materials Research, Tallinn Technical University, Ehitajate tee 5, 0026 Tallinn, Estonia.

Titanium-based coatings deposited by PVD techniques are used routinely to improve the wear and corrosion resistance of a surface. TiN-coated stainless steel shows good corrosion resistance. Further improvement of the corrosion behaviour can be achived by the deposition of multilayer coatings, including an intermediate layer with isolator properties or another type of conductivity. The investigated single- and multilayer coatings show high values of polarisation resistance. The coatings deposited within the Ti-N, Ti-Cr-O-N and Ti-O-N systems onto austenitic stainless steel substrates (AISI 321) significantly decrease the density of the corrosion current and move the corrosion potential of coated specimens to the passivity zone of the substrate. At the same time, there is no significant difference in the corrosion behaviour of single- and multilayer coatings. The factors of structure perfection predominate over those of the electron properties of the coating materials.

As the result of investigations cathodic arc evaporation system «Bulat-Pro» was developed.

K-II/P19 TECHNOLOGICAL PROBLEMS IN INDUSTRIAL IMPLEMENTATION OF PAPVD METHODS OF INCREASING TOOLS AND MACHINES PARTS DURABILITY, J. Walkowicz, J. Smolik, K. Miernik, J. Bujak, Institute for Terotechnology, 26-600 Radom, ul. Pulaskiego 6/10, Poland.

Implementation of PAPVD technologies of hard wear-resistant coatings deposition into industry causes many different problems: technical, economic and connected with co-operation between industrial and research groups. The said problems are exemplified by vacuum-arc deposition of nitrides and carbides of transition metals on tools and machine parts for engineering industry. The most difficult problems are those connected with technology development and execution, because they must consider: the type of the tool material and the type of termochemical treatment preceding the process of deposition, variety of tool shapes and sizes as well as customer demands. It is shown in the paper that all these problems can be solved correctly only with close co-operation between the customer and coating centre. Open exchange of technical and operating information is necessary for the development of surface treatment technology, which is the best for real working conditions. This co-operation is also an important factor stimulating development of new technologies and search for new coating materials. It is pointed out that costs of technology depend on versatility of technological equipment and adequate accessories.

K-II/P20 STRUCTURAL AND MECHANICAL CHARACTERIZATION OF MULTILAYERED SPUTTERED TiN/ZrN COATINGS, C.J. Tavares(1), L. Rebouta(1), B. Almeida(2), J. Bessa e Sousa(2), S. Ramos(3), (1)Departamento de Fisica, Universidade do Minho, Azurém, 4810 Guimaraes, Portugal, (2)Departamento de Fisica, Universidade do Porto, 4100 Porto, Portugal, (3)Departamento de Eng. Mecânica (polo2), F.C.T. da Universidade de Coimbra, Pinhal de Marrocos, 3030 Coimbra, Portugal

TiN/ZrN multilayers have been deposited with combined dc and rf magnetron sputtering. Experimental XRD and computational refinement of the latter has undergone to achieve the basics to elucidate the structural properties of the mentioned multilayers. Both high angle and low angle XRD have been employed for that purpose. Special attention has been considered regarding phenomena occurring at the interface. Therefore, with the assistance of XRD refinement techniques it was possible to obtain the degree of interfacial roughness, the strain profile of the individual layers near the interface and length of interdiffusion. Through RBS, it was possible to determine the concentration profile of the multilayers and reevaluate the interfacial roughness. Mechanical properties have also been investigated. More precisely, the dynamic hardness of the multilayers, their adhesion to the high speed steel substrates and stress relaxation on the thin films.

K-II/P21 NITRIDING OF AUSTENITIC STAINLESS STEELS USING PLASMA-IMMERSION-ION-IMPLANTATION, R. Günzel, S. Mändl, E. Richter, Research Center Rossendorf, Institute for Ion Beam Physics and Materials Research, PO.Box 510119, 01314 Dresden, Germany

Nitriding of stainless steels is still an unresolved problem as the conventional methods, e.g. bath nitriding, gas nitriding or plasma nitriding, achieve an increased hardness and a reduced wear but the corrosion resistance is significantly reduced due to the formation of chromium nitrides as treatment temperatures above 550°C are necessary to obtain nitriding depths of several µm in a reasonable time. At these temperatures the passivating chromium oxide layer at the surface of the stainless steel, which acts as a diffusion barrier for the penetrating nitrogen, is irreversibly transformed into chromium nitride.

One possibility to circumvent this problem and harden stainless steels without losing the corrosion resistance is plasma immersion ion implantation (PIII) of nitrogen. Here, the samples are immersed in a plasma, and, by applying negative high voltage pulses, positive ions are accelerated from the plasma through the expanding plasma sheath and implanted behind the surface layer of chromium oxide. Hence no diffusion barrier must be overcome and a treatment temperature of 400°C is sufficient to obtain a fast diffusion.

Here we present improved hardness and wear behaviour of austenitic stainless steel (X6CrNiTiMol7.12.2) implanted with nitrogen PIII at different voltages and doses, as determined with a micro-indenter and a pin-on-disk tribometer, respectively. Compared to untreated stainless steel the hardness can be increased up to a factor 4, depending on the amount of implanted nitrogen. The wear behaviour was improved by 1-2 orders of magnitude. A layer of «expanded austenite» of up to ten µm was formed in less than one hour, as determined with GDOS. No detrimental formation of chromium nitride was observed with XRD for the samples implanted at 400°C.

K-II/P22 THE COPPER-GRAPHITE NANOCRYSTAL COATINGS, T. Kopan, V. Kopan, N. Novikov, S. Vasnov, Department of Metal Physics, Kyev Taras Shevchenko University, 6 Glushkov, 252022 Kyev, Ukraine

The wear process was studied at slide friction in steel pair of shaft-bearing. Copper-graphite coatings was created in oil suspension with nanoparticles (2-26 nm). Nanoparticles weld together to surface shaft and bearing. Mechanics alloing start-up.

The suspension feeded in slide bearing. Suspension from nanoparticles was prodused by magnetron evaporation of target (80% atomic C+20% Cu) and thermal evaporation of oil "BΨK-94» with simultaneously condensation on one surface. Nanoparticles coagulation removing. The wear process decrease in pair of friction Δd/d (d=10 mm, d-diameter of shaft) when nanoparticles concentration increase to (9-12)% in volume and grow again. The wear process Δd/d increase when nanoparticles diameters increas. If rotation velocity grow Δd/d<0. The wear process of coating is more then build up process of one. It is exist optimal condition and parameters of coating at Δd/d=0.

K-II/P23 SURFACE QUALITY OF GREY CAST IRONS IN THE CONTEXT OF NITRIDING AND OXYGEN-SULPHUR-NITRIDING, J. Baranowska, Technical University of Szczecin, al. Piastow 19, 70-310 Szczecin, Poland.

In the paper author present the influence of thermo-chemical treatment (nitriding and oxygen-sulphur-nitriding) on the state of surface for different kinds of cast irons. After nitriding of grey cast iron the strong drop of surface quality was observed which had a big importance for practical use of workpieces such as piston rings for example. The tenfold increase of R_a parameter was measured.

The results wer controlled by metalographic testings (scanning and light microscopy) an by roughness measurement. The phases compositions of the layers were evaluated by X-ray diffraction.

(...) defects creation during nitriding which had a influence on increasing roughness of cast iron surface after treatment. The dependence of roughness parameters on the shape and size of the graphite was also observed. The mechanism of nitride layer forming was discussed.

The smaller negative influence on surface quality in the case of oxygen-sulphur-nitriding was observed. Moreover the two-steps nitriding with polishing is proposed to eliminate this negarive effect.

K-II/P24 SIMULTANOUS SURFACE AND BULK TREATMENT OF HSS STEELS, B.G. Wendler, Inst. Mat. Eng., Technical University of Lodz, ul. Stefanowskiego 1, 90-924 Lodz, Poland.

A method of HSS surface and bulk hardening in a single operation has been elaborated, in which specimen of an annealed HSS steel coated with thin carbide-forming metal layer is being submitted to a unique heat treatment (in vacuum or in nitrogen atmosphere). In the result the bulk hardness of specimen is increasing to a value of 62-66 HRC and the one of the surface increases to a value of 2500- 3600 VHN (the latter due to the solid state reactions Me⇒MeC or Me⇒MeCN). At the same time the impact toughness of the steel substrate is nearly twice as great as that after conventional heat treatment of the relevant steel.

4µm thick, single, bilayer as well as multilayer carbide coatings of transition metal carbides of groups IV and V (Hf, Nb, Ta, Ti, V and Zr) with dense, ultra fine-grained uniform or modulated structure, excellent adhesion to M2, ASP23 and ASP60 HSS substrates and approximately the same smoothness of the coatings as that of the substrates before deposition have been obtained with use of the method. Durabilty of numerous HSS tools (in particular of those for cold working of metals) coated with the carbide layers according to the method was 2÷10 times greater than that for same tools without any coating.

With no pollution of the environment, very low capital investments and production costs as well as simplicity of the method makes easy its application in small factories and for short batches.

K-II/P25 POLYMERIZATION OF N-VINYL-2-PYRROLIDONE UNDER ANODIC POLARIZATION : CHARACTERIZATION OF THE MODIFIED ELECTRODE AND STUDY OF THE GRAFTING MECHANISM, C. Doneux(1), R. Caudano(1), J. Delhalle(2), (1)Laboratoire LISE, (2)Laboratoire CTSI, FUNDP, rue de Bruxelles 61, 5000 Namur, Belgium, J. Charlier, C. Bureau and G. Lécayon, CEA, DSM-DRECAM-SRSIM, 91191 Gif-sur-Yvette Cedex, France.

The application of an anodic potential to highly concentrated solutions of NVP leads to the formation of PVP films onto Pt electrodes. These films are insoluble in a good solvent of the commercial polymer. In the present contribution, we have studied the influence of the anodic polarization shape, of the working and the initial potential amplitudes on the adhesion and the quality of the formed PVP films. XPS, UPS and IRAS spectroscopies have been used to characterize the polymer films. Their thickness has been established by profilometry. In situ quartz crystal microbalance measurements show that the formation mechanism of polymer films cannot be attributed to an initiation in solution followed by precipitation of the polymer on the surface but rather to a gradual growth of the polymer on the electrode. This result is confirmed by the analysis of the electrochemical medium which does not reveal the presence of polymeric chains in solution. Both a radical and a cationic mechanism are examined to explain the grafting and the growth of polymer films. A detailed theoretical analysis of plausible reaction intermediates suggests that only the cationic mechanism is able to account for all experimental results.

K-II/P26 ELECTROSYNTHESIS OF POLY (4-VINYLPYRIDINE) FILMS ON METALLIC SURFACES UNDER ANODIC AND CATHODIC POLARIZATIONS : STRUCTURE AND PROPERTIES OF THE ORGANIC COATINGS, C. Lebrun, G. Deniau, P. Viel, and G. Lécayon, CEA, DSM-DRECAM-SRSIM, 91191 Gif-sur-Yvette Cedex, France.

We study the electrochemical synthesis of polymer films grafted on metallic surfaces in a strictly controlled aprotic medium.

In this work, we present results about a vinylic monomer : 4-vinylpyridine, which is electroactiv under anodic and cathodic polarization.

The application of both potential modes to highly concentrated solutions of monomer leads to the formation of a poly (4-vinylpyridine) film grafted on the electrode surface.

Depending on the type of electrochemical polarization (anodic, cathodic, or cathodic polarization followed by reoxidation) cationic, anionic or radical polymerization developp : properties and structure of the resulting polymer film differ.

The films are studied by IRAS, XPS and UPS spectroscopies. Growing of the polymer films are also followed by in-situ quartz crystal microbalance. Reactional mechanisms are proposed.

K-II/P27 INDIUM-DOPED TRANSPARENT CONDUCTING OXIDES OF ZrO_2, S.B. Qadri(1), H.R. Khan(2), E.F. Skelton(1), P. Lubit(1), (1)U.S. Naval Research Laboratory, Washington, D.C. 20375, USA, (2)FEM, Katharinenstrasse 17, 73525 Schwäbisch Gmünd, Germany

Optically transparent semiconducting oxides such as In_2O_3, SnO_2 and ITO (90wt.%In_2O_3 and 10wt.%SnO_2) are used for applications, such as antistatic coatings, transparent resistive heaters and electrical electrodes for flat panel display and electrochromic devices. ITO is not chemically stable at high temperatures. Recently, investigated ZrO_2-ZnO films. (l) show their chemical stability above 400 °C and good optical and electrical properties. In this study, we report the deposition of ZrO_2-In_2O_3 films by e-b evaporation and stabilized in the tetragonal phase of zirconia. The electrical resisistivity of these films can be tuned, by composition Variation. Results on their resistivites as a function of temperature and optical transparency as a function of wavelengths will be presented. (l. S.B. Qadri, E.F. Skelton, P. Lubitz, N. V. Nguyen, and H. R. Khan; Thin Solid Films 290-291 (1996), 80-83.).

K-II/P28 INFLUENCE OF THE SURFACE TREATMENT OF THE SUBSTRATE IN THE LCVD OF CN_x FILMS, A. Crunteanu, R. Cireasa, R. Alexandrescu, I. Morjan, V. Nelea, I. N. Mihailescu, National Institute of Physics of Lasers, Plasma and Radiations, P.O. Box MG-36, Bucharest, Romania; A. Andrei, Institute for Nuclear Reactors, Pitesti, Romania.

Since Liu and Cohen predicted the existence of a new material, carbon nitride, with spectacular structure and properties, many methods were used for its synthesis. Among the different techniques employed, LCVD was the less exploited.

In this paper we are reporting an attempt in producing hard protective coatings of CNx by LCVD method on alumina substrates, from a mixture of carbon-nitrogen containing gases, as $C_2H_4/N_2O/NH_3$. The KrF laser radiation (λ= 248 nm) was directed perpendicularly onto substrates

A special emphasys was given to the preparation of the substrate surface in order to catalyse the deposition. For this purpose either a catalytic Ti/TiO_x film was predeposited or a preactivation of the bare substrate was performed with the KrF laser. The structural modifications of alumina induced by laser are believed to enhance the deposition mechanism. The photolytic process seems to be competed by a pyrolytic one as a result of a temperature rise of the substrate provoked by the laser. The dependence of C/N ratio on the partial pressures of NH_3/N_2O and surface preparation was investigated using different surface analysis, like XPS, SEM, XRD.

K-II/P29 THE PROTECTIVE $Si_{1-x}C_x$-SiC COATINGS ON THE HIGH TEMPERATURE CARBON GRAPHITE MATERIALS FORMATION FOR HEATERS AND CONTAINERS, V.A. Krasnov, Inst. of Semicond. Phys., Ukrainian Acad. Sci., Kherson Depart., PO Box 76, 325008 Kherson, Ukraine.

Carbon graphite materials are used in semiconductor metallurgy and ultrapure substance technology widely. In particular, it serves as the base of making of the different heaters, details of equipping and appliances, which work in unfriendly environments (low vacuum, hydrogenous or inert gas stream in the remanent oxygen and water steams presence, etc.).

For oxidized erosion prevention of such materials the technology of $Si_{1-x}C_x$ - SiC protective coatings formation in surface layers of the details made of present materials is proposed in this work. Probe technology included the following repartitions (macrooperations):

- capillary impregnation of the surface layers of product details, ~50...1000µm, by overheating silicon melt, $T_m \cong$ 1550...1650°C,
- the synthesis in consequence of diffusion - exchange interaction of solid solutions in Si - SiC system,
- the removal of residual oxygen from synthesis zone,
- the stabilize thermotreatments of details.

It is showed, in particular, that formation of the dense protective $Si_{1-x}C_x$ - SiC coatings onto the graphite heater elements permits to exploit them in air environment at 1500 - 1800°C. Their reliability and durability also rise. The investigations of structural, mechanical and electrophysical properties are carried out.

K-II/P30 STRUCTURAL CHARACTERIZATION OF HARDFACED PLATE WITH HYPEREUTECTIC CHROMIUM WHITE IRON, F.A. Ribeiro Serra and I.G. Solorzano, DCMM-PUC/Rio, C.P. 38008 Gavea, 22452-900 Rio de Janeiro, Brasil.

The electric arc powder deposition of hardfacing process offers the possibility to choose the deposit composition in view of specific applications. For the present study, samples were produce with a new system that allows higher deposition rate, permitting, therefore, to be used for obtaining thicker coatings than through conventional procedures.

The present contribution reports the characterization resulting from the following hardfaced coating compositions:

- standard for wear resistance (5.3%C, 30%Cr, 1%Mn, 1%Ni, 1%Nb);
- wear and heat resistance (5.3%C, 30%Cr, 1.5%Mn, 3%Mo, 1,5%Ni, 5%Nb);

Both plain carbon steel and stainless steel as base materials are under investigation. The later intended for heat resistant applications.

Light Optical as well as Scanning Electron Microscopy have been extensively used in order to characterize the different microstructures and correlate these observations with microhardness measurements in longitudinal and cross section of the coated samples.

It is clear that the microstructure has a great influence in wear behavior. Specifically, carbide morphology and orientation as well as base metal dilution are discussed in terms of the predicted tribological application.

K-II/P31 POLYMER COATINGS ON THE BASE OF POLYAMIDOIMIDES FROM DIHYDRAZIDES AND ALICYCLIC DIANHYDRIDES, V.A. Solomin, V.V. Lyapunov, B.A. Zhubanov, Institute of Chemical Sciences, Kazahk National Academy of Sciences, 106 Sh. Ualikhanov Str., 480100 Almaty, Kazakhstan.

Polyamidoimides (PAI) on the base of dihydrazides of dicarboxylic acids are of perspective for the development of new coatings for surface protection with improved physico-mechanical and tribological characteristics. The new approach to the synthesis of PAI in water- organic mixtures was elaborated by authors. It is distinguished by comparatively soft conditions of the process realization, industrial availability of the apparatus designing. High-molecular - weight polyamidoimide coatings and films were casted directly from reaction mixtures diluted with organic solvents, polycyclocondensation was carried out 3-4 hrs at 65 °C. Influence of monomers concentration on molecular weight of PAI had a strongly marked tendency in the case of aromatic dihydrazides. Inhearence viscosity of PAI depended from the reaction temperature less than in case of polyimides synthesis. Ultimate strength upon breaking of PAI coatings depended on molecular weight and its distribution as well as the nature of organic solvents used for synthesis. Obtained PAI are tractable from solutions and melts, demonstrate good adhesion to different surfaces, thermo- and hydrolytic stability, good physico-mechanical properties.

K-II/P32 METALIZATION OF SILICON SURFACES-ELLIPSOMETRIC CHARACTERIZATION, D.A. Tonova and J.E. Karmakov, Department of Condensed Matter Physics, Faculty of Physics, Sofia University, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria.

Much work is devoted to understanding the basic mechanisms of the silicide formation and the associated reaction kinetics. The studies involve powerful but expensive surface-sensitive methods-XPS, RBS, SIMS, AES, REEM and TEMs.

For very thin films of metals, metallic alloys and silicides the spectroellipsometry is a sensitive tool for investigations. It gives some insight into reaction mechanisms of intermetallic layer growth and phase transformation during annealing. As an example we present our spectroscopic ellipsometry studies of evolution with time of $CoSi_2$ formation from thin Co film on silicon during RTA. Compositional profiles of cobalt silicide layer are determined by proper models and algorithms from ellipsometric data. Obtained results are consistent with the theory of grain boundary diffusion in thin polycrystalline films. Effective diffusion coefficient of moving species is determined.

K-II/P33 TiN and TiAlN COATINGS DEPOSITED AT ROOM TEMPERATURE BY ENERGETIC CLUSTER IMPACT (ECI), H. Haberland, Y. Qiang, B. Knühl, J. Kraft, O. Rattunde and Th. Reiners, Freiburg Materials Research Center, Stefan-Meier-Str.21, 79104 Freiburg, Germany.

Smooth, well adherent TiN and TiAlN hard coatings have been deposited at room temperature by Energetic Cluster Impact (ECI). TiN or TiAlN clusters were produced by combining magnetron sputtering with reactive gas aggregation

(1 - 4% N_2 in Ar). Ionized clusters were accelerated electrically and deposited onto a variety of substrates (steel, Si, glass, Teflon and ceramic ...). The composition, morphology, and microstructure of the coatings have been studied by RBS, EDX, AFM and SEM. By increasing the impact energy of the clusters up to 10 eV/atom, the root mean square (RMS) surface roughness could be decreased below 1 nm The films show no columnar structure, even though the deposition was performed at room temperature while standard PVD methods work in the range of 400°C. Mechanical properties such as adhesion and stress of the coatings will be discussed.

K-II/P34 TRIBOLOGICAL PROPERTIES OF DUPLEX COATINGS, B. Skoric, D. Kakas, University of Novi Sad, Faculty of Technical Sciences, Trg. D. Obradovica 6, Novi Sad, Yugoslavia and T. Gredic, Institut of Nuclear Research, Belgrade, Yugoslavia.

The wear of high speed steel cutting tools is of great importance for the manufacturing industry and it is characterized by extreme contact conditions at tool-workpiece interface.

Physical Vapour Deposited (PVD) TiN coating is used as a wear resistant coating on cutting tools. To enhance the adhesion of the coating a plasma nitriding on low pressure, of substrates is used. Cutting tests were performed on special designed test equipment which gives opportunity to monitoring continuosly friction forces, friction coefficient and contact temperature.

The coating properties, as well as the properties of the substrate material and the conditions at the interface, influence the tribological properties at the contact surface. The wear zone morphology and characteristics of surface layer as well as important properties were investigated by scannig electron microscopy (SEM) and X-ray diffraction analysis (XRD). Whilst TiN coatings are with strong (111) preferred orientation and dense grain structure.

Notes

ICAM/E-MRS'97 SPRING MEETING

SYMPOSIUM L

III-V Nitrides Semiconductors and Ceramics: from Material Growth to Device Applications

Symposium Organizers

B.K. MEYER, Justus Liebig Univ. Giessen, Giessen, Germany

B. GIL, CNRS - GES, Montpellier, France

I. AKASAKI, Meijo University, Nagoya, Japan

H. MORKOÇ, Univ. of Illinois at Urbana-Champaign, Urbana, U.S.A.

SYMPOSIUM L

Monday June 16, 1997
Lundi 16 juin 1997

Afternoon
Après-midi

Session I - GaN Growth Methods

L-I.1 - invited - 14:00-14:30

EFFICIENT AND UNIFORM PRODUCTION OF III-NITRIDE FILMS BY MULTIWAFER MOVPE, R. Beccard, **B. Wachtendorf**, D. Schmitz and H.Jürgensen, AIXTRON GmbH, 52072 Aachen, Germany

We present results on the growth of Ga-In-Al-N films in multiwafer Planetary Reactors® with 7x2» wafer capacity. The unique design of these reactors allows to combine high efficiency (Ga efficiency in GaN around 30%) and excellent uniformity. Thickness uniformities better than ±5% on a 2» wafer are routinely obtained. Compositional uniformity of GaInN is better than 2 nm. Wafer-to-wafer and run-to-run reproducibility concerning thickness and composition is within the 1%-range. Besides this, the material grown also has a high purity. Hall mobilities above 500 cm^2/Vs are obtained for GaN.

Furthermore, the design of the reactors is dedicated to the growth of complex nitride heterostructures. Fast switching manifolds for various group III precursors and different carrier gases allow a flexible design of the growth runs including nucleation, bulk layers (doped/undoped) and quantum wells. The extremely low thermal mass of the reactor permits to perform very rapid changes of the deposition temperature between room temperature and 1300°C (optional: 1600°C). Of course p- and n-type doping is also possible. Doping uniformities are below 1% indicating extremely uniform wafer temperatures. The results demonstrate that Planetary Reactors® reliable and efficient tools for the mass production of ble-green optoelectronic devices.

L-I.2 14:30-14:50

2D/3D GROWTH OF GaN BY MOLECULAR BEAM EPITAXY: TOWARDS GaN QUANTUM DOTS, B. Daudin, F. Widmann, G. Feuillet, Y. Samson, M. Arlery, J.L. Rouvière, Département de Recherche sur la Matière Condensée CEA-Grenoble, SP2M/PSC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

The observation of intense Reflection High Energy Electron Diffraction (RHEED) oscillations allowed us to optimize the growth of hexagonal AlN and GaN as a function of the metal/N ratio. It was found that a ratio close to unity corresponded to an optimized 2D growth for which intense and narrow band edge photoluminescence was observed. The band edge peak width at half maximum and the intensity of the deep yellow band were found to strongly depend on the metal/N ratio.

AlN/GaN superlattices were also achieved. High Resolution Electron Microscopy revealed that the interfaces were abrupt at the atomic scale, with no interdiffusion observed. On the other hand, when increasing the growth temperature of GaN on AlN, an elastic relaxation through 3D islanding after deposition of 2.5 monolayers was observed, corresponding to a Stransky-Krastanov growth mode. GaN islands with heights ranging from 1.6 nm to 2.0 nm and lateral dimensions from 8 to 13 nm are clearly evidenced by AFM. These dimensions are typical of dots where quantum effects could in principle be observed.

L-I.3 14:50-15:10

PLASMA ASSISTED MBE GROWTH OF GaN, S. Einfeldt, U. Birkle, C. Thomas, M. Fehrer, H. Heinke, D. Hommel, University of Bremen, Institute of Solid State Physics, PO Box 33 04 40, 28334 Bremen, Germany

Growth conditions are known to have a strong impact on the physical properties of epitaxial GaN layers emphasizing the need for a systematic analysis of the growth process. In this paper we focus on nitrogen plasma assisted MBE growth of GaN on basal plane sapphire. The plasma source was successfully used for the nitridation of sapphire as confirmed by the variation of the lattice constant in the RHEED pattern and XPS measurements. Surprisingly, GaN was found to nucleate on sapphire as twodimensional layer even without nitridation or the predeposition of a low temperature buffer layer. On the other hand the layer properties are mainly influenced by the growth temperature and the V/III flux ratio as shown by X-ray diffraction, photoluminescence (PL) and atomic force microscopy measurements. The opportunity to bias samples in the MBE chamber enabled us to study the role of charged species during plasma assisted growth. Pronounced differences in the PL spectra are discussed in terms of a crystal damage by nitrogen ions. Whereas non optimized growth conditions are commonly expected to result in a high background carrier concentration, typical values for our layers are in the order of 10^{15} cm^{-3} for a wide range of growth conditions. The low mobility and its temperature dependence suggest a non-bandlike carrier transport process.

L-I.4 15:10-15:30

GROWTH OF GaN AND AlN THIN FILMS BY LASER INDUCED MOLECULAR BEAM EPITAXY, M. Gross, G. Henn and H. Schröder, DLR Stuttgart, Institute of Technical Physics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

The laser induced MBE was used for the growth of wurtzite GaN and AlN thin films on sapphire and SiC substrates. Nitride formation took place by pulsed laser ablation of a liquid Ga or a solid Al target in a nitrogen ambient. The N_2-pressure used in these experiments was 10^{-2}-1 mbar. The growth temperature was between 700 C and 1100 C. Prior to the growth of the films a buffer layer was deposited on the substrate.

The films were characterized for their structure, morphology and composition by XRD, SEM, EDX, Raman spectroscopy, and AFM. To study the optical properties of the films, PL spectroscopy was performed. Smooth, stoichiometric nitride films were prepared. The XRD diffraction patterns show together with the substrate peaks only (0002) and (0004) reflections of the nitrides. No other reflection is present, indicating that the films are predominantly oriented along [0001] direction. The clear appearance of the E_2 and A_1 (LO) phonon modes in the Raman spectra show that the deposited films contain pure AlN or GaN phase. In the PL spectra a broad band in the yellow region as well as a clear band-edge luminescence is observed at room temperatures. The results show, that laser induced MBE can be used for the preparation of optically active thin films with good quality.

L-I.5 15:30-15:50

GaN THIN FILMS PRODUCED BY PULSED LASER DEPOSITION, D. Cole, J.M.D. Coey, J.F. Donegan, F.P. Logue, J.G. Lunney, Department of Physics, Trinity College, Dublin 2, Ireland

Well-oriented GaN films were grown by pulsed laser deposition on (1120) sapphire substrates in ultra-high vacuum and in N_2 and NH_3 atmospheres in the pressure range 0.1 mbar to 0.3 mbar. The film quality is comparable to that obtained by conventional epitaxial techniques. Films deposited at a laser fluence of 2.0 J cm^{-2} and 700°C showed a pure wurtzite phase. Scanning electron microscopy indicated that at 700 °C and 2.0 J cm^{-2} smooth, continuous and droplet-free GaN films are obtained. The band-gap, obtained from transmission measurements is 3.7 eV. All the samples showed violet photoluminescence centered at 3.2 eV with a full width at half maximum of 0.2 eV. Samples prepared in ultra high vacuum also showed a yellow photoluminescence centered at 2.1 eV.

L-I.6 15:50-16:10

GROWTH AND CHARACTERIZATIONS OF GaN ON SiC SUBSTRATES WITH BUFFER LAYERS, G.C. Chi, Department of Physics, National Central University, Chungli, Taiwan, and C.F. Lin, H.C. Cheng, M.S. Feng, Department of Electronics Engineering, National Chio Tung University, Hsinchu 30049, Taiwan

High quality GaN epitaxial films were grown on various buffer layers over 6H SiC substrates by using low-pressure metalorganic chemical vapor deposition (LP-MOCVD) method. Samples with a 3-period of $GaN/Al_{0.08}Ga_{0.92}N$(l00Å/l00Å) as buffer layer produce good quality GaN epitaxial films.The mobility and carrier concentration are 612cm^2/Vs and 3X $10^{17}cm^{-3}$(at 300K) for the GaN epitaxial layer.We also report the observation of the enhanced electron mobility in the $Al_{0.08}G_{0.92}N/GaN$ heterostructures. The structure composed of 500Å AlGaN layer deposited on an 1.3μm GaN epitaxial layer. By using theVan der pauw method of Hall measurement. the sheet carrier density and mobility for $Al_{0.08}G_{0.92}N/GaN$ heterostructure are 5.8x$10^{12}cm^{-2}$ and 5300cm^2/Vs at 4.2K, respectively. Strong SdH(Shubnikov-de Haas) oscillations were observed thus confirm the presence of a two-dimensional electron gas (2DEG) at the AlGaN/GaN heterointerface. We also observed the addition of two SdH oscillations which might indicate that a second 2DEG channels of AlGaN/GaN heterointerface exist. Thus, the AlGaN/GaN heterointerface at the interface of GaN/buffer layer should be a good quality interface.

16:10-16:40 **BREAK**

Session II - Characterization of GaN

L-II.1 16:40-17:00

CHARACTERIZATION OF AlN BUFFER LAYERS ON (0001) SAPPHIRE SUBSTRATES, Y.M. Le Vaillant, GES, Université de Montpellier II, CC074, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France and R. Bisaro, J. Olivier, O. Durand, J. Y. Duboz, Thomson-CSF LCR, Domaine de Corbeville, 91404 Orsay Cedex, France, and S. Clur, O. Briot, B. Gil, R.L. Aulombard, Université de Montpellier II, CC074, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

It is now established that low temperature-grown buffer layers are needed to improve the structural and electronic properties of GaN layers grown on sapphire. Using x-ray diffraction, we have studied the dependence on temperature and annealing time of the recrystallization of AlN buffer layers grown by low pressure MOVPE. Warren-Averbach method applied to the broadening and shape analysis of the (0002) and (0004) x-ray diffraction peaks has allowed us to separate grain size distribution from microstrain effects. The obtained evolution of the relative frequency distribution of the grain sizes with annealing conditions is correlated with atomic force microscopy experiments (dynamic mode). The angular distribution of the c-axis of the grains is determined from x-ray rocking-curves experiments. X-ray reflectometry experiments and a simulation procedure have given us access to the roughness and the chemical composition of the sapphire-buffer layer interface and to the thickness and the roughness of the AlN really grown.

L-II.2 17:00-17-20

HIGH-RESOLUTION X-RAY DIFFRACTION ON GaN EPITAXIAL LAYERS, H. Heinke, S. Einfeldt, U. Birkle, D. Hommel, University of Bremen, Institute of Solid State Physics, PO Box 330440, 28334 Bremen, Germany

GaN/Al_2O_3(0001) layers were found to be an interesting material for high-resolution, X-ray diffraction (HRXRD) despite their relatively poor structural quality. Triple-axis (TA) measurements with a resolution of 10 arcsec show a pronounced anisotropy of the structural perfection of GaN layers which is directly demonstrated by (0002) reciprocal space maps (RSM). Large peak widths in ~-direction (1:30..800 arcsec) are faced by very narrow peaks (20 arcsec) for ω-2θ scans as well as by thickness fringes confirming the large coherence length along [0001]. This can be expressed in terms of the typical columnar growth of GaN layers. However, additional measurements of asymmetrical reflections are necessary to fully characterize GaN layers. TA measurements for these reflections allow to determine both the type and the density of dislocations providing a new tool for a fast nondestructive analysis of defects in GaN layers. This has been used to study the dependence of structural properties on the growth temperature and the doping level. In both cases, (0002) RSM show an asymmetry in ω-2θ direction, varying with the growth parameters. This asymmetry is discussed with respect to a nonstoichiometric growth or varying thermal strain. Temperature dependent HRXRD in a wide temperature range (T=4..630K) enables both effects to be separated.

L-II.3 17:20-17:40

EXAFS STUDIES OF PLASMA-ENHANCED MBE GROWN GROUP-III NITRIDES, A.V. Blant, T.S. Cheng, C.T. Foxon, N.J. Jeffs, Department of Physics, University of Nottingham, NG7 2RD, UK, C. Bailey, P.G. Harrison, Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK, and A. Dent, CLRC, Daresbury Laboratories, Warrington, Cheshire, WA4 4AD, UK

The properties of the Group-III Nitrides are not as well established as those of other III-V compounds and alloys. In particular, whether phase separation occurs for the Group-III Nitride alloys has not been reported. This is of great important since the active regions in visible and blue semiconductor lasers consist of (InGa)N quantum wells. EXAFS can provide unique information on the bond lengths and co-ordination ofthe alloys, and indicate whether phase separation does take place.

We report the first EXAFS studies of $In_xGa_{1-x}N$ alloys grown using a modified MBE method on Si substrates. Additional data on the structural and chemical composition of the alloys will be presented.

L-II.4 17:40-18:00

DRIFTS CHARACTERIZATION OF A NANOSTRUCTURED GALLIUM NITRIDE POWDER AND ITS INTERACTIONS WITH ORGANIC MOLECULES, M.I. Baraton, LMCTS, Faculté des Sciences, 87060 Limoges, France, G. Carlson and K.E. Gonsalves, Polymer Program at the Institue of Materials Science & Department of Chemistry, University of Connecticut, Storrs, CT, USA

Due to its wide bandgap, gallium nitride has become one of the most suitable materials for blue emitters. The still increasing demand for blue light emitting diodes and lasers has resulted in exhaustive studies of this material. While most of the synthesis processes concentrate on thin films deposition, the first zincblende nanostructured gallium nitride powder has been synthesized at the University of Connecticut. The powder actually consists of primary domains of 5 nanometers diameter which agglomerate.

Since the surface chemical composition of gallium nitride must be controlled because it can affect the electronic properties, we will present the first surface studies of this GaN nanostructured powder by diffuse reflectance infrared Fourier transform spectrometry (DRIFTS). As the GaN nanopowder deagglomerates after sonication and disperses into poly(methyl methacrylate) (PMMA), we also studied by DRIFTS the interactions between the GaN first atomic layer and organic molecules bearing related functional groups (acetone, ethyl acetate ...). The behavior of the nanostructured powder under pure oxygen and water vapor was then followed in situ to check its resistance to oxidation and the possible modifications of its first atomic layer.

L-II.5 18:00-18:20

EXCITON PHOTOLUMINESCENCE OF GaN BULK CRYSTALS GROWN BY AMONO METHOD, R. Dwilinski, R. Doradzinski, J.M. Baranowski, M. Kaminska, Institute of Experimental Physics, Warsaw University, Hoza 69, 00-681 Warsaw, Poland, J. Garczynski, L. Sierzputowski, Dept. of Chemistry, Warsaw Univ. of Technology, Pl. Politechniki 1, 00-661 Warsaw, Poland

GaN in form of microcrystals was obtained by a new technique, named AMONO method. The growth was performed at relatively low temperature and pressure conditions, in comparison with other techniques used for GaN growth. The idea of AMONO method is recrystallisation of nitride in supercritical ammonia at temperature gradient. Such mechanism of crystallisation is a direct chemical analogy to the mechanism which is a principle of hydrothermal method, commonly used for industrial growth of quartz crystals.

All GaN crystals obtained by AMONO method revealed very intensive and homogenous luminescence. At helium temperature exciton recombination dominated photoluminescence spectra. The exciton lines were extremely narrow with FWHM down to 1 meV energy what could be only compared with the width of luminescence lines observed for best homoepitaxial GaN layers. The exciton line energies were not sample dependent. It was in contrast to small changes of line energies commonly observed for epitaxial GaN layers and related to strain present in them. Therefore AMONO crystals which are strain free can be treated as a model material for measurements of basic optical parameters of GaN.

Although present dimensions of AMONO GaN crystals are up to 25 micrometers, the analogy to quartz crystals allow to consider the AMONO method as a potential technology for production of nitride substrates, necessary for nitrides homoepitaxy and ultraviolet lasers.

Tuesday June 17, 1997 — Morning
Mardi 17 juin 1997 — Matin

Session III - Optical Properties of GaN, Part 1

L-III.1 - invited - 8:30-9:00

LUMINESCENCE AND REFLECTIVITY STUDIES OF UNDOPED, n- AND p-DOPED GaN ON (0001) SAPPHIRE, **M. Leroux**, B. Beaumont, N. Grandjean, P. Lorenzini, S. Haffouz, J. Massies and P. Gibart, CRHEA-CNRS, Rue Bernard Grégory, 06560 Valbonne, France

GaN grown by three diffferent techniques (MOVPE, GSMBE and HVPE) have been studied using T dependent reflectivity and luminescence (PL): Both non intentionnally doped (MOVPE, GSMBE and HVPE) and n- and p- doped samples (MOVPE) have been investigated. Reflectivity is used to obtain intrinsic transition energies, varying with the amount of strain in the crystal. Growth parameters influencing this strain state are discussed. Using MOVPE (Tg ~ 1050°C) and GSMBE (Tg ~ 800°C), it is possible to grow heteroepitaxial samples whose low temperature PL spectra are dominated by free and bound excitons and their phonon replication. Intentional n-type doping up to ~10^{20} cm^{-3} is easily achieved using Si. A Si donor depth of 34 meV is tentatively deduced from the PL spectra at low doping level, whereas the spectra for n >> 10^{18} cm^{-3} exhibit a blue shift, attributed to band filling.

p-type doping has been attempted using Mg, C and Ca. Ca doping led to compensated samples. C doping using CCl_4 resulted in n-type samples, due to simultaneous oxygen incorporation in the layers; a strong enhancement of the 3.27 eV donor-acceptor pair PL is also observed in that case. p-type doping up to 10^{18} cm^{-3} has been achieved with Mg. With increasing Mg doping, new acceptor levels, deeper than the residual one, are observed on the PL spectra. For high Mg doping, the spectra are dominated by a blue band around 2.8 eV. This band is shown to be composite, and certainly involves deep electron levels.

L-III.2 9:00-9:20

CHARACTERIZATION OF Ca AND C IMPLANTED GaN, B. Mensching, C. Liu, B. Rauschenbach, Universität Augsburg, Institut für Physik, Memminger Str.6, 86135 Augsburg, Germany, and K. Kornitzer, W. Ritter, Universität Ulm, Oberer Eselsberg, Abteilung Halbleiterphysik, 89081 Ulm, Germany

Structural, electrical and optical properties of GaN after ion implantation and subsequent annealing have been studied.

The GaN layers used in the experiments were 0,2-2µm thick grown on sapphire substrate by MBE. ^{40}Ca and ^{12}C ions were implanted at doses of $5*10^{13}$-$1*10^{16}$cm^{-2} and energies of 60-180keV. Post implant annealing was performed in a RTA furnace.

Investigation by RBS-Channeling and XRD before and after annealing indicates reduction of ion-beam induced damage during implantation The agreement between the structural measurements and simulations is good. The electrical properties were determined by Hall measurements. For background carrier densities >$5*10^{16}$cm^{-3} Ca implant results in a strong decrease of the free-carrier concentration Possible reasons are compensation or the formation of a depletition area. Optical characterization was performed by PL- and Raman spectroscopy.

L-III.3 9:20-9:40

ORIGIN OF THE Q=11 meV BOUND EXCITON IN GaN, B. Santic(1), C. Merz(2), U. Kaufmann(2), K. Bachem(2), R. Niebuhr(2) and H. Obloh(2), (1)R.Boskovic Institute, Bijenicka 54, 10000-Zagreb, Croatia, (2)Fraunhofer Institut für Angewandte Festkörperphysik, Tullastr.72, 79108 Freiburg, Germany.

In addition to neutral donor bound excitons D^0X with a localisation energy Q of about 6 meV, high-purity undoped GaN films also exhibit a bound exciton PL line S with a localisation energy Q=11 meV. Line S has been observed in both VPE, and MOCVD GaN layers but so far only in high resistivity material. We have studied the dependence of its intensity on temperature and excitation power as well as its phonon coupling. These results neither support previous assignments to a deeper neutral donor bound exciton nor to a neutral acceptor bound exciton A^0X. However, our experimental results for line S are consistent with an ionised donor bound exciton. From theoretical stability criteria one expects this type of exciton to be stable in GaN. Therefore the best model for line S is an ionised donor bound exciton D^+X.

L-III.4 9:40-10:00

OPTICAL PROPERTIES OF GaN EPILAYERS GROWN ON Si (111) AND Si (001) SUBSTRATES, M. Godlewski, Inst. of Phys., PAS, Warsaw, Poland, J.P. Bergman and B. Monemar, Dept. Phys. & Meas. Technol., Linköping Univ., Sweden, U. Rossner and A. Barski, CEA/GRENOBLE, DRFMC/SP2M, Grenoble, France

We report the observation of relatively bright photoluminescence (PL) emission from two types of GaN epilayers grown by novel modifications of conventional molecular beam epitaxy (MBE) process. Wurtzite phase GaN/Si (111) is grown by gas source MBE process, whereas good quality cubic phase GaN epilayers are grown on (001) Si covered by thin SiC film in the process of Si annealing in propane prior to the GaN growth. PL emissions observed for two types of GaN/Si epilayers are identified based on the results of detailed PL and time-resolved PL investigations. In the case of cubic phase GaN «edge» part of PL is related to bound excitonic emission and free-to-bound and shallow donor - shallow acceptor pair recombination transitions. From the spectral position of the latter PL emissions we confirm recent suggestion that acceptors in cubic phase GaN epilayers have likely smaller ionization energies than the acceptors in wurtzite phase GaN. The smaller ionization energy may result in a higher concentration of free holes at room temperature in p-type films. For wurtzite phase GaN we observe an efficient up in energy transfer from bound to free excitons. This process is explained by large difference in PL decay times for two types (free and bound (donor, acceptor)) of excitonic PL emissions.

10:00-10:30 **BREAK**

Session IV - Optical Properties of GaN, Part 2

L-IV.1 - invited - 10:30-11:00

OPTICAL AND MAGNETO-OPTICAL CHARACTERIZATION OF HETEROEPITAXIAL GALLIUM NITRIDE, **B.J. Skromme**, Department of Electrical Engineering, Arizona State University, Tempe AZ 85287-5706, USA

Gallium nitride is currently of intense interest for optoelectronic as well as high power/high frequency electronic applications. However, many of the fundamental properties of the material are as yet poorly understood. We will describe our efforts to elucidate the properties of excitons, defects, and impurities in this material as well as the effects of strain using optical techniques such as photoluminescence, reflectance, Raman scattering, and magnetospectroscopy. Energies of the *A*, *B*, and *C* exciton ground states have been studied as a function of stress, which is measured by a method that does not require knowledge of unstrained bulk parameters. Our results suggest that bulk materials and epilayers previously widely thought to be strain-free may actually be under significant strain. Dependence of strains on measurement temperature will be discussed, which has been ignored until now. The theory of the strain splittings will be discussed using new parameter definitions that are more easily interpreted than the conventional ones. We have also observed the n=2 states of the free excitons using magnetospectroscopy, and obtain a binding energy of 26.5 meV, which is significantly larger than some other recent determinations. Excited states of donors have been studied in high magnetic fields in material grown by MOCVD, MBE, and hydride VPE, yielding accurate donor binding energies. The results are analyzed with the aid of variational calculations. The properties of shallow Mg acceptors and the effects of H incorporation have been studied. In particular we describe the observation of acceptor-bound excitons, two-hole transitions, and donor-to-acceptor and band-to-acceptor transitions involving this acceptor level.

L-IV.2 11:00-11:20

MAGNETOOPTICS OF WURTZITE GaN : EXCITONS ZEEMAN SPLITTING AND PHOTOLUMINESCENCE, M. Julier, J. Campo, D. Coquillat, D. Scalbert, J.P. Lascaray, O. Briot, Groupe d'Etudes des Semiconducteurs, URA 357 CNRS, Université Montpellier II, place Eugène Bataillon, 34095 Montpellier Cedex 5, France

We use magnetocircular dichroism to determine fondamental material parameters of wurtzite GaN on (0001) sapphire. Magnetoreflectance dichroism is a unique way of measuring weak Zeeman splitting of excitons in quite unhomogeneous materials such as GaN, among other parameters.

Photoluminescence of GaN in magnetic field is also investigated and its polarization is precisely analyzed using a similar technique, which gives rise to original results that are complementary with those obtained from time-resolved photoluminescence.

Fondamental investigation of III-V Nitrides is interesting in terms of academic research as well as in order to improve the growth techniques, and for the design of the upcoming device applications.

L-IV.3 11:20-11:40

EMISSIONS OF EXCITON-POLARITONS IN GaN, I.A.Buyanova, J.P. Bergman and B. Monemar, Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden, H. Amano and I. Akasaki, Department of Electrical Engineering, Meijo University, Tempaku-ku, Nagoya 468, Japan

Excitonic properties of wide band gap semiconductors with dipole-allowed direct band-to-band transitions can be properly described only within the polariton concept, which takes into account strong exciton-photon coupling. The polariton approach has been shown to be relevant for GaN, consistent with a rather large value of the estimated longitudinal-transverse splitting. However, the detailed properties of the exciton polariton in GaN, as well as parameters of the exciton-phonon interaction, are still unknown.

We have performed temperature dependent studies of intrinsic excitonic emission in GaN epilayers in order to investigate the exciton-phonon interaction in the material. It is shown that spectral properties of FEs can be described within the polariton concept. The unusual behavior of the exciton-polariton in GaN, such as the energy independent probability of the 1-L0 assisted transitions, as well as an enhanced intensity of the nophonon (NP) FE emission in comparison with its LO-phonon replicas, is revealed and is discussed in terms of strong defect/impurity scattering. The parameters of the exciton coupling with lattice phonons, indicating a higher strength of exciton-phonon interaction in GaN than in the other compound semiconductors, are also estimated from the analysis of thermal broadening of the NP line of FE recombination. The interaction with acoustic phonons is shown to be the dominant broadening mechanism in the temperature range below than 150K, while the contribution from the interaction with optical phonons is essential for the higher temperatures.

L-IV.4 - invited - 11:40-12:10

SPECTROSCOPIC ELLIPSOMETRY AND LOW TEMPERATURE REFLECTANCE: COMPLEMENTARY ANALYSIS OF III-N THIN FILMS, **N.V. Edwards**,(1) S.D. Yoo,(1) M.D. Bremser,(1) M.N. Horton,(2) N.R. Perkins,(2) T.W. Weeks Jr.,(1) H. Liu,(2)* R.A. Stall,(3) T.F. Kuech,(2) R.F. Davis,(1) and D.E. Aspnes,(1) (1)NCSU, Raleigh, NC, (2)U. of Wis., Madison, Wi, (3)EMCORE, Somerset, NJ; *now at Hewlett-Packard, San Jose, CA, USA

We report spectroscopic ellipsometry (SE) and low-temperature reflectance data on epitaxial GaN thin-film samples covering the widest range of tensile and compressive stress (-3.8 to 3.5 kbar) thus far. Lineshape ambiguities that hindered previous interpretations have been resolved with reciprocal space analysis, allowing us to (1) obtain band parameters such as Δ_{SO} = 17.0±1 meV and Δ_{CF} = 9.8±1 meV with increased confidence and (2) explicitly show the nonlinear behavior of the B-A and C-A splittings vs. the energy of the A exciton. Emphasis will be given to a discussion of the variation of these lineshapes with choice of substrate and growth parameters and to the resolution of said ambiguities, including dead layer and dispersion effects that prevent simple interpretations. This includes the Edn/dE contribution to dispersion, crucial for Fabry-Perot mode spacing calculations, as welll as the use of SE to assess the preparation of smooth and abrupt GaN surfaces by chemical treatments in real time. About 20-50Å of overlayer typically can be removed from air-exposed samples, enabling the observation of the near-bandedge excitonic features. $Al_xGa_{1-x}N$ data for n + Edn/dE for $0 \leq x \leq 1$, and specialized real-time surface preparation techniques for both InGaN and AlGaN will be presented as well.

L-IV.5 12:10-12:30 INFLUENCE OF Si DOPING LEVEL ON THE RAMAN AND IR REFLECTIVITE SPECTRA AND OPTICAL ABSORPTION SPECTRUM OF GaN, G. Bentoumi and A. Deneuville, LEPES CNRS, BP 166, 38042 Grenoble Cedex 9, France and B. Beaumont and P. Gibart, CRHEA CNRS, Parc de Sophia Antipolis, 06500 Valbonne, France

Doping is needed to achieve electronic devices with GaN. We report here large effects of Si doping in the concentration range $5x10^{17}$ to $5x10^{19}$ cm^{-3} on both the Raman spectrum and the sub band gap absorption of GaN.

Several microns thick GaN films are prepared by MOCVD, with Si doping atoms introduced from SiH_4 in the vapor phase and deposition on sapphire around 1080°C.

At low doping levels, the Raman peaks positions are obtained around 568 (E_2), 532 (A_1TO), 560 (E_1TO), 735 A_1LO and 741 cm^{-1}. At the higher doping level, while the E_2 and E_1TO modes remains rather similar, there is large change on the position of the A_1TO mode (520 cm^{-1}), on the relative intensities of the A_1 and $E_1(LO)$ modes and a wide band appears below 640 cm^{-1}.

The minimum of the IR reflectivity decreases systematically from around 2400 cm^{-1} to lower values as the doping level decreases from $5x10^{19}$ cm^{-3}.

Finally while the abrupt absorption edge has few change, the sub band gap absorption increase from the 10^3 to the 10^4 cm^{-1} range as the doping level increases from $5x10^{17}$ to $5x10^{19}cm^{-3}$.

The relative influence of the doping and the defects induced by doping will be discussed.

12:30-14:00 **LUNCH**

Tuesday June 17, 1997 — Afternoon
Mardi 17 juin 1997 — Après-Midi

Session V - Quantum Phenomena, Part 1

L-V.1 - invited - 14:00-14:30 MICROSCOPIC GAIN THEORY FOR GROUP III NITRIDES, **S. Koch**, University of Marburg, Germany

L-V.2 - invited - 14:30-15:00 NANOSECOND PUMP-AND-PROBE STUDY OF WURTZITE GaN, **T. Deguchi**, T. Azuhata, and T. Sota, Department of Electrical, Electronics, and Computer Engineering, Waseda University, Shinjuku, Tokyo 169, Japan, S. Chichibu, Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278, Japan, N.Sarukura, H.Ohtake, and T.Yamanaka, Instruments Center, Insitute for Molecular Science, Myodaiji, Okazaki 444, Japan, and S.Nakamura, Department of Research and Development, Nichia Chemical Industries Ltd, 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

The phonon structure of GaN with the wurtzite structure is quite different from that of typical cubic compound semiconductors with the zincblende one. In particular, frequencies of longitudinal optical (LO) phonons, which are considered to play a key role in the cooling process of hot carriers through the Fröhlich interaction, in GaN are approximately three times those in GaAs, InAs, and ZnSe. Thus, it is interesting and important to study the effect of the phonon structure on the energy transfer from carriers to the lattice.

We present a nanosecond optical study of wurtzite GaN using a pump-and-probe method under the excitation condition that the carrier-LO phonon scattering channel does not take part in the energy relaxation process. A very slow energy relaxation rate is found. It is shown that the origin of the slow relaxation rate is due to the phonon structure in GaN.

L-V.3 15:00-15:20 OPTICAL PUMPING IN GaN CAVITIES WITH ETCHED MIRROR FACETS, F. Binet, J.Y. Duboz, N. Laurent, P. Collot, F. Hanauer, Laboratoire Central de Recherches, Thomson-CSF, 91404 Orsay, France, O. Briot, B. Gil, GES, Universitè Montpellier II, 34095 Montpellier, France, F. Scholz, V. Härle, 4.Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

GaN and its related compounds have recently allowed the achievement of electrically pumped lasers on either sapphire or spinel substrates. However, in this horizontal geometry, the fabrication of output facets remains a severe issue due to the difficult cleaving of the substrate. Therefore, etched mirrors are usually employed.

We report the fabrication and the characterization of GaN resonators with vertical etched facets. The cavities were realized by means of Chemically Assisted Ion Beam Etching with Cl_2/Ar gases. This process was adjusted to obtain high etch rates and anisotropic profiles. The verticality and roughness of the etched sidewalls were estimated from electronic microscopy to beless than 100nm. The optical scattering on the etched GaN facets was evaluated at different wavelengths and compared to that on a cleaved GaAs facet. Optical pumping was performed in cavities of different sizes and geometries. Stimulated emission and laser action are clearly seen in these resonators. Results on pumping thresholds, polarization will be shown as a function of the geometry of the cavity and the quality of the etched sidewalls.

L-V.4 15:20-15:40 TWO-PHOTON SPECTROSCOPY IN GaN, M. Steube, K.Reimann, and D. Fröhlich, Institut für Physik, Universität Dortmund, 44221 Dortmund, Germany, S.J. Clarke, Department of Chemistry, Cornell University, Ithaca, N.Y., USA

Two-photon spectroscopy was performed on unstrained bulk crystals of wurtzite GaN at a temperature of 7K. The crystals were grown form a Na flux using Na, NaN_3, and Ga. Their photoluminescence spectra are dominated by the D°X luminescence at 3.475 eV, having a line width of 10meV. Two-photon transitions were observed by monitoring the intensity of this luminescence as a function of twice the incident laser photon energy. The two-photon spectra show a background due to continuum absorption and three clearly resolved peaks with line widths between 1.3 and 1.7meV. These peaks are identified as the A 2P, B 2P, and C 2P excitons. Assuming the excitons to be hydrogen-like, from their energies it is possible to calculate precisely the three band gaps and the corresponding exciton binding energies. Whereas the exciton binding energies for A and B excitons are found to be equal, the C exciton binding energy is larger. From this one can conclude that the average hole mass for the C valence band is higher than for the A and B valence bands.

L-V.5 15:40-16:00 SPATIALLY RESOLVED INVESTIGATIONS OF THE EXCITONIC LUMINESCENCE IN GaN, A. Hoffmann, L. Eckey, H. Siegle, C. Thomsen, Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstrasse 36, 10623 Berlin, J. Christen, F. Bertram, D. Schmidt, Otto-von-Guericke Universität Magdeburg, Institut für Festkörperphysik, PO Box, 39016 Magdeburg, K. Hiramatsu, Nagoya University, Department of Electronics, Nagoya 468-01, Japan

We present results from spatially-resolved cathodo-luminescence and Raman measurements on GaN epilayers grown on sapphire by hydride vapor phase epitaxy. The cathodo-luminescence (CL) experiments with a spatial resolution less than 500 nm show that different excitonic transitions appear depending on the distance to the substrate interface. The half-widths of the different excitonic lines in the spatially-resolved investigations are less than 0.5 meV while in the integral CL spectra half-widths of more than 2 meV were observed. It can be clearly demonstrated that at 4.2 K the excitonic luminescence corresponds to sample regions with higher dislocation densities whereas at room temperature the luminescence intensity from these areas is reduced drastically. Furthermore, the influence of the strain on the excitonic luminescence originating from the lattice mismatch between substrate/GaN layer and from impurity distribution was studied. Our micro-Raman investigations yield additional data to understand quantitatively the strain and impurity distribution in these samples.

16:00-16:30 **BREAK**

Session VI - Electronic Properties

L-VI.1 - invited - 16:30-17:00

ELECTRICAL TRANSPORT PROPERTIES OF III NITRIDES, **D.C.Look**, University Research Center, Wright State University, Dayton, Ohio 45435, USA

The quality of III-V nitride material has improved greatly over the last few years; For exmple, donor and acceptor concentrations in undoped epitaxial layers have decreased from the 10^{25}cm^{-3} to the 10^{16}cm^{-3} range during this period, and 300-K mobilities of close to 1000cm^{2}/V s can now be obtained. In this work, we will mainly deal with the elecrical properties of some of the best GaN on sapphire layers grown by each of the three major epitaxial techniques: HVPE, MOCVD, and MBE. Hall mobility data, over the temperature range of 7-400 K, are flued by an accurate solution of the Boltzmann equation, and the most sensitive fitting parameter is the acceptor concentration N_A. Then, the donor concentration N_D and the donor activation energy E_D are determined by a fit of the Hall concentration data to the charge-balance equation; in the case of HVPE material, a highly degenerate n-type layer at the GaN/sapphire must be taken into account for accurate values of N_D, N_A, and E_D to be obtained. Without correction for this interface layer, a falses curvature in in(n) vs 1/T is introduced, and is normally interpreted as a deeper donor; in good MOCVD material, single-phonon hopping between shallow donors is evident below 20K, whereas in some of the best MBE material, multiphonon hopping is dominant at all temperatures, up to 700K. Finally, the donor/acceptor properties of two point defects, the nitrogen vacancy and interstitial, respectively, can be firmly established by Hall analysis of high-energy electron-irradiated material.

L-VI.2 17:00-17:20

ZINC-BLENDE GaN : AB INITIO CALCULATIONS, J.L.A. Alves, H.W. Leite Alves, C. de Oliveira, R.D.S.C. Valadào, DCNAT-FUNREI, CP 110, 36.300-000 Sào Joào del Rei, MG, Brazil, and J.R. Leite, DFMM-IFUSP, CP 66318, 05389-970 Sào Paulo, SP, Brazil

The purpose of this paper is to contribute with a theoretical basis for understanding future wide-gap device concepts and applications based on III-V nitride semiconductors. The electronic properties of zinc-blende structure GaN and their (110), (100) and (111) surfaces are investigated using ab initio calculations based on the Full Potential Linear Augmented Plane-Wave (FPLAPW) method, within the large unit cell approach, and on the molecular Gaussian 92 code. Lattice constant, cohesive energy, bulk modulus are obtained from total energy calculations. Light-hol, heavy-hole and spin-orbit splitting effective masses along (100), (111) and (110) directions and electron masses at Γ point are extracted from band structure calculations and compared with previous ones based on pseudopotential methods. The hydrostatic pressure dependence of the $\Gamma\Gamma$, ΓX and ΓL energy gaps are also obtained. Comparing our band structure and «molecular cluster» calculations, the relaxations of the surfaces are found to be mostly determined by local rehybridization or valence effects and are basicallly independent of energy band features.

Wednesday June 18, 1997 **Morning**
Mercredi 18 juin 1997 Matin

Session VII - AlGaN and AlN

L-VII.1 - invited - 8:30-9:00

PROPERTIES AND APPLICATIONS OF MBE-GROWN AlGaN, **M. Stutzmann,** O. Ambacher, H. Angerer, R. Dimitrov, R. Höpler, A. Cros, D. Brunner, F. Freudenberg, R. Handschuh, Walter Schottky Institut, Am Coulombwall, 85748 Garching, Germany

AlGaN films on sapphire, covering the entire compositional range from GaN to AlN, have been grown by plasma-enhanced MBE. The alloy samples have been characterized by optical absorption, luminescence, X-ray diffraction, Raman scattering, spin resonance and transport measurements in order to obtain a complete picture of the structural and electronic properties of this nitride alloy system. In our contribution, we will focus on the preparation conditions, optical properties (bandgap, bowing parameter, refractive index and its temperature dependence), deep defects, doping, and charge transport as the parameters most relevant for device applications. The use of AlGaN layers and heterostructures in UV light-emitting diodes, MODFETs, Bragg reflectors, and surface acoustic wave devices will be discussed.

L-VII.2 9:00-9:20

MOVPE GROWTH AND CHARACTERIZATION OF $Al_xGa_{1-x}N$, S. Clur, O. Briot, B. Gil and R.L. Aulombard, GES-CNRS, CC074 Univ. Montpellier II, Pl. E. Bataillon 34095 Montpellier Cedex 5, J.L. Rouviere, CEA-Grenoble, DRFMC/SP2M, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

AlGaN is an important material for the design of nitride devices. However, few is known concerning its growth for high Al contents. We have studied the MOVPE growth of GaAlN by low pressure MOVPE (76 Torr), using triethylgallium, trimethylaluminum and ammonia as precursors. The solid composition versus gas phase composition relationship was determined experimentally and was fitted using a kinetic model. Then, the structural properties of the layers (x=0 to 1) were studied, using x-ray diffraction, scanning electron microscopy and transmission electron microscopy. We demonstrate that at high Al content, the buffer layer defects are replicated into the AlGaN layer. The electronic quality of the layers was also assessed using low temperature reflectance, and these results will be correlated to the structural quality of the layers.

L-VII.3 9:20-9:40

A PARAMETRIC STUDY OF AlN THIN FILMS GROWN BY PULSED LASER DEPOSITION, P. Verardi, CNR-Istituto di Acustica "O.M.Corbino", Via Cassia 1216, 00189 Rome, Italy, M. Dinescu, C. Stanciu, Laser Department, INFPLR, P.O. Box MG-16, 76900 Bucharest, Romania, C. Gerardi, L. Mirenghi, PASTIS-CNRSM, 72100 Brindisi, Italy, V. Sandu, INFM, P.O. Box MG-16, 76900 Bucarest, Romania

High quality AlN thin films were grown at 20 - 450 °C on sapphire substrates by laser ablation of Al targets in nitrogen reactive atmosphere The nitrogen pressure was varied between 10^{-3} - 10^{-1} torr. The reactive gas pressure during irradiation and the temperature of the substrate were found to essentially influence the quality of the layers. X-ray diffraction analysis evidenced the formation of highly oriented structures for a very restrictive set of parameters. Other analysis techniques, like scanning and transmission electron microscopy, x-ray photoelectron spectroscopy, secondary ion mass spectroscopy, optical transmission spectroscopy have been used to evidence the good stoichiometry and purity of the films. The characteristics of these films were compared with those of similar AlN thin films deposited in the same experimental conditions on Si(100) and Si(111) substrates.

L-VII.4 9:40-10:00

GROWTH OF COLUMNAR AlN LAYERS ON Si(111) BY MBE, S. Karmann, H.P.D. Schenk, U. Kaiser, A. Fissel and W. Richter, Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Max-Wien-Platz 1, 07743 Jena, Germany

AlN thin films are deposited by MBE technique using thermally evaporated aluminum ($T \approx 1100°C$) and RF-plasma excited nitrogen gas ($P \approx 300W$, $\Phi \approx 1$ sccm) as source materials. The films grown on Si(111) at substrate temperatures $\theta = 600 - 1000°C$ with maximum rates of 130 nm/h all consist of hexagonal AlN with the epitaxial relation AlN (0001) // Si(111).

Optimizing growth conditions to increase the crystalline quality, we obtain XRD-peaks with a FWHM of 0.4° for the AlN(00.2) reflex in the ω-scan. The layers reveal a highly c-axis ordered columnar growth (cross-section TEM) and subsequently the surfaces are textured with rms-roughness up to 40 nm (AFM measurement). In general, an increasing Al flow coupled with a higher growth rate supports the generation of AlN columns. The initial state of growth is traced using short time deposition experiments (t = 1..10 seconds) combined with RHEED, AFM and TEM examinations of the formed AlN seeds. By that we find growth conditions to avoid the formation of columns and to enhance the coalescence of the AlN seeds. For the resulting layers surface roughness is reduced below 1 nm, but XRD line width is broadened at the same time to some degrees.

We thank J. Kräußlich, G. Peiter, Ch. Schmidt, J. Schulze and K. Pfennighaus (all FSU Jena) for characterization of AlN thin films.

10:00-10:30 **BREAK**

Session VIII - TEM Studies

L-VIII.1 - invited - 10:30-11:00

CHARACTERIZATION OF EXTENDED DEFECTS IN GaN LAYERS, **J.L. Rouvière,** M. Arlery and A. Bourret CEA-Grenoble, Département de Recherche Fondamentale sur la Matière Condensée/SP2M/ME, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

In this communication, we review the extended defects (dislocations, stacking faults, inversion domains, nanopipes) observed by transmission electron microscopy in wurtzite GaN layers grown on sapphire.

In particular, we show how the defect content crucially depends on the polarity of the layer. For instance, columnar inversion domains propagate throughout the layers in N-polar material, whereas they tend to be annihilated in Ga-polar layers; nanopipes have not been observed in N-polar layers.

We mention how the strain in the GaN layer can be released by the different types of dislocations. A special attention will be devoted to the perfect screw dislocations that dissociate or recombine, opening and closing holes (nanopipes) in the GaN layers and how these dislocations can be revealed by a chemical etching of the surface.

L-VIII.2 11:00-11:20

DEFECT POPULATION AND ELECTRO-OPTICAL PROPERTIES OF GaN ON SAPPHIRE, S. Christiansen, M. Albrecht, H.P. Strunk, Institut für Werkstoffwissenschaften, Lehrstuhl VII, Universität Erlangen, Cauerstr. 6, 91058 Erlangen, Germany, M. Mayer, P. Kamp, K.J. Ebeling, Universität Ulm, Albert Einstein Allee 45, 89069 Ulm, Germany

Wurzite gallium nitride (GaN) films deposited on c- and r- sapphire substrates by gas source molecular beam epitaxy (GSMBE) and metal organic vapour deposition (MOVPE) are investigated as regards their defect structure. We use conventional and high resolution transmission electron microscopy. The different substrate orientations and in addition the different nitridization and buffer layer treatments lead to the generation of a variety of different defect populations (dislocations, planar defects such as stacking faults and partial loops).

We compare specimens that are characteristically different in defect population and luminescence:

i) those, which show an additional defect related luminescence line at 569nm in photoluminescence and spectrally and locally resolved cathodoluminescence (CL) spectra and those which do not show such a line. The occurence and missing of the line and the occurrance and missing of a certain defect, the so called Frank partial loop, give an indirect proof that this defect is related to the additional UV line.

ii) those, which show a strong yellow luminescence peak at arround 220nm and those which do show only a faint one. This peak seems to be directly correlated to the density of screw dislocations (U = [0001]).

The physical reason for the occurrance of additional lines (point defects such as interstitials, vacancies, antisite defects, impurity atoms gettered by extended de-fects such as dislocations and stacking faults) is discussed. We take into account the role of reconstruction of charging of the dislocation core. Uncharged cores such as that present in dislocations with Burgers vector b = 1/2[0001] and b = [0001], can cause additional luminescence lines.

L-VIII.3 11:20-11:40

THE STRUCTURE OF DEFECTS IN GaN/AlN LAYERS GROWN ON SiC AND SAPPHIRE SUBSTRATES BY MBE, P. Ruterana, P. Vermaut, V. Potin, G. Nouet, LERMAT 6004 CNRS, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France, and A. Botchkarev, A. Salvador, and H. Morkoç, University of Illinois, Materials Research Laboratory, Urbana, IL 61801, USA

A comparative study of the defects at the interface and inside layers was carried out in GaN-AlN epitaxial layers on (0001) SiC and sapphire.

Whereas the surface cleaning of the sapphire substrates has been rather standardized, the SiC surfaces were either cleaned in the now conventional way of chemical etching followed by a hydrogen plasma treatment or a more sophisticated technique which minimizes the residual impurities and the surface damages. In epitaxial growth, an important role is played by the lattice parameter: the (0001) sapphire surface has a 3m symmetry and a lattice mismatch of 16% with GaN. The SiC (0001) surface has 6mm symmetry identical to that of GaN and the lattice mismatch is of 3.5%.

The investigated growth methods are all MBE, but either ECR nitrogen plasma nitrogen or a NH_3 gas source system, was used in order to obtain atomic nitrogen.The comparative analysis was made starting from the dislocation densities and type of the interface structure, as well as atomic structure of the defects present inside the epitaxial layers.

L-VIII.4 - invited - 11:40-12:10

CHARACTERISATION OF DISLOCATIONS, NANOPIPES AND INVERSION DOMAINS IN GaN BY TRANSMISSION ELECTRON MICROSCOPY, **D. Cherns**, H.H.Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

12:10-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-Midi

Session XI - GaAsN

L-IX.1 - invited - 14:00-14:30

III-V NITRIDE COMPOUNDS FOR INFRARED APPLICATIONS, **J. Salzman**, Technion, Haifa 32000, Israel and H. Temkin, Texas Tech University, Lubbok TX 79409, USA

Ternary and quaternary III-V compounds containing Nitrogen, and As or P can be grown on GaAs or InP substrates, with band gaps corresponding to near infrared wavelengths. Recent progress in the growth of these low band gap compounds promises major improvements in the performance of photonic devices based on III-V materials and their heterostructures. However, the growth of these compounds is still in its infancy and only small nitrogen fractions have been reported.

We report systematic experiments in the growth of high quality $GaAs_{1-x}N_x$ on GaAs, and $Ga_xIn_{1-x}As_yN_{1-y}$ on InP by Plasma Activated Metalorganic Molecular Beam Epitaxy and Metalorganic Vapor Phase Epitaxy. The growth rate was in the range of 0.6 to 10 µm/hr, independent of the N content of the layer. We prepared single phase $GaAs_{1-x}N_x$ with x up to 0.1. Higher concentrations were obtained in polycrystalline samples. The samples were evaluated by X-ray Diffraction (XRD), Secondary Ion Mass Spectroscopy (SIMS), Photoluminescence (PL), Raman Spectroscopy, and Atomic Force Spectroscopy.

In the range of growth temperatures used in our experiments the N/As and N/P flux ratio play a crucial role in the growth of single phase layers, suggesting that the N and As (or P) atoms compete with each other for the same anion sites. This was further confirmed by SIMS measurements. By adjusting the N/As (and N/P) ratios (instead of simply supplying a sufficient N flux), we were able to control the N incorporation. High resolution XRD shows that our ternary and quaternary layers are single phase and of high quality. Powder XRD shows the absence of other phases. Room temperature PL measurements show good luminescence properties of the mixed compounds, and confirm earlier predictions of band gap shrinkage.

L-IX.2 14:30-14:50

OPTICAL CHARACTERISATION OF MBE-GROWN GaAsN, G. Pozina, I. Ivanov, and B. Monemar, Dept of Physics, Linköping University, 581 83 Linköping, Sweden; J. Thordson and T.G. Andersson, Dept of Physics, Chalmers Institute of Technology, 412 96 Göteborg, Sweden

Recently there has been an increasing interest in studying the growth and properties of nitrogen-containing III-V materials like GaAsN, because it can be lattice matched to Si. We present optical studies of GaAsN layers of several microns thickness with different nitrogen concentration. The GaAsN layers were grown by molecular beam epitaxy on GaAs substrates at a temperature of 580°C. The nitrogen content in the layers was determined by SIMS and X-ray diffraction. From X-ray data three different phases were identified in the layers: GaAs, GaAsN, and GaN. An attempt was made to characterise these three phases by optical techniques. The GaAs phase in the layers was easily monitored in low temperature photoluminescence (PL) spectra. The GaAsN phase gave no PL, but was possible to detect in transmission via its absorption edge below the GaAs bandgap. The GaN phase finally was studied via UV PL data. A complicated PL spectrum was observed at photon energies below 3.4 eV. The variation of these optical properties for a number of samples covering a broad composition range will be discussed.

L-IX.3 14:50-15:10

THE EVOLUTION OF a-$GaAs_{1-x}N_x$ / c-GaAs INTERFACE STATES AS A FUNCTION OF Ar - NH_3 PLASMA, K. Aguir, D.B.B. Lollman and H. Carchano, Laboratoire EPCM, Service A62, Faculté des Sciences de Saint Jérôme, Université d'Aix-Marseille III, 13397 Marseille Cedex 20, France

We have studied the electrical properties of amorphous $GaAs_{1-x}N_x$ thin films grown on GaAs substrates. Film deposition was carried out by RF sputtering of a GaAs target by adding a nitrogen carrier gas (NH_3) to an Ar plasma.

Chemical etching of substrates followed by different plasma treatments (like reverse bias or NH_3 glow discharge) prior to film deposition have been studied. The effects of substrate and growth temperature and of total pressure in the reactor have been analysed.

C(V) and C(T) characteristics have enabled us to put in evidence the evolution of interface states of the a-$GaAs_{1-x}N_x$/c-GaAs junctions. The amorphous $GaAs_{1-x}N_x$ thin films might be potentially used as dielectrics in GaAs-based MIS structures, due to their relatively high resistivity values, or as passivating layers on GaAs devices.

15:10-16:00 **BREAK**

Session X - Poster Session

16:00-18:00 See programme of this poster session p. L-21 to L-23.

Thursday June 19, 1997 | Morning
Jeudi 19 juin 1997 | Matin

Session XI - Optical Properties of GaN, Part 3

L-XI.1 8:30-8:50

COMPARATIVE STUDY OF HEXAGONAL AND CUBIC GaN GROWN BY RF-MBE, F. Widmann, B. Daudin, G. Feuillet, M. Arlery, J.L. Rouviere, CEA Grenoble, Département de Recherche Fondamentale sur la Matière Condensée, 38041 Grenoble Cedex, France

The cubic and hexagonal phases of GaN have different optical, electronic and structural properties which might bear some significance for device performances.

We wish here to comment upon the different physical properties of the two phases for GaN grown by RF-MBE. Hexagonal c-oriented GaN was grown either on homoepitaxial MOCVD GaN epilayers or directly on c-plane sapphire and exhibits a sharp (FWHM=8meV) exciton related PL peak centered at 3.47 eV. On the other hand, cubic (001) GaN was grown on CVD (001) SiC layers deposited on (001) Si: in this case PL spectra consist in both a free exciton peak centered at 3.27 eV, with a FWHM of about 19 meV and a D-A pair related peak. The yellow band centered at about 2.1 eV commonly observed in hexagonal GaN- the intensity of which is shown here to depend upon the flux stoichiometry and growth temperature - is absent in cubic phase GaN . These results are discussed in the light of TEM results concerning the nature of defects present in the two types of materials.

L-XI.2 8:50-9:10

PHOTOLUMINESCENCE STUDY OF MBE GROWN GaN/LiGaO$_2$ LAYERS, A.V. Andrianov, D.E. Lackison and J.W. Orton, Department of Electrical and Electronic Engineering, University of Nottingham, Nottingham, UK, T.S. Cheng, N.J. Jeffs and C.T. Foxon, Department of Physics, University of Nottingham, Nottingham, UK, K.P. O'Donnel and J.F.H. Nicholls, Department of Physics and Applied Physics, University of Strathclyde, Glasgow, UK.

The use of unique physical properties of GaN are still impeded by the large density of crystal defects that have a strong influence on the optical and electrical properties of the material. At present the most widely used substrate for practical applications of GaN is c-plane of sapphire. However the 16% lattice mismatch of sapphire compared with GaN can put severe limits on attempts to improve the quality of real devices. One of possible ways to solve this problem is homoepitaxy of GaN, but the bulk GaN crystals are not yet freely available. Recently the orthorhombic ternary compound LiGaO$_2$ has attracted attention as a possible substrate material for the group-III nitrides since it has a mismatch of only 0.2 % to GaN.

In the present work GaN films on LiGaO2 substrates have been grown by a modified MBE method and studied in detail by a photoluminescence (PL) spectroscopy technique. The experimental data allow us to conclude that the films contains both hexagonal and cubic crystallites. The main PL lines (6 K) are due to emission of excitons bound on neutral donors in hexagonal and cubic phases of the epitaxial film (3.472 eV and 3.263 eV), D-A pair recombination (3.154 eV) and free electron- neutral acceptor transition (3.185 eV) in c-GaN. The involved acceptor has a binding energy of about 115 meV. The estimated average distance between D-A pairs is 30-40 nm. The X-ray diffraction data also suggest the existence of both c- and h-GaN in the epitaxial layers. However the PL signal from cubic phase is greater than PL from hexagonal one. This enhancement of emission of cubic phase with respect to hexagonal one could be caused by a preferential overflow of nonequilibrium photoexcited carriers to narrow band gap cubic phase.

L-XI.3 9:10-9:30

DISLOCATION GENERATION AND REDUCTION IN GaN HETEROEPITAXY, J.S. Speck(1), X.H. Wu(1), P. Fini(1), E.J. Tarsa(1), D. Kapolneck(1), S. Keller(2), U.K. Mishra(2), and S.P. DenBaars(1,2), (1)Materials Dept. and (2)ECE Dept. Univ. of California, Santa Barbara, CA 93106, USA

Experimental results and models are presented for the mechanisms of threading dislocation (TD) generation and reduction in GaN growth on sapphire. The optimal nucleation layers (NLs) for achieving low TD density material (with high electron mobility, >700 cm^2/Vs at 298 K, sand strong PL) consist of mixed cubic/hexagonal GaN, which sustains its stacking disorder and island-like morphology after heating to HT. The HT growth proceeds by the formation of coarse islands which then coalesce. The HT island coalescence is accompanied by rapid surface smoothing. Isolated HT islands generally contain a small number of mixed or pure screw character TDs, whereas the majority of the edge TDs are generated at island coalescence. Under optimal conditions, a total TD density of ~5x10^{8}cm^{-2} can be achieved. Using identical NLs (Material A conditions in previous reports), controlling the HT growth conditions can markedly change the HT island nucleation density and lead to changes in the TD density by as much as two orders of magnitude.

We present dislocation-based models to the TD generation and evolution, for which the essential features have been verified by TEM studies. The stacking disorder between the NL and HT GaN is accommodated by Frank and Shockley partial dislocations, which do not generate TDs, whereas regions of the NL that have coalesced and transformed to hexagonal GaN are a source of TDs in the HT GaN.

L-XI.4 9:30-9:50 COMPARISON OF LUMINESCENCE AND PHYSICAL MORPHOLOGIES OF GaN EPILAYERS - AN OVERVIEW, C. Trager-Cowan, P.G. Middleton and K.P. O'Donnell, Department of Physics and Applied Physics, University of Strathclyde, Glasgow, Scotland, UK

Our recent studies of disparate GaN epilayers using atomic force microscopy (AFM), scanning electron microscopy (SEM) and cathodoluminescence (CL) imaging and spectroscopy has demonstrated that the morphological and luminescence properties of samples can vary dramatically. Some samples contain large hexagons of various dimensions - up to tens of microns across and several microns high - while others exhibit a net-like structured surface. For the hexagon-containing material there is a definitive correlation between surface structure and the luminescence properties, while for those samples with the net-like structure we observe little correlation. The hexagon-containing samples show no deterioration in emission intensity even under very high electron beam excitation (≈GWatts/cm^2), whereas for the net-like structured samples, the luminescence is quenched under electron beam excitation.

Sasaki [1], for example, has shown that morphology depends strongly on growth conditions. In work presently being carried out, using AFM, SEM and CL and PL studies we aim to elucidate the link between growth conditions, physical morphology and luminescence properties by a systematic study of a number of series of samples. For each series only one growth parameter has been varied, for example the gas flux and the buffer layer growth conditions.

We are grateful to Nottingham, Gent, Minnesota, Joseph Fourier and Montpellier Universities for the provision of samples.

[1] T. Sasaki, J. Cryst. Growth 129 (1993) 81-90.

L-XI.5 9:50-10:10 STRONG MORPHOLOGICAL DEPENDENCE OF LUMINESCENCE EFFICIENCY AND EMISSION WAVELENGTH IN HEXAGONAL GaN CRYSTALLITES DIRECTLY IMAGED BY SCANNING CATHODOLUMINESCENCE MICROSCOPY, F. Bertram, J. Christen, M. Schmidt, Inst. für Experimentelle Physik, Otto-von-Guericke-Uni., Uni-Platz 2, 39106 Magdeburg, Germany and M. Topf, S. Koymov, S. Fischer, B.K. Meyer, Justuts-Liebig-Uni., H.-Buff-Ring 16, 35392 Gießen, Germany.

Microscopical variations of local band gap and luminescence wavelength on the a- and c-planes of hexagonal GaN-crystallites are directly mapped by means of low temperature scanning cathodoluminescence (CL) and CL wavelength imaging (CLWI)[1].20 µm thick films of hexagonal GaN-layer were grown by low pressure chemical vapor deposition[2] on (0001) sapphire substrates, consisting of single crystal hexagonal columns with typical diameters of 5-20µm. In CLWI we find significant difference between the luminescence from the a-plane and the top c-plane forming the microcrystallites: Beside minor fluctuation of emission energy from crystallite to crystallite, the a-planes show a pronounced red shift of emission energy of more then 50meV with respect to the emission form the center region of the c-plane. Obviously different strain for a- and c-plane are shown. Even more pronounced is a blue shift in the CLWI of ≈22meV at the (0001) edges at each hexagonal corner between the a-planes. The c-plane itself shows additional inhomogeneity on a micron scale. Strongly red-shifted luminescence ($\lambda \geq 380$nm) originals from the very center regions of the c-planes. Here we found a high dislocation density in TEM analysis. The CL intensity shows a reticulated structure on the c-plane visualizing the local dislocation network.

[1] J. Christen, M. Grundmann, D. Bimberg, J. Vac. And Technol. B9, 2358 (1991)

[2] M. Topf, et al., III-V Nitrides, Eds. T.D. Moustakar et al., Mat. Rev. Soc. Sym. Proc. 449 (1997)

10:10-10:40 **BREAK**

Session XII - Quantum Phenomena, Part 2

L-XII.1 10:40-11:00 NONLINEAR PROPERTIES OF GaN, H. Haag, S. Petit, P. Gilliot, R. Lévy, IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France, O. Briot, R.L. Aulombard, Université de Montpellier, Groupe d'Etudes des Semiconducteurs, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

We studied luminescence and induced absorption of GaN grown on sapphire substrate by MOCVD.

We measured the nonlinear behaviour of the luminescence spectra, by using an excitation at 308 nm from an excimer laser. A tunable dye laser enables us to measure the excitation spectra of the luminescence.

The induced absorption was studied using a pump and probe configuration. With the excimer laser as pump beam and a dye continuum, we measured the variation of absorption of GaN as a function of the intensity of the pump beam. The tunable pump dye laser is used to obtain the excitation spectrum of the induced absorption. The dynamics of this absorption variation was studied in the same configuration using the third harmonic of a picosecond Nd-YAG laser as pump beam and a spectrally broad dye emission as probe beam with variable delays between pump and probe pulses.

L-XII.2 11:00-11:20 ROLE OF THE V/III PRECURSOR RATIO ON EXCITON DYNAMICS IN GaN MOCVD EPILAYERS, P. Lefebvre, J. Allègre, S. Clur, O. Briot and H. Mathieu, Groupe d'Etude des Semiconducteurs, CNRS, Université Montpellier 2, CC 074, 34095 Montpellier Cedex 5, France

Time-resolved photoluminescence spectroscopy is performed on strained epilayers of GaN, grown by MOVPE on Al_2O_3 substrates. As the V/III precursor ratio R is increased so as to approach the ideal stoechometry, the decay time of the donor-accepter pair (DAP) recombinations at ~3.22 and ~3.29eV is changed from ~lns to much more than 20ns. Coherently with this change, the X_A and X_B free excitons and a donor-bound exciton D_0X lying 5.7 meV below X_A are subject to significant variations. For R~8000, DAP transitions are fast and the D_0X recombination dominates the spectrum at T=8K, with decay times of ~35-45ps, while free excitons decay on a ~25ps time scale. For R~10000, the DAP transitions are very slow and all excitonic recombinations become faster : times of up to ~80ps are obtained for D_0X and 35ps for the X_A line, which now dominates the time-integrated spectrum. Exciton dynamics in GaN epilayers can thus be controlled by the V/III precursor ratio, which is tentatively related to the variation of density of nitrogen vacancies.

L-XII.3 11:20-11:40 QUANTUM BEAT SPECTROSCOPY OF EXCITONS IN GALLIUM NITRIDE, R. Zimmermann, M. Hofmann, D. Weber, J. Möbius, A. Euteneuer, and W.W. Rühle, Fachbereich Physik und Zentrum für Materialwissenschaften, Renthof 5, 35032 Marburg, Germany, E.O. Göbel, Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany, B.K. Meyer, 1.Physikalisches Institut der Universität Giessen, Heinrich-Buff-Ring 16, 35393 Giessen, Germany, H. Amano and I. Akasaki, Department of Electrical and Electronic Engineering, Meiji University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-01, Japan

Quantum beat spectroscopy by means of transient four wave mixing experiments in the spectral regime of excitonic resonances has been prooven to be a powerful tool for the precise determination of small energetic differences as, e.g. excitonic and biexcitonic binding energies [1,2]. We present to our knowledge the first four wave mixing experiments on excitons in GaN and observe pronounced beats. The resulting energy splittings as well as the respective dephasing times are discussed in detail.

[1] M. Koch, J. Feldmann, E.O. Göbel, P. Thomas, and K. Köhler. Phys. Rev. Lett. 69, 3631 (1992).

[2] E.J. Mayer, G.O. Smith, V. Heukeroth, J. Kuhl, K. Bott, A. Schulze, T. Meier, S.W. Koch, P. Thomas, R. Hey, and K. Ploog. Phys. Rev. B50, 14730 (1994).

L-XII.4 11:40-12:00 GaN/AlGaN QUANTUM WELL: EFFECT OF BIEXCITON, E.Hartung and B.S.Monozon, Dept. of Chemistry, University of North Carolina at CH, USA, Dept. of Physics, Marine Technical University, St. Petersburg, Russia

It has been demonstrated by a research group of R.F Davis at NCSU that the photoluminescence spectra of GaN and AlGaN films reveal strong bound exciton emission with a FWHM of 4 meV. An investigation is reported of an analytical model in which the application of a magnetic field allows us to distinguish this feature from bound excitons and provides evidence of its biexciton nature. A method of approximate solution is suggested for the two-photon absorption in a GaN/AlGaN quantum well using the system of Schrodinger equations describing the exciton-exciton interaction in III-V compounds in the presence of a magnetic field. In the two- band approximation. the analytic expressions depending explicitly on the GaN system parameters are obtained for the oscillator strength of the transitions.

L-XII.5 12:00-12:20 III-V NITRIDES : WURTZITE SYMMETRY AND OPTICAL ABSORPTION, P. Bigenwald, P. Christol, L. Konczewicz, P.Testud, LPM, UFR Sciences, 33 rue Pasteur, 84000 Avignon, France and B. Gil, GES-CNRS, Université de Montpellier II, CC 074, 34095 Montpellier Cedex 5, France

R&D electronic engineers are requested to demonstrate smart chips meeting tight criteria in terms of speed and reduced overheating. Multimedia explosion and its subsequent need of large storage capacities and fast telecom networks urged the issue of applications such as the DVD (digital video disk). III-V nitrides achieve the optical and electronic efficiency in the visible and UV range and are already available on the market. But the knowledge of their intimate physical properties has still to be extended. The engineering developed for GaAs can not be totally transferred since nitrides generally adopt the wurtzite crystal symmetry.

Optical efficiency of a SC diode (emission/absorption) depends basically on exciton properties, we shall give the dispersion relations for bulk GaN and AlN materials and effective masses for mixed A, B and C valence bands as a function of the in-plane wavevector. The second part of this communication will deal with single AlN-(Al,Ga)N quantum wells. We will present the results of our calculations on the exciton (oscillator strength, Rydberg energies, exchange interaction) taking into account the strain related to the lattice mismatch.

12:20-14:00 **LUNCH**

Thursday June 19, 1997
Jeudi 19 juin 1997

Afternoon
Après-Midi

Session XIII - InGaN

L-XIII.1 - invited - 14:00-14:30

COMPOSITION FLUCTUATIONS IN GaInN HETEROSTRUCTURES AND QUANTUM WELLS : LIMIT TO DEVICE APPLICATIONS ?, **F. Scholz**, A. Sohmer, J. Off, V. Syganow, A. Dörnen, J.-S. Im, A. Hangleiter, 4.Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany, J.Y. Duboz, P. Galtier, E. Rosencher, Thomson CSF, Physics Lab., Lab. Central de Recherche, 91404 Orsay, France, and H. Lakner, Werkstoffe der Elektrotechnik / FB9, Gerhard Mercator Universität, 47048 Duisburg, Germany

GaN and related compounds have attracted great interest due to their possible application in short wavelength optoelectronics. However, nitride semiconductor laser diodes are still a challenge, and only very few groups succeeded to realize first ultraviolet light emitting laser diodes. Besides the basic problems in growing nitrides, the growth of $Ga_{1-x}In_xN$ - necessary to tune the emission wavelength into the visible spectrum - has turned out to show additional problems. Thermodynamic calculations predict a large miscibility gap for x exceeding about 6 to 8%. Furthermore, the large strain between GaInN and GaN may play an important role.

We have studied the growth of GaInN hetero structures by low pressure MOVPE. The In incorporation efficiency into GaInN, only significant for reduced growth temperatures of 700 to 800°C, could be increased by reducing the H_2/N_2 flow ratio in the main carrier gas and by increasing the TEGa flow rate, i.e. the growth rate. However, our spectroscopic data show that GaInN layers with larger In content contain some structural defects. This may be caused by composition fluctuations in these ternary layers as further evidenced by scanning transmission electron microscopy.

L-XIII.2 14:30-14:50

CATHODOLUMINESCENCE STUDY OF CRYSTALLINE QUALITY OF (Al, Ga, In) N HETEROSTRUCTURES, Q. Liu, H. Lakner, A. Meinert, and E. Kubalek, Gerhard-Mercator-Universität Duisburg, Werkstoffe der Elektrotechnik, 47048 Duisburg, Germany, and F. Scholz, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

Group III-nitride heterostructures have recently emerged as important semiconductor materials with applications to high power devices and light emitting devices in the visible and ultra-violet range. For improved device performance and reliability the concentration of deep levels caused by defects needs to be minimized. The goal of this work is non-destructive, spatially resolved characterization of defects and microstructures of MOVPE-grown wurtzite (Al, Ga, In)N heterostructures in correlation with growth parameters. We applied spectral and panchromatic cathodoluminescence (CL) combined with secondary electron (SE) imaging to investigate the electro-optical as well as the structural properties of (Al, Ga, In)N heterostructures, such as various energy levels, radiative recombination centers, interfacial quality and crystalline defects. Our CL study on various group-III nitride quantum well structures shows distinct correlations between defects and luminescence behaviours. Panchromatic CL micrographs exhibit typically inhomogeneous emission intensity. Further studies using spatially resolved spectral CL measurements show, that the regulated intensity inhomogeneity (on a - 1μm scale) is related to local variations of the interface quality, while CL-spectra recorded from dislocation sites are dominated by the so-called «yellow- emission». Additionally, high resolution x-ray diffractometry (HRXRD) and scanning transmission electron microscopy (STEM) were used to examine the structural properties and their correlation to CL results.

L-XIII.3 - invited - 14:50-15:20

GAIN SPECTRA IN CW InGaN/GaN MQW LASER DIODES, T. Deguchi, T. Azuhata, and **T. Sota,** Department of Electrical, Electronics, and Computer Engineering, Waseda University, Shinjuku, Tokyo 169, Japan, S. Chichibu, Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278, Japan, and S. Nakamura, Department of Research and Development, Nichia Chemical Industries Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

Stimulated emission peaks, on the one hand, have shown a blue-shift in comparison with the spontaneous emission one in the current injected cw and pulsed operation InGaN LDs as well as in the optical pumped GaN/AlGaN SCH structure, GaN/AlGaN vertical cavity surface emitting laser, and cleaved cavity InGaN/GaN laser. On the other hand, a lot of works for III-nitrides have reported a red-shift of the peak of the stimulated emission compared with the spontaneous one. The controversy seems to make it difficult to assign the stimulated emission mechanisms.

We will present a systematic study on the stimulated emission by means of optical pumping in the cw operation InGaN LDs' wafers with the use of the variable excitation-stripe length method to get an insight into the stimulated emission mechanisms. Discussions will be given on obtained gain spectra under a variety of conditions.

L-XIII.4 - invited - 15:20-15:50

RECOMBINATION DYNAMICS OF LOCALIZED EXCITONS IN SELF FORMED InGaN QUANTUM DOTS, **Y. Kawakami**, Y. Narukawa, Shizuo Fujita and Shigeo Fujita, Department of Electronic Science and Engineering, Kyoto University, Kyoto 606-01, Japan, S. Nakamura, Department of Research and Development, Nichia Chemical Idustries Ltd., Anan, Tokushima 774, Japan

Currently, much interest has been focused on $In_xGa_{1-x}N$-based semiconductors because of both the realization of incandescent blue, green and yellow light emitting diodes (LEDs),[1] and the first operation of purplish blue laser diodes (LDs) at room temperature (RT) under continuous wave (CW) mode.[2] Although the achievement of the high quantum efficiency of these devices is owing to the use of InGaN ternary alloys as the active layer, little has been known about the optical properties of InGaN quantum wells (QWs).

Detailed nature of the exciton localization in a $In_{0.20}Ga_{0.80}N$ multiple quantum well (MQW) LD structure has recently been revealed by means of transmittance (TR), electroreflectance (ER), photoluminescence excitation (PLE) and time-resolved PL (TRPL) spectroscopy, where the main spontaneous emission was attributed to localized excitons whose trap center is located below the lowest n=1 quantized level by about 250meV. [3] The depth of the trap center was so large that the localized excitons dominated the PL spectra even at RT.

Structural analysis has been performed on this structure, by employing transmission electron microscopy (TEM) and energy-dispersive X-ray microanalysis (EDX), both of which are assessed from cross sectional direction. It has been found that the contrast of light and shade in the well layers corresponds to the difference of In composition. Consequently, the origin of exciton localization has been attributed to In-rich region in the wells acting as quantum dots (QDs) which are self-formed by spinodal phase separation.[4]

In this symposium, dynamics of excitons in $In_xGa_{1-x}N$-based QWs will be presented based on localization, radiative and nonradiative recombination processes.

(l) S. Nakamura et al., Jpn. J. Appl. Phys. 34, L797 (1995).
(2) S. Nakamura et al., Appl. Phys. Lett. 70, 868 (1997).
(3) Y. Narukawa, Y. Kawakami, Sz. Fujita, Sg. Fujita and S. Nakamura, Phys. Rev. B 55, R1938 (1997).
(4) Y. Narukawa, Y. Kawakami, M. Funato, Sz. Fujita, Sg. Fujita and S. Nakamura, Appl. Phys. Lett. 70, (1997, 24 February issue) in press.

L-XIII.5 15:50-16-10

STIMULATED EMISSION OF GaN LAYERS AND DEVICES, K.P. O'Donnell(1), M. Umlauff(2), M. Kraushaar(2), H. Kalt(2), O. Briot(3), (1)Department of Physics and Applied Physics, University of Strathclyde, Glasgow, Scotland, UK, (2)Institute for Applied Physics, University of Karlsruhe, Germany, (3)Groupe d'Etude des Semiconducteurs, Montpellier II, France

Stimulated emission of epitaxial GaN layers is readily obtained at photo-excitation densities of order 1 MW cm^{-2} at temperatures up to room temperature. We report surprising spectral differences between stimulated emission obtained using surface and edge emission geometries for particular samples. While stimulated emission from the surface of such samples is only weakly downshifted from the GaN bandgap, the photon energy of the edge-emitted light is approximately 100 meV less. The same downshift is observed in the edge emission spectrum of a commercial Nichia light emitting diode. The anomalous stimulated emission peak may be due to population inversion at stacking faults or domain boundaries.

L-XIII.6 16:10-16:30

INVESTIGATIONS OF SELECTIVELY GROWN GaN/InGaN EPITAXIAL LAYERS, O. Gfrörer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter, 4. Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

Selective growth is a very promising method for the realization of integrated optoelectronic devices. We have studied GaN/lnGaN samples grown by selective area low pressure metalorganic vapor phase epitaxy (LP-MOVPE) on partially masked substrates. On the c-face of the sapphire substrate we grow an about 10nm AlN nucleation layer and a 1 µm GaN buffer layer. Then SiO_2 was deposited. Using photolithography and wet etching, quadratic and circular areas of 500 µm were opened. On these areas, InGaN layers of various thickness were embedded between a second GaN buffer layer and a GaN top layer.

In the heteroepitaxial growth of the group III-nitrides it is well known, that the mismatch in thermal expansion coefficients between the nitrides and the substrates results in strain of the layers depending on their thickness and composition. Cathodoluminescence investigations we made to probe the local dependencies of the resulting strain in the selectively grown samples. The results were compared to the ones for growth on plain sapphire substrates where relaxation of the stress can be observed at cleaved edges for the GaN layers and the InGaN layers. The influence of the pressure on the spatial variation of the Indium incorporation and the growth rates was investigated as well as the local dependencies of the growth rates at the edges of the masked areas where growth enhancement can be seen.

Friday June 20, 1997 **Morning**
Vendredi 20 juin 1997 Matin

Session XIV- LEDs and LDS with InGaN

L-XIV.1 - invited - 8:30-9:10

RT CW OPERATION OF InGaN MULTI QUANTUM WELL STRUCTURE LASER DIODES, **S. Nakamura**, Department of Research and Development, Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

Major developments in wide-gap III-V nitride semiconductors have recently led to the commercial production of high-brightness blue/green light-emitting diodes (LEDs) and to the demonstration of room- temperature (RT) violet laser light emission in InGaN/GaN/AlGaN-based heterostructures under pulsed currents and continuous-wave (CW) operation. Recombination of localized excitons was proposed as an emission mechanism for the spontaneous emission of the InGaN quantum-well-structure LEDs and LDs. The fundamental properties of semiconductor lasers are specified by the optical gain. However, experimental data regarding the optical gain of RT CW-operated III-V nitride-based LDs have not been reported. Recently, RT CW operation of the InGaN MQW LDs with a lifetime of 35 hours has been achieved. Using these RT CW-operated LDs, it is interesting to measure the characteristics of the LDs in detail especially those of the emission mechanism.

Here, we report the optical gain and the emission characteristics of InGaN single-quantum-well (SQW) LEDs and MQW LDs. The carrier lifetime and the threshold carrier density were estimated to be 2-10 ns and 1 x 10^{20}/cm^3, respectively. For the measurement of the gain spectra of the LDs, the Hakki-Paoli technique was used. The differential gain coefficient, the transparent carrier density, the threshold gain and the intrinsic loss were estimated to be $5.8\text{x}10^{-17}$ cm^2, $9.3\text{x}10^{19}$ cm^{-3}, 5200 cm^{-1} and 46 cm^{-1}, respectively, from the measurement of the gain spectra.

L-XIV.2 - invited - 9:10-9:40

CHARACTERIZATION OF MOCVD GROWN InGaN/AlGaN HEREROSTRUCTURES FOR BLUE LED APPLICATIONS, **C.A. Tran**(1), R.F. Karlicek Jr.(1), M. Schurman(1), T. Salagaj(1), Y. Li(2), I. Ferguson(1), Z.C. Feng(1), A.G. Thompson(1), R.A. Stall(1), Y. Park(2), A.G. Choob(2) and H.S. Park(2), (1)EMCORE Corp., 394 Elizabeth Avenue, Somerset, NJ 08873, USA, (2)Departement of ECE, Rutgers University, Piscataway, NJ 08855, USA, (3)SAIT, PO Box 111, Suwon 440-600, Korea

In this paper we describe the metalorganic chemical vapor deposition (MOCVD) growth and characterization of InGaN/AlGaN heterostructures for LED applications. The growth was carried out in a large area multi-wafer (6x2') rotating disc low-pressure MOCVD system designed for LED mass production. The characterization includes measurements of structural properties (X-ray diffractometry, transmission electronic microscopy), optical properties (photoluminescence (PL), transmission) and electrical properties for n- and p-GaN (Hall and contactless resistivity). The real-time monitoring of the growth process using in-situ reflectance will be presented and discussed. It was found that under certain growth conditions phase separation of both InGaN bulk layer and $In_xGa_{1-x}N/In_yGa_{1-y}N$ multi-quantum wells can occur. The influence of indium inter-diffusion on PL wavelength and the shape of X-ray satellite peaks will be discussed. The electroluminescence spectra of LEDs with different active layer structures will also be presented.

L-XIV.3 9:40-10:00

THE OPTICAL LINEWIDTH OF InGaN LIGHT EMITTING DIODES, P.G. Middleton and K.P. O'Donnell, Department of Physics and Applied Physics, University of Strathclyde, Glasgow, Scotland, UK, T. Breitkopf and H. Kalt, Institute for Applied Physics, University of Karlsruhe, Germany, and W. Van der Stricht, I. Moerman and P. Demeester, IMEC- INTEC, University of Gent, Belgium

The optical linewidths of photo- and electroluminescence from high-quality InGaN epilayers and commercial single quantum well light emitting diodes (LEDs) were compared. In both cases, optical linewidths are found to be temperature-insensitive and to increase systematically with luminescence peak energy. By assessing quantitatively the contribution of three mechanisms to the linewidth - alloy fluctuations, well width fluctuations, and strain effects - we show that the observed broadening of the emission lines is an intrinsic property of InGaN alloys. For the purpose of this investigation the existence of a random alloy has been assumed. However, we highlight the issue of immiscibility in InGaN alloys and the consequences of quantum dot formation in the active layer. The piezoelectric effect in wurtzite semiconductors is suggested as a novel line-broadening mechanism in LEDs.

10:00-10:30 am **BREAK**

Session XV - GaN for Opto, Part 1

L-XV.1 - invited - 10:30-11:00

DIFFUSION LENGTH OF PHOTOEXCITED CARRIERS IN GaN, **J.Y. Duboz**, F. Binet, N. Laurent, Laboratoire Central de Recherches, Thomson-CSF, 91404 Orsay, France, O. Briot, B. Gil, GES, Université Montpellier II, 34095 Montpellier, France, F. Scholz, J. Off, A. Sohmer, 4.Physikalisches Institut, Universität Stuttgart, 70550 Suttgart, Germany

GaN based materials have already demonstrated their large potential for optoelectronic applications. Devices for light emission and detection have been demonstrated and exhibit excellent performances. Besides remaining difficulties related to the growth, additional problems as the limited diffusion of photoexcited carriers have been pointed out.

We present an extensive study of the diffusion length in GaN. Various experiments will be presented. The measurement of the photoresponse in back-side illuminated Schottky diodes, its spectral analysis and a model based on a one-dimensional diffusion gave a hole diffusion length of about 0.1 µm. This result was compared with measurements in Schottky diodes with various GaN thicknesses below the metal. The temperature dependence of the diffusion was studied in this geometry from 300 K down to 80 K. Contrary to these measurements of diffusion along the growth direction, transport measurements in the plane of the layers can also be performed and results will be given. Finally, a study of the diffusion based on photoluminescence measurements in InGaN/GaN quantum wells will be shown. The temperature evolution of the diffusion in these heterostructures will be given.

L-XV.2 - invited - 11:00-11:30

GaN BASED LEDs BY MOVPE, B. Beaumont, **P. Gibart**, M. Leroux, CRHEA-CNRS, Sofia Antipolis, Rue B. Grégory, 06560 Valbonne, France; E. Calleja and E. Munoz, Dept. de Ing Electronica, ETSIT, 28040 Madrid, Spain

For almost two decades, p-doping of GaN was not feasible. Since the ionization energy of any acceptor species is greater than 200 meV, the hole concentration obtained by p-doping is only one hundreth of the acceptor impurity concentration. Mg has been so far the most typical dopant used for p-type GaN. In MOVPE, the precursor was the bismethyl-cyclopentadienyl Mg (MeCp2Mg). However two severe drawbacks must be overcome. The Mg precursor and ammonia react in the vapour phase to give solid particles. In addition H is incorporated during the growth process, thereby a post growth annealing is required. The Mg doped GaN samples studied were grown by MOVPE on (0001) oriented sapphire substrates. With proper design of the growth chamber and thermal annealing, doping densities up to 1.5.10^{18}cm^{-3} have been reached. Pl and Photocapacitance data reveal in addition to the shallow acceptor deep states most likely related to Mg complexes. N-doping is straightforward. Si is easily introduced via silane and allows to reach free carriers concentration up to 10^{19}cm^{-3}. Henceforth a p-n junction, LEDs were achievable. Under high injection (~4kA/cm^2) these LEDs, the blue-W emission dominates.

L-XV.3 - invited - 11:30-12:00

ELECTRICAL AND OPTICAL PROPERTIES OF p-SiC/n-GaN HETEROSTRUCTURES, **M. Topf**, D. Meister, I. Dirnstorfer, G. Steude, S. Fischer, B.K. Meyer, 1. Physikalisches Institut, Justus-Liebig-Universität Giessen, 35392 Giessen, Germany, A. Krtschil, H. Witte, J. Christen, Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, 39016 Magdeburg, Germany, T.U. Campen, W. Mönch, Laboratorium für Festkörperphysik, Universität Duisburg, 47048 Duisburg, Germany

SiC/GaN pn-hetero-diodes were fabricated with low pressure chemical vapor deposition (LPCVD) by growing GaN films on p-type 6H-SiC substrates.

The samples were investigated by means of temperature dependent current-voltage as well as frequency dependent admittance measurements. The diodes exhibited a good rectifying behaviour with a maximum forward to reverse current ratio of 10^5 at room temperature. Capacitance-voltage-characteristics revealed an interfacial layer at the heterojunction. This leads to an capacitance plateau at low forward bias (V=2...5V) and to a very small dependence of the depletion capacitance on the applied bias. Assuming a thermionic emission, the effective barrier was determined to 168 meV from temperature dependent current voltage characteristics in forward direction. Thermal admittance spectra (TAS) show a bias independent maximum in conductivity and a step in capacitance at temperatures between 120...200K with an activation energy of 166±1 meV. Furthermore a step in capacitance at 200K was found in TAS spectra of the heterostructure biased in forward direction. This step shows a strong dependence on the bias voltage. Such behaviour is characteristic for near interface defect states. In addition temperature dependent photoluminescence (PL) and electroluminescence (EL) of the p-SiC/n-GaN diodes was performed. The PL spectra are dominated by the excitonic emission of GaN around 3.4 eV at room temperature. However the EL consists of two emission bands peaking around 2.4 eV and 2.8 eV.

In the view of the electrical and optical data the band offsets in the heterostructure are discussed including a barrier caused by the interfacial layer.

12:00-14:00 **LUNCH**

Friday June 20, 1997
Vendredi 20 juin 1997

Afternoon
Après-Midi

Session XV - GaN for Opto, Part 2

L-XVI.1 14:00-14:20

FREQUENCY RESPONSE OF UV PHOTODETECTORS BASED ON GaN GROWN BY MBE, L.B. Flannery, I. Harrison, D.E. Lacklison, Department of Electrical and Electronic Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK, and T.S. Cheng, C.T. Foxon, Department of Physics, University of Nottingham, University Park, Nottingham NG7 2RD, UK

There have been several reports of photoconductive devices based on GaN and AlGaN. These in the main have been grown by MOCVD. We report here results from photoconductive experiments on both n and p-type material grown by MBE. In other III-IV materials, the different growth methods give rise to traps with different signatures. GaN is believed to be an exception to this rule. We have measured the photoresponse as a function of frequency and from this estimated the lifetime of the trapped carriers. By varying the temperature over the range -25°C to 40°C, we have been able to measure the energy of the trap controlling the photoconductive process. These results will be presented in this paper.

L-XVI.2 14:20-14:40

THE GROWTH, FABRICATION AND CHARACTERIZATION OF III-NITRIDE MSM AND P-N JUNCTION ULTRA-VIOLET PHOTODETECTORS, J. Ferguson, C.A. Tran, Y. Li and R.F. Karlicek Jr. , EMCORE Corporation, Somerset, NJ 08873, USA, and S. Liang, Department of ECE, Rutgers University, Piscataway, NJ 08855., USA

Interdigital metal-semiconductor-metal (MSM) and p-n junction Ultra-violet (UV) photodetectors have been successfully grown and fabricated from GaN based materials. All the structures were grown in a multi-wafer rotating disc low pressure MOCVD system developed specifically for the epitaxial growth of III-Nitrides. Excellent uniformity of material properties as that required for the commercial production of large area UV focal plane arrays, ty ically 1-2% variation, was obtained during the simultaneous deposition of III-Nitrides on 7 x 2» wafers. The MSM devices were produced using two types of GaN; high-resistive GaN and Mg doped GaN. For the high-resistive GaN detector, the lowest dark current is ~0.1 nA and the UV responsivity of the device was about 460 A/W at a DC bias of 30 V. The Mg doped GaN exhibited larger gains, 1150 A/W at 2.0 V, but at much higher dark currents, 400 nA. The high gain in this device is not well understood but has attributed to an 'avalanche' effect and is under further investigation. The feasibility of a photovoltage detector structure based on alloys of GaN has also been proven. A GaN/GaInN structure exhibited a cut-off at 2.9 eV with a responsivity of 0.28 A/W at zero bias for an active region of only 500 Å thick.

L-XVI.3 14:40-15:00

COMPARISON OF WURZITE AND ZINC-BLENDE III-V NITRIDES FET's/A 2D MONTE CARLO DEVICE SIMULATION, F. Dessenne$^{(1)}$, D.Cichoka$^{(2)}$, P.Desplanques$^{(1)}$ and R. Fauquembergue$^{(1)}$, $^{(1)}$Institut d'Electronique et Microelectronique du Nord - DHS, University of Lille, 59652. Villeneuve d'Ascq, France ; $^{(2)}$Instytut Fizyki, Politechnika Warszawska 00662 Warszawa, Poland

The III-V Nitrides have recently attracted considerable attention for their application in short wavelength optoelectronic devices. They are also very appealing because their thermal stability, their high breakdown voltages due to a wide band gap and their high electron velocities make these materials suitable for high power and high temperature electronic devices. When grown on Sapphire or SiC substrates, III-V nitrides cristallize in the Wurzite (hexagonal) phase, whereas on Si or GaAs substrate, the Zinc- Blende (cubic) phase is obtained and exhibits better electronic transport properties than the Wurzite one [1]. Recently, microwave Heterojunction Field Effect Transisors (HFET's) on III-V Nitrides in the Wurzite form have been demonstrated, exhibiting interesting performance in terms of current densities, transconductances, current cut-off frequencies...[2]

In this work, we report on the theoretical comparison of Wurzite and Zinc- Blende III-V Nitride FET's with very short gate length (0.12µm). Using a 2D Monte Carlo device simulation, we investigate the capabilities of a GaN MESFET and $Al_{0.15}Ga_{0.85}N$/GaN HFET. For the cubic phase MESFET, we obtained transconductance of 330 mS/mm and cut-off frequency of 135GHz against 240mS/mm and 100GHz in the Wurzite form. In the cubic form, the HFET structure exhibits transconductance of 480 mS/mm, cut-off frequency of 180GHz and current densities in excess of 900mA/mm.

[1] J. Kolnik et al., J. Appl. Phys. 78 (2), 15 july 1995, 1033-1037
[2] M. Asif Khan et al., Electron. Lett. 32,1996, 357-358

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SYMPOSIUM L
POSTER SESSION

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session
16:00-18:00

L-X/P1

PHOTOLUMINESCENCE PROPERTIES OF NANOCRYSTALLINE AlN LAYERS GROWN BY PULSE PLASMA ASSISTED CVD, R. Dwilinski, J. Siwiec, M. Kaminska, Institute of Experimental Physics, Hoza 69, Warsaw University, 00-681 Warsaw, Poland, A. Olszyna, J. Konwerska-Hrabowska, A. Sokolowska, Faculty of Matérials Science & Eng, Warsaw Univ. of Technology 02-524 Warsaw, Nabutta 85, Poland

In this work results of photoluminescence measurements on Pulse Plasma Assisted CVD layers of AlN and other nitrides for comparison are presented. Nanocrystalline layers grown on silicon substrates were excited by 3 mW He-Cd laser (325 nm line) at temperatures in the range 4.2 - 300K. All samples revealed wide luminescence band of low intensity in the case of BN and C_3N_6 and much higher intensity in the case of AlN, most probably due to indirect and direct bandgap respectively. This wide band (1,7 to 3.2 eV) with maximum at 2.2 eV covers all visible light spectrum and in case of AlN is easy eye detectable. The efficient luminescence of nanocrystalline AlN layers, obtained under not optimal conditions, i.e. relatively low energy excitation (energy bandgap of AlN is twice higher than the laser energy) seems to be very perspective for light emitting application of this material.

The above results were complemented with measurements of UV-VIS absorption. All kinds of samples were characterised by direct, forbidden absorption transitions, band to band relevant, and by the bandgap levels transitions. These studies allowed to estimate the bandgap energy values for all studied nitrides. Generally, optical properties of these materials in nanocrystalline form do not differ as much as in the case of monocrystals, and are dominated by deep midgap electron levels.

L-X/P2

TEM CHARACTERISATION OF MOCVD GROWN GaN LAYERS, B. Pécz(1), M.A. di Forte-Poisson(2), L. Toth(1), G. Radnoczi(1), V. Papaioannou(3) and J. Stoemenos(3), (1)Research Institute for Technical Physics of the Hungarian Academy of Sciences, 1325 Budapest, P.O.Box 76, Hungary, (2)Thomson LCR, Domaine de Corbeville 91401 Orsay, Cedex, France, (3)Aristotle University of Thessaloniki, 540 06 Thessaloniki, Greece

1.4 µm thick GaN layers were grown onto (0001) sapphire by MOCVD using a two step procedure. At first a nucleation layer was deposited at 510°C onto both exact and miscut (3.5° off) substrate. The growth temperature of the GaN layer varied between 960 and 1000°C.

The grown layers were characterised by TEM, by X-ray and by AFM measurements. Typical FWHM values evaluated from the high resolution X-ray measurements are: 210» for the (0002) peak. The GaN layers are hexagonal and epitaxial to the sapphire substrate. Mirror like surfaces were obtained at certain growth conditions despite hexagonal based pyramids were found by AFM on the growth surface of GaN. The typical size of the base diameter is 50-100 µm, the typical height is about 3 µm.

The defects in the layers were studied by TEM and the results will be discussed in details. A thin layer of AlN was also detected at the interface.

L-X/P3

NITRIDES CERAMICS THICK FILMS : MANUFACTURE AND POSSIBILITY OF DEVICE APPLICATIONS, O.I. Shulishova, I.A. Shcherbach, D.I. Shcherback, N.V. Shevchuk, Inst. for Problems of Materials Science, Krjijanovsky str., 3, 252142 Kiev, Ukraine

Superconducting zirconium and niobium nitrides of pressed metals powders in chamber with nitrogen pressure at high temperature were received. Synthesized nitrides were grinded to the powder with dispersion about some micrometer. The pastes of nitrides' and borosilicate glass' powders and organic binder were prepared. Thick films obtained by screen technique on alumina ceramic substrates were used. The resulting composite films possess unusual combination of properties both in normal and superconducting state. Changing the paste composition and conditions of termal processing one can obtain films with normal resistivity renging from hundredths to dozens of Ohm/sq, TCR any value and sign, superconducting transition temperature and range within 0 to 16 K. The possibility to easily regulate the properties of resulting composite films as well as the reproductibility and stability of their characteristics prompt their use as cryogenic fluid level detectors, cryogenic resistance thermometers, thermal keys, conducting elements with zero electric loss.

L-X/P4

RADIATION SPECTRA IN LED BASED ON GaN EPITAXIAL FILMS UNDER INJECTION-THERMAL PROCESSES, S.V. Svechnikov, P.PH. Oleksenko, G.A. Sukach, P.S. Smertenko, S.I. Vlaskina, V.L. Gromashevski, ISP NASU, Kyiv, Ukraine

The effect of the factors due to through current (I) upon the intrinsic UV band of luminescence ($\lambda\sim370$ nm) and the impurity blue one ($\lambda\sim430$ nm) and upon the overheat temperature of the active region of LED has been investigated. It has been shown that the peak of intrinsic emission band shifts, according to the theory, to longer wavelengths and the band intensity increases quadratically, whereas the peak of more long wavelength band at the currents up to 15 mA shifts to higher energies. In the region of 15 - 50 mA the peak position is practically constant and shifts to the same longer wavelength region (current heating) under further increase of current. Such behaviour evidences that the recombination occurs through donor-acceptor pairs.

The overheat temperature of the active region of LED (ΔT_{AR}) had linear behaviour for the currents over 15 mA. Maybe the more weak dependence ΔT_{AR} (I) at $I < 15$ mA is due to the fact that at forward biases $V < Eg/e$ all the power terminated to device is released in space charge region ($w \leq 0.3$ µm). In this case the main region of generation of radiation is far off diffusion length minority current carriers $L_D = 4$ µm >>w.

As the forward bias which applied to p-n-junction grew ($V > Eg/e$), the barrier on the boundary of n- and p- regions was straightened. This leads to expansion of device heating region which gives the linear relation between ΔT_{AR} and current I. So the behaviour of ΔT_{AR} (I) evidences about space division of the radiation generation region and the region of energy release.

L-X/P5 SMALL-ANGLE SCATTERING OF X-RAYS (S-AS) OF GaN, DEPOSITED ON SiC AND Al_2O_3 SUBSTRATES, M.E. Boiko, Yu.G. Shreter, E.N. Mokhov, A.F.Ioffe Physical-Technical Institute, 26 Polytekhnicheskaya, 194021 St.Petersburg, Russia

The modified S-AS have been applied in studying of the defect structure GaN films.

We used for our x-rays measurements thick films (0.2- 0.3mm) of the GaN deposited on (0001) plane of SiC substrate and thin (0.003-0.005mm) films GaN deposited on sapphire (α-Al_2O_3). X-ray rocking curves show difference in full width at half maximum (FWHM) of those structures. (S-AS) shows quite different picture for those samples. GaN films deposited on the SiC had the three-dimensional disoriented domains. GaN domains distribute in liquid cluster model. It is seen by presence of strong incident peak and weak size-peak. The grid of GaN domains looked like the network of 120 or 60 degrees 50 nm cell. Estimation the length (perpendicularly surface) of those hexagonal prism were 200-300nm. The transmission mode S-AS carried out on GaN deposited on sapphire showed that variation of density distributed by a gas-like model.

L-X/P6 INITIAL STAGES OF GROWTH OF GaN OVER (0001) Al_2O_3 SUBSTRATES USING MBE : A CRYSTALLOGRAPHIC ANALYSIS OF THE DEFECTS, V. Potin, P. Ruterana, G. Nouet, LERMAT 6004 CNRS, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Sapphire has been used to demonstrate that devices such as violet emitting laser can be obtained in GaAlN alloys. The tremendous research effort now going on has demonstrated the critical effect of the buffer layers in the formation of inversion boundaries in MOCVD grown samples.

In MBE, the growth mode is found to be always three dimensional. Making a comparison between AlN and GaN growth, the AlN buffer layer is made of small polycrystallites having a common [0001] axis parallel to that of the substrate. They are rotated around this axis and angles can be as large as 20°. These grain boundaries have been analyzed and their atomic structure was determined. The thickness of the AlN layer is close to 50 nm and no IDB formation was found inside active GaN layer.

When no buffer layer is used, the growth is also three dimensional and the GaN layer contains nanometric inversion domains which are limited by {1010} planes and which cross the whole epitaxial layer. Their density is very high ($10^{+10}cm^{-2}$) and their boundary structure corresponds to the Holt model in which every atom presents two wrong bonds.

L-X/P7 THE NATURE OF THE ORIENTATION RELATIONSHIPS IN THE EPITAXIAL SYSTEMS «III-V NITRIDES ON SAPPHIRE», A.N. Efimov and A.O. Lebedev, Ioffe Institute, 194021 St.-Petersburg, Russia

Sapphire substrates of various orientations are usually successfully used for the epitaxial growth of III-V nitrides despite the difference in symmetry as well as in lattice parameters of wurtzite and sapphire structures. All Orientation Relationships (ORs) in the system under study both published earlier and original, reported for AlN, GaN, InN and their solid solutions, grown by the various epitaxial techniques on the different sapphire orientations have been summarized and considered.

It is shown that the usual notation of OR (i.e. H//K, h//k, where H,h,K,k are the plane and the direction of the substrate and the layer, respectively) is not only possible one and does not allow to identify spatially equivalent ORs observed at the different substrate orientations. Using mathematics of linear operators and presenting OR by linear operator M such that HM=K and Mk=h one can remove all ambiguities and carry out a correct comparison between ORs to reveal equivalent ones. As result, all ORs in the system «GaN on sapphire» have been systematized into 8 groups on the basis of criterion of almost the same spatial correspondence of the conjugated crystals' lattices.

It is shown, that the dependence of ORs on both sapphire cut orientation and layer compound can not be recognized within the framework of commonly accepted coincidence site lattices concept. Nevertheless, the dependence of ORs on layer compound for (0001) and (11. 0) sapphire substrate has been successfully described, without using any fitting parameters, by symmetry analysis earlier proposed by the authors and computer Monte Carlo simulation of initial stage of epitaxy.

L-X/P8 OPTICAL ABSORPTION AND FARADAY EFFECT IN GALLIUM NITRIDE, A.I. Savchuk, S.V. Medynskiy, I.D. Stolyarchuk, A.M. Lyakhovich, Dept of Phys. Electronics, University of Chernivtsi, 274012 Chernivtsi, Ukraine

Although gallium nitride GaN has been studied extensively with respect to fundamental properties only a few papers have been devoted to the magnetooptical study of this material. Here we report results of investigation of optical absorption and Faraday effect in GaN crystals. The bulk GaN crystals were grown by high-pressure synthesis method. Simultaneous measurements of absorption and Faraday rotation spectra were carried out at temperatures 77-300 K. Faraday rotation experiments were performed in the static magnetic field up to 3.5 T and pulsed magnetic field up to 25 T.

The Faraday rotation is observed to be positive in the spectral region 400-1000 nm. The maximum rotation observed for all studied samples at room temperature is about 4 deg/kG cm. It has been found similarity in the spectral dependence of Verdet constant for GaN and other III-V and II-VI semiconductor compounds.The obtained data on interband Faraday rotation were compared to the theory of Boswarwa, Howard and Lidiard (BHL) as well as the theory of Roth. From comparison between experimental data and theory BHL the effective direct band gap energies 3.40 eV at 300 K and 3.45 eV at 77 K have been estimated. The estimations coincide very closely with those from absorption edge analysis.

L-X/P9 PHOTOLUMINESCENCE PROPERTIES OF NANOCRYSTALLINE AlN LAYERS GROWN BY PULSE PLASMA ASSISTED CVD R.Dwiliñski, J.Siwiec, M.Kamiñska, Institute of Experimental Physics, Hoza 69, Warsaw University, 00-681 Warsaw, Poland, A.Olszyna, J.Konwerska-Hrabowska, A.Sokonowska, Faculty of Materials Science & Eng, Warsaw Univ. of Technology 02-524 Warsaw, Narbutta 85, Poland

In this work results of photoluminescence measurements on Pulse Plasma Assisted CVD layers of AlN and other nitrides for comparison are presented. Nanocrystalline layers grown on silicon substrates were excited by 3 mW He-Cd laser (325 nm line) at temperatures in the range 4.2 - 300K. All samples revealed wide luminescence band of low intensity in the case of BN and C3N6 and much higher intensity in the case of AlN, most probably due to indirect and direct bandgap respectively. This wide band (1,7 to 3.2 eV) with maximum at 2.2 eV covers all visible light spectrum and in case of AlN is easy eye detectable. The efficient luminescence of nanocrystalline AlN layers, obtained under not optimal conditions, i.e. relatively low energy excitation (energy bandgap of AlN is twice higher than the laser energy) seems to be very perspective for light emitting application of this material.

The above results were complemented with measurements of UV-VIS absorption. All kinds of samples were characterised by direct, forbidden absorption transitions, band to band relevant, and by the bandgap levels transitions. These studies allowed to estimate the bandgap energy values for all studied nitrides. Generally, optical properties of these materials in nanocrystalline form do not differ as much as in the case of monocrystals, and are dominated by deep midgap electron levels.

L-X/P10 HVPE GROWTH OF AlGaN ALLOYS, Y. Melnik, A. Nikolaev, S. Stepanov, A. Zubrilov, I. Nikitina and V. Dmitriev, PhysTech WBG Research Group, A.F. Ioffe Institute, 194021 St. Petersburg, Russia

Epitaxial layers of AlGaN alloys were grown by hydride vapor phase epitaxy (HVPE). The alloys were grown on GaN layers deposited on SiC substrates by HVPE [1,2]. Layers thickness ranged from 0.5 to 5 µm. Growth rate was controlled from 0.5 to 1.5 µm/min. Material composition was measured by Auger Electron Spectroscopy, SIMIS and x-ray micro probe to be around 50 mol.% of AlN. Alloy crystal structure was investigated by x-ray diffraction and transmission electron microscopy. Optical properties were characterized by cathodoluminescence. Characteristics of the layers will be compared with those for AlGaN grown by MOCVD. Results on conductivity measurements will also be presented.

[1] Yu.V. Melnik, I.P. Nikitina, A.S. Zubrilov, A.A. Sitnikova, Yu.G. Musikhin and V.A. Dmitriev, Inst. Phys. Conf. Ser. 142, 863 (IOP 1996).

[2] Yu.V. Melnik, I.P. Nikitina, A.E. Nikolaev and V.A. Dmitriev, presented at the 1st ECSRM, Greece Oct. 1996.

L-X/P11 EFFECTS OF INDUCTIVELY COUPLED PLASMA CONDITIONS ON THE ETCH PROPERTIES OF GaN AND OHMIC CONTACT FORMATIONS, H.S. Kim, Y.H. Lee, and G.Y. Yeom, Dept. of Materials Eng., Sung Kyun Kwan Univ., Suwon, 440-746 Korea, T. Kim, J.W. Lee, M.C. You, and T.I. Kim, Photonics Semiconductor Lab., Samsung Advanced Institute of Technology, P.O.Box 111, Suwon, Korea

To fabricate GaN-based laser diode successfully, reproducible etching process with high etch rates, vertical etch profile, and damage-free surface is required. In this study, GaN etching was performed by planar inductively coupled plasma and the effects of process parameters such as inductive power, bias voltage, pressure and gas combination on the plasma characteristics (ion density, ion energy, and radical density, and etc.) were studied using Langmuir probe, optical emission spectroscopy(OES), and quadrupole mass spectrometer(QMS). Various gas combination of $C1_2$, $BC1_3$, Ar, HBr, and H_2 were used to etch GaN and to its examine etching mechanism. GaN etch rates increased with the increase of the chlorine radical and ion energy (bias voltage), and the etch rates close to 4000Å/min could be obtained without substrate heating over 100°C . GaN etch rate enhanced by reactive radical such as Cl or reactive ion could be confirmed by OES focused on the GaN surface being etched. On the other hand, plasma conditions with chlorine-rich gas chemistry and high ion energy induced considerable changes in the surface composition (Ga/N ratios) of both n-type and p-type GaN layer. After the plasma etching of p-type and n-type GaN with the same etch depth condition, contact resistivities was measured by TLM technique. Contact resistivity changed not only by the radiation damage by energetic ion bombardments and hydrogen implantation, but also by the surface composition change caused by the selective etching (Ga for chlorine-rich plasmas, N for hydrogen-rich plasmas).

L-X/P12 SYNTHESIS OF AlN BY REACTIVE CATHODIC SPUTTERING, F. Andriamora, J.C. Bruyère and A. Deneuville, LEPES CNRS, BP 166, 38042 Grenoble Cedex 9, France

From its very wide band gap 6.2 eV, AlN exhibits a negative electron affinity, which suggests in particular its use as cold cathode in flat panel display. For this type of application, large areas are required, which discards preparation by MBE or MOCVD. On the contrary, reactive cathodic sputtering appears especially well suited. First, we are looking for obtaining films of the wide gap semiconductor AlN, then for improving their quality.

Films are obtained from sputtering an Al target in various He/ Ar/ N_2 reactive mixture on Si and silica substrates at temperatures between 50 and 650°C.

From the occurence of its specific Infra Red (TO at 673 cm^{-1}) and Raman (E2 at 660 cm^{-1}) peaks, and of a forbidden gap around 6 eV, a large set of preparation conditions are found for deposition of polycrystalline films with the hexagonal phase of the semiconductor AlN on both Si and silica.

We look for optimum conditions both from the minimisation of the widths of the IR and Raman peaks and of the residual optical absorption for subband gap excitation. Although work is still in progress, we have already obtained at low deposition temperature < 300°C, on silica a residual sub band gap absorption in the 10^3 cm^{-1} range, and on Si around FWHM around 60 cm^{-1} for the IR band and around 11 cm^{-1} for the Raman peak. In conclusion, good quality polycrystalline AlN films are already obtained by reactive cathodic sputtering.

Notes

ICAM/E-MRS'97 SPRING MEETING

ICAM-97

E·MRS

SYMPOSIUM M

Materials, Physics and Devices for Molecular Electronics and Photonics

Symposium Organizers

J. ZYSS, France Télécom/CNET, Bagneux, France

F. GARNIER, CNRS, Laboratoire des Matériaux Moléculaires, Thiais, France

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A.J. HEEGER, University of California, Santa Barbara, CA, USA

V. AGRANOVICH, Russian Academy of Sciences, Troitsk, Russia

The assistance provided by

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is acknowledged with gratitude.

SYMPOSIUM M

Monday June 16, 1997
Lundi 16 juin 1997

Afternoon
Après-midi

Session I

M-I.1 - plenary - 15:00-15:45 SINGLE MOLECULE SPECTROSCOPY, **U. Wild**, Laboratory of Physical Chemistry, ETH Zürich, Universitätstraße 22, 8092 Zürich, Switzerland

M-I.2 - invited - 15:45-16:15 NON LINEAR OPTICAL SPECTROSCOPY OF SINGLE MOLECULES IN LOW-TEMPERATURE SOLIDS, F. Jelezko, B. Lounis and **M. Orrit**, C.P.M.O.H., CNRS et Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cedex, France

A single molecule in a crystal matrix is a very good example of a two-level system. We describe a new system for single molecule spectroscopy, dibenz-anthanthrene in a naphthalene crystal, which we use to illustrate some well-known and some less usual effects of the coupling of an electronic two-level system to a laser field. We studied optical saturation, and photon bunching due to a metastable triplet level. The triplet population rate and triplet lifetime are so low, that the bottleneck effect of the triplet may be neglected. We also observed variations of the single molecule radiative linewidths, which we attribute to spontaneous emission modifications by surface effects.

Pump-probe experiments were also performed on this system with strong resonant fields. We observed light-shifts of the transition in the near resonant regime, the hyper-Raman resonance corresponding to an amplification of the probe beam and the multiphotonic sub-harmonic oscillations. These are related to a kicked-oscillator dynamics of the Bloch vector in the total laser field resulting of the beating of pump and probe beams.

16:15-16:30 **BREAK**

Session II

M-II.1 - invited - 16:30-17:00 MOLECULAR-SCALE CONTROL OF SYMMETRY-BREAKING IN SELF-ASSEMBLED CONJUGATED THIN FILMS, **F. Charra** and J. Cousty, Commissariat à l'Energie Atomique, DRECAM-SRSIM, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France

Some important physical properties of molecular materials are conditioned by a symmetry breaking in their molecular arrangement. We show, from near-field microscopy studies of the growth of self-assembled conjugated molecular thin films, that centrosymmetry breaking and chirality can arise spontaneously from the molecular arrangements themselves. These symmetry-breaking orderings are achieved through the control of weak intermolecular and molecule-surface interactions. We present examples of such orderings based on pyrene- and triphenylene-cored molecules, epitaxially self-assembled at liquid-solid interface. In the particular case of octupolar triphenylenes with D_{3h} symmetry, we have obtained a transition from a centrosymmetric phase towards non-centrosymmetric and chiral phases depending on a side-chain controlled « aspect ratio » of the molecule, and the nature of the surface. Such a transition involves the packing of molecules into closed gear-like structures. Optical measurements coupled to a scanning tunneling microscope gives further insights into the influence of such asymmetric phases on the electronic properties of the conjugated cores.

M-II.2 - invited - 17:00-17:30 SELF-ORGANIZATION OF CONJUGATED POLYMERS AT NANOSTRUCTURED SURFACES OBSERVED BY SCANNING PROBE MICROSCOPIES, **J.P. Rabe**, Department of Physics, Humboldt University Berlin, Invalidenstr. 110, 10115 Berlin

M-II.3 17:30-17:55 CHARACTERIZATION OF MICRO-CONTACT PRINTED PATTERNED SELF-ASSEMBLED MONOLAYERS BY ATOMIC FORCE MICROSCOPY, G. Bar, R. Brandsch, Freiburger Materialforschungszentrum, Albert-Ludwigs University, 79104 Freiburg, Germany and M.H. Whangbo, Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, USA

Several patterned monolayers of alkanethiols $CH_3\,(CH_2)_{n-1}SH$ on an Au substrate were prepared by using micro-contact printing and solution deposition methods. The surfaces were examined by IR, ellipsometry, and atomic force microscopy (AFM) in the contact and tapping mode. AFM can detect differences in packing density of chemically identical molecules which are too small to be detected by IR, ellipsometry, and wetting measurements, and suggests that the tip-sample contact area is an important parameter governing the contrast of AFM images. Stiffness images obtained with Force Modulation depend on changes in the Young's modulus of a sample surface as well as in the tip-sample contact area. As a result a surface region of small modulus can have a large stiffness mode images, the relative contrast of chemically different regions depends sensitively on the set-point amplitude ratio r_{sp} and driving amplitude A_0 values. As the tip-sample force is increased from small to large, phase and height images can undergo a contrast reversal. The dependence of e phase shift and amplitude damping on r_{sp} and A_0 can be qualitatively discussed using the expressions derived under thassumption that the primary consequence of tip-sample force interaction is to slightly change the force constant of the cantilever.

M-II.4 17:55-18:20

ANALYSIS OF THE POLARIZATION DISTRIBUTION IN A POLAR ORGANIC NANOTUBE MATERIAL BY SCANNING PYROELECTRIC MICROSCOPY, A. Quintel, P. Rechsteiner, J. Hulliger, Department of Chemistry and Biochemistry, University of Berne, Switzerland, M.Wübbenhorst, Department of Polymer Technology, Delft University of Technology, The Netherlands

The polarization distribution in a polar perhydrotriphenylene (PHTP) inclusion compound has been studied by scanning pyroelectric microscopy for the first time.

Co-crystallization of PHTP with a variety of linearly shaped donor (D) and acceptor (A) disubstituted nonlinear optical compounds produces PHTP-NLO inclusion compounds exhibiting polar macroscopic properties in more than 90% of 34 investigated cases. The guest molecules form aligned dipole chains in parallel channels built up by a honeycomb-type host-lattice of PHTP. In the case of PHTP-NNPP (NNPP: 1-(4-nitrophenyl)piperazine) scanning pyroelectric microscopy showed that the majority of NNPP dipoles are oppositely directed at the end faces of needle shaped crystals. This results in a formation of a 180° twinned domain state. A thermodynamic theory explains the occurrence of polar domains by a mechanism driven by the difference in -D···D- and -A···A- intermolecular interaction energies.

M-II.5 18:20-18:45

CORRELATION BETWEEN SIZE DISTRIBUTIONS OF PORES AND SIZES OF SILICON CLUSTERS FORMED IN SOL-GEL GLASSES (SGG), D.P. Savin, S.A. Gevelyuk, I.K. Doycho, N.P. Kovalenko, Y.O. Roizin, Odessa State University, Ukraine, E. Mugenski, Wroclaw Institute of Low Temperatures, Poland

Quantum-size silicon clusters were formed in the SGG matrix by local reduction of silicon dioxide;

It was shown that size distribution of pores in SGG is one of the limiting factors, affecting the sizes of formed silicon clusters and, consequently, dielectric properties and photoluminescence spectra of fabricated materials. A novel technique of capacitance spectrometry for obtaining the size distribution of pores was employed. The interferometry measurements of the size distribution of pores were performed in parallel. The photoluminescence spectra of SGG with different size distributions are analyzed and a model is proposed that describes the photoluminescence in terms of tunnel dispersive transport of nonequilibrium charge carriers.

Tuesday June 17, 1997
Mardi 17 juin 1997

Morning
Matin

Session III

M-III.1 - plenary - 8:30-9:15

CONJUGATED POLYMERS AS MATERIALS FOR THIN FILM SOLID STATE LASERS, F. Hide, M.A. Diaz-Garcia, M. McGehee, B.J. Schwartz and **A.J. Heeger**, Institute for Polymers and Organic Solids, UC Santa Barbara, Santa Barbaran CA 93106, USA

Optically pumped gain narrowing and lasing have been demonstrated in submicron thick films, neat and undiluted, of photoluminescent conjugated polymers. The dramatic collapse of the emission line width occurs at very low pump energy thresholds (~10 $\mu J/cm^2$). Gain narrowing is found in over a dozen different conjugated polymers representing a variety of molecular structures, including poly(p-phenylenevinylene), poly(p- phenylene) and polyfluorene derivatives; the emission wavelengths in these materials span the visible spectrum. The short gain lengths in conjugated polymers are attributed to the high density of chromophores, the large density of states associated with the interband (π-π^*) transition in quasi- one-dimensional systems, and the Stokes shift which minimizes self- absorption and allows optical pumping to the excited state without simultaneously stimulating emission (thereby yielding population inversion). Lasing and gain narrowing are compared for a soluble poly(phenylene vinylene) derivative using two different resonant structures: planar waveguides and microcavities. In both cases, the gain narrowing threshold is at 0.05 - 0.1 μJ per 10 ns pulse focused to approximately 1.5 mm Single mode microcavity lasers are obtained when a cavity resonance occurs at the wavelength where the gain of the polymer is a maximum. Low threshold lasing (threshold more than an order of magnitude below that observed in planar waveguides and microcavities) has also been demonstrated using distributed feedback in a planar thin film configuration.

M-III.2 - invited - 9:15-9:45

POLYMER LED'S AT SMALL DIMENSIONS, **O. Inganäs**, Laboratory of Applied Physics, Dept. of Physics (IFM), University of Linköping, 592 29 Linköping, Sweden

M-III.3 9:45-10:10

ERBIUM LUMINESCENCE IN SOL-GEL DERIVED GLASS FILMS AND CERAMICS, N.V. Gaponenko, A.V. Mudryi, O.V. Sergeev and V.E. Borisenko, Belarusian State University of Informatics and Radiolectronics, P. Browka 6, Minsk 220027, Belarus, E.A. Stepanova, A.I. Rat'ko, A.S. Baran, Institute of General and Inorganic Chemistry, Surganova 9, Minsk 220027, Belarus, and S.V. Baran, "PHARMEC" Scientific and Production Enterprise, Masherova 107, Minsk 220020, Belarus and J.F.McGilp, Trinity Colllege, Dublin 2, Ireland

Sol-gel derived SiO_2,ZrO_2,Al_2O_3,In_2O_3,Y_2O_3,Fe_2O_3 free standing an spin-on films containing 10 wt% Er_2O_3 were fabricated, and erbium photoluminescence (PL) in the region of 1.53 μm was investigated. The erbium doped spin-on SiO_2 films fabricated on porous alumina and monocrystalline silicon were characterised by SIMS analyses. It was founded, that in comparison with thermally grown SiO_2 films the spin-on sol-gel derived films are enriched with carbon (1 at%). A strong influence of the host matrix on the electron structure of Er ions was observed in the Er PL. Room temperature Er luminescence from In_2O_3 appeared after annealing at 573 K, 400 K lower than sol-gel derived SiO_2 and 200 K lower than sol-gel derived Al_2O_3 The optoelectronics engineering potential of low temperature processing of Er-doped In_2O_3 sol-gel films on porous alumina is discussed.

10:10-10:30 **BREAK**

Session IV

M-IV.1 - invited - 10:30-11:00

DESIGN AND OPTICAL PROPERTIES OF NOVEL INTRAMOLECULAR DONOR-ACCEPTOR SYSTEMS, **J.P. Ferraris**, Department of Chemistry, The University of Dallas Richardson, Texas 75083, USA

Molecular and polymeric systems possessing donor (D) and acceptor (A) moieties exhibit unusual properties including very fast energy transfer, enhanced photoconductivity and narrowed energy gaps (E_{gap}) We have been studying two families of such materials: (1) polyalkylthiophenes (D) onto which C_{60} (A) has been remotely grafted and (2) polycyclopenta-dithiophenes (D) possessing a variety of electron withdrawing units (A). Two approaches have been used to generate the systems in family 1: (a) design and synthesis of C_{60}-bearing electropolymerizable monomers or (b) derivatization with C_{60} of preformed polymers possessing remote functionalization. The first approach leads to materials which have a fixed D:A ratio and a relatively well defined sequence distributions but are non- processible. The second affords random copolymers amenable to solution processing. A further advantage is that the D:A ratio can be widely varied. The redox properties of the D and A moieties appear only slightly or not-at-all affected by the presence of the other for this family. In contrast, the redox and optical properties of the systems in family 2 can be directly controlled by judicious choice of the electron withdrawing groups. In several cases polymers with $E_{gap}<0.7$ eV have been obtained. We will discuss the design strategy and syntheses that led to these systems and their electrochemical and optical properties.

M-IV.2 11:00-11:25

OLIGOTHIOPHENE S,S-DIOXIDES: TOWARDS n-TYPE SEMICONDUCTOR OLIGOTHIOPHENES? C. Arbizzani(1), G. Barbarella(2), A. Bongini(1), M. Mastragostino(3), P. Ostoja(4), 0. Pudova(5), M. Zambianchi(2), (1)Dipartimento di Chimica 'G. Ciamician', Universita', Via Selmi 2, 40126 Bologna, Italy, (2)I Co.C.E.A., L.A.M.E.L., Area Ricerca C.N.R., Via Gobetti 101, 40129 Bologna, Italy, (3)Dipartimento di Chimica Fisica, Universita', Via Archirafi 26, 90123 Palermo, Italy, (4)Institute of Organic Synthesis, Aizkraukles str. 21, Riga 1006, Latvia

α-Conjugated oligothiophenes are being actively investigated for their electric conductivity and related electric properties. Thin film field effect transistors based on ultrapure α-sexithiophene have sufficiently high charge mobilities and on/off ratios to envisage practical applications in large-area electronic circuits. A variety of oligothiophenes functionalized with electron-donating or electron-releasing groups have been described, but so far the performance of unsubstituted sexithiophene as p-type semiconductor organic material remains unequaled.

We are reporting here the synthesis and the electrochemical characterization of a new class of end-capped oligothiophenes selectively oxidized at the sulfur atom of the terminal thiophene rings. These new oligothiophene S,S-dioxides are very stable materials characterized by a greater electron delocalization than the parent compounds. Cyclic voltammetry shows that, contrary to the parent oligothiophenes, oligothiophene S,S-dioxides are more easily reduced than oxidized and that the reduction potentials, which depend on the oligomers length, are less negative than -1.5 V vs. Ag.

The synthesis of oligothiophene S,S-dioxides having much greater electron affinity than the parent compounds is of some interest since this could be the first step towards the realization of n-type semiconductor oligothiophenes.

M-IV.3 11:25-11:50

A NEW PATHWAY TO GaN, C. Winter(1,2), J. Käshammer(1), S. Mittler-Neher(1), and R. Fischer(2), (1)Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany, (2)Institut für anorganische Chemie, Universität Heidelberg, INF 503, 69120 Heidelberg, Germany

GaN is a very sucessful material for blue laser sources in optoelectronic devices and as a III-V-semi-conductor in high-temperature electronic devices. Typicall preparation methods are electron cyclotron resonance assisted molecular beam epitaxy (ECR-MBE) or chemical vapor deposition from organo-metallic precursors (MOCVD). MOCVD has traditionally been carried out using mixtures of trimethyl-gallium ($Ga(CH_3)_3$) and ammonia (NH_3) at a very high substrate tempertature, typically ~ 900°C. These methods rule out a coating of thermally labile substrates. Tailor-made single-source precursors for GaN may represent a solution, if these compounds can be converted into GaN under mild conditions. As a first step towards this goal we studied the reactivity of ($GaN_9 \cdot NEt_3$) with OH-terminated self assembled monolayers. In 1996, we presented an alternative preparation method, using a so-called single source precursor, which contains both the Ga and the N source in one molecule.Now we present a preparation route, which makes it possible to immobilize GaN at low temperature (at room-temperature or only a little higher) to OH-terminated self assembled monolayers (SAM's). We choose triethyl-galliumtriazide (GaN_9NEt_3), which was prepared in a two step synthesis from $GaCl_3$, as single source precursor. We exposed a self-assembled-monolayer (SAM) of 1 l-mercapto-l-undecanole on gold to a solution of GaN_9NEt_3 in dry toluene for 24 hours. Mass-spectra were taken with a home-built SD-TOF-mass-spectrometer. We found peaks, which indicate a covalent binding between the OH-terminated monolayer and the gallium-azide precursor, which had lost NEt_3.

Studies to convert the deposited galliumazide on functionalyzed SAM's into GaN by illuminating the sample with UV-light are in progress.

M-IV.4 11:50-12:15

CONTROLLING SURFACES AND INTERFACES OF SEMICONDUCTORS USING ORGANIC MOLECULES, R. Cohen(1), S. Bastide(1), D. Cahen(1), J. Libman(2), A. Shanzer(2), (1)Depts. of Materials & Interfaces (2),and of Organic Chemistry Weizmann Institute of Science, Rehovot, 76100 Israel

Control over the physics and chemistry of semiconductor surfaces is essential to permit fine-tuning of semiconductor device properties. Guided by this we have formulated chemical strategies for surface modifications of semiconductors using specially designed organic molecules with, in one molecule, several groups, each of which performs a different function.

Because one or more of these are binding groups, they chemisorb, also under ambient conditions, on CdTe, GaAs, CdSe, InP or $CuInSe_2$ crystals. This strongly changes the electron affinity (≤ 770 mV) and, under certain conditions, also the surface state distribution or occupation, i.e. band bending (≤ 500 mV). These changes are roughly linearly correlated with the molecules' dipole moments (electron affinity) and their LUMO energy (band bending). Thus, in principle, this approach allows full control over the semiconductor electrical properties that are crucial for the opto-electronic properties of semiconductor junctions and a basis for molecule-based electronics.

M-IV.5 12:15-12:40

TWO-DIMENSIONAL LANGMUIR-BLODGETT AND SELF-ASSEMBLED ARRANGEMENTS OF ULTRASMALL GOLD CLUSTERS, M. Burghard(1), G. Philipp(1), S. Roth(1), K. von Klitzing(1) and G. Schmid(2), (1)Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany, (2)Universität-GH Essen, Universitätstr. 5-7, 45117 Essen, Germany

Metal clusters are promising candidates as components of ultrasmall electronic devices that operate with only a few electrons. For such devices the ability to control the cluster arrangement is essential. Two possible means to achieve this are the Langmuir-Blodgett (LB) and self-assembly techniques.

For the LB studies we used gold clusters stabilized by a phosphine ligand shell (nominal formula $[Au_{55}(PPh_3)_{12}Cl_6]$). These clusters were embedded in a polymeric LB matrix and the transferred layers were characterized by TEM and UV/Vis absorption spectroscopy. We discuss the cluster arrangement as observed in the TEM depending on the chemical nature of the polymer matrix and the subphase composition. The different aggregation types of the clusters are reflected in the optical absorption properties of the films. Through a suitable combination of exchanged ligands and ions in the subphase, ordered cluster architectures can be prepared that are of interest as electronically active parts between metal contacts.

The self-assembled films are based on the same clusters but with negatively charged ligands. These clusters can be self:-assembled into a monolayer via chemical modification of the surface of SiO_2 or Si_3N_4 coated Si wafers. In this way cluster films can be prepared on thin membranes that are suitable for TEM investigations.

12:40-14:00 **LUNCH**

Tuesday June 17, 1997
Mardi 17 juin 1997

Afternoon
Après-midi

Session V

M-V.1 - plenary - 14:00-14:45

POLYMER LIGHT EMISSION: CONTROL OF PROPERTIES THROUGH CHEMICAL STRUCTURES, MORPHOLOGY AND DEVICE FABRICATION, **D.D.C. Bradley**, Centre for Molecular Materials and Department of Physics, University of Sheffield, Hounsfield Road, Sheffield S3 7RH, UK

M-V.2 - invited - 14:45-15:15

PHOTOINDUCED SPONTANEOUS AND STIMULATED EMISSION IN SEXITHIOPHENE SINGLE CRYSTALS, **G. Horowitz**, P. Valat, F. Garnier, F. Kouki and V. Wintgens, CNRS, Laboratoire des Matériaux Moléculaires, 2 Rue Henry Dunant, 94320 Thiais, France

Photoinduced stimulated emission in electroluminescent organic polymers has attracted much attention recently, because it would open the way towards organic based laser diodes. In the present communication, we show evidence for stimulated emission in sexithiophene (6T) single crystals. At room temperature, the PL spectrum presents three peaks, of which the two low energy peaks are interpreted as vibronic replica of the high energy peak. As the temperature decreases, a second and a third set of peaks appears successively at higher energies. The respective origin (0-0 peak) of the three sets is 16860, 17510 and 17980 cm^{-1}. Owing to the fact that the emission level of the 0-0 peak of the high energy (low temperature) set is much lower than that of its replica (0-1 and 0-2 peaks), we attribute this set to the $2A_g \leftarrow 1A_g$ forbidden transition, made partially allowed by vibronic coupling. Furthermore, the low temperature excitation spectrum presents a fine structure, with a very narrow 0-0 peak at 18350 cm^{-1}, which is very close to the A_g state estimated from two photon excitation. At low excitation level, the transient PL presents a single exponential decay with a time constant of 1.9 ns. At higher excitation levels, a shorter and more intense emission is superimposed to the low excitation signal. We attribute this fast component to stimulated emission. This is confirmed by the emission spectrum, which consists of a very narrow peak (FWHM≈100 cm-l) centered at 16775 cm^{-1}, close to the origin of the room temperature steady state emission. We therefore attribute the latter transition to the bottom of the B_u exciton band.

M-V.3 15:15-15:40

DOPING AND TRAP STATES IN PPV LIGHT EMITTING DEVICES, E. Werner, K. Zuleeg, J. Scherbel, M. Meier, S. Karg, W. Brütting, M. Schwoerer, Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

It has been shown by transport and optical measurements that single layer polymer light emitting devices (ITO/PPV/metal) with poly-phenylene-vinylene (PPV) as the active emitting material are well described within the Schottky diode model. The p-type doping of the polymer, required for the Schottky model, occurs during the thermal conversion process of the precursor to the conjugated PPV on the ITO substrate.

Using impedance spectroscopy, thermally stimulated currents and intemal photoemission we have been able to determine the energetic distribution of trap states in PPV and can ascribe them to specific impurities. The conversion of PPV on ITO substrates creates shallow traps with a depth of about 0.1-0.2eV, which act as a dopant in PPV. The total density of this trap species is of the order of 10^{16}-$10^{17} cm^{-3}$ at room temperature. Exposure to air creates additional trap states with trap levels at 0.8-0.9eV. Their density can be varied by applying vacuum to the devices.

By using non-reactive anode materials in combination with controlled doping of the polymer, partially conjugated polymers or additional electron transport layers the efficiency of PPV based devices can be largely increased.

M-V.4 15:40-16:05

TWO DIMENSIONAL EXCITONS DYNAMICS IN THIN FILMS OF THIOPHENE OLIGOMERS, G. Lanzani(1,2), L. Rossi(3), S. Stagira(2), G. Cerullo(2), S. De Silvestri(2), and F. Garnier (4); (1)Istituto di Matematica e Fisica Univ; di Sassari, Italy; (2) CEQSE-CNR, Politechnico di Milano, Italy; (3)Dipartimento di Fisica «A. Volta», Univ. di Pavia, Italy; (4)Laboratoire des Matériaux Moléculaires CNRS, France.

Photoexcited states in thiophene oligomers have been studied by using femtosecond transient and cw photomodulation spectroscopy. Sexithiophene was substituted by hexyl groups both on the terminal α position (α,ωDH6T) and as pendant group in the ß position (ß,ß'DH6T). α,ω)DH6T is a pure two dimensional highly ordered organic semiconductor in which excitonic coupling is quite evident, while ß,ß'DH6T behaves as an ensamble of non interacting molecules. α,ωDH6T shows a broad photoinduced absorption (PA) band centered at 1.6 eV, and photobleaching which appears about 200 ps after the excitation. ß,ß'DH6T shows very different ultrafast dynamics: we distinguish stimulated emission around 1.78 eV and photoinduced absorption at 1.3 eV, consistently with the results obtained in solution. Long lived by-products of photoexcitation are detected by photomodulation in the ms time domain. PA for ß,ß'DH6T shows a PA band at 1.58 eV which is assigned to triplet-triplet transitions and very weak polaron PA bands at 0.7 and 1.4 eV, respectively. The PA spectrum in α,ωDH6T is assigned to doubly occupied states, namely π-dimers and bipolarons. Intrinsic charge photogeneration via bulk CT excitons and a topological dependent charge separation can well explain the results.

16:05-16:25 **BREAK**

Session VI

M-VI.1 16:25-16:50

EFFICIENT CHARGE CARRIER GENERATION IN POLYPARA-PHENYLEN/C_{60} COMPOUNDS, C. Waldauf, W. Graupner, S. Tasch, G. Leising, Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria and A. Gügel, U. Scherf, A. Kraus, M. Walter, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

The improvement of dissociation of singlet excitons by electron or hole capturing species like C_{60} is essential for efficient photovoltaic cells based on conjugated systems.

We investigate the charge transfer in blends of methylsubstituted laddertype poly-(paraphenylen) (m-LPPP) with new well soluble C_{60}-derivatives, which are characterized by sidegroups of different electronic properties (donor-acceptor-nature).

It is shown, that the electronic properties of the C_{60}-sidegroups strongly influence the efficiency of the charge transfer in these blends and hence significant different behaviours in the photoluminescence, the electroluminescence, the photocurrent and photoinduced absorption is observed.

M-VI.2 16:50-17:15

(PHOTO)CONDUCTIVITY OF CONJUGATED OLIGOMER FILMS: HOW ARE MOBILE CHARGE CARRIERS FORMED?, D. Oelkrug, H.J. Egelhaaf and L. Lüer, Institute of Physical Chemistry, University of Tübingen, Germany

In ambient atmosphere, films of conjugated oligomers are electric semi-conductors of conductivity σ_D, which typically increases upon illumination by several orders of magnitude to σ_L.We investigated DC- and AC-conductivities of vacuum-deposited films of oligothiophenes Tn, oligophenylenevinylenes PVn and titaniumoxophthalocyanines Pc with different chain lengths n and a series of distance controlling substituents as function of temperature, irradiation time and intensity, annealing preconditions, and composition of the surrounding atmosphere. The most important of these variables is the oxygen partial pressure $p(O_2)$. Extrapolation of the conductivity data to $p(O_2) \to 0$ yields $\sigma_D \to 0$ and approximately also $\sigma_L \to 0$ .Hence we conclude that mobile electric charge carriers can be created in the films only in presence of additional electron acceptors (we consider electroneutral films and disregard charge injection).

In all examples the minimum dissociation scheme is given by $M(*) + M(O_2) \to M^+ + M(O^-_2)$, where $M(*)$ is a ground state or excited state (*) film constituting molecule, and $M(O_2)$ the vdW complex with O_2. From the dissociation enthalpies in the dark and upon illumination it follows that photoconductivity is always initiated from the singlet exciton ($M^* \cong S_1$) and not from the triplet state. In addition, CT-complexes (MO_2) can be formed in the dark or in a photoassisted process.These complexes are able to create free charge carriers by direct irradiation into the CT-band but, in a side reaction, also irreversibly oxidized photoproducts.

M-VI.3 17:15-17:40

ELECTRONIC TRANSMISSION ACROSS A METAL/CONJUGATED-OLIGOMER/METAL STRUCTURE : ROLE OF INTRINSIC AND EXTRINSIC DISORDER, A. Saxena, Z.G. Yu, D.L. Smith and A.R. Bishop, Los Alamos National Lab. , NM 87545 USA

We study the transmission coefficient of an electron across a metal/conjugated-oligomer/metal structure as a function of (i) the work function of the two metals, (ii) the thickness of the oligomer layer, and (iii) the electronic parameters (e.g. Peierls gap, hopping, electron-phonon and electron-electron interactions) of the oligomer. The electronic structure of the oligomer is modeled using a tight-binding model. The effect of both the intrinsic disorder (e.g. quantum lattice fluctuations; single and multi-phonon thermal effects) and extrinsic disorder (site/bond impurities) is studied on the transmission coefficient assuming coherent electron tunneling. The role of effects that explicitly break the electron-hole conjugation symmetry, i.e. electronic correlations, difference in on-site energies (e.g. an AB-type oligomer) is also considered. The results are interpreted in the context of possible experimental implications and charge transport in electroluminescent devices based on PPV-like light-emitting polymers.

M-VI.4 17:40-18:05

POLY (ARYLENE ETHYNYLENE) COPOLYMERS : A MODEL STUDY IN MOLECULAR ENGINEERING FOR PHOTONIC DEVICES, A. Davey, O. O'Connor, E. Bourdin and W.J. Blau, Physics Department, Trinity College Dublin, Dublin 2, Ireland

It is established that polydiacetylenes possess some of the largest optical nonlinearities observed in conjugated polymers. Similarly, it is well known from the example of the PPV polymer family that the inclusion of arylene moieties into the polymer backbone can yield highly fluorescent materials. We have therefore decided to combine these two properties and to develop a family of poly(arylene ethynylene) copolymers whose fluorescence properties may be tuned by the appropriate choice of an arylene moiety and who also will possess a large nonlinearity, in particularly a large multi-photon absorption. Starting from semi-empirical quantum chemical geometry optimisation models we determined the relevant optical properties of the molecules by configuration interaction. Subsequently a number of members of this copolymer family were syhthesised with emissions ranging from blue to red, and whose fluorescence quantum yield is above 50% in some cases. Light emitting diodes were fabricated with efficiencies similar to those of simple PPV devices. Similarly, laser action was observed under ultraviolet laser pumping. The sign and magnitude of the second order hyperpolarisability was determined at 1064 nm and 532 nm. At 532 nm, a strong two photon resonance enhanced response is observed with values of the hyperpolarisability of $2\ 10^{-32}$ esu, mainly real negative. Intense fluorescence was stimulated by three photon absorption at 1064 nm which indicated a good potential to use such polymers for frequency up-conversion of near infrared laser pulses.

Poster Session I

18:05-20:00 See programme of this poster session p. M-14 to M-23.

Wednesday June 18, 1997 — Morning
Mercredi 18 juin 1997 — Matin

Session VII

M-VII.1 - plenary - 8:30-9:15

HYBRID FRENKEL-WANNIER-MOTT EXCITONS AT INTERFACES AND IN MICROCAVITIES, **V. Agranovich**, Institute for Spectroscopy, Troitsk, Moscow obl. 142092, Russia, G. La Rocca and F. Bassani, Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy, H. Benisty and C. Weisbuch, Laboratoire de PMC, Ecole Polytechnique, 91120 Palaiseau, France

We discuss the linear and nonlinear optical properties of organic- inorganic nanostructures (quantum wells and superlattices) brought about by resonance interactions between Frenkel excitons in organic QWs and Wannier-Mott excitons in semiconductor QWs. We show that such a coupling (Coulomb dipole-dipole at an interface and through the cavity photons in a microcavity) is responsible for the appearance of mixed Frenkel-Wannier-Mott excitations.

We demonstrate that the new hybrid states and their dispersion curves can be tailored to engineer the enhancement of resonance optical nonlinearity, fluorescence efficiency and relaxation processes.

M-VII.2 - invited - 9:15-9:45

OPTICAL EXCITATIONS IN NOVEL FORMS OF OLIGOTHIOPHENES, **R. Tubino**, Dipartimento Fisica - Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

M-VII.3 9:45-10:10

EXCITATIONS AND OPTICAL PROPERTIES OF PHENYLENE-BASED CONJUGATED POLYMERS AND OLIGOMERS, S. Brazovskii(1,2), N. Kirova(1), A.R. Bishop(1), V. Klimov(1), D. McBranch(1), N.N Barashkov(1), J.P. Ferraris(1), (1)LANL, Los Alamos, NM 87545, USA, (2)LPS, Université Paris Sud, 91405 Orsay, France

Phenylene-based conjugated polymers have attracted widespread interest in both their fundamental properties and their potential for future applications. The optical properties of these materials remain extremely controversial, with many unresolved questions on the nature of the photoinduced excitations. We present time-resolved and intensity-dependent studies of the photoinduced absorption and stimulated photoemission, as well as CW luminescence and optical absorption data for MEH-DSB oligomer solutions and thin films. To place the experimental features of this model oligomer in context, we will review earlier existing data and available theoretical descriptions.

We have developed a new theoretical picture which unifies features of both a semiconductor band model (delocalized excitations), and a molecular exciton model (localized excitations). On this basis we identify the most important optical features for both high (4-6 eV) and low (2-4 eV) photon energies. Our picture includes electronic delocalization, while invoking the necessary corrections for electron-hole interactions. This approach allows us to present a qualitative picture of various excited states which matches all of the experimental features in MEH-DSB solutions, which represents the limit of noninteracting oligomers. This picture will then facilitate the prediction of optical and electronic properties of this class of materials in even more complicated situations (side chain substitution, solid-state effects, different backbone structure, etc.)

10:10-10:30 **BREAK**

Session VIII

M-VIII.1 - plenary - 10:30-11:15

POLYMER WHISPERING GALLERY MODE LASER, **M. Kuwata-Gonokami**, Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan and K. Takeda, Tsukuba Research Laboratory, JSR Co. Ltd, Tsukuba, Ibaragi, Japan

Micro dielectric spheres, disks and cylinders or rings are known to act as efficient optical micro-resonators, which have very high quality factor and very small mode volume. Such resonance modes are called optical whispering gallery modes (WGM's). We reported the efficient lasing of dye doped polymer spheres with diameter of 10 μm to 100 μm region [1]. Here we report the quantitative analyses of the resonance characteristics of the WGM's of dye-doped polymer spheres of down to 2 μm in diameter showing their fluorescence spectra. We also examine the spontaneous emission coupling constant of WGM, that is called ß value, by the threshold behavior of WGM laser under optical excitation. Observed ß value is about 30% for 5 μm spheres. We numerically calculated the vacuum field distribution as a function of position and frequency and evaluate the ß value and obtained good agreement between theory and experiment. With these results, we discuss the potentiality of WGM to current injection lasers with organic materials.

[1] M. Kuwata-Gonokami, Kennji Takeda, Hiroaki Yasuda, Kazuhiro Ema:» Laser Emission from Dye-Doped Polystyrene Microsphere,» Jpn. J. Appl. Phys. Lett. 31(1992) L99, Mol. Crys. Liq. Cryst. 216 (1992) 21.

M-VIII.2 - invited - 11:15-11:45

HIGH FINESSE ORGANIC MICROCAVITIES, **S.E. Burns**, N. Tessler, G.J. Denton, R.H. Friend, The Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, UK

High finesse light-emitting microcavities were constructed from the conjugated polymer poly(p- phenelenevinylene) and high reflectivity distributed Bragg reflectors. The modification of the absorption, photoluminescence and electroluminescence of these mirrors by confinement of the photon field were investigated. Spontaneous emission enhancements of 2 orders of magnitude were found in the forward direction. The stimulated emission of these devices was also investigated using short-pulse laser excitation. Comparisons were made with previous studies on microcavities incorporating metal mirrors where lasing occurred. Findings were complimented by simulations using multi-layer stack theory and transfer matrices.

M-VIII.3 11:45-12:10 PREPARATION AND CHARACTERIZATIONS OF REGULARLY ALTERNATE MULTIPLE-QUANTUM-DOTS : POLYAZOMETHINES, S. Destri, W. Porzio, C. Botta, Istituto di Chimica delle Macromolecole del C.N.R., via E. Bassini 15, 20133 Milano, Italy

We have prepared and characterized soluble copolymers in which low band-gap sequences (thenylenic segments) regularly alternate with high-gap portions (phenylenic segments) linked by azomethine moieties hence maintaining the overall π- conjugation.The polymer series with three, six and eight thienylenic residues showed interesting non linear optical properties together with evidences of electronic confinement in low-gap segments, superlattice structure, clearly envisaging applications as LED, photovoltaic or photonic devices. The products, obtained from polycondensation reaction of dialdehydes and diamines, end with carbonilic groups; hence they can be used in nanostructured substrate preparation (hydrophilic substrate), as already checked with starting dialdehydes self-assembled onto quartz slabs. These self-assembled structures can be obtained either by evaporation in high vacuum or by a proper thermal treatment, depending on the molecular weight of the molecules.As an example, dialdehydes can be arranged in different inclinations with respect to the substrate as a function of the film preparation procedure. Self-assembled structures with higher molecular weight materials using sublimation techniques could be obtained using depositions in ultra-high vacuum chamber. Several synthetic routes have been followed to prepare these polyazomethines obtaining materials showing different thermal and structural properties as a function of the ratio of two possible isomers at imino linkage. The order degree also influences the optical properties in fact luminescence data are strictly related to the percentage of the two isomers. On the contrary Raman scattering measurements, which show an electronic confinement in thienylenic blocks for all the polymers are not affected by the nature of imino linkage. Luminescence data of oligomers and polymers will be presented and discussed in view of their constitutional, configurational and conformational structure.

M-VIII.4 12:10-12:35 MODIFIED SPONTANEOUS EMISSION IN OLIGO (p-PHENYLENE VINYLENE) PLANAR MICROCAVITIES, L. Berthelot(1), J. Tardy(1), A. Gagnaire(1), J. Joseph(1), B. Masenelli(1), V.H. Tran(2), H. Rigneault(3), (1)Ecole Centrale de Lyon - LEAME (UMR CNRS 5512), 69131 Ecully, France, (2)LMOPS (UPR CNRS 9030) 69390 Vernaison, France, (3)Laboratoire d'Optique des Surfaces et des Couches Minces (UPRES A CNRS 6080), Ecole Nationale Supérieure de Physique de Marseille, Domaine Universitaire de St Jérôme, 13397 Marseille Cedex 20, France

We report on the luminescence characteristics of planar microcavities formed by Oligo (p-PhenyleneVinylene) (OPV) sandwiched between two dielectric mirrors or between a dielectric mirror and a metallic mirror. The dielectric mirrors were made up with TiO_2/SiO_2 distributed Bragg reflectors (DBR). Thc OPV-n (n= 5-13) layers were deposited by vacuum evaporation.

The materials were first optically characterized to determine their refractive indexes and their absorption spectra as a function of n.

The structures were characterized by photoluminescence (PL). The spectra were compared with those of OPV films without microcavity. The influence of the microcavity is significantly evidenced through a spectral narrowing of the PL spectrum. The width of the emission line of the cavity is about 10 nm against 80 to 100 nm for the material PL. Secondly. the emission at the resonance wavelength is strongly enhanced. Both the spectral narrowing and the intensity increase were observed to be dependent on the structure of the microcavity (two dielectric mirrors or a combination of dielectric and metallic mirror).

The angular emission was also observed to be strongly affected by the microcavity effect. The wavelength of the nominal resonant mode (emission normal lo the axis of the cavity) is emited in a very narrow cone (half angle ~15°). Off-axis resonance is blue shifted as expected.

12:35-14:00 **LUNCH**

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Session IX

M-IX.1 - invited - 14:00-14:30

CHIRALITY IN SURFACE NONLINEAR OPTICS, M. Kauranen, T. Verbiest, and **A. Persoons**, Laboratory of Chemical and Biological Dynamics and Center for Research on Molecular Electronics and Photonics, University of Leuven, Celestijnenlaan 200 D, 3001 Heverlee, Belgium

The efficiency of second-harmonic generation from chiral surfaces and thin films is different for left- and right-hand circularly-polarized fundamental light. Such optical activity can occur in the electric-dipole approximation. However, to explain our results for chiral polymer films, magnetic contributions to the nonlinearity must be included. A technique that uses a quarterwave plate to continuously vary the polarization of the fundamental beam was used to determine the relative complex values of the components of the tensors that characterize the nonlinear interaction. The largest magnetic components were ~20% of the largest electric components.

Second-harmonic generation from achiral anisotropic surfaces can also lead to optical activity. This occurs if the orientation of the anisotropic sample makes an otherwise achiral experimental arrangement chiral. The effect occurs in the electric-dipole approximation and changes sign as the handedness of the setup is reversed.

M-IX.2 - invited - 14:30-15:00

NEW MOLECULAR ENGINEERING SCHEMES FOR ELABORATION OF NONLINEAR OPTICAL POLYMERS VIA ELECTRIC- OR OPTIC FIELD ORIENTATION, **I. Ledoux**, I. Cazenobe, S. Brasselet, J. Zyss, Centre National d'Etudes des Télécommunications, France Télécom UA 250, 196 avenue Henri Ravera, 92220 Bagneux, France

We will review some recent advances in molecular design towards highly efficient dipolar chromophores as well as multidimensional molecules for elaboration of active polymers suitable for optoelectronic devices and systems.

Optimization of the electro-optic factor of merit will be discussed in terms of molecular nonlinearities and dipole moments, associated with high thermal stability and low transmission losses in the near infrared. The influence of the amorphous matrix and chromophore concentration will be examined in terms of their DC-field orientation above Tg versus orientational stability at temperatures of operation.

2- and 3-dimensional charge transfer schemes increase the number of structural parameters for optimization of the macroscopic nonlinearity. The advantages of the newly developed all-optica poling scheme will be discussed with respect to electric-field poling, in terms of a local and tensorial control of the optically induced $\chi_{ijk}^{(2)}$ coefficients. Finally we will discuss preliminary molecular engineering schemes for efficient all-optical poling, involving photoisomerization, conformational effects and electronic resonances.

M-IX.3 - invited - 15:00-15:30

POLING AND RELAXATION DYNAMICS OF SIDE-CHAIN AND CROSSLINKABLE COPOLYMERS, **F. Michellotti**, Università di Roma "La Sapienza", Dipartimento di Energetica, Via A. Scarpa 16, 00161 Roma, Italy, E. Toussaere and J. Zyss, France Telecom-CNET, 196 Av. Henri-Ravera, 92225 Bagneux, France

A review of our recent experimental and theoretical results on poling of side-chain copolymers, either in a dc or pulsed electric field, is presented. A technique for the in-situ measurement of the electro-optic coefficient is described. Experimental results, obtained for Disperse Red 1 side-chain PMMA and its crosslinkable variant Red Acid Magly, show Williams-Watts-Kohlrausch isothermal relaxation of the 2nd order response and Vogel-Fulcher-Tamann-Hesse temperature dependence of the relaxation time constant, above glass transition Tg. On the theoretical side, the growth of the macroscopic 2nd order nonlinear optical (NLO) properties of side-chain and crosslinkable copolymer species, under application of a periodic electric poling field, is modelled. Rotational diffusion of diazo-dye dipoles, in the presence of crosslinking sites randomly distributed in the copolymer matrix, is discussed. The influence of the poling field frequency and of the density of crosslinking sites on the asymptotic 2nd order NLO properties is shown. Numerical results are compared with experimental ones, for two cited copolymers, showing a good agreement. The model can be used in order to optimize the copolymer parameters, in order to maximize the final 2nd order NLO properties.

M-IX.4 - invited - 15:30-16:00

POLYMER BASED WAVEGUIDES AND OPTICAL SWITCHING, **M.A. Bader**, H.M. Keller, G. Marowsky, Laser-Laboratorium Göttingen e.V., Hans-Adolf-Krebs-Weg 1, 37077 Göttingen, Germany

Optical nonlinear devices are necessary to control the processing of fast optical signals. Polymeric materials are particularly suited to be applied to realizing new all-optical switching concepts. A bistable switching device based on a periodically structured nonlinear waveguide has been demonstrated [1], so-called gap solitons stabilizing the switching process. A polymer based device would signify a tremendous progress in integrated optics.

The fabrication of Bragg gratings in different polymeric films with high optical nonlinearity, e.g. PPV (polyphenylene-vinylene) or PDA (poly-diacetylene) is under progress. Experimental work is concentrated on the characterization of the nonlinear periodic planar waveguide structure considering different aspects, like refractive index modulation, absorption or thickness of the polymeric films, and on the proof of the band gap. The next step will be the investigation of the nonlinear switching process.

Calculations based on the coupled-mode theory [2] simulating the switching process under real conditions are carried out parallel to the experiments to verify the experimental results and define the requirements to optimize the switching performance.

[1] N. D. Sankey et al., Appl. Phys. Lett. 60, 1427 (1992)
[2] C. M. de Sterke and J. E. Sipe in Progress in Optics XXIII, ed. by E. Wolf, Elsevier Science (1994)

16:00-16:25 **BREAK**

Session X

M-X.1 - invited - 16:25-16:55 FERROELECTRIC LIQUID CRYSTALS AND ELECTROOPTICAL DEVICES, DEVELOPED IN TECHNICAL UNIVERSITY DARMSTADT, **W. Haase**, and L. Beresnev, Institute of Physical Chemistry Technical University Darmstadt, Petersenstr.20, 64287 Darmstadt, Germany

The overview report about development of electrooptical devices, based on FLC's will be presented. The unusual physical properties of some FLC materials, will be discussed starting from X-ray, dielectric, electrooptic and pyroelectric investigations.

The description of such developed FLC devices will be done, as: flat electroclinic modulators with response time less 5 microseconds, DHF modulators with response time 100 microseconds and driving voltage less 5 V, prism shutters, using electrically controlled total internal reflection, aperture 3-4 cm^2, response time 50 microseconds, contrast of order 10^6, computer controlled diffraction grating with resolution 40 mm^{-1} and operation frequency 1 kHz, optically addressed spatial light modulators, using the silicon and ZnSe based photoconducting layers and DHF materials, with resolution 100 lp/mm, sensitivity less 50 $microW/cm^2$, operation rate up to 1 kHz. The application of discussed devices will be demonstrated for such functions of optical processing as switching of optical patters in non-polarized non-monochromatic light, for local suppression of light in the field of view of eye or video camera, for fast shuttering light beams with high intensity.

M-X.2 16:55-17:20 MOLECULAR RECTIFICATION IN ORIENTED POLYMER STRUCTURES, C. Sentein, C. Fiorini, A. Lorin and J.M. Nunzi, LETI (CEA-Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France

We underline the intrinsic rectifying nature of an oriented polymeric material. Orientation of the initially symmetric structure is performed through DC-field ordering of the polar molecules contained in the polymer. The internal field induced in the polymeric material is evidenced by the induction of a rectifying current-voltage characteristic. Second-harmonic generation and time-of-flight experiments confirm the molecular-diode nature of the individual molecules. This opens a new route for the improvement of organic semiconductor devices efficiency. Indeed, molecular orientation induces a band structure which is equivalent to a distributed p-n homojunction within a single polymer film. Additionally, it lowers the potential barrier for charge injection at electrodes and it enhances drift-mobility of the charge carriers.

M-X.3 17:20-17:45 NEW LOW-Tg ORGANIC PHOTOREFRACTIVE MATERIALS, L. Mager, C. Melzer, M. Barzoukas, A. Fort, J. Muller, GONLO, IPCMS, 23 rue du Loess, BP 20 CR, 67037 Strasbourg Cedex, France, and S. Méry, J.F. Nicoud, GMO, IPCMS, 23 rue du Loess, BP 20 CR, 67037 Strasbourg Cedex, France

With the discovery of organic photorefractive materials, one has access to numerous different structures. They are built by the association of photoconductive and nonlinear optic (NLO) moieties. So, one can select the different components and the way to associate them in order to obtain given properties. A low T_g makes the material easily processed and allows reorientation of the molecules at room temperature. This reorientation was found to enhance the performances, because of the anisotopy of the linear polarisability.

We present new results on three different kinds of low T_g materials.

The first material is a photoconducting functionalized polysiloxane which has been doped with novel NLO molecules. Important net gain has been observed at 514 nm the material showing low absorption at this wavelength.

The second type of materials are multifonctional polymers. In these structures the photoconductive and NLO moieties are both attached to the polymer backbone. The investigated materials are polysiloxane functionalized with carbazole groups insuring the photoconduction, and with modified carbazole groups exhibiting NLO properties.

The last material is a novel bifonctional molecule (photoconductive and NLO) leading in itself to an organic glass without the use of any binder polymer. This kind of material exhibits a remarquable low viscosity at room temperature. Measurements at 633 nm show very important photorefractive gain.

M-X.4 17:45-18:10 NOVEL PHOTOREFRACTIVE SOL-GEL MATERIALS, F. Chaput, K. Lahlil, J.P. Boilot, Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, URA CNRS 1254D, Ecole Polytechnique, 91128 Palaiseau, France, V. Alain, M. Blanchard-Desce, Département de Chimie, Ecole Normale Supérieure, URA CNRS 1679, Paris, France, B. Darracq, Y. Levy and A. Brun, Groupe d'Optique Non Linéaire, Institut d'Optique Théorique et Appliquée, URA CNRS 14, Orsay, France

Interest in photorefractive polymeric materials has been growing rapidly since the demonstration of the first organic polymer based photorefractive system in 1991. Studies in this field have been motivated by the wide variety of potential applications and by the desire for a better understanding of photorefractivity in such systems.

We report in this study design, synthesis and optical characterizations of photorefractive sol-gel materials, which contain different second-order chromophores and charge transporting molecules covalently attached to the silica based backbone. We show that gel films exhibit large and stable quadratic nonlinearities as deduced from second harmonic and electrooptic measurements ($r_{33}\approx17pm/V$ at 633nm). Large net optical gains of about $200cm^{-1}$ at a zero external electric field were measured using two-beam coupling experiments.

M-X.5 18:10-18:35 NONLINEAR OPTICAL PROPERTIES OF MULTI-DIMENSIONAL CHARGE TRANSFER FUNCTIONAL GROUPS IN FERROELECTRIC LIQUID CRYSTALS, Yi Luo, M. Lindgren, and H. Agren, Institute of Physics and Measurement Technology, Linköping University, 58183 Linköping, Sweden

The design of Ferroelectric Liquid Crystals (FLCs) possessing large second -order nonlinear optical susceptibilities is accomplished by the introduction of functional groups with large microscopic hyperpolarizabilities. Currently, only one-dimensional charge transfer functional groups, such as p-nitroanilines and p-nitrophenol, have been used. In this case, the mesomorphic character of FLCs can be disturbed, since there is a strong permanent dipole moment along the donor-acceptor direction which is almost perpendicular to the molecular axis. In this report, several new multi-dimensional charge transfer functional groups, which lack dipole moment along the direction perpendicular to the molecular axis, are proposed and studied. The undertaken ab initio calculations indicate that the hyperpolarizabilities of such functional groups are comparable with those of one-dimensional charge transfer molecules. The changes of hyperpolarizability of functional groups in different hosts have also been studied.

Poster Session II

18:35-20:00 See programme of this poster session p. M-24 to M-32.

Thursday June 19, 1997 — Morning
Jeudi 19 juin 1997 — Matin

Session XI

M-XI.1 - plenary- 9:00-9:45

POLYMER OPTICAL FIBERS (Title to be confirmed) **K. Sasaki**, Faculty of Science and Technology, Keio University, Lab. 3-14-1, Hiyoshi, Yokohama 223, Japan

M-XI.2 - invited - 9:45-10:15

PHOTOCHROMIC AND PHOTOREFRACTIVE POLYMERS FOR HOLOGRAPHIC DATA STORAGE, **D.M. Burland**, Center on Polymer Interfaces and Macromolecular Assemblies, Almaden Research Center, IBM Research Division, 650 Harry Road, San Jose, CA, USA

In recent years there has been an increase in interest in the use of photoactive polymers for the holographic storage of digital information. Two general classes of materials have been considered: photochromic systems in which an irreversible or reversible photochemical reaction is used to record the data and photorefractive systems in which photogenerated charges are used. The use of these systems in data storage applications places severe requirements on the physical properties of these polymers. These requiremetns will be discussed and measurements of the performance of existing holographic polymer systems will be presented. A new class of promising photorefractive materials, doped glasses, will be described.

10:15-10:30 **BREAK**

M-XI.3 - invited - 10:30-11:00

POLYMERIC THERMO-OPTIC SPACE SWITCHES FOR OPTICAL COMMUNICATIONS, **M.B.J. Diemeer**, Akzo Nobel Central Research, RGE Department, 6800 SB Arnhem, The Netherlands

Solid state optical space switches based on the thermo-optic effect in polymeric optical waveguides have now reached the commercial stage. The application of these switches is in network protection and network reconfiguration functions for fiber optic communications systems. The requirements for these applications include polarization and wavelength independence, low insertion loss, low cross talk, low drive power with step-like (digital) response, millisecond switching times and small size. In addition the reliability of the component must meet the demanding requirements of telecom applications.

It will be shown that polymeric thermo-optic space switches can meet all functional requirements due to the exceptional thermal and thermo-optic effects of polymers combined with their tunability and processing versatility. Furthermore, it will be shown that polymer optical chips and packaged and pigtailed components can withstand extreme liftime tests with success.

Session XII

M-XII.1 - invited - 11:00-11:30

TOWARDS ELECTROLUMINESCENT POLYMER DISPLAYS, **P. Robin**, P. Le Barny, C.M. Bouché, H. Facoetti, F. Soyer, M. Vergnolle, G. Vériot, Thomson-CSF Laboratoire Central de Recherches, Domaine de Corbeville, 91404 Orsay, France

Electroluminescent polymers are now studying by numerous researchers in academic and industrial laboratories. Luminance of 10000 cd/m^2 are now obtained with voltage from 4 to 10 volts. The life times are continuously increasing and 5000 hours for 100 cd/m^2 have been now demonstrated.

During the presentation, we will describe the possibilities to built displays with these materials: brightness, passive multiplexability, active matrix addressing, current density, heat dissipation.

M-XII.2 - invited - 11:30-12:00

STABILITY OF POLYMER LEDS, **P. van de Weijer**, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Polymer LEDs have a number of attractive properties that make them suitable for many applications. Operating at low voltage, bright large-area devices can be made by simple technology. One of the limitations that prohibited industrialization of polymer LEDs was their limited lifetime.

An overview of the technological progress in polymer LED processing and its encapsulation at Philips is presented. The improved polymer LED performance during the last year for 8 cm^2 devices is reflected by lifetimes of many thousands of hours, while operating at daylight visibility under ambient conditions.

A few examples will be given of analytical measurements that have contributed to our qualitative understanding of the degradation mechanism of polymer LEDs. Some of the bottlenecks for further improvement of the device performance will be discussed.

12:00 **LUNCH**

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SYMPOSIUM M
POSTER SESSIONS

Tuesday June 17, 1997 **Afternoon**
Mardi 17 juin 1997 Après-midi

Poster Session I
18:05-20:00

M-I/P1 APPLICATION OF POLYMER PHOTOSENSITIVE LAYERS IN LIQUID CRYSTAL SPATIAL LIGHT MODULATORS, N.V. Kamanina, Vavilov State Optical Institute, St.Petersburg, 199034 Russia and N. A.Vasilenko, Karpov Research Physical-Chemical Institute, Moscow 103064, Russia.

Polyimide systems hold a special position among high resolution media, where the reversible recording of information is realized at spatial frequency up to 1500 mm^{-1}. Recently we investigated an enhancement of speed for the liquid crystal spatial light modulators (LC-SLMs) based on polyimide by varying a delay between a write laser pulse and a supply voltage pulse and by choosing an alignment film (SiO, CeO_2, GeO, polyvinyl alcohol, and a-C:H).

In the present work we investigated the possibilities for an achievement of the limiting sensitivity and of the maximum resistance to laser irradiation damage in the polyimide - liquid crystal system. In this experiment a write energy density was varied in a range 100 μJ cm^{-2}- 0.2 J cm^{-2} and a width of supply voltage pulse was changed from 30 ms to 380 ms. The investigated LC-SLMs showed the holographic sensitivity in the range $5x10^{-7}$-$1x10^{-6}$ J cm^{-2}.

M-I/P2 MULTISTEP RELAXATION IN RESONANT LIQUID CRYSTAL MEDIA., V. V. Danilov and N. V. Kamanina, Vavilov State Optical Institute, St.Petersburg, 199034 Russia.

In the present paper the relaxation of a holographic grating has been investigated in the nemato-chiral system doped with a dye, when the effect of diffraction suppression of absorption, an optical analog of the Borrmann effect, is occurred.

For the recording and the readout of the holographic grating using the second harmonic (530 nm) of Nd-laser nanosecond pulses and cw He-Ne laser (633 nm), respectively, the time dependence of a diffraction efficiency was investigated. Three regions were clearly separated from this dependence. Region I is associated with the resonant interaction of the short laser pulses with the impurity nemato-chiral system, when the laser wavelength falls within the overlapping region of the selective reflection band for the liquid crystal mixture with the absorption band of the dye. Region II is characterized by the dependence of the relaxation time of a write spatial frequency. Here the relaxation of the deformation of the cholesteric spiral occurs. Region III exhibit the longest characteristic time. In this case the relaxation of smectic phase regions is observed. It should be noticed that the mechanisms, which are corresponded to these regions, have been found to switch on sequentially.

M-I/P3 ELECTRONIC INSTABILITY OF ONE-DIMENSIONAL MOLECULAR SYSTEM AS PHYSICAL BASE FOR DESIGNING ELECTRONIC DEVICES, Ju.H. Krieger, Institute of Inorganic Chemistry, Lavrentiev ave. 3, 630090, Novosibirsk, Russia

The designing of the molecular electronic devices demands the solution of various problems. On the one them is the problem of determining a physical principle of operating molecular system.

Our concept in achievement of this purpose is based on use of electronic structural instability effect, which can take place in one dimensional molecular systems. This phenomenon has a number of useful properties which allow us to use it as a physical principle for designing molecular electronic devices:

—this phenomenon occurs in molecular systems with size about 100 Å
—the electrical conductivity of such a system can be controlled by external effect (electrical fields, light, chemical compounds, and so on);
—this conductivity can be ten orders and more varied;
—this allows us to control of one or several molecules and convert their condition in macroscopic conductivity of the one dimensional systems;

This property will allow us to create various molecular electronic devices: molecular transistor, memory element, chemical sensor, artificial neurone and so on.

M-I/P4 MEMORY CELL BASED ON ELECTRICAL FIELD INDUCED CHANGING CONDUCTIVITY OF MOLECULAR FILMS, Ju.H.Krieger, S.B. Vaschenko, N.F. Udanov, Institute of Inorganic Chemistry, Lavrentiev ave. 3, 630090, Novosibirsk, Russia

We propose using the quantum effect of electronic instability, which is realized in one-dimensional molecular systems for a creation of the molecular electronic devices, in particular, molecular memory cells.

The electrical field induced changing conductivity and memory phenomena are observed in the molecular thin films sandwiched between two metal electrodes which called as memory cell. Electrophysical parameters of the cell were measured. It was established that it has an S-shaped voltage-current characteristic with memory. The threshold voltage is usually lies in the range of 0.15-0.3 volt. The several type of the memory is observed depends on the type of the molecular system and a condition of the switching. The conductivity of the memory cell could be fixed in the wide interval (100ohm-10megaohm) depending on the switching condition. The time of information recording is about 10-100 ns and the time information storage from 10 sec to 2 months and more depending on recording regime, molecular system composition. The number of write-erase cycles was more than 10^8.

We believe that on the basis of the given molecular memory cell it is possible to design and build DRAM and SRAM devices with a high information density without the expensive fabrication facilities.

M-I/P5 NONLINEAR RESONANT TUNNELING THROUGH DOUBLE DEGENERATE STATE OF QUANTUM WELL, V.N. Ermakov and E.A.Ponezha, Bogolyubov Institute for Theoretical Physics, Kiev, Ukraine

In an approach of low transparency of barriers tunneling of electrons through a double barrier system with an account of their Coulomb interaction in an interbarrier space (quantum well) has been considered. The state of electrons in the quantum well is supposed to be two-fold degenerated. It was shown that the dependence of tunneling current on applied voltage has a steplike character at low temperatures and in a region of small applied bias there is a threshold value. The considered system also has bistability properties due to the appearance of two electrons in the upper splitting levels in the well. Such tunneling state is possible because the tunneling system is unequilibrium but stable. The charge fluctuations in the well are also discussed.

M-I/P6 FULL COLOUR ELECTROLUMINESCENCE USING DYE DISPERSED POLYMER BLENDS, S. Berleb, G. Egerer, W. Brütting, M. Schwoerer, Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany and R. Wehrmann, A. Elschner, Bayer AG, Zentrale Forschung und Entwicklung, Werk Uerdingen, 47829 Krefeld, Germany

The use of molecular dyes as dopants in polymer light emitting devices offers the possibility to optimize separately the basic processes charge carrier injection, transport and recombination. By blending suitable dyes into poly-N-vinylcarbazole (PVK) we have fabricated devices which emit light in the whole visible range. Using ITO and Al as electrodes we have achieved relatively high external quantum efficencies (up to 0.1%) in a simple single-layer structure.

The current-voltage-characteristics can be described by space-charge limited currents (SCLC) with effective trapping of the carriers by the dye molecules, while the light intensity shows a Fowler-Nordheim-like behaviour as a function of the mean electric field. We were able to model the electroluminescence characteristics by assuming tunneling of the minority charge carriers through a triangular barrier. The obtained barrier heights showed a strong dependence on the dye molecules, suggesting that the injection of the minority carriers takes place directly into the LUMO-levels of the chromophors. The recombination along with the space charge leads to a steeper increase of the current and a Fowler-Nordheim-like I-V-characteristics in the electroluminescent regime though the majority carrier current is not injection-limited.

M-I/P7 NEW ELECTRON CONDUCTING COPOLYMERS IN OLEDs, J. Pommerehne, A. Selz, W. Heitz and H. Bässler, Fachbereich Physikalische Chemie und WZMW der Philipps-Universität, 35032 Marburg, Germany

A new conducting, non-crystalline polymer based on a polystyrene backbone with substituted quarterphenyle side chains (PQP) is presented. In a monolayer device with calcium cathode the current is found to be space charge limited. From Child's law an electron mobility of $\cong 10^{-9}$ cm^{-2} $V^{-1}s^{-1}$ is obtained. Double layer devices consisting of a 85 nm Tristilbenamine(TSA)/Polysulfone film overcoated by a 80 nm thick PQP layer show electroluminescence of the TSA with efficiencies of 1% (Al-cathode) and 1.4% (Mg-cathode), respectively. To study the kinetics of electroluminescence transient measurements were performed upon adressing single and double layer devices by rectangular voltage pulses. An unusually sharp rise of the El signal after a delay time of up to 100 ms is observed suggesting the involvement of a trap-saturation effect. Further investigations are in progress.

M-I/P8 A NEW PRECURSOR TO ELECTROCONDUCTING CONJUGATED POLYMERS : OPTO-ELECTRICAL PROPERTIES OF LUMINESCENT DEVICES (LEDs AND LECs) BASED ON THESE PPV DERIVATIVES, W. Bijnens, M. Van Der Borght, D. Vanderzande, J. Gelan, J. Manca, W. De Ceuninck and L. De Schepper. Instituut voor Materiaal Onderzoek, Limburgs Universitair Centrum, Universitaire Campus gebouw D, 3590 Diepenbeek, Belgium.

Despite the interesting properties and the large spectrum of possible applications for precursors to electroconducting conjugated polymers, a lot of problems have to be over come. Typically the Wessling precursor route is used for polymer LED's. This route is an illustration for the polymerisation behavior of p-quinodimethane systems. The method has several drawbacks and limitations which complicate the precise control of the previous history of the material.

We have been able to define the boundary conditions that are necessary for the polymerisation of substituted p-quinodimethane systems. This has offered the possibility for improved precursor routes which have led to the synthesize of new conjugated polymers with well defined structure and morphology. Here a hydrogen chlorine is eliminated under basic conditions during polymerisation and a non-charged sulphinyl group, a thermally labile group, is removed during the conversion to the actual conjugated polymer. In this way we have been able to synthesis poly(4,4'-bisphenyle vinylene), poly(2,6-naphtalene vinylene) and methyl and methoxy-substituded poly(p-phenylene vinylene).

Here we report in detail on the opto-electrical properties of devices by current-voltage measurements and impedance spectroscopy, powerful techniques for the study of these devices. As well light emitting diodes (LEDs) as light emitting electrochemical cells (LECs) will be discussed in detail.

M-I/P9 INTERNAL ELECTRICAL FIELD DISTRIBUTION IN DOUBLE LAYER POLYMER STACKS AS STUDIED BY ELECTROABSORPTION, S. Grossmann, S. Saal, T. Weyrauch, W. Haase, Institut für Phys. Chemie, TH Darmstadt, Petersenstr. 20, 64287 Darmstadt, Germany

Electrical field poling of polymer multi layer structures is of basic interest for fabricating a variety of integrated optic polymer devices e.g. waveguide devices with selectively located passive and active electrooptic (EO) polymers. Due to different resistivities and interface effects the electric field is not homogeneous over the whole stack. In order to achieve efficient poling of these polymer structures a large part of the applied voltage must be applied to the active layer. Up to now no direct methode to investigate the inhomogeneous field distribution in a multi layer polymer stack is known.

The aim of this work is to present a method, which allows to measure the field strength selective in the EO active polymer layer. The investigated polymer structures are made up of two layers: A polycarbonate layer containing an EO chromophore and a cladding layer, from epoxy resin or polyimide. In order to measure the electric field strength in the active layer an electric AC field is applied to the sample in addition to the DC poling field. Because of the different spectral behaviour of the quadratic and the linear electroabsorption (Stark) effect we may distinguish between effects caused by the internal electric field and the polar order of the chromophores, respectively. Thus the value and the time dependency of the internal field in the active layer was detectable. The influences of different layer conductivities and interface charges on the internal field can be studied. One also gets informations about time course and magnitude of the polar order of the EO chromophores.

M-I/P10 RELAXATION-PROCESSES OF CHROMOPHORES IN POLYMER MATRICES DETERMINED BY ELECTRO-ABSORPTION EXPERIMENTS, S. Saal, S. Großmann, T. Weyrauch and W. Haase Institut für phys. Chem, Technische Hochschule Darmstadt Petersenstrasse 20, 64287 Darmstadt, Germany

In order to understand the general behaviour of poled polymers the study of the relaxation of chromophores in the matrix is an important task. To measure the dynamics of the chromophores dielectric spectroscopy has some disadvantages since this method is sensitive to all dipole groups in the sample. The electroabsorption technique, however, is selectively sensitive to the chromophores.

Assuming a rigid sample the electroabsorption spectroscopy allows one to determine the difference of the dipole moment $\Delta\mu$ and the difference in polarizability $\Delta\alpha$ between optical ground and excited state due to the quadratic Stark effect. In poled polymers the linear Stark effect is also observable. It has been shown that the polar order parameter $<\cos\Theta\sin^2\Theta>$ may be determined by this effect as function of time.

In the case of a non-rigid sample a contribution to the electroabsorption occurs due to the orientation of the molecules in the electric field. The orientation of the chromophores by the electric modulation field is observable in the quadratic-in-field measurements by two means:

(i) a contribution proportional to the absorption spectrum due to the linear dichroism of the molecules
(ii) an apparent change of $\Delta\alpha$ due to the polar orientation of the chromophores.

This technique developed by us is sensitive to an amount of less than 1 wt-% of dye in the frequency range 10 mHz to 10 kHz.

M-I/P11 ELECTROCHEMICAL DOPING IN A SERIES OF α,α' DIMETHYL END-CAPPED OLIGOTHIENYLS. A FT-RAMAN CONFIRMATION OF A RADICAL CATION GENERATION, J. Casado(1), T.F. Otero(2), S. Hotta(3), V. Hernandez(1), F.J. Ramirez(1) and J.T. Lopez Navarrete(1), (1)Dpt.de Quimica Fisica, Universidad de Malaga, 29071-Malaga, Spain. (2)Dpto. Ciencia y Tec.de Polimeros, Facultad de Quimicas, 20080 San Sebastian, Spain. (3)Matsushita Research Inst.Tokyo, 3-10-1 Higashimita, Tamaku, Kawasaki 214, Japan

Conjugated conducting polymers and oligomers constitute a subject of research lying at the interface between solid-state physics and molecular science. In this field, Raman spectroscopy is a powerful tool for studying the structures of polarons and bipolarons, which are associated with the electrical and optical properties of the polyconjugated materials. In this work, the thiophene oligomers ($n = 4$, 5 and 6) α,α'dimethyl-protected were investigated with a spectroelectrochemical system where the optical absorption spectra were recorded on a in situ cyclic voltammetry experiment. In order to get a caracterization of the oxidized samples we have recorded the FT-Raman spectra in a non simultaneous registration system.This results will be utilized to propose the molecular species associated to the conduction mechanism in oligomeric and polimeric systems derived from thiophene.

M-I/P12 CONSTRUCTION OF THE ENERGY DIAGRAM OF THE DTPP/SnO_2 HETEROJUNCTION BY SURFACE PHOTOVOLTAGE SPECTROSCOPY, E. Moons, M. Eschle, M. Grätzel, Lab. de Photonique et Interfaces (L.P.I.), Ecole Polytehnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Solid layers of various thickness of the hole conductor dithioketopyrrolopyrrole (DTPP) were evaporated on conducting transparent SnO_2. The work function of these organic layers were measured by the Kelvin Probe technique. By back and front side illumination of the layers, the p-type conductivity type was confirmed and space charge layers were found to be located at the air/DTPP and at the DTPP/SnO_2 interface. For thick layers of DTPP, the front and back side illumination allowed us to separate these two fields and thus to calculate their respective contributions to the total photovoltage. These results in the construction of the energy diagram of the DTPP/SnO_2 junction. For thinner layers the photovoltage is a superposition of the front side signal and back side signal, modulated by an inner filter effect by the organic layer itself. Surface Photovoltage Spectroscopy (SPS) of evaporated layers showed a weak spectral dependence of the photovoltage. However, spectral changes upon solvent vapour treatment of the layers could be observed. The Kelvin Probe and SPS technique have also proven to be useful to study interfaces involving other solid organic layers, such as other DPP derivatives, PTCDA, porphyrins[1] and phthalocyanines[2].

(l) Moons, E.; Savenije, T.; Goossens, A. J. Phys. Chem. 1997, submitted,
(2) Pfeiffer, M.; Leo, K.; Karl, N. J. Appl. Phys. 1996, submitted,

M-I/P13 ELECTRICAL CHARACTERIZATION OF $CuInSe_2$ THIN FILMS, O. Tesson, M. Morsli, A. Bonnet, L. Cattin, Université de Nantes, Laboratoire de Physique des Matériaux pour l'Electronique, G.P.S.E., 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03 and G.Massé, Université de Perpignan, Centre d'Etudes Fondamentales, 52 Avenue de Villeneuve, 66860 Perpignan, France

Deposition of $CuInSe_2$, a promising photovoltaïc material, had been carried out by using a simple and low cost close-spaced vapour transport method. Nearly stoichiometric large area polycristalline thin films were grown for different source and substrate temperatures. Direct current electrical resistivity, Hall effect and thermoelectric power measurements have been performed in a wide temperature range (80-500K). Experimental results are described for some representative samples. An eventual grain boundary contribution to the transport properties is discussed on the basis of all experimental results. In the low temperature range, it appears that conduction mechanisms are mainly governed by variable range hopping at Fermi level in the localized states of a band which originates from non-stoichiometry and residual impurities. At higher temperatures, the contribution of the extended states of the conduction and valence bands becomes predominant.

M-I/P14 POLYCARBAZOLE THIN FIMS OBTAINED BY ELECTROCHEMICAL OXIDATION, H. Taoudi, J.C. Bernede, A. Bonnet, M. Morsli, and O. Tesson, Laboratoire de Physique des Matériaux pour l'Electronique, G.P.S.E., 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03, France

A comparative characterization of polycarbazole obtained either by electrochemical oxidation of carbazole in solution or vacuum deposited carbazole films is described. The first method starts from conducting electrodes in an electrolyte solution containing the carbazole monomer. In the second, the oligomer source consists in thin films deposited under vacuum on conducting SnO_2 coated glass substrate. After oxidation, thin films obtained by the second method are amorphous while some crystallites with carbazole structure are present in other ones. The electrical conductivity of the polycarbazole obtained by oxidation of predeposited thin films is higher and thermogravimetric measurements show that it is more stable. These results could be attributed to a longer averaged chain lenght in agreement with X-ray diffraction spectra which show that probably some monomers and/or oligomers are effectively present in the polycarbazole obtained from carbazole in solution.

M-I/P15 X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF POLYANILINE-POLYSTYRENE BLENDS, V. Jousseaume, M. Morsli, A. Bonnet, O. Tesson, Université de Nantes, Laboratoire de Physique des Matériaux pour l'Electronique, G.P.S.E., 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03 and S. Lefrant, Institut des Matériaux de Nantes, Laboratoire de Physique Cristalline, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03, France

The electronic structure of polyaniline (PANI) films and conducting polyaniline - polystyrene (PANI - PSt) blends have been studied by X-Ray Photoelectron Spectroscopy (X.P.S.). Different counterions were used to simultaneously protonate polyaniline and induce solubility of conducting PANI in m-cresol. The proportion of benzenoid amine, quinoid imine and protonated units in each samples is deduced from X.P.S. analysis. The Nls level spectrum decomposition allowed to estimate the doping rate and the localization of the charge transfer on the chain. Blending polyaniline with polystyrene do not induce important modifications in the polymer electronic structure.

M-I/P16 TRANSPORT PROPERTIES AND STABILITY OF POLYANILINE - POLYSTYRENE BLENDS, V. Jousseaume, M. Morsli, A. Bonnet, O. Tesson, Université de Nantes, Laboratoire de Physique des Matériaux pour l'Electronique, G.P.S.E., 2 rue de la Houssinière , BP 92208, 44322 Nantes Cedex 03 and S. Lefrant, Institut des Matériaux de Nantes, Laboratoire de Physique Cristalline, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03, France

Doped polyaniline (PANI) is one of the most attractive conducting polymers for electronic applications. The codissolution method allowed us to obtain conducting polyaniline - polystyrene (PANI - PSt) composites with a high electrical conductivity and good mechanical properties. The dependence of the electrical conductivity with volume fraction of polyaniline in the blend is found to be characteristic of a percolation system with a low percolation threshold. Electrical conductivity and thermoelectric power measurements have been performed in a wide temperature range (80K-300K) and are interpreted on the basis of hopping mechanisms between polaronic clusters. The thermal study puts in evidence a good stability of these composites with time and temperature.

M-I/P17 IN SITU CHARGE-MODULATION SPECTROSCOPY OF OLIGOTHIOPHENE FIELD-EFFECT DIODES : FROM SEXITHIOPHENE TO POLYTHIOPHENE, M.G. Harrison, Cavendish Laboratory, Cambridge, UK, CB3 OHE and F. Garnier, A. Yassar, and D. Fichou, CNRS Laboratoire des Matériaux Moléculaires, 2 rue Henri Dunant, 94320 Thiais, France

We have fabricated semi-transparent Metal-Insulator-Semiconductor (MIS) diodes in which the semiconductor is an oligothiophene, including α-6T, α-8T and α-12T. The charge density within the oligomer layer is controlled by the voltage applied to the gate electrode. By modulating the gate voltage and probing the resulting modulation of optical absorption at the same frequency, we have obtained optical spectra characteristic of the charged excitations in these oligomers within real solid-state field-effect devices.

Analysis of the phase response and dependence on modulation frequency, gate voltage and temperature enables us to assign the new charge-induced optical transitions to radical cations, dications and charged aggregates such as π-dimers. We investigate the equilibrium between these species as a function of the oligomer chain length and compare the extrapolations with spectra on poly(alkylthiophene)s We also discuss the polymeric polaron / bipolaron model in view of our new data on oligomers.

M-I/P18 BOND LENGTH ALTERNATION IN PUSH-PULL POLYENES AND THE RELATIONSHIP BETWEEN ELECTRONIC AND VIBRATIONAL MOLECULAR HYPERPOLARIZABILITIES, C. Castiglioni, M. Del Zoppo, P. Zuliani and G. Zerbi, Dept. of Industrial Chemistry, Politechnico di Milano, P. L. Da Vinci, 32, 20133 Milano, Italy

During the last few years theoretical calculations and experimental data on organic conjugated systems have shown a close correspondence between electronic molecular hyperpolarizabilities (ß^{e} and γ^{e}) and their vibrational counterpart (ß^{v} and γ^{v}) .

Some of these compounds are known to have a strongly solvent dependent N.L.O. behaviour. Theoretical studies on push pull polyenes pointed out that the solvent effect is accompained by relevant changes of the molecular structure in terms of variation of the bond alternation along the polyenic chain.

Analogously the vibrational hyperpolarizabilities are affected by changing the intermolecular sourroundings as shown by experimental and computed vibrational spectra.

The study of these effects based on a simple two state model allows to establish a precise correspondence between electronic and vibrational hyperpolarizabilities.

M-I/P19 MODEL OF PHOTO-INDUCED NEUTRAL-IONIC PHASE TRANSITION IN ORGANIC CHARGE-TRANSFER SALTS, V.M. Yartsev, Centro de Fisica, IVIC, Apartado 21827, Caracas 1020A, Venezuela

Organic charge-transfer crystals with mixed-stack structures may be classified into two types with a neutral and an ionic electronic ground states. We calculated [l] charge distribution in isolated small clusters: a donor-acceptor dimer and a donor-acceptor-donor trimer. Electron-intramolecular vibration coupling was shown to be responsible for a sharp neutral-ionic phase transition and characteristic hysteresis in the degree of ionicity dependence upon pressure. Now we consider a possibility of neutral-ionic transition upon local photo-induced charge-transfer excitation. The results are used for interpreting the experimental data obtained for single crystals of tetrathiafulvalene-p-chloranile [2] and polydiacetylenes [3].

[l] S. Matsuzaki, S. Basaki, and V.M. Yartsev, J. Phys. Soc. Jpn. 64, 858 (1996).
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M-I/P20 PHOTOPHYSICAL PROPERTIES OF ß-ALKYLATED QUATER-, OCTA-, DODECA- AND HEXADECA-OLIGOTHIOPHENE, H.J. Egelhaaf, D. Oelkrug, Inst. for Phys. Chem., Univ. of Tübingen, 72076 Tübingen, W. Gebauer, M. Sokolowski, E. Umbach, Inst. for Physics, Univ. of Würzburg, Th. Fischer, P. Bäuerle, Inst. for Organic Chem., Univ. of Ulm, Germany

In order to elucidate the effect of chain-length on photophysical properties, soluble ß-alkylated oligothiophenes with n = 4, 8, 12 and 16 thiophene rings were investigated by UV/Vis-absorption, steady-state and time-resolved fluorescence spectroscopy.

In solution, absorption bands are unstructured, whereas fluorescence spectra show vibrational structure, indicating torsional mobility of the molecules in the ground state and planarization in the excited state. Absorption maxima are blue-shifted by about 1000 cm^{-1} compared to unsubstituted oligothiophenes, due to steric hindrance by the alkyl chains. No such shift is observed for fluorescence spectra, supposing that the extent of planarization in the excited state is the same as for the unsubstituted species. Torsional mobility is also reduced in rigid environments, e.g. in microcrystallites, resulting in well resolved vibrational structure in both fluorescence and fluorescence excitation spectra.

The chain-length dependence of the spectral positions of absorption and fluorescence maxima in solution and in the solid state cannot be approximated by the l/n relationship for n > 8. However, the dependence is well described over the whole range of n by a modified HMO method, which takes alternating bond-lengths into account. As a consequence, the 'band gap' transition energy for polythiophene is significantly higher than predicted by the l/n rule.

Fluorescence is dipole allowed in all of the investigated compounds, both in solution and in the solid state. The values for the radiative rate constants are the same, whether they are calculated from the area under the main absorption band or from lifetimes and quantum yields of fluorescence. This result is confirmed by the coincidence of the 0-0- transitions of fluorescence and fluorescence excitation spectra at T = 4 K.

M-I/P21 THERMAL PROPERTIES OF METALLIZED POLYIMIDE FILMS, A. Kupchishin, B. Tepikin, K. Tlebaev, Abai State University, 13 Dostyk, 480100, Almaty, Kazakhstan and S. Kudaikulova, V. Kravtsova, G. Boiko, B. Zhubanov, Institute of Chemical Sciences, 106 Valihanov, 480100 Almaty, Kazakhstan

New method of metallizing of films on the basis of aromatic and alicyclic polyimides (PI) has been worked out. It is shown that quality of metallization depends on following factors: cyclization degree of the polyimides, nature of complexing and reducing agents.

Since the mechanical and electrical properties of PI films are widely investigated, their thermal properties are not well understood. In this work the thermal conductivity, thermal diffusivity and specific heat of (non)metallized films have been investigated in the wide temperature range: 80 -330°K. The thermal properties were measured by a transient heating method. It is shown that metallization significantly changes thermal properties. Relation between thermal properties and metal's nature is established.

Metallized PI films reversibly change form upon heating, probably it is due to phase transition.

M-I/P22 PRODUCING OF METAL LAYERS ON THE SURFACE OF THIN POLYIMIDE FILMS BY CHEMICAL CONVERSION, S. Kudaikulova, I. Shalabaeva, B. Zhubanov; Institute of Chemical Sciences, 106 Valihanov, 480100 Almaty, Kazakhstan

Polyamideacids (PAA) on the basis of isophtaloilchloride and methylenedianthranilic acid were synthesized. It was shown that thin films on the basis of nonsoluble salts of PAA were chelated by ions Ag^{+}, Cu^{2+}, Ni^{2+}, Co^{2+}. Structure of chelated complexes was determined.

Reduction of Me^{n+}/PAA leads to formation of metallized films. Reduction of Cu^{2+} has some peculiarities: it results in the formation of black CuH/PAA film. Main factor which determines degree of reduction of Cu^{2+} ions is relation between Cu^{2+}ions and reducing agent (α). CuH/PAA film is very active. Immersion of this film into the solution of AgNO$_3$ leads to the reduction of Ag^{+} ions and formation of bright metallized film of combined (Ag/Cu) structure. Two methods of full reduction up to Cu^{o} are suggested: reduction of Cu^{1+}/PAA film and reduction of Cu^{2+}/PAA film through complex forms.

Electroconductivity of metallized films is in range 10^{-4}-10^{2} S/cm depending on metal's nature.

M-I/P23 POLYIMIDE FILMS CHEMICALLY DOPED WITH AZODYES, S. Kudaikulova, G. Boiko, B. Zhubanov, Institute of Chemical Sciences, 106 Valihanov, 480100 Almaty, Kazakhstan

At present time polymers doped with azodyes are perspective materials for nonlinear optic devices. One of the main factors which determines effectiveness of optical polymer-azocompound system is chemical bond between them.

Two methods of producing of polyimides (PI) of different thickness on the basis of alicyclic dianhydrides and aromatic diamines doped with azodyes are suggested. 1.Azocompound is catalyst of reaction of PI formation and significantly rises PI's molecular mass. It is shown that azodyes with chlorinetriazinic fragment form stable covalent bound wwith the end groups of PI chain. 2. Synthesis of PIs with active side groups. Interaction of azodyes with functionally active PIs leads to formation of stable colored (doprd) PIs. Chemical bonding of azodye with PI chain was investigated by IR, UV-spectroscopy and by special experiments with inactive forms of dyes.

Azodoped PIs are stable to the effect of UV-radiation. Parameters of radiation damage are determined. Azodyes stabilize photodestruction.

M-I/P24 GROWTH OF THE NON-LINEAR OPTICAL CRYSTALS OF LITHIUM TRIBORATE AND BETA BARIUM BORATE, H.G. Kim, J.K. Kang, S.J. Park, S.J. Chung, Division of Materials Science and Engineering, Seoul National Univ., Seoul 151-742, Korea

LiB_3O_5 (abbreviated to LBO) and ß-BaB_2O_4 (abbreviated to BBO) have excellent non-linear optical characteristics in THG, OPO fields.

There are some problems to grow the LBO single crystals of high quality from high temperature solution due to the high viscosity of B_2O_3 solution and the formation of second phase. It was recently reported that the formation of second phase could be prevented by N_2 gas flow[I]. In this work, LBO single crystals were grown from B_2O_3 self flux solution without N_2 gas flow. The effects of seed orientations and rotation rate on crystal quality and crystal size were investigated. At the rotation rate of 20rpm, the crystal grown from the seed perpendicular to (011) face was larger than from the seed parallel to <001> direction. As the rotation rate was increased to 50rpm, crystal yield increased. Second phase formation has not been observed in our experiments without N_2 gas flow. The defects of the grown crystals were observed by x-ray topography.

BBO crystals were grown by the TSSG technique using NaF as well as Na_2O as the flux. Although Na_2O has been known to be the best flux, this flux system has many problems such as high viscosity and flux inclusions. The crystals grown from NaF solution had larger thickness than those grown from Na_2O solution. This morphology change is attributed to low viscosity of NaF solution. The defects in grown crystals could be reduced by decreasing the cooling rate.

[I] E. Brück et al., J. Cryst. Growth, 128, 993-937, 1993

M-I/P25 RECORD AND POSTEXPOSITIONAL AMPLIFICATION OF HOLOGRAMMS IN POLYMER FILMS WITH HIGH ATTENUATION, E. Kovalenko, E. Pen, S. Sharangowich, V. Shelkovnikov, State Academy of Automatic Control Systems and Radioelectronics, 40 Lenin Av., 634050 Tomsk, Russia

Non-uniformity of holographic grating record in photopolymer medium even in case of thin films is very high. Light beam attenuation in a film of 50 mkm thick goes up to 90% and more. Under this condition when describing record kinetics it is necessary to take into consideration the attenuation. The record non-uniformity influences much on diffraction characteristics of the holograms, their efficiency and selective properties. In the report the results of solution of the problem about the recording dynamic and postexpositional amplification of holograms in polymer films are given. Radical photopolymerization kinetics, monomer diffusion and connected with this process the displacement of the inert component are considered. The dependence of the diffusion on the polymerization level and the light beam attenuation in the direction of the propagation is taken into consideration. The dependences of the diffraction efficiency and hologram selectivity on the six of model parameters are defined. The methods which enables to define the parameters of the models on the basis of the experimental data are discussed. The results of the researches and processing of the experimental data for some polymer systems are given. The dynamics of the record, postexpositional amplification and optical amplification after the dark amplification period having been over. The comparison of the experimental data and mathematical model enabled us to find out its main parameters and showed the satisfactory correlation of the predicted and experimental data.

M-I/P26 SECOND HARMONIC GENERATION STUDIES OF NOVEL PYROELECTRIC LIQUID CRYSTAL POLYMERS, M. Lindgren, IFM, Linköping University, 581 83 Linköping, U.W. Gedde, A. Hult, F. Sahlén, M. Trollsas, J. Ortegren, Dept. of Polymer Technology, Royal Institute of Technology, 100 44, Stockholm, D. Hermann, L. Komitov, S.T. Lagerwall, P. Rudquist, B. Stebler, Physics Department, Chalmers University of Tech., 412 96 Göteborg, Sweden

Pyroelectric liquid crystal polymers (PLCP) were prepared by photopolymerisation of binary mixtures of two monomers which exhibit a ferroelectric chiral smectic C phase. A2c: 4"-{(R)-(-)-2-[(10-acrylo-yloxy)decyl]-oxy}-3nitrophenyl 4-4'-[(11-acryloyloxy) undecyloxy]-phenyl}benzoate. A1b: 4»-((R)-(+)-2-octyloxy)-3»-nitro phenyl 4-(4'-((11 -acryloyloxy)undecyl-oxy)phenyl) benzoate. Both monomers have an in-built NO_2 function to enhance electrooptical properties, and one of the monomers, A2c, enables polymerisation to a cross-linked polymer. During the polymerization an electric field of approximately 50 V/µm was applied over the FLC cells. All cases of polymers formed from the chiral smectic C phase showed an SHG-signal with no external field present, indicating that polar order became fixed. The associated d_{22}-coefficient was found to vary in the range 0.2-2.8 pm/V. Experimental results of different polarization combinations of the pump and frequency doubled light are presented and discussed.

M-I/P27 STRUCTURE AND ELECTRONIC PROPERTIES OF POROUS SILICON, OBTAINED BY LASER ABLATION, D.P. Savin, S.A. Gevelyuk, Y.O. Roizin, Odessa State University, Ukraine, E. Mugenski, I. Sokolska, Wroclaw Institute of Low Temperatures, Poland

We have fabricated luminescent porous silicon by the method of laser ablation. The crystalline silicon surface was treated by a focused beam of a low power UV laser in different gaseous atmospheres. As a result a porous material containing silicon quantum size clusters and a certain amount of oxygen was formed. Structure investigations, photoluminescence spectral measurements and photoconductivity measurements of the fabricated material were performed. It was shown that such a material, similar on the whole to porous silicon prepared by electrochemical etching, offers new technological options, in particular the possibility to process chips with dimensions less then 20 mkm.

M-I/P28 INFLUENCE OF OXYGEN ON THE ELECTRICAL CHARACTERISTICS OF PPV-LED'S, J. Manca, W. Bijnens, W. De Ceuninck, L. De Schepper, D. Vanderzande, J. Gelan and L. Stals, Limburg University Centrum, Institute for Materials Research, Wetenschapspark, 3590 Diepenbeek, Belgium

With impedance spectroscopy and IV-measurements it has been shown that the presence of oxygen in the surrounding atmosphere exerts an important influence on the electrical characteristics of organic electroluminescent diodes using 100 nm poly(p-phenylene vinylene) (PPV) Indium Tin Oxide (ITO) anodes and aluminium cathodes.

From the impedance spectroscopy data an equivalent circuit has been substracted composed of a resistance R_s in series with a parallel circuit consisting of resistance R_p and capacitor C_p. The presence of oxygen in the surrounding atmosphere mainly affects the parallel resistance R_p which in air increases with at least one order of magnitude with respect to inert atmosphere. The evolution of the forward current at a fixed DC-bias shows important changes as the oxygen contents of the surrounding atmosphere is changed, which demonstrates the potential usefulness of the given material system as gas sensor.

IV-measurements in different atmospheres lead to the observation of two types of IV-curves. In oxygen-rich atmospheres the IV-curves have the form of 'classical', smooth Shockley-diode-characteristics. In vacuum and N_2, however, the IV-curves differ considerably from the Shockley-diode-characteristics since they feature systematically anomalies in the form of negative resistance sections. Similar negative resistance sections in IV-curves are typical for a special class of anorganic diodes, the so-called Esaki- or tunnel-diodes. The observation of a tunnel-diode behaviour for organic LED's in an oxygen-free atmosphere is a very important result since up to now the electrical behaviour of these devices has mainly be described in terms of Schottky-emission, Poole-Frenkel mechanism and Fowler-Nordheim-tunneling.

M-I/P29

COMPLEX OPTICAL LIMITING DEVICES BASED ON THE Z-SCAN TECHNIQUE, P.O. Arntzen(1), A. Eriksson(2), M. Lindgreen(2), S. Svensson(1), (1)Defence Research Establishment, Department of Sensor Technology, P.O.Box 1165, 581 11 Linköping, Sweden, (2)Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden

The z-scan technique, which is a method to characterise the non-linear refractive index and absorption coefficient of a sample, has been developed to allow for non-Gaussian laser beams. The new method is based on a mode expansion of the electric field of the laser beam into Gaussian-Laguerre modes. The electric field at the exit plane of a sample is expanded as a sum of Gaussian-Laguerre modes. From the final mode expansion the intensity distribution at the detector plane can be calculated. With this formalism it is possible to use an arbitrary non-Gaussian beam when fitting the experimental z-scan data. We present z-scan simulations and measurements of a variety of complex optical limiting devices, such as stacks of samples with different material parameters, and thick samples with a variation of material parameters along the z-axis. The efficiency of the limiting device can be optimised by simulations employing the new method.

M-I/P30

SYNTHESIS, STRUCTURE AND OPTICAL PROPERTIES OF LOW-DEFECT POLYACETYLENE, V.M. Kobryanskii(1), D.Yu. Paraschuk(2) , E.M. Nechvolodova(1), A.N. Shegolichin(1), S.A. Arnautov(1), (1)Institute of Chemical Physics RAS, Kosygin st. 4, Moscow 117977, Russia, (2)Physics Department, Moscow State University, Moscow, 119899, Russia

The acetylene polymerization in sutурated polymer solutions and the influence of the synthesis conditions on the final product properties was studied. A new class of acetylene polymerization catalysts - binuclear clusters of Re - was discovered. Such catalysts give possibility to prepare «soluble» polyacetylene compositions with extremely high stability of their optical properties. High-quality films and coatings on various substrates were obtained from solutions.

The results of thermochromism, electroabsorption, Raman scattering and photoinduce spectroscopy studies of «soluble» polyacetylene films and solutions show that the properties of the trans- and cis- isomers differ dramatically: the trans- isomer reveals considerably higher Raman scattering activity, electroabsorption, thermochromism, and sensitivity of vibrational modes to temperature. Besides, the values of the coefficients calculated from the data obtained, as a rule, exceeded the corresponding values for typical semiconductors (Si, Ge, GaAs). The measured values of the cubic non-linear optical susceptibility were up to 10^{-8} esu.

M-I/P31

PREPARATION, STRUCTURE AND OPTICAL PROPERTIES OF HIGH-ORIENTED VACUUM-DEPOSITED POLY-PARA-PHENYLENE FILMS, V.M. Kobryanskii, S.L. Kotova, N.V. Zhidkova, Institute of Chemical Physics RAS, Kosygin st. 4, Moscow 117977, Russia

Investigations of structure and optical properties of vacuum-deposited poly-para-phenylene (PPP) films showed that the selection of proper evaporation conditions and initial PPP powder molecular-weight could provide a high oriented films with high efficiency of luminescence and high optical anizotropy.

It was demonstrated that in IR-spectra of PPP films prepared with high-molecular-weight PPP powder an extremely strong band at 1375 cm^{-1} is observed that is not typical for the currently familiar PPP modifications. Based on the IR spectral data, the model of formation of PPP chain with quinoid fragments in the ground electronic state is proposed. The structure of defects that inevitably spring up at the benzoid-quinoid transition is discussed. High intensity of the band a 1375 cm^{-1} is associated with changing the order of the «defect» C-C bond between adjacent quinoid and benzoid units.

M-I/P32

POLYMER LIGHT-EMITTING ELECTROCHEMICAL CELLS FROM OLIGO(ETHYLENE OXIDE) SUBSTITUTED POLYTHIOPHENES, T. Johansson(1), W. Mammo(2), M. Andersson(2), and O. Inganäs(1), (1)Laboratory of Applied Physics, Linköping University, 581 83 Linköping, Sweden, (2)Organic Chemistry, Chalmers University of Technology, 412 96 Göteborg, Sweden

Substituted polythiophenes can be used as the emissive polymer in light-emitting electrochemical cells. The active layer in this kind of devices must be a material with both ionic and electronic conductivity. Polythiophenes with oligo(ethylene oxide) side chains provide both these properties and make processing easier. These substituted polythiophenes mixed with a salt ($LiCF_3SO_3$) is layered between two ITO coated glass slides. The turn on voltage for light emission in the red-orange range is less than 2 V.

M-I/P33

CONDUCTING LANGMUIR-BLODGETT FILMS BASED ON TTF DERIVATIVES WITHOUT LONG ALKYL CHAIN, H. Ohnuki, T. Noda, and M. Izumi, Tokyo University of Mercantile Marine, Koto-ku, Tokyo 135, Japan, T. Imakubo, Dept. of Chem., Graduate School of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan, R. Kato, ISSP, The University of Tokyo, Minato-ku, Tokyo 106, Japan

We report the physical properties of the conducting LB films that retains metallic conductivity down to 14 K. The mixed LB films of BEDO-TTF and behenic acid shows a metallic conducting property without secondary treatment, and the maximum conductivity reached 40 S/cm at room temperature. The key to achieve the higher conductivity with the simple donor molecule and behenic acid can be attributed the formation of a bilayer film on the water surface: upper layer of the bilayer film is made of behenic acid governing the lateral packing of the film and lower one is made of donor molecule. The Y-type films fabricated from the bilayer are expected to have two structural advantages for electrical conducting LB films. 1) The donor molecules forms a 2-D network of closer contact between the molecules, and the 2-D states for conducting electron arises. 2) The insulating domains made of behenic acid is difficult to appear, and the uniform layered structure can be constructed. We report our strategy followed by the above study preparing a highly conducting LB films with TTF derivatives.

M-I/P34

INFRARED SPECTROSCOPIC CHARACTERIZATION OF THE ORIENTATION AND ORDER OF THIN OLIGOTHIOPHENE FILMS, M. Kramer and V. Hoffmann, Institute of Physical and Theoretical Chemistry, Auf der Morgenstelle 8, 72076 Tübingen, Germany

Thin layers (12 - 100nm) of oligothiophenes (4T, 5T, 6T) were prepared by Knudsen evaporation on Si/SiO_2 and ZnSe. Variation of preparation conditions (evap.-rate, substrate temp.) gives different layer structures.

By FTIR-spectroscopy (transmission, ATR, DRIFT) information about molecular orientation and the order of these films can be obtained.

Polarized spectra of uniaxially oriented layers of thiophenes allow the calculation of the tilt angle α of the molecules relative to the surface normal[1] (5T: $\alpha = 29°$).

The γ-CH-vibration of 5T shows a factorgroup splitting (fgs) if sublimated on a non-heated substrate with high evaporation rate (≈10 Å/s) in comparison with CS_2-solution, indicating a liquid crystal (LC) smectic phase with 2 molecules/cell. The intensity ratio gives a hering bone angel τ of (69 ± 5)°. Further fgs in 4 components (4 molecules/cell) is measured for a layer prepared on a heated substrate (105°C). The spectrum of 6T layers shows the doublets of 2 different LC phases (smectic and nematic). After annealing only the higher ordered smectic phase remains.

1a H. Egelhaaf, P. Bäuerle, K. Rauer, V. Hoffmann, D. Oelkrug. J. Mol. Struct., 293 (1993) 249

1b P. Lang, R. Hajlaoui, F. Garnier, B. Desbat, T. Buffeteau, G. Horowitz, A. Yassar. J. Phys. Chem., 99 (1995) 5492

M-I/P35 THE INTERFACE STRUCTURE OF POLYIMIDE GUIDES ETCHED BY ION IRRADIATION, J.P. Moliton, B. Mazière, C. Devilder, T. Trigaud, UMOP, Université de Limoges, 123 avenue Albert Thomas, 87060 Limoges Cedex, France

Optical waveguides are here etched by means of ion irradiation in the energy range [30-500] keV. As the quality of an optical waveguide is given by its optical loss, depending on the structure of the interface where the refraction occurs, we are here concerned with the characterization of the layer resulting from the ion bombardment.

In a first step, the damaging process of polyimide (PMDA-ODA), when exposed to ions is described by means of VBDOS (Valence Band Density Of States). The etched depth is evaluated as a function of the ion fluence. The optimal conditions for etching are then deduced.

Secondly, the process of etching is exposed. The structure of the interface layer is qualitatively deduced. Characterizations by different methods : SIMS, XPS, electrical conductivity, quantitatively define the layer.

M-I/P36 STUDY OF RADIATION DEFECTS ON THE BASIS OF VARIATION OF SPECTRA OF CHANNELLED ELECTRONS AND ACCOMPANYING RADIATION, E.K. Balafanov, K.K. Istekov, V.A. Kovtunetz, L.G. Kolodin, A.I. Kupchishin, A.S. Mirzoyan, N.A. Kupchishina, Almaty State University, Almaty 480100, Kazakhstan

Electrons,when passed through crystal, generated Kumachov and braking radiation, effect of electron channelling was observed.

The paper covers the result of the set of experiments connected with control, formation and transport of electron beam, automation of researches, diagnostics of radiation defects in crystals using the data on charge in spectra of Kumachov and braking radiation. General expressions for differential and integral cross-sections of generation of Kumachov radiation fluxes, of X-ray radiation at different depths crystal were obtained. Technique of diagnostics of radiation and other defects on the basis of change in various spectra and parameters was developed. Algorithm was made and calculations were performed using IBM PC/486 DX. Model calculation and experiment were carried out for Si crystals.

M-I/P37 RESONANT ENERGY ABSORPTION BY SOME POLYMERS, A.A. Kupchishin, A.I. Kupchishin, N.V. Slyunyaeva, B.G. Tepikin, K.B. Tlebaev, Almaty State University, Almaty, 480100, Kazakhstan

It is known that curves of temperature dependence of heat capasity C (T) and thermal cornductivity Λ (T) of some linear polymers exhibit peaks resulting from structure changes.

We have studied dependence C (T) and Λ (T) for teflon with the range from 80 to 330 K using automated setup TAU-5. Two peaks have been found in the temperature range 290 - 310 K, magnitude of the first peak was ~ 50% and that of the second peak was ~ 10%. Autors attribute, the first peak to resonant absorption by polymeric chains of initial material and the second peak to oscillations of polymeric chains, after phase transition. When delivered energy is comparable with energy of oscillations of polymeric chains resonance occurs. Effect of electron irradiation (energy 6 MeV) on magnitude of peaks which shifted towards the left with increase of irradiation dose and disappeared at doses at all was studied.

M-I/P38 STUDY OF MECHANICAL PROPERTIES OF ELECTRON IRRADIATED POLYMERS, B.A. Kozhamkulov, A.I. Kupchishin, Almaty State University, Almaty 480100, Kazakhstan

The paper presents the results of the study of effect of irradiation on ruggeaness of thin poly terephthalyl polyimide, polytetrafluoroethellene and pheneje films with 2 Mev electrons. Structural changes in polymers due to irradiation have been investigated employing infrared spectroscopy. Elementary analysis has been performed. Molecular masses of polymers have been found. The study of doze dependence of characteristics of polymer film ruggedness has shown that from 4 kinds of films polytetrafluoroethelene film had minimal stability towards irradiation. Maximal stability towards irradiation was shown by polyimide film. Hence polymers having in their structure space cyclic groups (benzene ring, imide group) are the most stable toward irradiation ones. The results of infrared spectroscopy and cheruical analysis have been compared with the data of measurement of ruggedness of polymer films. Correlation between changes in structure and polymer ruggedness after irradiation has been found. At has been shown that decrease of ruggedness after irradiation was due to the process of destruction followed by decrease of molecular mass and increase the oxygen content.

M-I/P39 SEM-EPMA AND PHOTOELECTROCHEMICAL CHARACTERIZATION OF ELECTRODEPOSITED CIS ($CuInSe_2$) THIN FILMS FOR ENERGY CONVERSION APPLICATIONS, R. Perez(1), M.E. Calixto(2), S.A. Gamboa(2), P.J. Sebastian(2) and A.M. Fernandez(2), (1)Centro de Investigacion en Energia-UNAM, 62580 Temixco, Mor., Mexico, (2)Instituto Nacional de Investigaciones Nucleares, Km. 36.5, Carr. México-Toluca, 52045 Salazar, Edo. de Mexico, Mexico

The structural, morphological, compositional and photoelectrochemical properties of electrodeposited and selenized CIS thin films were characterized using various techniques. As-deposited as well as selenized films exhibited a compact or a granular morphology depending on the composition. The films stoichiometry was improved after selenization at 550 C in a tubular furnace. The film conductivity type, carrier concentration and flat-band potential were determined from the photoelectrochemical studies. The films are formed with a mixed composition of the binary as well as the ternary phases. From the results of these studies, a model is suggested for the superficial as well as the bulk conductivity types of the film.

M-I/P40 OPTICAL PROPERTIES OF p-HEXAPHENYL POLYCRYSTALLINE FILMS, A. Mura and G. Bongiovanni, Dipartimento di Scienze Fisiche, Cagliari, Italy, G. Lanzani and A. Piaggi, Istituto di Matematica e Fisica, Sassari, Italy, W. Graupner, G. Leising, and F. Meghdadi, Institut für Festkörperphysik, Graz, Austria

p-Hexaphenyl (PHP) is a very interesting material which has been successfully used as highly efficient blue-light emitting layer in electroluminescent devices. We investigate the emission properties of polycrystalline PHP films by combining time-resolved photoluminescence and photoinduced absorption measurements with site-selective spectroscopy. Absorption and site-selective photoluminescence results give evidence of important short range disorder, as confirmed by the very fast - within 1 ps - polarization-memory loss of the photoexcitations. We observe long photoluminescence lifetime (400 ps at 300 K and 1 ns at 10 K) and an almost exponential decay, which indicate that emission has molecular character. Photoinduced absorption, gain and photoluminescence have the same temporal dynamics showing that they are originated by the same emitting species. No evidence of intermolecular excited states has been observed. Disorder does not favour the H-aggregate formation, and this agrees with the high photoluminescence quantum yield of PHP.

M-I/P41 INVESTIGATIONS OF NEW π-CONJUGATED MATERIALS USED AS CHARGE TRANSPORT LAYERS IN ORGANIC LIGHT EMITTING DIODES (OLED's), B. Winkler, R. Muellner, S. Tasch, F. Meghdadi, W. Fischer, G. Leising, and F. Stelzer, SFB Elektroaktive Stoffe, Institut für Chemische Technologie Organischer Stoffe, TU-Graz, Stremayrgasse 16, 8010 Graz, Austria

To obtain OLED's of high quality (low driving voltage, high quantum efficiency, high brightness and stability) transport layers between the emissive conjugated polymer and electrodes are used.

Based on our former studies, we show a systematic investigation of the dependency of the performance of multi-layer OLED's on transport layers of conjugated oligomers of different types, which also contain substituents with different electron affinities.

Therefore we have prepared several substituted oligoazomethines by condensation reactions and fluorinated oligo(p-phenylene)s and oligo(p-arylene-vinylene)s by Pd(0)- or Ni(0)-catalysed coupling reactions. The first substances are used for hole transport layers (HTL), the second ones for electron transport layers (ETL). Very efficient multi-layer devices (ITO/HTL/PHP/ETL/Al) have been prepared by chemical vapour deposition of these oligomers and of p-hexaphenylene (PHP) as light emitting material.

M-I/P42 TOWARDS EPITAXIAL GROWTH OF THIN ORGANIC FILMS : COMMENSURATE PHASES OF QUATERTHIOPHENE ON Ag(111), W. Gebauer, M. Sokolowski, and E. Umbach, Experimentelle Physik II, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

During the past five years a large number of investigations concerning organic films on inorganic substrates have been undertaken. Although there is clear evidence that the substrate has a strong influence on the growth mechanism and hence the structural quality of organic films [1], only very few efforts have been made to establish preparation routines for true epitaxial growth of organic materials on inorganic crystalline substrates, which may be compared to inorganic MBE processes.

Here we present an extensive UHV study on the structure of vapour- deposited quaterthiophene films with film thicknesses in the range up to 100 Å. Since usual X-ray cristallography cannot be used for ultrathin organic films in laboratory experiments due to the small X-ray scattering cross-section, we used low energy electron diffraction (LEED), which is a well established technique for the analysis of surfaces.

Our experiments reveal four different highly commensurate structural phases of quaterthiophene layers on Ag(111) single crystal substrates as a function of substrate temperature and film thickness. As shown earlier [2] these epitaxial films lead to highly resolved optical spectra and allow new insight into the optical properties of oligothiophene films. By an additional analysis of the LEED spot profiles, our experiments reveal a very high level of structural order and new insight into the geometrical structures. The fundamental processes which determine the molecular ordering in the film will be discussed as a general approach towards organic molecular beam epitaxy.

[1] W. Gebauer et al., Synth. Met.; [2] W. Gebauer et al., Chem. Phys. Lett., in press

M-I/P43 ELECTRONIC STRUCTURE AND ELECTRON-MOLECULAR VIBRATIONAL COUPLING IN BEDT-FFT k-PHASE ORGANIC CONDUCTORS : OPTICAL STUDY, O.O. Drozdova, V.N. Semkin, R.M. Vlasova and R.N. Lyubovskaya, A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

Polarized reflectance spectra of BEDT-TTF based conductors k-$(ET)_2[Hg(SCN)Cl_2]$ and $(ET)_2[Hg(SCN)_2Br]$ are measured over the range 700-40000 cm^{-1}.

The quantitative analysis of optical conductivity obtained after Kramers-Kronig transformation, is performed in the framework of the «phase phonons» theory. The accurate parameters of the electronic structure and electron-molecular vibrational (EMV) coupling are determined. It is concluded that conductors have apparently narrower allowed electron bands, stronger electron correlations and smaller λ value as compared to related superconductors. The deuteration effect on the EMV coupling is found.

This work is supported by Russian Scientific-Technical Programme on Superconductivity, Projects No 94055 and No 93030.

M-I/P44 EXCITON DEPHASING TIMES IN CuBr QUANTUM DOTS, J. Moniatte, P. Gilliot, IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France, J. Valenta, Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Praha 2, Czech Republic, A.I. Ekimov, A.F. Ioffe Physico-Technical Institute, Polytechnicheskaya 26, 194021 St. Petersburg, Russia

We perform degenerate four-wave mixing on CuBr quantum dot samples on a femtosecond time scale. Due to inhomogeneous broadening, we observe a so called photon-echo signal. The signal dynamics measured at different pump intensities provides information on the dephasing time. We study this dephasing time at 5K in different samples, containing quantum dots of different mean size.

We determine also the homogeneous absorption linewidth by spectral hole burning measurements, in the same samples, at 5K, using a nanosecond dye laser excitation. Being an alternative indirect method to determine dephasing times, we can compare both our results. We then conclude on the difficulties to measure dephasing times in confined systems by the latter method.

M-I/P45 AN EFFICIENT ELECTRON-TRANSPORTING POLYMER FOR HIGH BRIGHTNESS POLYMER LIGHT-EMITTING DIODES, S. Dailey, M. Halim, E. Rebourt, I.D.W. Samuel and A.P. Monkman, Department of Physics, University of Durham, South Road, Durham, DH1 3LE , UK

The discovery that semiconducting polymers can be used as the active layer in light-emitting diodes (LEDs) has stimulated great interest in the physics of these materials and offers enormous potential for making highly visible flat large-area colour displays. The efficient operation of LEDs requires balanced injection and transport of electrons and holes, and this has stimulated a search for suitable electron-transporting materials.

We report the use of polypyridine as an efficient electron-transporting polymer. We have achieved a substantial advance in the performance of poly(p-phenylene vinylene) (PPV) LEDs by incorporating polypyridine as an electron-transporting layer and optimising layer thickness to balance transport of electrons and holes. These bilayer devices have ITO and aluminium contacts, and we have compared their efficiency with single-layer PPV LEDs with ITO and aluminium or calcium contacts. We find that the efficiency of the bilayer devices is more than two orders of magnitude greater than single layer PPV LEDs with the same contacts, and an order of magnitude greater than single layer PPV LEDs with calcium as the electron-injecting contact. The emission spectrum is similar to that of PPV, and peaks at 550 nm. An exciting implication of this work is that the use of polypyridine as an electron-transporting layer should improve the performance of polymer LEDs made from a wide range of light-emitting polymers.

M-I/P46 NONLINEAR OPTICAL PROPERTIES OF THE PHOTOELASTIC ORGANIC MEDIA, O.Y. Semchuk, L.G. Grechko and V.M. Ogenko, Institute of Surface Chemistry National Academy of Sciences Ukraine, 31 Lauka Avenue, Kyiv 252022, Ukraine

The present study is concerned with non-coherent light scattering due to interaction of an incident electromagnetic wave with fluctuations of Rayleigh surface waves at the isotropic photoelastic organic medium boundary. Two mechanisms of the interaction of an electromagnetic wave with Rayleigh surface waves are considered:

a). Interaction of the electromagnetic waves and the surface acoustic wave by means of the inhomogeneity of the dielectric constant under boundary conditions.

b). Interaction of an electromagnetic wave and surface one by means of the photoelast mechanism.

Values of the light reflection coefficient calculated in this work and peak position on Brillouin scattering are good agreement with experimental date.

M-I/P47 THE EFFECT OF METAL FILMS ON THE PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE OF CONJUGATED POLYMERS, H. Becker, S.E. Burns and R.H. Friend, Cavendish Laboratory, Madingley Rd, Cambridge CB3 0HE, UK

We report the modification of photoluminescence (PL) and electroluminescence (EL) from conjugated polymers due to the proximity of metal films. The presence of a metal film alters the radiative decay rate of an emitter via interference effects and also opens up an efficient non-radiative decay channel via energy transfer to the metal film. We show that these effects lead to substantial changes in the PL and EL quantum efficiencies and the emission spectra of the polymers studied here (cyano derivatives of poly(p-phenylenevinylene), PPV) as a function of the distance of the emitting dipoles from the metal film. Using the spectral dependence of the emission we have been able to investigate the effect of interference on the radiative rate as a function of the wavelength and the distance between the emitter and the mirror.

We compare our results with simulations of the radiative power of an oscillating dipole in a similar system. From our results we can determine the orientation of the dipoles in the polymer film, the branching ratio that gives the fraction of absorbed photons leading to singlet excitons and the extent of the recombination zone in light-emitting diodes (LEDs). We propose design rules for LEDs and photovoltaic cells that optimise the effects of the metal film. By making optimum use of above effects we have substantially increased the EL quantum efficiencies of PPV/cyano-PPV double-layer LEDs.

M-I/P48 INVESTIGATION OF THE TWISTED EXCITED STATE BEHAVIOUR IN A META-LINKED PHENYLATED PPV-DERIVATIVE, A. Koch, R.H. Friend, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK, and N. Haylett, R. Daik, W.J. Feast, Chemistry Department, South Road, Durham, DH1 3LE, UK

The polymer poly-(1,3-phenylene diphenylvinylene) (m-PPV-DP) is distinguished from PPV by the diphenyl-substitution and the meta-linkage of the in-chain phenylene. Due to the phenylation m-PPV-DP exhibits a strong steric hindrance and hence a very disordered structure. The meta-link effectively breaks the π-conjugation along the polymer. We report a comparative study of m-PPV-DP and the molecule Tetraphenylethylene (TPE), showing that the twisted excited state geometry of TPE explains most of those photophysical properties of m-PPV-DP that differ significantly from PPV.

M-I/P49 INCREASED PHOTOSTABILITY OF PPV-DERIVATIVES BY DIPHENYL-SUBSTITUTION, A. Koch, N.T. Harrison, R.H. Friend, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK, and N. Haylett, R. Daik, W.J. Feast, Chemistry Department, University of Durham, South Road, Durham, DH1 3LE, UK

We report that the UV-photodegradation of the PPV-derivatives PDPV (poly-(4,4'-diphenylene diphenylvinylene)) and m-PPV-DP (poly-(1,3-phenylene diphenylvinylene)) is slowed down in comparison to PPV by the removal of the vinylene bond aliphatic hydrogens by a diphenyl-substitution. The photoluminescence decay and the photoluminescence excitation spectra were measured as a function of UV-irradiation time. Both results are modelled on the basis of a small set of assumptions about the degradation process. FTIR-studies reveal that the degradation process is oxidative and is rate limited with respect to the oxidation.

M-I/P50 BLUE LIGHT EXCIMER LUMINESCENCE FROM POLY(ETHYLENE NAPHTALATE) : PEN, J. Davenas, G. Seytre, Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, UMR 5627 CNRS, Université Claude Bernard Lyon 1, 43 Bd du 11 Novembre, 69622 Villeurbanne, France

Poly (ethylene 2, 6 naphtalate): PEN, appears as an alternative polymer for electrical engineering due to its high stability, in particular for use in capacitors. The interest for this polymer led to extended studies of its dielectric properties in relation with the film morphologies. Fluorescence attributed to an excimer mechanism of the ß phase has been recently reported. We have performed a study of the photoluminescence and electroluminescence of PEN films. Blue electroluminescence with a maximum at 430 nm is induced when applying an electric field of the order of 1 MV/ cm. This luminescence is very sensitive to the molecular order and is interpreted by an excimer resonance of the aromatic chromophores belonging to adjacent polymer chains. The decrease of the film thicknesses and progress in the control of the morphologies will allow in a next future the formation of optimized electroluminescent diodes.

M-I/P51 ANISOTROPY OF THE PHOTOINDUCED TRANSLATION DIFFUSION OF AZOBENZENE-DYES, P. Lefin, C. Fiorini, and J.M. Nunzi, LETI (CEA-Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France

Large-amplitude holographic surface relief gratings are optically induced by resonant visible exposure in azobenzene dye-containing polymers. We propose a simple diffusion model accounting for the essential features of surface relief grating formation. It is based on the anisotropic diffusion of azobenzene-dyes in polymer matrices further to their photoinduced trans-cis isomerization cycles. The essential feature of the model is that dye-molecules undergo a 1D-random-walk along their excitation direction. The model accounts for intensity, grating-pitch and polarization dependencies. Understanding of this process appears essential for holography applications. It opens new perspectives associated with optically controlled anisotropic diffusion.

M-I/P52 MULTIPHOTON ABSORPTION IN ORGANIC DYE SOLUTIONS, S. Delysse, V. Dumarcher, C. Fiorini and J.M. Nunzi, LETI (CEA-Technologies Avancées), DEIN-SPE, Groupe Composants Organiques, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France

We report on the determination of the two-photon absorption spectra of non-centrosymmetric dyes. We compare two complementary experimental techniques : Kerr-ellipsometry and fluorescence up-conversion. The two-photon spectra are interpreted in terms of a tree-level system accounting for all virtual paths. Above a critical dye concentration, two-photon absorption is dramatically increased. We present an original model accounting for such enhanced absorption in concentrated dye solutions. The related nonlinear absorption which is induced in the transparency region of the dye solutions may reach levels as high as using excited absorptions. This open new directions for the realization of blue up-conversion laser sources.

M-I/P53 SPATIAL CORRELATIONS BETWEEN CHROMOPHORES IN THIN FILMS BY FEMTOSECOND HYPER-RAYLEIGH SCATTERING, G. Olbrechts, K. Clays, and A. Persoons, Center for Research in Molecular Electronics and Photonics, Department of Chemistry, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

Femtosecond hyper-Rayleigh scattering has been used to probe the spatial orientational fluctuations between nonlinear optical chromophores as dopants in spincoated polymer films. The fluctuation in the second-order incoherently scattered light intensity upon translating the sample is indicative of the degree of spatial correlation between the chromophores. The decay of the autocorrelation function of this fluctuating signal is characterized by a spatial correlation length. Electric-field poling of chromophores is shown to increase this length. The temporal characteristics of this correlation length have been studied and compared with relaxation times, obtained with coherent second-harmonic generation. This correlation length decays much faster than the second-harmonic intensity. Possible implications will be addressed.

M-I/P54 SPACE CHARGE ANALYSIS IN DOPED ZINC PHTHALOCYANINE THIN FILMS, B. Remaki(1), G. Guillaud(1), D. Mayes (2), (1)Laboratoire d'Electronique des Solides (L.E.S,.EA 621), BAT. 201, Université Claude Bernard - Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France. (2)School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

We present an improved method for the determination of the space charge density in organic semiconductors used as active layers in Schottky barriers. These measurements provide a powerfull tool for the interpretation of basic properties such as the rectifying effect, doping process and carrier trapping mechanisms of films together with a way to assess the potential for sensor applications.

Metal/molecular semiconductor Schottky junctions were prepared on zinc phthalocyanine layers doped by a controlled exposure to the ambient air. The organic material is deposited on aluminium or heavily doped silicon substrates, in order to make a Schottky barrier (film thickness 200-300 nm). An ohmic contact is obtained by a gold deposition on the strongly doped side of the molecular material.

We have investigated the current-voltage and capacitance-voltage characteristics. The results are interpreted in terms of a space charge region at the interface with the substrate, followed by an extended semi-insulating layer.The contribution of these two regions to the total impedance is analysed in well improved conditions of temperature and frequency measurements combined with an unsteady state regime.

In the case of a heavily doped silicon substrate, the Schottky effect and the stability are enhanced in comparison with junctions on aluminium . A 10^{17}-10^{18} cm^{-3} space charge density decreasing towards the interface is then revealed in the 3 to 10 nm prospected zone . The barrier height is 0.5 eV with a strong serial bulk resistance corresponding to a conductivity of 10^{-9} - 10^{-8} S/cm. These results are successfully interpreted and related to the sample preparation process.

M-I/P55 MULTILAYER LIGHT EMITTING DIODES USING A PPV BASED COPOLYMER, L.C.Chen, T.P. Nguyen, Institut des Matériaux de Nantes, 2 rue de la Houssinière, 44332 Nantes Cedex 3, France, X. Wang, Institute of Material Physics, Tianjin Institute of Technology Tianjin 300191, China, and Z. Huang, Department of Chemistry, North-East Normal University, Changchun 130022, China

We report the investigations on new multilayer light emitting diodes using poly(2,5 bis methoxy)-poly(p-phenylene vinylene) copolymer as the emitting layer. In order to improve the polar charge injections, poly(phenylquinoxaline) and poly(p- phenylene vinylene) layers were chosen as electron and hole transport layers in bilayer sandwiched configuration. The electrical behavior of the diodes, determined by the current- voltage characteristics was improved with the use of the charge transport layers and showed low threshhold voltages. Bright yellow emission light could be observed from these diodes with the forward current flow. Electroluminescent intensity of the multilayer diodes was greatly enhanced as compared to that obtained in single layer ones. The emission peak in the multilayer diodes was shifted with regard to the copolymer one and was attributed to the recombination process occurring in different regions of the structure.

M-I/P56 LIGHT-EMITTING DIODES WITH NAPHTALIMIDE SIDE-CHAIN POLYMERS : BASIC PROPERTIES AND ROLE OF POLYMER THICKNESS IN 2-LAYER DEVICES, F.Cacialli, R.H. Friend, Cavendish Laboratory, Cambridge University, Madingley Road, Cambridge CB3 OHE, UK, C.M. Bouche, P. Le Barny, H. Facoetti, F. Soyer, M. Vergnolle, and P. Robin, Laboratoire Central de Recherches-Thomson-CSF, 91404 Orsay, France

We report the fabrication of efficient green light-emitting diodes using a side-chain random copolymer based on a high-electron affinity (EA) naphtalimide moiety (PNI). The chromophore is attached to a polymethacrylate backbone through a spacer, and emits in the green with high efficiency (30% photoluminescence quantum yield). In single-layer light-emitting diodes (LEDs), we find that the electroluminescence (EL) efficiency is not limited by Al cathodes as for poly(p-phenylene-vinylene), PPV, and we attribute this to the increased EA. We report maximum internal efficiencies of about 1.7% for Ca and 0.9% for Al in double-layer devices where PPV serves as both hole-injector and emitter. Compared to some oxadiazole based electron injection/transport layer, PNI gives higher efficiencies at high currents, and longer lifetimes (time to reach 50% of the initial emission). Tuning of emission in the red is possible by dye-doping the PNI and causing the emission to happen in this layer. We discuss the properties of the different device configurations with a view to the electronic structure of the materials and in particular to the influence of the thickness of the individual layers on efficiency and driving conditions.

M-I/P57 CONJUGATED MOLECULAR RODS SELF-ASSEMBLED INTO NEEDLES WITH MOLECULAR CROSS-SECTIONS, P Samori and J.P. Rabe, Department of Physics, Humboldt University Berlin, Invalidenstr. 110, 10115 Berlin, V. Francke and K. Müllen, MPI for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Conditions were found for self-assembling poly(2,5- dihexyl-phenylene-ethynylene) (PPE) into needles on mica. The needle shapes were determined by Tapping Mode-Scanning Force Microscopy (SFM), taking into account the SFM-tip shape. A constant needle thickness as well as a distribution of widths was found, indicating that the width corresponds to the length of a single molecule. The molecular weight distribution is determined from the analysis of needle widths, and compared to gel permeation chromatography (GPC) data, as well as to theoretical predictions for a polycondensation reaction, indicating that the SFM based method is valid and has its advantages. Interestingly, also α,ω thio–PPE can be self-assembled into needles, which are capable of bridging gold nanoelectrodes. This opens the possibility of fabricating molecular wires between nanoelectrodes, where the length of the wire is that of a single extended conjugated molecule.

Wednesday June 18, 1997
Mercredi 18 juin 1997

Afternoon
Après-midi

Poster Session II
18:35-20:00

M-II/P1 INTERFERENCE PHENOMENA IN POLYMER LIGHT-EMITTING DIODES, F. Cacialli, S.E. Burns, Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, UK

While the interference of light in optical resonators and the application to the control of spontaneous emission have been the focus of many theoretical and experimental studies in both inorganic and organic luminescent devices, less interest has been devoted to the effects generated by the presence of a single reflecting electrode in organic and polymeric light-emitting diodes. Nonetheless these effects can change drastically the properties of the emission, both in terms of the spectral distribution and of the intensity. The spectral changes can also be used as diagnostic tools for evaluating specific properties of the radiative processes, such as the extent of the recombination zone in electro-luminescent devices. In this paper we present studies of interference effects in single-layer diodes with indium-tin oxide (ITO) on glass and Al or Ca electrodes, where we used poly(p-phenylene vinylene) (PPV) as the luminescent polymers. We find that optical (PL) and electrical (EL) excitation of the radiative species produce different results which we can analyse in terms of interference phenomena.

M-II/P2 GROWTH AND CHARACTERISATION OF CONJUGATED OLIGOMERS GROWN BY ORGANIC MOLECULAR BEAM EPITAXY, J.J.W.M. Rosink, M.A. Blauw, L.J. Geerligs, E. van der Drift and S. Radelaar, DIMES, PO Box 5046, 2600 GA Delft, The Netherlands

The possible application of organic polymers or oligomers in electronics and optoelectronics has led to a vast amount of research on carrier transport in conjugated molecules. The study of conductance of molecular chains is complicated by the random distribution of molecular orientations and chain lengths. In this work we aim for short molecules grown segment by segment, yielding an ordered array of parallel and π-conjugated oligomers. When sandwiched between two electrodes, such an arrangement of molecules will enable the study of the quasi 1-dimensional electrical transport in a most controlled fashion.

Starting point is a Au(111)/mica substrate on which a monolayer of 4-aminothiophenol is grown by self assembly. Next, the segment by segment growth follows by alternate evaporation of 1,4-benzenedicarboxaldehyde and 1,4-benzenediamine in vacuum, employing imine-formation by condensation polymerisation. The growth is monitored by in-situ ellipsometry and a quartz crystal film thickness monitor. For chemical characterisation X-ray photoelectron spectroscopy (XPS) is used.

In this contribution we discuss the growth of the first monolayers. Chemical composition and arrangement was evidenced by XPS. Scanning tunnelling spectroscopy on 4-ATP films showed a staircase-like pattern in I-V curves. This could be attributed to resonant tunnelling Coulomb charging effects.

M-II/P3 ELECTROABSORPTION STUDIES OF PPV AND MEH-PPV, S.J. Martin, H. Mellor, D.D.C. Bradley, Centre for Molecular Materials and Department of Physics, University of Sheffield, Hounsfield Road, Sheffield S3 7RH, UK, and P.L. Burn, Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, UK

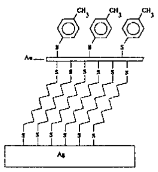
We report the results of an electroabsorption (EA) spectroscopy study of the electronic structure of the conjugated polymer PPV and its soluble derivative MEH-PPV. We find that the EA response of both polymers is dominated by a Stark shift of the $1B_u$ exciton. Comparison of the EA spectrum with the Third Harmonic Generation (THG) and two-photon fluorescence spectra for PPV allows us to address the question of the exciton binding energy in these materials. We estimate the binding energy to be 0.8(±0.15)eV for PPV and 0.7(±0.15)eV for MEH-PPV. We discuss the difference between the optically determined binding energy and that estimated via indirect electrical methods. We also present data for the EA response of higher lying transitions and discuss these in terms of current theoretical models.

M-II/P4 CHARACTERIZATION OF 6PV PHENYLENE VINYLENE OLIGOMER THIN FILMS, T.P. Nguyen, C. Stéphan, P. Le Rendu, Institut des Matériaux de Nantes, 2 rue de la Houssinière, 44072 Nantes Cedex 3, France, and V.H. Tran, LMOPS, CNRS, 69390 Vernaison Cedex, France

Investigations of phenylene vinylene oligomer thin films with 7 phenyl, 6 vinyl units (6PV) have been carried out for the first time by optical and electrical measurements. Optical characterizations including infrared, Raman and UVIS spectroscopies were performed and the obtained results were discussed by comparison with those obtained on poly(p-phenylene vinylene) (PPV). Electrical characterizations of oligomer based diodes were studied by measuring the current-voltage-temperature characteristics and the thermally stimulated currents. For the conduction mechanisms in these devices, two distinct temperature ranges were observed: at high temperatures (>300 K), a field assisted mechanism occurs involving locaized states in the oligomer bulk while in Low temperature range, hopping conduction is probable. Thermally stimulated currents showed asymmetric characteristics which may be related to trapped charges in the oligomer-metal interface.

M-II/P5 CHEMICAL VAPOR DEPOSITION OF GOLD ON ALKANEDITHIOL SELF-ASSEMBLED MONOLAYERS, J. Käshammer(1), J. Weiss(2), C. Winter(1,2), P. Wohlfart(1), R.Fischer(2), S. Mittler-Neher(1), (1)Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany, (2)Institut für Anorganische Chemie, Universität Heidelberg, Im Neuenheimer Feld 503, 69120 Heidelberg, Germany

Due to the Chemical Vapor Deposition (CVD) technique with precursors it is possible to deposite ultra thin layers of metals onto any substrate. Here we demonstrate the deposition of gold onto thiol-functionalized self assembled organic monolayers. The thiol functionalization was chosen to preferentially bind the gold to the SAM surface and to enhance the adhesion of the gold due to chemisorption. With these kinds of ultra thin gold layers integrated optical devices can be used with a wide variety of thiol functionalizations for sensor purposes with only little losses due to the metal coating. Self assembled alkanethiol monolayers were CVD coated with trimethylphosphane gold(I)methyl as a precursor. Spontaneous Desorption Time of Flight Mass-Spectroscopy, Rutherford Back-Scattering, Atomic Absorption Spectroscopy, Surface Plasmon Spectroscopy and Contact Angle Measurements were used for the characterization of the gold layer. An increase in surface density with increasing deposition time was found for the functionalized SAM surface only. In a second step the CVD deposited gold layer was used for the self-assembly of an additional thiol layer 4-Thiokresol. The characterization have shown a successful second SAM step ontop of the deposited gold.



M-II/P6 EVALUATION OF POLYMER BASED THIRD ORDER NONLINEAR INTEGRATED OPTICS DEVICES, A. Driessen, H.J.W.M. Hoekstra, F.C. Blom, F. Horst, G.J.M. Krijnen, J.B.P. v. Schoot, P.V. Lambeck and Th.J.A. Popma, MESA Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands, and M.B. Diemeer, Akzo Nobel Research, P.O. Box 9300, 6800 SB Arnhem, The Netherlands

Nonlinear polymers are promising materials for high speed active integrated optics devices. In this paper we describe the steps needed to arrive at realistic devices. These steps include materials characterization, design and realization of the waveguiding structures and evaluation of the device performance.

In our experimental work we applied mainly Akzo Nobel DANS side-chain polymer that exhibits large second and third order coefficients. This material has been characterized by third harmonic generation, Z-scan and pump-probe measurements. In addition, various waveguiding structures have been used to measure the nonlinear absorption (two photon absorption, TPA) on a ps time-scale. Finally an integrated optics Mach Zehnder interferometer has been realized and evaluated.

It is shown that the DANS side-chain polymer has many of the desired properties: the material is easily processable in high-quality optical waveguiding structures, has low linear absorption and its nonlinearity has a pure electronic origin. More materials research has to be done to arrive at materials with higher nonlinear coefficients to allow switching at moderate light intensity (< 1 W peak power) and also with a lower TPA coefficients.

M-II/P7 DIELECTRIC RELAXATION SPECTROSCOPY STUDIES IN LIQUID CRYSTALLINE IONOGENIC COPOLYMERS, D. Ionescu, T. Pop, Department of Physics, "Polytehnica" University of Bucharest, Splaiul Independentei 313, 77206 Bucharest, Romania and E.B. Barmatov, V.P. Shibaev, Department of Chemistry, Moscow State University, 119899 Moscow, Russia

Dielectric relaxation spectroscopy was used to investigate the molecular dynamics in liquid crystalline copolymers containing cyanobiphenyl mesogenic groups and acrylic acid as nonmesogenic adding.

The intramolecular H-bonding between the carboxylic groups within the polymer structure determines the backbone flexibility. Therefore, the phase behaviour of these copolymers changes with the acrylic acid concentration and influences the molecular dynamics in electric field. The dielectric loss and the dielectric permitivity were recorded for copolymers of different composition. The relaxation parameters are discussed in terms of temperature and acrylic acid concentration.

M-II/P8 MEAN-FIELD THEORY OF OPTICAL STORAGE IN LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS, T.G. Pedersen, and P.M. Johansen, Optics and Fluid Dynamics Department, Riso National Laboratory, 4000 Roskilde, Denmark

Liquid crystalline side-chain polymers are very promising materials for optical storage due to the high long-term stability (several years) and the large values of photoinduced anisotropy ($\Delta n \approx 0.1$). In this presentation a simple mean-field theory of the storage process is presented and compared to experiments for azobenzene polyesters[1]. The multi-domain structure of the polymer material is taken into account and intermolecular interactions are described using a Maier-Saupe mean-field theory. We demonstrate how the mean-field model combined with a molecular reorientation mechanism based on photoinduced trans↔cis isomerization provides an explanation for the stability as well as the intensity dependence of the photoinduced anisotropy. A detailed comparison with experiments shows an excellent agreement over the entire range of intensities.

[1] N.C.R. Holme et al., Appl. Opt. 35, 4622 (1996).

M-II/P9 COMPOSITE SYSTEMS FOR DISPLAY APPLICATIONS FROM CELLULOSE ELASTOMERS AND NEMATIC LIQUID CRYSTALS, M.H. Godinho, A.F. Martins, Dept. Ciência dos Materiais and CENIMAT, FCT/UNL, 2825 Monte da Caparica, Portugal, and J.L. Figueirinhas, CFMC-UL, Av. Prof. Gama Pinto 2, 1699 Lisboa Codex, Portugal and IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

Composite systems made from cellulose derivatives solid films impregnated by a nematic liquid crystal can be used as electro-optical devices [1, 2]. The electro-optical behaviour of such cells depends on the nature of the cellulose derivative used, the preparation conditions of the cellulosic film, and the rugosity of the films'surface [2]. In this work we study the influence of preparation techniques, number of polymer layers (1- 3 layers each 9 μm thick), thickness of the liquid crystal layer (8- 18 μm) and aging (1 week- 9 months), upon the electro-optical response of the cells. The cells used in this work were shown to exhibit high transmission coefficients (up to 82%) in the activated state and high contrast (up to 266). The cells'optical behaviour is strongly dependent on the number of films' layers.

[1] H.V. Craighead, J. Cheng, S. Hackwood, Appl. Phys. Lett., 40, 22 (1982); [2] M.H. Godinho, J.L. Figueirinhas, A.F. Martins, Liquid Crystals, 20(3), 373 (1996).

M-II/P10 PREPARATION OF THIN LEAD OXIDE FILMS USING LANGMUIR-BLODGETT TECHNIQUE, Y.N. Savin, A.V. Tolmachev, A.V. Voynov, P.V. Matejchenko, A.N. Shekhovtsov, O.N. Bezkrovnaya, Institute for Single Crystals, Lenin Ave., 60, 30001 Kharkov, Ukraine

Thin lead oxide films have been prepared from corresponding fatty acid salt on Si and quarz substrates using Langmuir-Blodgett (LB) technique. Monomolecular films of lead stearate were formed on the aqueous subphase surface using the standart LB procedure at the surface pressure p=30 mN/m and then transferred onto solid substrates. Samples so obtained were annealed in air at 473K, 573K, 773K. Using optical absorption method is shown that, during the heating, desorption of the organic component from lead stearate molecule occurs and thin layer of lead oxide is formed on the substrate. Thickness of these films was determined by elipsometry method. Morphology of lead oxides films was studed by scanning electronic microscopy method. Stoichiometric composition of the films was determined before and after heat treatment using XPS method.

M-II/P11 THE FORMATION OF Q-STATE PbS AND GaS PARTICLES IN 10,12-TRICOSADIYNOIC ACID LB FILMS, Y.N. Savin, A.V. Tolmachev, M.V. Dobrotvoskay, A.G.Fedorov, N.R Sumskaya, A.V. Koval', Institute for Single Crystals, Lenin Ave., 60, 310001, Kharkov, Ukraine

The formation and grows of Q-state plumbum and gallium sulfide in 10,1 2-Tricosadiynoic acid are investigated. The phase diagrams (π/A isotherms) of Langmuir monolayers on the surface of subphase with a different degree of dissociation of COOH-group of surfactant, different concentration and type of metal cations as well pH of subphase are studied. The Q-state semiconductor particles in LB films are obtained by exposing films to H_2S. The difference in degree of bonding of metal cations with the monolayer and the nanocrystal formation at the air-water interface depend on the concentration and type of cation as well pH of suphase is found.The phase composition and stoichiometry as well ordering of LB films are studied by X-ray photoelectron spectroscopy and X-ray small angle diffraction methods. Scanning tunnelling spectroscopy method are used to determinate the size of Q-state particles.

M-II/P12 FLUORESCENT LANGMUIR - BLODGETT FILMS, N.I. Voronkina, K.B. Vodolazhsky, V.M. Zuber, A.V. Tolmachev, Institute for Single crystals, Lenin Ave., 60, 310001, Kharkov, Ukraine

Langmuir-Blodgett technique is used for obtaining fluorescent films of organic luminophores (oxazoles, oxadiazoles, pyrazolines) in inert stabilizing matrix and in the one containing chromophore fragments. The concentration dependences of photo- and radioluminescence in LB films are investigated for the luminophore content varying from 0.5 to 100 mol. %. The revealed anisotropy of luminescence in LB films is bound up with the orientation of luminophore molecules and clusters in the monolayer plane and in the volume of the films The intensity of specific radioluminescence is by 20 times higher in comparison with that of polymer fluorescent films. The constants of electron excitation energy transfer run from 10^7 to 10^{11} s^{-1}, depending from the luminophore concentration. Such films are promising for using as detectors of heavy charged particles and electroluminescent diodes.

M-II/P13 CHARGE TRAPPING IN POLYMER ELECTROLUMINESCENT DEVICES, A.J. Campbell, D.D.C. Bradley, D.G. Lidzey, Centre for Molecular Materials, Department of Physics, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield, S3 7RH, UK

We report studies focusing on the nature of trap states present in single layer ITO/polymer/metal devices of poly(phenylene vinylene) and its soluble derivatives. The current-voltage (IV) and impedance characteristics, the electroluminescence spectrum and the transient capacitance and conductance response to a voltage or light pulse were recorded for temperatures between 11 and 290K. The IV and impedance measurements show that for about 0.5 to $1.5x10^6$V/cm the device characteristics are dominated by bulk transport. The IV relationship in this regime can be successfully modelled by space charge limited current theory with a pseudo-exponential distribution of traps and a temperature dependent mobility derived from hopping conduction theory. The capacitance and conductance transients are non-exponential and approximately follow a power-law relationship with time whose decay rate decreases with decreasing temperature. A simple analytical model shows that this can be related to the emptying of the trap distribution deduced from the SCLC analysis. Due to variations in structure, conformation and environment, the polymer consists of a distribution of chains with different energy gaps. These form a distribution of sites between which hopping conduction occurs. It is proposed that the chains with the smallest energy gaps (about 1 to 0.1% of sites) in the tail of the distribution act as the observed traps for both positive and negative carriers. The same sites dominate the photo- and electroluminescence emission spectra.

M-II/P14 THE PHOTOVOLTAIC EFFECT IN POLY (P-PHENYLENE-2, 3'BIS (3, 2'DIPHENYL) QUINOXALINE -7-7'-DIYL), C. Giebeler, R.N. Marks, A. Bleyer, D.D.C. Bradley, Department of Physics and Centre for Molecular Materials, Sheffield University, Sheffield S3 7RH, UK, S. Schrader, Institut für Angewandte Chemie Adlershof e.V.12484 Berlin-Adlershof, Germany

We have investigated the photovoltaic properties of non-ether poly(p-phenylene-2, 3'-bis(3, 2' diphenyl) quinoxaline-7-7'-diyl) (PPQ) which has previously been identified as a potential electron transporting material. The photocurrent action spectrum peaks at the onset of absorption, indicating that the current is limited by recombination effects in the device. When a voltage of 1.4V is applied to the device (ITO positive) to reverse the sign of the internal field, the action spectrum becomes slightly more red-shifted, suggesting that the mobility of holes in PPQ is lower than that of electrons.

We synthesised tetra(l-dimethylamino-phenyl)-ethylene as a p-type dopant for PPQ, and used blends of PPQ and the dopant in devices. Doping leads to an increase in the quantum efficiency of the devices by three orders of magnitude relative to pure PPQ to 1.55 % at a radiation density of $6.8x10^{-4}$ mW/cm^2 at 415nm. Although the efficiency of the device improves, the spectral response remains approximately constant which suggests that exciton dissociation increases but that the charge transport properties are unchanged.

M-II/P15 EFFICIENT MULTI-LAYER ELECTROLUMINESCENCE DEVICES WITH POLY(m-PHENYLENEVINYLENE-co-2,5-DIOCTYLOXY-p-PHENYLENEVINYLENE) AS THE EMISSIVE LAYER, D. O'Brien, A. Bleyer, D.D.C. Bradley, Department of Physics and Centre for Molecular Materials, University of Sheffield, S3 7RH, UK, and T. Tsutsui, Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan

We report on the use of a new highly luminescent conjugated polymer as an emissive layer in single and multi-layer electroluminescence devices. Poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) [PmPV-co-DOctOPV] was prepared via a Wittig synthesis reaction. The resulting polymer has a high photoluminescence quantum efficiency in the solid state with an emission spectrum peaked at 506 nm (2.45 eV) in the green. Electroluminescence devices were fabricated with an ITO anode and a MgAg cathode. Three different structures were studied: (i) Single layer devices containing only PmPV-co-DOctOPV; (ii) Double layer devices with PmPV-co-DOctOPV and an evaporated film of 1,3- bis(4-tert-butylphenyl-1,3,4-oxadiazoyl)phenylene [OXD-7] as an electron transport layer; (iii) Triple layer devices containing PmPV-co-DOctOPV, OXD-7 and in addition a polyvinylcarbazole [PVK] hole transport layer. Electroluminescence external quantum efficiencies for these devices were found to be respectively up to 0.08%, 0.55% and 1% respectively, corresponding to luminous efficiencies of ≈ 0.5, ≈ 3 and ≈ 6 lm/W and power efficiencies of 8.5×10^{-5}, 5.9×10^{-4} and 6.0×10^{-4} W/W.

M-II/P16 ON THE ROLE OF THERMAL STRAIN FOR MICO-RAMAN DETERMINATION OF CARRIER CONCENTRATIONS IN MOVPE-n-GaN, N. Wieser, M. Klose, R. Dassow, G.C. Rohr, Institut für Technische Physik, DLR Stuttgart, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany, and F. Scholz, J. Off, 4. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

We have investigated the thermal strain and its relaxation at cleaved edges of MOVPE-n-GaN by micro-Raman scattering. This is indicated by E_2 and A_1(LO) mode frequency shifts. Our experimental observed shifts are compared with shifts of the zone center E_2 and A_1(LO) phonon modes calculated ab initio within the framework of density functional pertubation theory. By micro-Raman measurements at the cleaved edge the thermal strain induced shifts of the LO phonons are eliminated for using the Hon-Faust model to estimate carrier concentrations and mobilities from LO phonon plasmon coupled modes. This is shown for intrinsic and low S-doped GaN films, for instance.

M-II/P17 RELATIONSHIP BETWEEN STRUCTURE AND ELECTRO-LUMINESCENCE OF OLIGOPHENYLENEVINYLENES, U. Stalmach, H. Detert, H. Meier, Institut für Organische Chemie, Universität Mainz, J.J. Becher-Weg, 18-22, 55099 Mainz, Germany, V. Gebhardt, D. Haarer, Experimentalphysik IV, A. Bacher, H.W. Schmidt, Makromolekulare Chemie I, Universität Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

The preparation of LEDs with poly(p-phenylenevinylene) [PPV] as the emitting material is well established. However, due to the presence of polymer sequences with a distribution of chain lengths, systematic investigations of the electroluminescence with polymeric materials is difficult, as far as the optical emission is concerned.

We are studying the relationship between structural variation of substituted oligophenylenevinylenes and their corresponding electro-luminescent behaviour using a homologuous series of monodisperse oligo-(2,5-dipropyloxy-1,4-phenylenevinylene)s with up to 11 repeating units. This series covers the spectrum from monomer to polymer. By building LEDs by vapor deposition or spincoating of the oligomers in a polystyrene matrix, the influence of the chainlength on electroluminescence can be investigated. The comparison of PL- and EL-spectra shows that the photophysical properties of the oligomers are strongly altered by aggregation phenomena. Incorporation of the oligomers into a polymer matrix significantly enhances the performance properties of the LEDs.

M-II/P18 WITHDRAWN

M-II/P19 WITHDRAWN

M-II/P20 POLYMERIC NONLINEAR OPTICAL WAVEGUIDES FOR ALL-OPTICAL SWITCHING AT TELECOMMUNICATION WAVELENGTHS, A. Boyle, and W.J. Blau, Physics Department, Trinity College Dublin, Dublin 2, Ireland

The construction and characterisation of a nonlinear fibre loop mirror of ultrafast all-optical switching and demultiplexing is described. The difficulties presented with using optical fibre as the active nonlinear element are discussed and the potential advantages of using polymer waveguides are presented. A complete characterisation of the nonlinear optical properties of a representative polymer channel waveguide is established in the near infrared at 1.3 µm and 1.55 µm. Nonlinear absorption results in a decrease of the propagating light intensity and its magnitude and potential influence on all optical switching is discussed. The nonlinear refractive index coefficient is measured by spectral broadening due to self - phase modulation and by pulse modulated Mach - Zehnder interferometry. The nonlinear refractive index coefficients are found to be 1.9 10^{-17} m^2/W at 1.32 µm and 1.0 $10^{-17} m^2/W$ at 1.55 µm. A balanced evaluation of linear and nonlinear losses and nonlinear refraction concludes with the need to improve the polymer material and waveguide quality, but a clear demonstration of the excellent application potential of this material class.

M-II/P21 THE COMPRESSION MICROMOLDING OF POLYMERS -A REPLICATION TECHNIQUE APPLIED FOR MICROOPTICS, N. Moldovan(1), J. Mohr(2), M. Ilie(1), P. Ruther(2), (1)IMT-Bucharest, PO Box 38-160, R72225, Romania, (2)FzK, Postfach 3640, 76021 Karlsruhe, Germany

The compression molding of PMMA and PC has been used as a replication technique for both diffractive and refractive optical components.
The results are presented: blazed diffraction gratings, microprisms, microlenses.
The mechanical, morphological, chemical properties of the molten materials are taken into account when establishing the process steps in order to obtain the individual optical components.
The encountered problems are discussed, the required properties are outlined.
The work was accomplished in the frame of the PECO-HCM program «Microfabrication with synchrotron radiation» (1995-1997)

M-II/P22 THEORY OF ORGANIC FIELD EFFECT TRANSISTORS, G. Paasch and R. Tecklenburg, IFW Dresden, 01171 Dresden, Germany, and S. Scheinert, Institut für Festkörperelektronik, Technische Universität Ilmenau, 98684 Ilmenau, Germany

Transistors with organic materials as active layer are at present essentially used to determine mobilities in these materials. Till now, in analyzing the measured current characteristics only the simplest (Shockley) model has been used which neither accounts for this type of thin film transitor (TFT) (operating in depletion and accumulation. the substrate acts as the gate) nor for the nature of the carriers. Starting from two-dimensional simulations for the analogous silicon-TFT we developed an analytical model for the TFT which accounts for several peculiarities of the current characteristics of this type of transistor. In addition, a modification has been developed which describes the situation when the charged states are polarons and bipolarons. Applications to published experimental current characteristics show that a general reanalysis will be needed. One special result is that in spite of the low mobilities a consistent description is possible only by iontroducing also for such materials a saturation velocity. Surprisingly, as in crystalline semiconductors the transition to saturation occurs in the region of 10^4V/cm.

M-II/P23 CONJUGATED POLYMERS WITH POLARONS AND BIPOLARONS AS CHARGED STATES, G. Paasch, IFW Dresden, 01171 Dresden, Germany, and P.H. Nguyen, Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany and IFW Dresden, Germany

The properties of space charge layers and the redox behaviour are in general determined by the connection between the particle densities and the (electro-) chemical potential. In conjugated polymers with non-degenerate ground state (as polyaniline. poly-(paraphenylene viniylene)) the charged states are not simply electrons and holes but polarons (charge ±e, s = 1/2) and bipolarons (charge ±2e, s = 0). These states are split off from the bands, their energies depend on their occupation and they are connected with alternations of the bond conjugation. Considering all these peculiarities we present for the first time an approximation for the dependence of both densities on the chemical potential including the transition to high densities (degeneration). With this approximation the properties of space charge layers (electric field vs. band bending, differential capacitance, different screening length's) are consistently described. Further, we obtain a complete (equilibrium) description of the redox behaviour of porous polymer layers (cyclic voltammogram, ESR, electrochemical impedance) for which a quantitative description was missing till now.

M-II/P24 VUV LIGHT-INDUCED DEPOSITION OF LOW DIELECTRIC CONSTANT ORGANIC POLYMER FOR INTERLAYER DIELECTRICS, J.Y. Zhang and I.W. Boyd, Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

The semiconductor industry's need for speed has created a strong interest in low dielectric constant materials, which promise to shorten RC time delays, thereby enabling faster chip operations. The polyimides are attractive for use in integrated circuited as interlayer dielectric materials due to their excellent properties such as low dielectric constant, ease of application, ease of patterning, and high thermal stability. However, in order to use them as interlayer dielectric, the complete imidization of the polyimide film is essential to take advantage of their excellent properties. The degree of imidization of the polyimide film during thermal curing has a significant effect on the chemical and physical properties of the polyimide.

In this work we explore the photo-assisted the conversion of polyamic acid spun onto Si and quartz substrates into thin polyimide films (less than 1 µm thickness), at low temperature using 172 nm radiation from a Xe_2* excimer lamp. The degree of imidization of the polyimide films during the UV curing at different exposure times and temperatures was investigated using Fourier transform infrared spectroscopy. Ellipsometry, UV spectrophotometry, capacitance-voltage, and current-voltage measurements were employed to characterise the polymer films and indicated them to be of high quality. Compared with conventional furnace processing, the photo-induced curing of the polyimide provided both reduced time and reduced temperature processing, which can give improved performance and reliability of semiconductor devices incorporating such layers. The current-voltage measurements showed that the leakage current density of irradiated polymer was reduced over an order of magnitude compared with those obtained by thermal processing. Therefore, these low dielectric constant polyimide films have very high applicability as interlayer dielectric layers for advanced VLSI devices.

M-II/P25 ELECTROLUMINESCENCE : ENHANCED INJECTION USING ITO ELECTRODES COATED WITH A SELF ASSEMBLED MONOLAYER, S.F.J. Appleyard and M.R. Willis, Chemistry Department, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

In a typical organic bilayer electroluminescent device the hole injecting electrode is almost invariably ITO glass, but a number of electron injecting metal electrodes are possible. Unfortunately the low work function materials used readily oxidise and restrict the lifetime of the device.
It is known that appropriate monolayers can change the work function of a solid and also that phosphonic acids can form self assembled monolayers on ITO glass. Using an ITO glass electrode coated with a self assembled monolayer of an electron accepting phosphonic acid (2- chloroethanephosphonic acid) and aluminium as the electron injecting electrode, it was found that the threshold voltage was significantly reduced to the same value as achieved with the less stable Mg:Ag electrode.
The use of such modified ITO electrodes would obviate the use of highly reactive metal electrodes and help to overcome one of the factors which limit device lifetime.

M-II/P26 SPECTRAL NARROWING PHENOMENA IN THE EMISSION FROM A CONJUGATED POLYMER, X. Long, A. Malinowski, M. Grell, D.D.C. Bradley, Dept. of Physics and Centre for Molecular Materials, Sheffield University, Sheffield S3 7RH, U.K., and M. Inbasekaran, E.P.Woo, The Dow Chemical Company, Midland MI 48674, USA

We report a study of the emission properties of a substituted polyfluorene in solid thin films. Spectral narrowing(SN) is observed for pump excitation energies of ≥1μJ per pulse (4ns, 10Hz Q-switched Nd:YAG laser at 355nm). The dependence of this phenomenon on the film morphology has been investigated and we report here on our findings.

The occurrence of SN is strongly dependent on film morphology and the excitation configuration. SN is easily observed in spin coated films. But after thermal treatment of the same films the SN disappeared. For films which are spin coated on a rubbed polyimide aligning layer, the situation is different. There is then no influence of thermal treatment of the film on the occurrence of SN. The combination of the pump polarization direction, film alignment direction and excitation area however now play an important role. The spectral location of SN peaks also varies with morphology and different region of the same sample can give different SN peaks.

We discuss the morphology dependence of the SN and other emission properties in terms of exciton-exciton interaction and the competition between amplified spontaneous emission and cooperative emission processes. The different roles of the intra- and inter-chain coupling are also considered.

M-II/P27 HIGH PEAK CURRENTS AND BRIGHTNESSES IN POLYMER LIGHT-EMITTING DIODES, N.T. Harrison, N. Tessler, C.J. Moss, R.H. Friend, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

We report measurements of peak current and brightness from polymer light-emitting diode structures based on poly(p-phenylenevinylene). The devices were operated at low duty cycles, supported peak currents in excess of 2500 A/cm^2 and produced peak brightnesses of up to 5xl0^6 cd/m^2. These results suggest that transient charge carrier mobilities in these materials are much higher than was previously thought, and that construction of an electrically pumped polymer laser diode is an attainable target.

M-II/P28 LOW LOSS, LOW REFRACTIVE INDEX FLUORINATED SELF-CROSSLINKING POLYMERS WAVEGUIDES FOR OPTICAL APPLICATIONS; J. Liang, E. Toussaere, R. Hierle, R. Levenson, J. Zyss, France Telecom, CNET/DTD, BP 107, 196 Av. Henri Ravera, 92225 Bagneux, and A.V. Ochs, A. Rousseau, B. Boutevin, ENSCM-L.C.A.- UPRESA 5076, 8 rue de l'Ecole Normale, 34296 Montpellier, France

Synthesis and optical applications of low loss methacrylate-based fluorinated polymers are described. The synthesis of well defined self-crosslinking fluorinated polymers has been carried in order to tune refractive index in the range of 1,39 ≤ n ≤ 1,45. After thermally crosslinking, one single lithographic step followed by reactive ion etching is necessary to monomode optical waveguide fabrication on silicon substrates. Optical losses lower than ldB/cm at 1300 nm and than 2dB/cm at 1550 nm were measured for highly confined modes. Efficient chip coupling to lensed optical fibers was obtained. Using waveguides with an effective index close to that of bulk silica, a significant coupling interaction between the guided modes and the whispering gallery modes of a silica microsphere was evidenced thus opening the way for new device applications.

M-II/P29 HIGH ELECTRO-OPTIC RESPONSE IN POLYMERS DOPED WITH NOVEL CHROMOPHORES WITH GOOD THERMAL AND ORIENTATIONAL STABILITY, I. Cazenobe, I. Ledoux and J. Zyss, France Telecom/ CNET, 196 avenue Henri Ravera, 92225 Bagneux Cedex, France, and P. Boldt, J. Wichern, T.H. Kirchberger, J. Rase and C. Ernst, Technische Universität Braunschweig, Institut für Organische Chemie, Hagenring 30, 38092 Braunschweig., Germany

Novel chromophores designed towards the elaboration of highly electro-optic (EO) polymers have been synthesised and characterised. $\mu\beta(0)$ factors as high as $9000*10^{-48}$ esu are obtained in molecules containing thiophene or thieno[3,2-b] thiophene rings and strong acceptors (pyrazolone, tricyanoquinodimethane, tricyanovinyl).

EO doped polymers were prepared and characterised using Second Harmonic Generation and the Teng and Man techniques at 1.3μm for measurements of d_{33} and r_{33} respectively. The measured values of d_{33} (31pm/V) and r_{33} (18pm/V) in a polycarbonate matrix doped with 5.5% of chromophore may be advantageously compared with d_{33}=10pm/V and r_{33}=3pm/V as observed in a DR1 doped (8.2%) polycarbonate. Good thermal stability (80°C during 1000 hours in polysulfone) qualify these materials for further elaboration in EO devices for optical signal processing.

M-II/P30 PHOTOINDUCED MULTIPOLAR SYMMETRY BREAKING IN MULTIPOLAR NONLINEAR MEDIA : FROM MOLECULAR TO PHOTONIC ENGINEERING, S. Brasselet and J. Zyss, France Telecom/ CNET, 196 avenue Henri Ravera, 92225 Bagneux France

By extension of the classical dipolar charge transfer conjugated systems based on the paranitroaniline-like molecular diode template, we introduce a general class of multipolar molecules renewing perspectives towards both molecular engineering and photonic applications. The macroscopic assembly of such systems is presented by way of an all-optical poling technique, connecting photochemical processes to a bichromatic nonlinear absorption scheme. We demonstrate, both theoretically and experimentally, the possibility to drive both the magnitude and tensorial anisotropy of an optically patterned macroscopic nonlinear tensor, in agreement with coupling rules between the molecular susceptibility and the optical poling field tensors. This approach opens the possibility to tailor new quasi-phase-matched structures at the micron scale, whereby the optical control of both linear and nonlinear properties complements the more classical molecular optimization schemes.

M-II/P31 DYNAMICS OF PHOTOEXCITATIONS IN HIGHLY FLUORESCENT ORGANIC GUEST-HOST-SYSTEMS, E.J.W. List, W. Graupner, M. Wohlgenannt, S. Tasch, G. Leising, Institut für Feskörperphysik, TU Graz, Austria, J. Partee, J. Shinar, Ames Laboratory, Iowa State University, Iowa, USA, and P. Schlichting, Y Geerts, U. Scherf, K. Müllen, Max-Planck-Institut für Polymerforschung, Germany

A guest-host-system, composed of a few 100 ppm of the red emitting poly(perylene-co-diethynylbenzene) (PPDB) dispersed in a film of a conjugated ladder-type poly(para-phenylene) (LPPP), can be used to build efficient white light emitting diodes [1]. Upon photoexcitation of the LPPP a very efficient excitation energy transfer (EET), involving the diffusion of an electron hole pair from the photoexcited LPPP to the PPDB, is observed. The results of optically detected magnetic resonance and photoinduced absorption, both of which are sensitive to charged species and triplet states of these guest-host-systems, are described and discussed.

[1] S. Tasch et al., submitted to Appl. Phys. Lett.; E.J.W. List et al. this meeting.

M-II/P32 EFFICIENT COLOUR TUNING (BLUE, RED, WHITE) OF LIGHT EMITTING DIODES BY EXCITATION ENERGY TRANSFER, E.J.W. List, S. Tasch, C. Hochfilzer, G. Leising, Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria and P. Schlichting, Y. Geerts, U. Scherf and K. Müllen, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

We present a colour tuning technique to control the emission colour of polymer light emitting diodes (PLEDs), which is of considerable interest for flat panel display applications.

The emission colour variation of the PLED from blue to red is achieved by blending small amounts of a red light emitting polymer into the active layer of a blue light emitting laddertype poly(paraphenylene) (LPPP). Using this new technique we realised highly efficient stable single layer PLEDs emitting different colours including white light emission.

Besides the colour tuning, which is established by an efficient excitation energy transfer (EET) from LPPP to the guest polymer, a significant increase of the photoluminescence and the electroluminescence quantum efficiency is observed.

M-II/P33 WHITE LIGHT AND RED-GREEN-BLUE (RGB) ELECTROLUMINESCENCE BY LIGHT COLOUR-CONVERSION, A. Niko, S. Tasch, F. Meghdadi, C. Brandstaetter, G. Leising, Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria

We present methods which provide colour-conversion of light emission from organic LED's using a multilayer structure, for the purpose of spectral colour control. These devices with multicolour emission are suitable for applications in flat panel colour display technology. The LED's produced using an active layer of Para-hexa-phenyl (PHP), a bright, stable source of blue light as a pump source can be efficiently combined with colour-converting layers consisting of green (Coumarin) and red (Lumogen F300) dyes in PMMA matrices.

By controlling the absorption and reflection mechanisms of multilayer device structures we are able to demonstrate the production of multicolour light (RGB emission) and in addition, the colour-mixing required to produce white light. By designing the colour-converting films with a specific thickness or concentration of the dye (thus tailoring the optical density of the converter layers), the spectral emission can thus be controlled. By investigating the colour-conversion process in a multilayer stack RGB device, a method of maximising the brightness by improved coupling between the multilayers is presented.

M-II/P34 Fe_2O_3 FILMS FOR $\chi^{(3)}$ OPTICS : RAMAN AND XAS CHARACTERIZATION, C. Baratto, P.P. Lottici, G. Antonioli, INFM and Dipartimento di Fisica, Università, Viale delle Scienze, 43100 Parma, Italy and A Montenero, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università, Viale delle Scienze, 43100 Parma, Italy

The third-order optical susceptibility $\chi^{(3)}$ of thin films of α-Fe_2O_3 has been recently reported as the highest among the inorganic oxides [1]. Its value, $5.8 x l0^{-11}$ esu, exceeds that of SiO_2 glass by about three orders of magnitude. In this work we report on the characterization by Raman and XAS (X-Ray Absorption) spectroscopy of films of α-Fe_2O_3 obtained by two different sol-gel routes. In the first one, the starting solution is iron nitrate $Fe(NO_3)_3.9H_2O$ in a mixture of 2- methoxyethanol and 2,4 pentanedione ($CH_3COCH_2COCH_3$) whereas in the second one the iron oxide is obtained by hydrolysis of $FeCl_3 \cdot 6H_2O$ at pH=9. The films were obtained by single and multiple dip coatings on silica and glass substrates.

The Raman spectra on the films have been measured in the Brewster configuration: for both prepaprations they show all phonon peaks of rhombohedral α-Fe_2O_3, when heated at 500 °C. Confinement effects due to the presence of nanocrystals both in the powders and in the films are discussed on the basis of frequency shifts and peak broadening. XAS measurements, taken at the Fe K-edge in fluorescence mode at ESRF, Grenoble, confirm the α-Fe_2O_3 local structure also in the films obtained by a single coating, which are hardly investigated by other techniques. Both XANES and EXAFS data were analyzed and the changes in the local coordination of iron is followed from the gel to the heat treated films.

[l] T. Hashimoto, T. Yamada, T. Yoko, J. Appl. Phys. 80, 3184 (1996)

M-II/P35 ANISOTROPY IN ALIGNED CONJUGATED POLYMER FILMS-PROBING BY POLARISED ABSORPTION, PHOTOCURRENT AND ELECTROLUMINESCENCE SPECTRA, M.G. Harrison and B.A. Weir, Cavendish Laboratory, Cambridge, CB3 OHE, U.K., and D.H. Hwang, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK

We have fabricated photodiodes in which a thin aligned film of the conjugated polymer MEH-PPV is sandwiched between ITO and semi-transparent Al electrodes. We have investigated the photocurrent action spectra in response to linearly polarised light and observe significant anisotropy. We evaluate our experimental data by comparison with quantitative simulations using models which consider the absorption depth and diffusion of excitons or charges. We also investigate polarised electroluminescence and temperature-dependence of the polarised absorption spectra. We study the microstructure of the films using transmission electron microscopy and diffraction. We discuss whether the microstructure and optoelectronic spectra support the use of a fringe-micelle type model in understanding 3-D interactions in semi-crystalline conjugated polymers, such as PPV.

M-II/P36 AIR ASSISTED PHOTOGENERATION AND DISSOCIATION OF EXCITON IN AN ORGANOMETALLIC CONJUGATED PLATINUM POLY-YNE., N. Chawdhury, and R.H. Friend, Cavendish Laboratory, Cambridge, CB3 0HE, U.K., and M. Younus, J. Lewis, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK

We have fabricated a photocell in which a thin film (250 nm) of the organometallic conjugated polymer Pt-poly-yne is sandwiched between ITO and Al electrodes. We have studied the photovoltaic response of the cell under vacuum after annealing and also after exposure to air. We observe significant change in the photovoltaic response. We find that air enhances exciton dissociation. We also find that air introduces sub-gap states for which absorption can occur. The enhancement of the photovoltaic response to air is found to be reversible after annealing under vacuum.

M-II/P37 NONLINEAR PROPERTIES OF POLYMOLECULAR LAYERS, V.A. Barachevsky, Center for Photochemistry of Russian Academy of Sciences, 7a Novatorov St., Moscow, 117421, Russia

The analysis of the literature and original results concerning the study of nonlinear properties for organic compounds in polymolecular layers prepared by Langmuir-Blodgett (LB) technique are presented. These LB films provide the possibility of observing nonlinear properties using accesible powers of laser irradiation.

Prominence is given to results of investigation for second - and third - order susceptibilities. It was shown that efficiency of second and third harmonic generation depend on compound nature, composition of LB films, conditions and procedure of their preparation as well as intermolecular interaction between molecules in LB layers, in particular their aggregation and complexing.

In summery, photoinduced effects for LB films are discussed. The perspectives of investigation in this line are associated with making photocontrol reversible harmonic transformers of laser irradiation.

M-II/P38 MAGNETO-OPTICAL STUDIES OF PERYLENE TETRA-CARBOXYLIC DIMIDE THIN FILMS, A. Morozov, E. Lifshitz and E. Ehrenfreund, Solid State Institute, Technion, Haifa 32000, Israel

The research focuses on the absorption (Ab), photoluminescence (PL), PL excitation (PLE) and PL detected resonance (ODMR) of N/N-dimethyl-perylene-3,4,9,10 tetracarboxylic diimide film. The Ab and PLE spectra indicate that the basic HOMO-LUMO energy gap is at ≈2 eV. The PL spectrum consists of three well-separated vibronic progression bands, Stokes shifted from the absorption onset, appearing at 1.89, 1.75 and 1.61 eV, respectively. The energy of the absorption band edge and of the luminescence bands indicates the existence of dimers in the film. The ODMR spectrum exhibits a narrow line, centered at $g \approx 2$, associated with a excited π radical ($S=1/2$). In addition, the spectrum contains a typical triplet powder pattern, centered at $g \approx 2$ and a half field resonance at $g \approx 4$. The latter corresponds to the existence of a triplet exciton ($S=1$) populated due to intersystem crossing. The spin Hamiltonian analysis of the powder pattern triplet spectrum yields dipole-dipole parameter $D \approx 0.78$kG, corresponding to an exciton dimension of about 3.5A, and random orientation of the dimers or monomers within the film.

M-II/P39 IONIC SPACE-CHARGE ASSISTED CURRENT INJECTION IN ORGANIC LIGHT EMITTING DIODES, J.C. De Mello, N. Tessler, S.C. Graham, and R.H. Friend, Cavendish Laboratory, Cambridge, CB3 OHE, UK

We have fabricated organic light-emitting diodes with mobile ions incorporated into the active polymer layer, similar in structure to light emitting electrochemical cells (LECs). We report electrical characteristics for devices fabricated with a range of ionic concentrations. The behaviour of these devices can be understood in terms of an electrostatic model. The accumulation of ionic space-charge in the vicinity of the two electrodes is shown to permit easier injection of electronic carriers than is possible in a conventional LED. We are able to explain the symmetric current-voltage characteristics observed in these devices and demonstrate both theoretically and experimentally that an ionic concentration in excess of 10^{20} cm^{-3} is required in order to improve charge injection significantly in a device of thickness 1000 Å. Our model accounts for the relative insensitivity of device characteristics to the workfunctions of the electrodes and predicts sharp increases in current density and light emission at biases close to the energy gap of the luminescent polymer (defined to be the free energy difference between positive and negative carriers).

M-II/P40 STUDY OF ORGANIZED $\chi^{(2)}$ SUSCEPTIBILITY IN GERMANOSILICATE OPTICAL FIBERS AND WAVEGUIDES, Y. Quiquempois, G. Martinelli, P. Bernage, M. Douay, P. Niay, L.D.M.P., U.S.T.L., 59655 Villeneuve d'Ascq Cedex, France and E. Delevaque, H. Poignant, B. Loisel, J.F. Bayon, C.N.E.T.-Lannion, 2 Avenue Pierre Marzin, 22307 Lannion Cedex, France

Poling has been achieved successfully in specially designed germanosilicate fibers and waveguides. The $\chi^{(2)}$ susceptibility was detected and measured through S.H.G. and refractive index change measurement using the interferometric method within the fiber and waveguides. Both the poling technics and the results concerning the linear E.O. effect will be presented at the conference.

M-II/P41 MONOLITHIC INTEGRATED FOUR DFB LDs ARRAY WITH POLYMERIC-BASED COMBINER FOR WDM APPLICATIONS, E. Toussaere, N. Bouadma, J. Zyss, France Telecom-CNET/DTD, BP 107, 196 Av. Henri-Ravera, 92225 Bagneux, France

Compact an low cost integrated photonic components will be of significant importance for a wider penetration of optical technologies into private customer access systems. Hybrid semiconductor/polymer integrated technologies are very promising to achieve this goal by virtue of the highly flexible nature of polymers at both molecular and material scale, of their compatibility with processing steps used in semiconductor technologies, and of their reasonably low cost.

One example is an integrated semiconductor 4-wavelength laser array with polymer based l-to-4 passive optical combiner on the same substrate. The polymer waveguide structure is a polysulfone material stripe embedded in PMMA cladding layers, and the laser structure is a burried ridge stripe (BRS). The optical coupling between the active and passive elements is a butt-joint coupling via a reactive ion beam etched (RIBE) semiconductor mirror facet. Such a photonic integration simplifies the optical coupling between a laser array and single mode fibres, while reducing the packaging cost.

This optical device has been achieved with interesting performances such as small dimension size (1.2 mm x 0.5 mm), low laser threshold current, and output powers for each laser from the polymeric waveguide port of at least l.5mW without additionnal on-chip optical amplification.

M-II/P42 EUROPIUM AND TERBIUM PHOTOLUMINESCENCE IN POROUS Al_2O_3 SPIN COATED WITH SOL-GEL FILMS OR ELECTROCHEMICALLY DOPED, N.V. Gaponenko, A.V. Mudryi, S.K. Lazarouk, O.V. Sergeev and V.E. Borisenko, Belarusian State University of Informatics and Radioelectronics, P. Browka 6, Minsk 220027, Belarus, E.A. Stepanova, A.I. Rat'ko, A.S. Baran, Institute of General and Inorganic Chemistry, Surganova 9, Minsk 220027, Belarus

Thin film planar Al_2O_3 optical waveguides doped with the optically active rare-earth elements hold considerable potential in the field of integrated optics. We are reporting about Eu and Tb photoluminescence (PL) in the range around 540-620 nm from porous Al_2O_3. Anodic Al_2O_3 films 1µm in thickness were formed on monocrystalline Si substrates by magnetron sputtering of Al followed by anodization in 10% aqueous solution at forming voltage 50 V. Tb and Eu were introduced in pores either during electrochemical doping or by spin-on technique of sol-gel derived SiO_2, TiO_2, In_2O_3, Al_2O_3 films. The PL of Eu and Tb was detected after drying at 473K. The strong influence of the sol-gel matrix and annealing treatment on Eu and Tb PL was observed. Two approaches (sol-gel or electrochemical doping) in fabrication of the Al_2O_3 optical waveguides are discussed.

M-II/P43 INVESTIGATION OF CHARGE INJECTION MECHANISM BY ELECTROLUMINESCENCE METHOD, A. Lachinov and T. Zagurenko, Polymer Physics Laboratory, Institute of Physics of Molecules and Crystals, Ufa Research Center, RAS, K. Marx Str. 6, Ufa 450025 Russia

The high conductivity (HC) of nondoped polymers of poly(arylenephthalide)s type has gotten a great importance for various devices. However the question of the HC mechanism formation is open. The paper presents the results of investigation of the injection mechanism role. The highly conducting state (HCS) was form by electric field. Appearing of monopolar injection in the low conducting state of polymer samples under the small of difference of voltages in the metal-polymer-metal system was shown. Bipolar injection observed under increasing of voltage. The injection process controlled by electroluminescense methods (EL) using for generation of electron-holes recombination irradiation. The obtained data analysis shown that the injection phenomena play a real role in the mechanism formation of the highly conducting state. However the properties of experimental systems changed after transition to HCS. Conductivity reached 5.10^5 $(\Omega.cm)^{-1}$ and more, does not thickness dependence of conductivity of $d^{1/3}$ type, current density may be 10^6 A/cm^2 and more. More over conductivity have gotten the metal type temperature dependence. There is the microscopic mechanism of insulator-to-metal type transition in the metal-polymer-metal system under influence of electric field discussed.

M-II/P44 STUDY OF THE ELECTRICAL PROPERTIES OF THE METAL-CALIXATENE-SEMICONDUCTOR STRUCTURES, R. Ben Chaabane and H. Ben Ouada, Département de Physique, Faculté des Sciences de Monastir, 5000 Monastir, Tunisie and M. Gamoudi, G. Guillaud, B. Remaki, Laboratorie d'Electronique du Solide, UCB Lyon I, 43 bd du 11 novembre 1918, 69622 Villeurbanne, France

The research made to use organic materials as active elements in the electronic components and sensors has attracted much attention during the last decade. One of the interesting properties of these materials is the possibility to easily prepare stable and homogenous thin films. In this work, we are interested by the study of the electrical properties of calixarene thin films using a Metal-Oligomer-Semiconductor structure. The electrical study of a such structure can contribute to provide a complementary information about the nature of the electrical conduction of the material and to elucidate the interface properties. The aim of this work is to study the I(V) characteristics and the behaviour of capacitance and conductance characteristics versus frequency. The annealing effects on the films are also investigated.

M-II/P45 MICROWAVE AND FAR-INFRARED PROPAGATION IN CONDUCTIVE MICROSTRUCTURED COMPOSITES, T.E. Huber, L. Luo and L. Silber, Polytechnic University, Brooklyn, NY 11201, USA

The design of composites has flourished in the last few years. We have prepared densely packed arrays (76% volume fraction) of 10-µm diameter parallel indium wires that exhibit an enhanced transmission, of $\sim 10^3$, relative to an indium foil of equal thickness for far-infrared ($f > 2.4x10^{12}$ Hz) propagating along the wire length. The absorption increases as $k^{0.45\pm0.07}$ and is explained by the dynamic Maxwell-Garnett model, which includes eddy current dissipation. Measurements of wire arrays in the 2-12 GHz frequency range, showing enhanced transmission and low reflectivity, will be discussed also. The implications for plasmons in conductive wire microstructures and for developing simultaneously transmissive and conductive composites are discussed.

M-II/P46 MORPHOLOGY AND ONL PROPERTIES OF THIN FILMS OF ORGANIC COMPOUNDS OBTAINED BY EPITAXIAL GROWTH, P. Damman, R. Vallée, M. Dosière, Laboratoire de Physicochimie des Polymères, 20 Place du Parc, 7000 Mons, Belgique, J. Zyss, E. Toussaere, France Telecom CNET, Département d'Electronique Quantique et Moléculaire, 196 Av. Henri Ravera, 92225 Bagneux, France

Oriented films of 2-methyl-4-nitroaniline (MNA) have been obtained by epitaxial growth from the vapor phase onto well oriented thin films of polytetrafluoroethylene (PTFE) prepared following the friction-transfer method. Grazing incidence X-ray diffraction and polarized micro Fourier transform infrared spectroscopy have been used to determine the morphology of these thin MNA films. A (-3,0,1) crystallographic plane has been determined as the contact plane for MNA. The non linear optical properties of these oriented MNA films have been determined by the second harmonic generation technique and show an anisotropy which is related to the orientation of the MNA molecules in the film.

M-II/P47 INFLUENCE OF STRETCHING LOAD ON MOLECULAR STRUCTURE OF ISOTACTIC POLYPROPYLENE, U.G. Gafurov, V.S. Presman, Institute of Nuclear Physics, Tashkent, Ulugbek 702132, Uzbekistan

By IR spectroscopy method the change of molecular structure of isotactic polypropylene in dependence on temperature,stretching load was investigated. It was mainly used the band 973 cm^{-1}. It has been shown that the reasons displacement of the absorption band and change of its form under stretching load are the extension(- deformation) and configuration distortion of helical structure of macromolecules with reorientation and conformation transformation of some sections of macromolecules and weakening of intermolecular interaction both in amorphous and crystalline polymer regions.

M-II/P48 ROTATION MODEL OF SELFDIFFUSION MOBILITY OF MACROMOLECULES IN CRYSTALLYTES OF FLEXIBLE CHAIN LINEAR POLYMER, U.G. Gafurov, Institute of Nuclear Physics, Tashkent, Ulugbek 702132, Uzbekistan

The model of the rotation mobility and selfdiffusion of linear macromolecules in the crystallits of flexible-chain polymers (type of polyetylene) has been proposed. It has been taking into account the interconnection of molecular degrees of freedom such as rotations of molecular groups and chain deformation in the intermolecular field. Varying the summary potential energy the expressions corresponding to the condition for chains equilibrium have been found for the considered model. Thus we have got complex nonhomogeneous equation with mixed terms. However, if accept that the solution changes slowly enough, one can restrict oneself only to terms including derivative of the lowest order and their products. In this case the solution is analogous to one of Frenkel-Kontorova's equation.

M-II/P49 MOLECULAR MODELS OF SLIPPAGE FOR STRAINED PASSAGE MACROMOLECULES IN AN ORIENTED CRYSTALLINE POLYMER, U.G. Gafurov, Institute of Nuclear Physics, Tashkent, Ulugbek 702132, Uzbekistan

An elementary act of polymer plastic deformation and of its creep is slippage of molecular chains. An oriented crystalline polymer with homogeneous chemical structure is studied. Models of the thermoactivated slippages of stressed macromolecules and of the relaxation of local loads on amorphous parts of these molecules are presented. The crystalline polymer is considered as two-phasic one with interchanging amorphous and crystalline regions in a microfibrille. For calculations Frenkel-Kontorova's soliton model is used. It is assumed that polymer crystallits are long enough the continuous matter approximation to be applicable.

In dependence on external load and amorphous region length two cases are realized. The first case takes place when the load is moderate. In this case the load on the amorphous section of a slipped out chain are completely relaxed and this section could change its conformation state. In the second case slipped out amorphous part of a macromolecule is in strained state but its strain is less than one of the macromolecule before its slipping out. The energy activation depen- dencies on molecular parameters and the local load are different for the two cases.

M-II/P50 THE MOLECULAR MODEL OF TENSION AND SLIPPAGE OF THE STRAINED PASSAGE MACROMOLECULES IN ORIENTED LINEAR CRYSTALLINE POLYMERS. COMPUTER SIMULATION, U.G. Gafurov and E. Pestrikova, Institute of Nuclear Physics, Tashkent, Ulugbek 702132, Uzbekistan

The biphase model of linear oriented crystalline polymer as linear polyethylene with real sizes crystalline and amorphous regions was used. This model considered passage macromolecules with strained section in one amorphous regions possessing the free conformational coiled sections in adjacent amorphous regions and the molecular chain with cross chemical bonds or strained loops (entanglement) on crystallite surfaces. With help of computer simulation the numerical calculate of local loads distribution along crystalline section of the strained passage macromolecules to and afterwards thermofluctuation kink formation was conducted. The condition of balance of strained chain in polymer crystallite was made with application of the Frenkel-Kontorova crowdion model. The kink formation is accompanied mechanically stimulation molecular chains slippage and local loads relaxation on them amorphous sections as well as by conformation reorganizations of these sections in some conditions. Is shown that the nature of distribution of local loads, kink form and its evolution in different degree and considerably besides of molecular parameters depend from longitudinal size of crystallits, load on amorphous sections of macromolecules.

The macromolecules slippage with non-loaded section on opposite end of crystallite the kink energy loss is accompanied. While the slippage of fixed passage molecular chain of cross bonds or strained loop (entanglement) on of polymer crystallite surface by increase of energy initial kink is accompanied. At unsufficiently high initial local loads on streined amorphous sections the molecular chain again pull in crystallite.

For such chains with growth their tension at increase of external load or at redistribution of local loads in chains sliding processes are created of condition for termofluctation rupture their stressed amorphous sections.

M-II/P51 EFFECT OF THE SOLVENT POLARITY ON THE CHAIN-LENGTH DEPENDENCE OF THE QUADRATIC POLARIZABILITY OF PUSH-PULL POLYENES, V. Alain, M. Blanchard-Desce, Ecole Normale Supérieure, Département de Chimie (URA 1679), 24 rue Lhomond, 75231 Paris Cedex 05, France and J. Muller, A. Fort, M. Barzoukas, Institut de Physique et Chimie des Matéraux de Strasbourg, Groupe d'Optique Nonlinéaire et d'Optoélectronique (UMR 046), 23 rue du Loess, 67037 Strasbourg, France

We have synthesized several series of push-pull polyenes of increasing size, bearing aromatic electron-donating end groups and various electron-withdrawing moieties. We have measured the quadratic hyperpolarizability, $\beta(0)$ of these compounds in different solvents. We present an analysis, based on a two-form two-state model, explaining how the dependence of $\beta(0)$ on the polyenic chain length varies with the solvent polarity.

M-II/P52 NEW NON-DIPOLAR STRUCTURES WITH SIGNIFICANT QUADRATIC HYPERPOLARIZABILITIES, M. Blanchard-Desce, J.B. Baudin, O. Ruel, L. Jullien, Ecole Normale Supérieure, Département de Chimie (URA 1679), 24 rue Lhomond, 75231 Paris Cedex 05, France and S. Brasselet, J. Zyss, Département d'Electronique Quantique et Moléculaire, France Télécom, 169 avenue Henri Ravera, 92225 Bagneux Cedex, France

«Octupolar» molecules are of particular interest in the field of nonlinear optics due to their potentially large quadratic nonlinearities.[1] Within this framework, we have designed organic chromophores of approximate tetrahedral symmetry and investigated their quadratic nonlinearities by performing Harmonic Light Scattering (HLS) experiments in solutions. Issues related to the molecular engineering of the nonlinearity-transparency trade-off have been addressed. As a result, molecules combining significant quadratic hyperpolarizabilities and excellent transparency have been identified.

[1] J. Zyss, Nonlinear Optics, 1991, 1, 3.

M-II/P53 THEORY OF ELECTRONIC STATES AND EXCITATIONS IN PPV, S. Brazovskii(1,2), N. Kirova(1), A.R. Bischop(1), (1)LANL, Los Alamos, NM 87545, USA, (2)LPS, Université Paris Sud, 91405 Orsay, France

Optical studies of conducting polymers are a topical agenda in both the physics and applications of organic semiconductors. In most of current theoretical models primary excitations are derived from the local excitations of the phenyl ring. But such pictures cannot provide the energies below $E_1 = 4.7$eV which is twice higher than that required for low energy absorption. We have developed a new theoretical picture which unifies features of both a semiconductor band model (delocalized excitations) and a molecular exciton model (localized excitations). Our model is based upon the analytical solution for the band structure of the PPV polymer, while invoking the necessary corrections for electron-hole interactions. The discret levels appear naturally on top of the delocalized states as excitons of intermediate range (between Frenkel and Wannier-Mott types). Even for these excitons the electrons are almost equally present at the phenyl ring and at the vinyl linkage. The lattice relaxation is provided by selftrapping of electrons or excitons due to libration modes.

M-II/P54 STABILITY OF BIPOLARONS IN CONDUCTING POLYMERS, S. Brazovskii(1,2), N. Kirova(1), Z.G. Yu(1), A.R. Bishop(1), A. Saxena(1), (1)LANL, Los Alamos, NM 87545, USA, (2)LPS, Université Paris Sud, 91405 Orsay, France

There is a considerable interest in effects of real space pairing of electrons. In nonmetallic materials these pairs are frequently referred as bipolarons (BP). While the existence of BPs have not been fully proved yet, their manifestations have been conjected in a number of different material. Conducting polymers suggest the most convinced evidences from optical and magnetic data. The BPs may be very important bringing new ingredients to the properties of electronic devices based on conducting polymers. They appear to be the main form of the charge collection. The main challenge to the existence of BPs comes from long range Coulomb repulsion which can ionize them into a pair of polarons. We report systematic studies of Coulomb effects for isolated BPs in the volume and near the metal contact as well as for the BP - impurity complexes. We have determined the parameter regions, where the BPs exist as a stable or metastable particles. The stability region is widely extended in a bound state with a dopant or near the metal surface due to Coulomb screening. Our studies confirm that the BPs or their liquids or superstructure indeed provide the main form of charge storage under doping or at the contacts. Their ability to carry current is limited to a restricted region of material parameters. The results are applied to calculations of optical and tunneling features related to the existence of BPs.

M-II/P55 OPTICAL EMISSION FROM CONFINED POLYTHIOPHENES, **O. Inganäs**, T. Granlund, M. Theander, M. Berggren, M. Granström, Laboratory of Applied Physics, Dept. of Physics (IFM), University of Linköping, 592 29 Linköping, Sweden, and M.R. Andersson, Dept. Polymer Technology, Chalmers University of Technology, 412 96 Göteborg, Sweden

The emission wavelength of substituted poly(thiophenes) cover the range from blue to near infrared. This emission may be strongly modified by separating chains from each other in polymer matrices, to avoid photoluminescence quenching. It may be combined by adding several polythiophenes in adjacent compartments, in polymer blends giving phase separation. The emission may also be spectrally and spatially selected by confinement in microcavity geometries. Enhanced photoluminescence is obtained from conjugated chains separated by non-conjugated side chains in a homopolymer of thiophene. Fast kinetics of these photoluminescence processes give evidence for stimulated emission. This emission can be expressed in polymer layers confined between dielectric mirrors in a microcavity device.

M-II/P56 OPTIMIZATION OF THE PHOTOREFRACTIVE PROPERTIES OF PUSH-PULL MOLECULES FOR OPTIMIZED PHOTOREFRACTIVE PROPERTIES, A. Fort, J. Muller and M. Barzoukas, IPCMS-GONLO, 23 rue du Loess, 67037 Strasbourg Cedex, France

Low glass transition temperature photorefractive polymers can exhibit large diffraction efficiency due to birefringence and Pockels contributions of the chromophores to the refractive indice modulations. We discuss in the frame of the MIX analysis previously developped for push-pull molecules the importance of these two effects, namely $\mu^2\Delta\alpha$ and $\mu\beta$, where μ is the molecular dipole moment, $\Delta\alpha$ the polarizability anisotropy and β the quadratic hyperpolarizability.

The theoretical predictions allow us to optimize the photoresponse in respect with the molecular structure of the chromophores depending on MIX.. The relevant experimental data, obtained with a special set-up for $\Delta\alpha$, for a series of push-pull molecules in different solvents confirm the predominant contribution of the birefringence effect to the photorefractive properties of doped polymers.

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