



Strasbourg (France)

E-MRS SPRING MEETING 2003

June 10 – 13, 2003

SYMPOSIUM B

Advanced multifunctional nanocarbon materials and nanosystems

Symposium Organizers:

Peter Scharff, Technische Universität Ilmenau, Germany

Hans Kuzmany, Universität Wien, Austria

Shen Cui, Tianjin University, China

Lothar Dunsch, Institut für Festkörper- und Werkstoff-forschung,
Abteilung Elektrochemie und leitfähige Polymere, Dresden, Germany

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Chemical Material Science” of the Kiev National Taras Shevchenko
University and NAS of Ukraine

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E-MRS 2003 SPRING MEETING

SYMPOSIUM B

Tuesday, June 10, 2003
Mardi 10 juin 2003

Morning
Matin

Session I: Nanoscience of Integrated Nanosystems 1

Session chair: Peter Scharff

9:00 **B-I.1** -Invited- MERGING CHEMISTRY AND PHYSICS AT THE NANOSCALE: ELECTRONIC DETECTION OF CHEMICAL REACTIONS

George Gruner, Nanomix Inc. and University of California Los Angeles, USA

Nanoscale electronic devices with carbon nanotubes as the conducting channel have been developed in recent years. This talk will explore the utilization of these devices for chemical and bio-sensing.

9:40 **B-I.2** NANOPARTICLE REACTIONS ON CHIP

Michael Kohler(a,b), Th. Kirner(a), J. Wagner(a), A. Csaki(b), R. Muller(b), W. Fritzsche(b), (a)Technical University of Ilmenau, Department for Physical Chemistry and Microreaction Technology, (b)Institute for Physical High Technology Jena, Biotechnical Microsystem Department, TU Ilmenau, Germany

The handling of heterogeneous systems in micro reactors is difficult due to their adhesion and transport behaviour. Therefore, the formation of precipitates and gas bubbles has to be avoided in micro reaction technology, in most cases. But, micro channels and other micro reactors offer interesting possibilities for the control of reaction conditions and transport by diffusion and convection due to the laminar flow caused by small Reynolds numbers. This can be used for the preparation and modification of objects, which are much smaller than the cross section of microchannels. The formation of colloidal solutions and the change of surface states of nano particles are two important tasks for the application of chip reactors in nanoparticle technology. Some concepts for the preparation and reaction of nanoparticles in modular chip reactor arrangements will be discussed. Nanoparticles are of particular interest for nano construction technologies and for molecular recognition, because they can behave both as small robust solids and specifically reacting chemical species. Therefore, they moved into the focus of interest for labeling procedures in biochip applications since few years. So, DNA-substituted Au nanoparticles are suited as labels for optical as well as for electrical detection of molecular interactions at DNA chips. A fast read-out of biochips and an optical detection of single binding events can be achieved if chemical amplification of nanoparticles by metal-catalyzed metal deposition is applied. It is assumed, that nanoparticle technologies will promote biochip application as well as chip reaction technologies in the near future.

10:00 **B-I.3** MANIPULATION OF CARBON NANOTUBES

Laszlo Forro, Institute of Physics of Complex Matter, FBS Swiss Federal Institute of Technology (EPFL), 1015 Lausanne, Switzerland

We will give the current status of chemical and mechanical manipulation of single walled, multiwalled carbon nanotubes and other inorganic tubular structures.

10:30 **BREAK**

Session II: Nanoscience of Integrated Nanosystems 2

Session chair: Vladimir L. Kuznetsov

10:50 **B-II.1** -Invited- NANOSTRUCTURED CARBIDE-DERIVED CARBONS: FROM DIAMOND TO CARBON ONIONS AND NANOTUBES

Yury Gogotsi, Alexei Nikitin, Department of Materials Engineering, Drexel University, Philadelphia PA 19104, USA

This paper will present an overview of recent advances in synthesis of nanostructured carbide-derived carbons (CDC). Amorphous and nanocrystalline graphitic carbon, single wall and multiwall nanotubes, carbon onions, nanocrystalline diamond, and ordered graphite can be produced by extraction of metals from carbides. This method allows synthesis of almost all known carbon structures. Since the metal carbide lattice is used as a template and metal is extracted layer by layer, atomic level control can be achieved in the synthesis process and the structure of the carbon can be templated by the carbide structure, with an opportunity for further modification by controlling the temperature, pressure, composition of the environment and other process variables. Linear kinetics of CDC growth in a broad temperature range allows transformation to almost any depth and synthesis of coatings, powders and free-standing CDC membranes. This is due to open nanometer porosity in the material. The pore structure of CDC can be tuned very finely by using different carbides, etching agents, and temperature. The average pore size can be controlled with a better than 0.1 nm accuracy and the pore size distribution produced is more narrow than in activated carbons derived from organic precursors and having a similar average pore size.

- 11:30 **B-II.2** NANOCARBONS IN CARBON MATERIALS
Michio Inagaki, Aichi Institute of Technology, Department of Applied Chemistry, Yakusa, Toyota 470-0392, Japan
Carbon materials consist of four families, diamond, graphite, fullerenes and carbyne. Each family has its own diversity in structure and texture. In the lecture, diversity of each family will be summarized and the definition of nanocarbons will be proposed.
- 11:50 **B-II.3** PHOTOCONDUCTIVE PROPERTIES OF SINGLE-WALL CARBON NANOTUBES
Akihiko Fujiwara, Japan Advance Institute of Science and Technology, 1-1, Asahidai, Tatsunokuchi, Ishikawa, 923-1292, Japan
Carbon nanotubes (CNTs) are nano-scale one-dimensional conductors. Extraction of photoconductive properties of CNTs is very important for the understanding of nature of carrier in one-dimension and for the application of photoelectric effect in nano-scale devices. We present our recent research on photoconductive properties of single wall carbon nanotube (SWCNT) bundles. Temperature dependence of photoconductivity has been investigated for film samples of SWNTs at 0.7eV which is energy gap of semiconducting SWCNTs. In order to clarify the effect of atmosphere on photoconductivity, measurements have been performed under helium and nitrogen gas flow in the temperature range from 10 K to room temperature (R.T.) and from 100 K to R.T., respectively. Photoconductive response monotonously increases with a decrease in temperature and tends to saturate around 10 K. No clear difference in photoconductive response under different atmosphere was observed. We discuss the mechanism of photoconductivity at 0.7eV from experimental results. We also review the related behaviors observed in SWCNTs presented by other groups.
- 12:10 **B-II.4** SPATIALLY RESOLVED PHOTOEMISSION SPECTROSCOPY OF CLUSTER-ASSEMBLED CARBON AND NANOCOMPOSITE CARBON/METAL FILMS
C. Lenardi, INFN-Ist. Fis. Gen. e Chim. Biolog., Via Trentacoste 2, 20134 Milano and LAMINA, Italy, and R.G. Agostino, T. Caruso, E. Colavita, INFN-Dipartimento di Fisica, Università della Calabria, Ponte Bucci, Cubo 33c, 87036 Arcavacata di Rende (CS), Italy, and S. La Rosa, M. Bertolo, Sincrotrone Trieste, S.S 14 km 163.5-in Area Science Park, 34012 Basovizza-Trieste, Italy, and E. Barborini, G. Bongiorno, P. Piseri, P. Milani, INFN-Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy and LAMINA, Italy
Inclusions of metals in the growth process of carbon cluster assembled materials (ns-C) induce modifications in the structural and electronic properties of the material. Loading of metal nanoparticles into carbon cluster based films is obtained by using a cathode with two distinct components (metal (Ti,Ni,Pt,Mo,Co)/graphite). The study of the spatially resolved valence band emission from nanocomposite carbon/metal films has been performed by means of photoelectron spectromicroscopy beamline at ELETTRA (photon energy = 95.0 eV). No evidence of significant spectral anisotropy has been detected. The influence of the photon irradiation has been studied as function of time. All the nanocomposite materials show an increment of the DOS population at the Fermi edge, particularly relevant and fast in the case of Ni containing specimens. The localized metallisation induced by photon irradiation can open new perspectives in carbon-based nano- and micro-electronics.
- 12:30 **LUNCH**

Tuesday, June 10, 2003
Mardi 10 juin 2003

Afternoon
Après-midi

Session III: Nanoscience of Integrated Nanosystems 3

Session chair: Petra Rudolf

14:00 **B-III.1** -Invited- USING POLYMERS AND COPOLYMERS FOR PURIFICATION AND FUNCTIONALIZATION OF CARBON NANOTUBES.

Robert Klement, Dimitrios Voulgaris, Pierre Petit, **Claude Mathis**, Institut Charles Sadron (CNRS-ULP), Strasbourg, France

Unlike common emulsifier that allow dispersing SWNT in water, block-copolymer like polystyrene-b-poly(2-vinylpyridine) allows dispersing SWNT even in organic solvent such as methanol. Due to the difference in solubility of the PS and the P2VP blocks in MeOH, the PS sequence stacks on the SWNT surface and the copolymer acts as a good emulsifier leading to suspensions stable for weeks. Destabilization of the "solution" by adding controlled amounts of THF (good solvent for both PS and P2VP) leads to precipitation of first impurities and finally SWNT. The entire polymer can be removed from these latter by adding large amounts of THF. This method, based on a fractionated precipitation process, can be employed for purification of "as produced" SWNT. Covalent grafting of polymer chains with a terminal amine group onto SWNT bearing on their side-walls acid functionalities, introduced either by an oxidizing acid treatment or via 1,3-dipolar cycloaddition of azomethine ylides, is discussed. Direct sidewall grafting of aminoacid terminated polymers has also been achieved using this latter method. Functionalization of carbon nanotubes results in solubilization of these latter in organic solvents. The grafted polymer chains allows to apply the classical polymer processing methods to these materials.

14:40 **B-III.2** ELECTRONIC AND GEOMETRIC STRUCTURES OF FULLERENES NETWORKED BY EXTERIOR METAL ATOMS

Atsushi Nakajima, Keio Univ., Japan and Koji Kaya, Institute for Molecular Science, Japan

The electronic and geometric structures of gas-phase exohedral atoms-C60 fullerene clusters were studied by mass spectrometry, photoionization spectroscopy (PIS) of the neutrals, and photoelectron spectroscopy (PES) of their anions. The exohedral atoms-C60 mixed clusters were produced by two laser vaporization methods. In the mass spectra of cationic vanadium(V)-C60, Vn(C60)m+, the abundant clusters were produced at the composition of (n, m) = (1, 1), (1, 2), (2, 3), (3-4, 4), and (5, 5). This pattern is explicable in terms of a multiple dumbbell structure; V atom and C60 are alternatively piled up. The ionization energy and the reactivity of the dumbbell clusters toward O2 and CO show V1(C60)2 takes a structure of V1(h6-C60)2. Furthermore, the electronic properties, HonC60 with n = 1-5, were studied by PIS of the neutrals and PES of their anions. Both spectroscopic analyses reveal that each Ho atom donates its three valence electrons to the unoccupied molecular orbitals of C60. The electron filling through the charge transfer allows us to observe the unoccupied levels of C60 due to high electron acceptability. For silicon (si) or germanium (Ge)-C60, however, behavior of Si and Ge atoms (or clusters) on the surface of a C60 has been revealed by using time-of-flight mass spectroscopy and photoelectron spectroscopy.

15:00 **B-III.3** CARBON NANOTUBE SIDEWALLS AND END CAPS AS TARGET SITES FOR CHEMICAL MODIFICATION

Sarbajit Banerjee, Stanislaus S. Wong, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794, USA Materials and Chemical Sciences Department, Brookhaven National Laboratory, Upton NY 11973, USA

Single-walled carbon nanotubes (SWNTs) have been the focus of intensive study due to their properties. For these quasi-molecular materials to fully realize their proposed potential in charge transport, high strength and high surface area applications requires the facile formation of SWNT based nanocomposites. This work discusses a number of different approaches to the derivatization of SWNTs. Chemical modifications through coordination to metal-containing molecular complexes can have significant effects on their properties. In fact, improved solubilization in organic solvents, charge transfer, and catalytic properties were noted in SWNTs functionalized with Iridium and Rhodium complexes. The adducts of SWNTs with these complexes have been extensively characterized by electron and atomic force microscopy. Optical properties have been extensively probed by means of UV-Vis-NIR, mass, and multinuclear NMR spectroscopy as well as by photoluminescence studies. Further extension of functionalization at the metal-nanotube interface has been achieved by tethering of quantum dots (such as CdSe) and oxide nanocrystals by oxygenated functional groups on the SWNT end caps and defect sites. Exhaustive structural characterization as well as charge transfer studies will be presented. In yet another approach at increasing the processability of SWNTs, they were dissolved in water and polar solvents by electrostatically functionalizing with an organic macrocycle. Recently, a more efficient method for functionalizing SWNT sidewalls with oxygenated functionalities has been developed using ozonolysis. Ozonation enables considerable control over the identity of the functional group as well as allowing the typical amide functionalization done at nanotube ends to be extended to the sidewalls.

15:20 **B-III.4**

MOLECULAR-SCALE IMAGING OF ORGANIC INTEGRATED NANOSYSTEMS.

N. Katsonis, A. Marchenko, D. Fichou, CEA-Saclay, Service de Physique et Chimie des Surfaces et Interfaces (SPCSI), DRECAM/DSM, Gif-sur-Yvette, France, Laboratoire de Chimie Organique, Université Pierre et Marie Curie, Paris, France

Self-assembled monolayers of organic films have been the subject of an extensive research effort because of their potential applications in bio and chemical sensing, corrosion inhibition and electronic devices. For these investigations STM has proven to be a very efficient tool, providing information about structural and electronic properties on the nanoscale. In particular, much attention has been given to studies of film growth using fullerene as a model adsorbate. In all these investigations, the overlayer results from a direct deposition in ultra high vacuum. Despite a large number of studies of C60 films, there are no investigations of fullerene adsorption at the liquid/solid interface, which could facilitate technological applications. We report for the first time on an in-situ STM investigation of structure and growth of the C60 and C70 overlayers formed at the liquid/solid interface. We demonstrate the possibility to manipulate and to carry out spectroscopy measurements with single C60 molecules in a liquid environment. We also present the results of systematic STM investigations of normal alkanes and long chain molecules terminated by trimethylsilyl and sulfur groups. The observed structures are discussed in terms of commensurability and of competition between molecule-substrate and molecule-molecule interaction. Proposed models are in a good agreement with obtained results.

15:50 **B-III.5**

SCANNING TUNNELING SPECTROSCOPY OF LIGHT EXCITED MOLECULAR FILMS

V. Arima, Fabio Della Sala, R. Blyth, R. Rinaldi, R. Cingolani, National Nanotechnology Laboratories of INFN and Dipartimento di Ingegneria dell'Innovazione Università degli Studi di Lecce, Via Arnesano, 73100 Lecce, Italy

Scanning tunneling spectroscopy (STS) is a powerful experimental technique to investigate electronic properties of single molecules or thin solid films. In fact STS can give informations about molecular electronic levels. These states can be modified by external perturbation. Here we report on STS measurements of spin-coated organic thin films under laser excitation. Three different prototype molecules has been considered, namely zinc-tetra-phenyl-porphyrin, nitrobenzene derivative and sexithiophene. I/V curve has been measured under different excitation wavelengths and powers, showing that the light excitation has a strong effect on the tunneling current. Molecular electronic levels of light-excited excited molecules are in fact different to that of molecules in equilibrium. The experimental results are compared with theoretical calculations.

16:05

BREAK

Session IV: Nanoscience of Integrated Nanosystems 4

Session chair: Alexandr Marchenko

16:20 **B-IV.1**

BUILDING CARBON NANOTUBE ARCHITECTURES FOR DEVICE APPLICATIONS

B.O. Wej, N. Chakrapani, Y.J. Jung, R. Vajtai, P.M. Ajayan, Department of Material Science and Engineering, A. Carrillo, R. Kane Howard, P. Isermann, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy NY 12180, USA

Carbon nanotubes have fascinating physical properties. In order to use these novel one-dimensional structures for applications (such as in electronic devices and mechanical reinforcements) the structure of nanotubes needs to be tailored. Some of our recent efforts are directed towards growing nanotubes by chemical vapor deposition in controllable ways, with site selection and orientation on templated planar substrates. The challenges and the ultimate goals in the creation of mesoscale nanotube-based architectures will be discussed. By performing chemistry on nanotubes to modify their interactions with solvents and matrices we show several approaches towards developing this material into useful, functional materials and devices. This study involves creating extremely dense patterns of carbon nanotubes by plasma functionalization of aligned nanotube arrays obtained directly from CVD method followed by appropriate chemical treatments. The defects and functional groups, which can be used to alter the surface character of nanotubes, can be generated by cold gas plasma in a controllable manner. The densely packed nanotube structures have potential in nanotube-membrane and actuator applications.

17:00 **B-IV.2**

[2+1] CYCLOADDITIONS FOR CROSS-LINKING SWCNTS

Michael Holzinger, Johannes Steinmetz, Damian Samaille and Patrick Bernier, GDFC, Université de Montpellier II, CC26, 34095 Montpellier Cedex 05, France

In recent years, several successful reactions for the functionalization of SWNTs have been developed. The direct sidewall functionalisation of SWNTs with organic addends is possible via reactions with reactive species such as nitrenes, carbenes and radicals. One of the most investigated derivatization method is the covalent sidewall functionalization with nitrenes. It demonstrates a reliable way to add a huge number of different organic species to the nanotube sidewalls. The success of this reaction led us to use it for the interconnection of single walled carbon nanotubes using long alkyl chains terminated with azidocarbonates at each end. After the reaction and work-up, a highly flexible and stable sheet of cross-linked SWCNTs was obtained. The resulting product is insoluble in water and all common organic solvents. With spectroscopic methods like NMR, XPS, Raman and IR, we can give evidence for the formation of akloxyaziridino-SWCNTs but not for the interconnection of the tubes. This must be proven by microscopic methods. Here, not only the interconnection can be seen but also the splitting of bundles can be observed, which is an already known side effect of this reaction. This method of interconnecting single walled carbon nanotubes represents a new possibility to process SWCNTs to form materials only made of nanotubes.

17:30 **B-IV.3**

ELECTRICAL, MAGNETO-TRANSPORT AND LOCALIZATION IN NANOCOMPOSITES BASED ON CARBON NANOTUBES

O. Chauvet, J.M. Benoit*, B. Corraze, IMN/LPC, Nantes University, 44322 Nantes, France, *now at MPI, Stuttgart, Germany

Singlewalled carbon nanotubes (SWNT) are nanomaterials which possess remarkable physico-chemical properties thanks to their nanometric size. The potential application field of these nanosystems is very broad, ranging from nanodevices to MEMS, actuators or sensors, chemical reactors.... Still, most of the practical sensing applications will involve an ensemble of SWNT rather than isolated nano-objects. To understand the evolution of the properties when putting the SWNT together is thus essential. This is the purpose of this paper in which we investigate the electrical transport and magneto-transport properties of an ensemble of SWNT, embedded into an insulating polymer matrix in order to build a nanocomposite. We show that the metallic character is lost in the nanocomposite. Intrinsic localization of the carriers at the bundle size is evidenced from the conductivity measurements. This is confirmed by magnetoresistance measurements which exhibit well defined quantum interference effects in the localized regime. By comparison with isolated SWNT, another difference is found in the role of the Coulomb interactions. Building an ensemble of SWNT allows a partial screening of these interactions as revealed from the ohmic and non ohmic conductivity temperature and field dependencies

18:00 **B-IV.4**

BIOMOLECULAR DEVICES: AN EXPERIMENTAL AND TEORETICAL STUDY

R. Cingolani, A. Bramanti, G. Maruccio, P. Visconti, E. D'Amone, P. Calogriuri, R. Rinaldi, NNL-National Nanotechnology Laboratory of INFN, Department of Innovation Engineering, University of Lecce, Via per Arnesano, 73100 Lecce, Italy

Molecular electronics requires the demonstration of a simple way to interconnect molecules. Between the various fabrication approaches proposed, planar nanojunctions allow transport experiments in self-assembled molecular monolayers, and permit to easily fabricate field effect devices. In this work, we investigate how to probe molecular transport and implement the related devices. Planar nanojunctions were fabricated by electron beam lithography and lift-off process and inspected by plan-view scanning electron microscopy (SEM). Open circuit resistances greater than 100 GOhm were measured. At high operating voltages (greater than 4 V), breakdown may cause contact failure, due to the electrode proximity and the discontinuity of the dielectric constant. Field simulations were carried out by the finite element method. The analysis identified a few small regions, strictly correlated to the critical breaking points evidenced in the images, where the electric field intensifies. Thus, careful design of the electrodes is required, avoiding discontinuities in their geometry, to prevent field-induced damage. Though a tip geometry is technologically convenient to obtain very close electrodes, especially with respect to lift-off problems, it might represent a cause of contact damaging. Thus, we present a trade-off solution - based on the field simulation - which conciliates process and operational needs. Finally, the model allows to analyze the field influence on transport.

18:30

DISCUSSION Nanoscience of Integrated Nanosystems

Participants: George Gruner, Michael Kohler, Laszlo Forro, Yury Gogotsi, Ernst Hammel, Michio Inagaki, Akihiko Fujiwara, R. G. Agostino, Martin Hulman, Claude Mathis, Atsushi Nakajima, Olexandr Marchenko, Fabio Della Sala, Stanislaus S. Wong, Bingqing Q. Wei, Michael Holzinger, Olivier Chauvet, Roberto Cingolani.

Wednesday, June 11, 2003
Mercredi 11 juin 2003

Afternoon
Après-midi

Session V: Theory, modeling
Session chair: R. Cingolani

- 14:00 **B-V.1** -Invited- INDIVIDUALITIES AND AVERAGE BEHAVIOR IN THE PHYSICAL PROPERTIES OF SMALL DIAMETER SINGLE-WALLED CARBON NANOTUBES
Jenő Kürti, Viktor Zólyomi, Department of Biological Physics, Eötvös University, Budapest, Hungary; Guangyu Sun, Miklós Kertész, Department of Chemistry, Georgetown University, Washington DC 20057, USA; Ray H. Baughman, Department of Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson TX 75083, USA; Hans Kuzmany Institut für Material Physics, University of Vienna, Vienna, Austria
Various properties of single-walled carbon nanotubes (SWCNTs) have been investigated theoretically. Density functional theory with periodic boundary condition has been used in the calculations. Geometry, electronic band structure and the frequency of the radial breathing mode in the Raman spectrum were investigated for armchair, zigzag as well as chiral SWCNTs with diameters starting from 0.4nm. In addition, the strain-charge curves were calculated for negatively and positively charged nanotubes. SWCNTs with small diameter exhibit characteristic deviations from the corresponding average behavior.
- 14:40 **B-V.2** CARBON NANOTUBES IN CHANNELS
Orest Dubay, Georg Kresse, Vienna University, Institut fuer Materialphysik, Sensengasse 8/12, 1090 Wien, Austria
An all-electron ab initio density functional method is used to study carbon nanotubes embedded in channels. Two classes of systems are investigated: nanotubes in zeolite crystals (AFI) and double-walled carbon nanotubes. A common feature of these systems is the confinement of the carbon nanotube by weakly (van der Waals) interacting channels. The impact of the channel environment on the electronic and vibronic properties of nanotubes is explored.
- 15:00 **B-V.3** SUPERCONDUCTIVITY IN CARBON NANOTUBES
Alessandro De Martino, Reinhold Egger, Institut für Theoretische Physik IV, Heinrich-Heine-Universität, 40225 Dusseldorf, Germany
I discuss the theoretical description of phonon-mediated attractive electron-electron interactions in individual single-wall Carbon nanotubes and the resulting superconducting instability. The possibility for a true superconducting phase transition in ropes is then studied by taking into account the Josephson coupling between the tubes in a mean-field approximation.
- 15:15 **B-V.4** THE ELECTRONIC STRUCTURE OF NANOTUBES AND THE TOPOLOGICAL ARRANGEMENTS OF CARBON ATOMS
István László, TU Budapest, Dept. of Theoretical Physics, Hungary
Various tree-coordinated tiling of the plane by hexagons, pentagons and heptagons are presented in order to obtain tubular, toroidal and helical carbon structures. Good initial topological coordinates are constructed by combining some thinking from chemistry (Hückel matrices), physics (zone folding) and modern mathematics (null spaceembedding of graphs). The final geometric structures were obtained with the help of Brenner-potential based molecular mechanics methods, and the electronic structures were determined with the help of tight-binding calculations.
- 15:30 **B-V.5** MODELLING AND IMAGING ONE-DIMENSIONAL CRYSTAL STRUCTURES IN CARBON NANOTUBES
Jeremy Sloan, Inorganic Chemistry Laboratory, University of Oxford, Malcolm L.H. Green, Inorganic Chemistry Laboratory, University of Oxford, Angus I. Kirkland, Department of Materials Science and Metallurgy, University of Cambridge, John L. Hutchison, Department of Materials, University of Oxford, OX1 3QR Oxford, U.K.
General approaches to the direct or indirect lattice imaging, interpretation and modelling of 1D crystal structures formed within predominantly single layer carbon nanotubes are described. Such structures may be produced in a "top down" fashion by selecting fragments derived from bulk crystal structures, which is an approach that may be used when the obtained 1D crystal structure is recognizably similar to that of the bulk. In the instance of simple packed structures, for example those derived from rocksalt (B1), such a derivation is straightforward although normally some distortion of the crystal fragment is required in order to mimic those that are observed experimentally. In the case of more complex 2D and 3D network structures, some reduction in coordination of the obtained fragment is normally required at the crystal surface. Where the obtained 1D crystal structure bears no obvious relation to a known bulk structure, an alternative strategy involves the derivation of a new crystal structure via a "bottom up" approach whereby the structure is constructed ab initio from the obtained lattice images of the 1D crystal/nanotube composite.

15:45 **B-V.6**

CARBON NANOARCHITECTURES CONTAINING NON-HEXAGONAL RINGS

Laszlo Peter Biro, G.I. Mark, J. Gyulai, Research Institute for Technical Physics and Materials Science, 1525 Budapest., Pf. 49, Hungary; J.B.Nagy, Laboratoire RMN, Facultes Universitaires Notre-Dame de la Paix, 5000 Namur, Rue de Bruxelles 61, Belgium; Ph. Lambin, Laboratoire de Physique du Solide, Facultes Universitaires Notre-Dame de la Paix, 5000 Namur, Rue de Bruxelles 61, Belgium

The structure and formation mechanism are of regularly coiled carbon nanotubes are exciting questions since several years. The early models were based on the very regular incorporation of a small fraction of non-hexagonal (NHx) rings in a perfect hexagonal lattice [1, 2]. However, it is difficult to understand by which mechanism takes place such a regular incorporation of isolated NHx rings. Recently a model based on a ratio of NHx/ H rings slightly larger than unity was proposed [3]. In this paper the tubular structures generated in a systematic way, following a similar wrapping procedure like for straight carbon nanotubes, are investigated. This model may account for the multiple coils, [4] and the various experimentally observed coils [5, 6, 7].

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2. S. Ihara, et al., Phys. Rev. B 48, 5643 (1993).
3. L. P. Biró, et al., Phys. Rev. B, 66, 165405 (2002).
4. C.-J. Su, et al., Chem. Comm., 5, 34 (2002)
5. S. Amelinckx, et al., Science, 265, 635 (1994).
6. L. P. Biró, et al., Europhys. Lett., 50, 494 (2000).
7. L.P. Biró, et al., J. Mat. Sci. Eng. C, 19, 3 (2002)

16:00

BREAK

Session VI: Technology, engineering

Session chair: Elena Obraztsova

16:20 **B-VI.1** -Invited- ELECTROCHEMICAL TUNING OF ELECTRONIC STRUCTURE OF CARBON NANOTUBES AND FULLERENE PEAPODS

Ladislav Kavan, J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, Lothar Dunsch, Institute of Solid State and Materials Research, Helmholtzstr. 20, 01069 Dresden, Germany, Hiromichi Kataura, Department of Physics, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

Single-walled carbon nanotubes (SWCNT) and fullerene peapods (C60@SWCNT, C70@SWCNT) were charged electrochemically in LiClO₄+acetonitrile or in butylmethylimidazolium tetrafluoroborate (ionic liquid). The second electrolyte allows broader window of electrochemical potentials to be applied. The used ionic liquid has also favorable optical properties for in-situ Vis-NIR and Raman spectroelectrochemistry of nanocarbons. Electrochemistry of both nanotubes and peapods is dominated by their capacitive double-layer charging. In-situ Vis-NIR spectra of nanotubes and peapods demonstrate reversible bleaching of the transitions between Van Hove singularities. At high anodic potentials, new optical transitions were activated. They were assigned to electron transfer within partly filled valence band. The bleaching of optical transitions, induced by charge-transfer, is mirrored by quenching of resonance Raman spectra in the region of tube-related modes. The Raman modes of intratubular C60 exhibit considerable intensity increase upon anodic doping of peapods, but these modes are not enhanced at cathodic charging. The "anodic Raman enhancement" is specific for C60@SWCNT only. In the case of C70@SWCNT, symmetric quenching is detected of the C70 Raman modes at both cathodic and anodic potentials. The difference is tentatively interpreted in terms of the mutual position of the HOMO-LUMO levels of intratubular fullerene C60/C70 vs. the Fermi level of the SWCNT wall.

17:00 **B-VI.2**

SYNTHESIS AND PROPERTIES OF ONION-LIKE CARBON: AN OVERVIEW'

Vladimir L. Kuznetsov, Yuriy V. Butenko, Borekov Institute of Catalysis, Lavrentieva 5, Novosibirsk 630090, Russia.

At present two main approaches of onion-like carbon (OLC) production based on (1) a condensation of initially evaporated atoms or small clusters of carbon and (2) a transformation of condensed carbon are known. Only few processes allow producing the significant quantity of OLC. We have developed new process generating hundreds of grams OLC in laboratory. It consists of thermal annealing of nanodiamonds (ND) with a size of 3-6 nm, which production is growing and reach several tons per year. The HRTEM study combined with kinetic investigation of diamond graphitization and the molecule modeling allowed elucidating the formation mechanism of OLC and new type of nanocomposites with different ratio of sp²/sp³ carbon. These OLC based systems were characterized by a wide variety of physical methods, namely Raman spectroscopy, XPS, XRD, EELS, ESR; X-ray emission spectroscopy. Measurements of temperature dependence of electrical resistivity and magnetoresistivity of carbon nanoparticles with different graphitization degrees was used for estimation of their electron transport properties. Two different types of OLC carbon can be produced by these methods: one contains spherical shells another one consists of polygonized shells. Study of X-ray emission spectra of the OLC combined with quantum-chemical simulation led us to conclusion that the spherical onions produced by ND annealing at the intermediate temperature (1400–1900 K) have holed structure of internal shells. The formation of such defects stabilized within nanoparticle volume can provide the appearance of new unusual properties of carbon materials (electronic, magnetic and optical properties). The areas of possible applications of OLC will be considered.

17:20 B-VI.3

ION BEAM PROCESSING OF CARBON NANOTUBE

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Ion beams can be used to modify the properties of carbon nanotubes in several interesting ways, as evidenced e.g. by the recent observations irradiation-induced graphite-to-diamond transformations in carbon onions, coalescence and welding of carbon nanotubes. Experiments also show that ion bombardment and carbon nanotubes may be employed for fabricating metal nanowires using multi-walled nanotubes as masks. Using classical and tight-binding interatomic interaction models, we are systematically studying the fundamental physics of ion irradiation effects in carbon nanotubes. By simulating impacts of energetic ions, we examine production of defects in individual nanotubes, both suspended and deposited on substrates. We demonstrate that even though energetic ions produce strong local damage, nanotubes can preserve their overall shape under ion bombardment and anneal much of the damage due to defect migration and dangling bond saturation. In order to determine to what extent nanotubes can be used as masks against irradiation, we simulate ion irradiation of multi-walled nanotubes. We derive an equation which for a given nanowire material allows one to estimate the theoretical limit on the minimum width of the wire. We also study ion bombardment of crossed nanotubes as a technique to join nanotubes. We demonstrate that ion irradiation should result in the welding of crossed nanotubes, both suspended and deposited on substrates.

17:40 B-VI.4

MULTIWALL CARBON NANOTUBES: FUNCTIONALIZATION AND MECHANICAL PROPERTIES OF MWNTs/EPOXY COMPOSITES

Y. Breton(a), G. Désarmot(b), R. Benoît(a), S. Delpoux(a), L. Boufendi(c), J.P. Salvetat(a), C. Sinturel(a), F. Béguin(a) S. Bonnamy(a), (a)CRMD, CNRS-Université, 1rue de la Férollerie, 45071 Orléans Cedex 2, France, (b)ONERA, 29 avenue de la Division Leclerc, 92322 Châtillon Cedex, France, (c)GREMI, CNRS-Université, 14 rue d'Issoudun, 45067 Orléans Cedex 2, France

Theoretical studies have shown that nanotubes could be good matrix reinforcing materials for the next generation of composites due to their intrinsic properties. In the present study, multiwalled nanotubes synthesized by catalytic decomposition of acetylene were submitted to several treatments in order to modify their surface chemistry and/or microtexture, then mechanical tests were performed on epoxy resin loaded with MWNTs. Cold RF plasma treatments performed in different atmospheres (argon/ammonia, oxygen and methyl methacrylate) allow a selective grafting of chemical groups on MWNTs surface or a coating of a thin PMMA derived film. The modifications due to chemical oxidation and thermal treatment were investigated by XPS and TEM. For mechanical tests, pristine and functionalized MWNTs (1 to 6 wt%) were dispersed in epoxy resin. Nanotubes surface functionalization leads to an increase of the Young modulus composite by 30% due to enhancement of the nanotubes wetting, improving the dispersion in the matrix and the interfacial shear strength. The influence of the specific surface area on nanotubes dispersion, therefore on rigidity, is also shown. In the case of annealed (2400 ÅC) then oxidized nanotubes, a 60 % increase of the modulus is obtained, due to intrinsic modulus increase of the nanotubes. However the tensile strength of the composites is reduced due to the high surface over volume ratio of nanotubes and their isotropic orientation in the matrix.

18:00 B-VI.5

PURIFICATION AND ISOLATION OF SINGLE WALLED CARBON NANOTUBES

Elizabeth Gregan, S. Keogh, T. Hedderman, L.O'Neill, G. Chambers, H.J. Byrne, Facility for Optical Characterisation and Spectroscopy (FOCAS), School of Physics, Dublin Institute of Technology, Dublin 8, Ireland Single Walled Carbon Nanotubes (SWNT) exhibit many unique physical and chemical properties. Although there are many different production methods none have been successful in producing large quantities of specific diameter, 100% pure tubes. This work involves the purification and isolation of SWNT initially produced from batch processes such as the HiPco process, using two different systems. The first involves the use of conjugated polymers such as PmPV and non conjugated polymers such as Perspex to selectively isolate certain tubes. These hybrid systems are explored using spectroscopic and thermal techniques to determine specific interactions. The second uses SWNT as templates for organic molecules such as terphenyl and anthracene. Improvements in the solubility of SWNT's are seen as a result of specific interactions with the oligomers. Suspensions formed in toluene with these oligomers and the SWNT's are seen to be stable over prolonged periods. Spectroscopic analysis clearly shows an interaction between the tubes and the oligomers. The electronic properties of the oligomers are greatly affected by the presence of the SWNT's and this is clearly shown in the quenching in the fluorescence of the oligomer on the addition of SWNT's. Raman studies further support the hypothesis of specific interaction as composite spectra of the oligomers and SWNT 's have been obtained

18:20 B-VI.6

INVESTIGATION ON PREPARATION OF CARBON NANOTUBES BY DC ARC DISCHARGE UNDER N₂ ATMOSPHERE

S. Cui, Peter Scharff, C. Siegmund, K. Risch, D. Schneider, S. Klutzer, Institute of Physics, Technische Universität Ilmenau, Ilmenau 98694, Germany, and L. Spiess, H. Romanus, J. Schawohl, Institute of Materials Science, Technische Universität Ilmenau, Ilmenau 98694, Germany

Preparation of carbon nanotubes (CNTs) and formation of carbon nanostructures (CNSs) by DC arc discharge under N₂ atmosphere were investigated. The effects of N₂ pressure and flow rate on the yield and morphology of CNTs and CNSs were investigated separately. SEM, TEM, HR-TEM, EDX in SEM and TEM, XRD, and investigation on air oxidation stability were used to characterize the products. Mainly multiwalled CNTs, and some single-walled and little double-walled CNTs were formed. The maximum yield of CNTs was obtained at a N₂ pressure of 300 Torr and a flow rate of 400 mL/min. And the CNTs formed in the cathode deposits were in an aligned state. The inner diameters proved to be increased with the increase of N₂ pressure. Several different CNSs were observed in the products collected from different parts within the arc evaporator. By XRD measurements we found that such CNSs were doped by nitrogen atoms.

Nanoscience of Integrated Nanosystems

Session Chair: Michael Kohler

B/PI.1 SCANNING PROBE MICROSCOPY AND SPECTROSCOPY OF CARBON NANORODS GROWN BY SELF-ASSEMBLY

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Nanotechnology can be operated by two opposite approaches labeled 'top down' and 'bottom up'. Whereas 'top down' methods will soon reach its limits, the 'bottom up' method is still in its infancy. But there is a principle in nature pushing forward the latter: self-organization. While the macroscopic characterization of self-assembled fullerene derivatives is routinely performed using TEM, optical absorption spectroscopy, XRD, AFM and light scattering measurements, there is surprisingly few direct experimental evidence available about the arrangement of the self-assembling units on the molecular/atomic level. We present a detailed STM/AFM report on fullerene based self-assembled entities using an ionic C₆₀ derivative, complemented by spectroscopic measurements and high-resolution light-microscopy. The observed structures appear either rod-like or dendritic. Characteristic features of the Raman and mid-IR spectrum allow us to differentiate between the bulk and the self-organized form of the material. Raman spectroscopy is also used to study the thermal stability of the system.

B/PI.02 PREPARATION AND PROPERTIES OF CARBON NANOCCLUSERS

Seraphin Supapan, Department of Materials Science and Engineering, The University of Arizona, Tucson, U.S.A

Morphologies and properties of carbon nanoclusters depend strongly on the preparation procedures. This presentation will provide an overview of the various carbon products from four different methods of preparation: the conventional arc discharge, the carbon monoxide disproportionation, the modified arc discharge, and the methane decomposition. The conventional arc discharge produces fullerenes in the soot and numerous carbon nanotubes in the cathodic deposit. The yield of fullerenes v.s. nanotubes can be adjusted by changing the pressure of the arc chamber, the current and the voltage between two electrodes.

Encapsulation of metals into the carbon nanocages provides new aspects of materials science for essentially two reasons. (1) The encapsulant consists of a small number of atoms that is measurably confined by the size of the carbon cage; (2) collective physical properties of these clusters are novel and can be studied as a function of the number of the atoms providing insight into size-dependent properties. In the nanometer size regime, the number of atoms in the bulk of the particle is close to that in the surface region. By varying the size of the particle, the effects of the bulk vs. surface region can be studied independently. These effects are pronounced in the group of the transition metals where the collective properties vary strongly depending on the number of electrons in d-orbitals. Specifically, the ferromagnetic properties of Fe, Co, and Ni particles inside carbon nanocages will be discussed.

B/PI.03 PORPHYRIN SELF-ASSEMBLED MONOLAYERS WITH A CONTROLLED ORIENTATION ON GOLD(111)

V. Arima, R. Blyth, R. Del Sole, F. Matino, G. Mele, G. Vasapollo, R. Rinaldi, R. Cingolani, National Nanotechnology Laboratory of INFN - Lecce and Department of Innovation Engineering, University of Lecce, Department of Innovation Engineering, Via per Arnesano, 73100 Lecce, Italy

Nano-scale electronic devices can be fabricated using single molecules or monolayers of molecules connected to metallic nano-contacts. Single molecule devices are expected to have interesting electronic properties, but devices based on molecular monolayers are easier to fabricate and could be potentially more reliable. Relatively stable and highly ordered conducting and semi conducting films can be simply produced by self-assembly method, e.i. attaching identical molecules to a flat gold surface through a covalent bond between Au and a molecular thiol group. Solid films of oriented porphyrins were realized through a simple procedure that allow the positioning of the macropilane of the molecule parallel to the electrode surface. We prepared a 4-aminothiophenol self-assembled monolayer (SAM) on gold(111) followed by in situ axial legation of Cobalt porphyrins. The SAMs with and without immobilized porphyrins were characterized by UHV Scanning Tunneling Microscopy (STM) and Spectroscopy (STS). We clearly observed Au(111) herringbone structure reconstruction probably due to adsorption/desorption processes of molecules. Moreover, STM atomic resolved images and Scanning Tunneling Spectroscopy (STS) measurements indicated that the immobilization of molecules induce electronic perturbation of gold surface. This effect is probably due to SAMs oriented dipole layers laying between the metal and the organic material.

B/PI.04 BIOMOLECULAR DEVICES: FIELD EFFECT TRANSISTOR AND FEASIBILITY REPORT

G. Maruccio, P. Visconti, S. D'Amico, V. Arima, A. Bramanti, R. Cingolani, R. Rinaldi, National Nanotechnology Laboratory of INFN, Università di Lecce, 73100 Lecce, Italy, S. Masiero, T. Giorgi, G. Gottarelli, Department of Organic Chemistry, University of Bologna, 40126 Bologna, Italy

The realization of a transistor-like device represents a starting point for the development of a molecular electronics roadmap. Recent demonstrations suggest that the obstacles to the accomplishment of molecular electronic devices are more technical than conceptual, mainly related to the tremendous interconnection problems. In this work, a field effect transistor based on a deoxyguanosine derivative (a DNA base) is reported and the main factors affecting long-term stability are faced. Nanodevices were fabricated by cast deposition of molecules on two Cr/Au arrow-shaped electrodes, with separation of about 30-40nm, defined by electron beam lithography. A Ag back electrode was deposited to produce a field-effect transistor. Current-voltage experiments were carried out at room temperature: typical curves are asymmetric with a rectification ratio around 3. The transconductance and the output resistance of the device are 146 pA/V and 5.2 GOhm, respectively, resulting in a maximum voltage gain as high as 0.76. An equivalent circuit of the device and a physical interpretation of the transport mechanism are also proposed. Several tens of nominally identical devices were investigated to test reproducibility of the device physical parameters, its reliability and time stability. We found that small differences in the self-assembly of molecules could partially limit the device reproducibility and that there could be some device damage during operation (mostly due to heating and field effects). Possible strategies to solve these problems are proposed.

B/PI.05 A FIELD EFFECT TRANSISTOR BASED ON REDOX PROTEIN AZURIN: DESIGN, FABRICATION AND CHARACTERIZATION

Adriana Biasco, G. Maruccio, P. Visconti, A. Bramanti, P. Calogiuri, R. Cingolani and R. Rinaldi, NNL - National Nanotechnology Laboratory of INFN - Lecce and Department of Innovation Engineering, University of Lecce, Via per Arnesano, 73100 Lecce, Italy

Molecular electronics intends to provide an alternative approach to scaling down electronic components to nanometer scale. In this work, the fabrication and characterisation of a field effect transistor (FET) based on redox protein azurin are reported. These metallo-proteins mediate electron transfer in the denitrifying chain of Pseudomonas bacteria and exhibit self-assembly properties, therefore they are good candidates for bio-electronic applications. Two arrow-shaped Cr/Au 100nm-separated electrodes are fabricated by means of electron beam lithography on Si/SiO₂ and a gate electrode is deposited on the Si backside. Azurin monolayers are self-assembled onto silane functionalised surfaces and characterized by atomic force microscopy. Transport experiments, carried out at room temperature and ambient pressure, show in some cases FET behavior with conduction modulated by the gate potential. We suggest that transport through the protein copper site is responsible for conduction whereas the modulation is correlated to the field effect. However, after some cycles of measurement, current level drops because of device aging, due to both molecular active layer degradation and electrode burning, as revealed by SEM investigation. A correlation between electrical response and morphological changes of the molecular active layer is observed. Though a better control of the main parameters affecting the reproducibility has to be achieved, the demonstration of such field effect device is an important step towards the development of molecular electronics.

B/PI.06 CATALYTIC CARBONIZATION OF WOOD CHARCOAL: GRAPHITE OR DIAMOND?

Toshimitsu Hatr(a), Tomas Vystavel(b), Paul Bronsveld(b), Jeff De Hosson(b), Hikari Kikuchi(c), Kouei Nishimiya(c), (a)Yuji Imamura Wood Research Institute, Kyoto University, Japan, (b)Department of Applied Physics, Materials Science Center, University of Groningen, The Netherlands, (c)S S Alloy, Japan

In a recent paper Banhart discusses the stability of diamond under the influence of an electron beam. The most stable bonding configuration of carbon at NTP is graphite with an energy difference of ~0.02 eV per atom over diamond (Saada, see also Wang et al.). Due to the high energetic barrier between the two phases, the transition from diamond to graphite at normal conditions is very slow. Moreover, in a certain temperature window and with a beam voltage above a characteristic accelerating voltage of 100 kV, diamond is more stable than graphite. Further exposure at room temperature does destroy the diamond structure again. The recent interest in diamond with respect to device technology and in diamond like coatings for tribological applications makes these findings of crucial importance as the dimensions are of a nano scale and transmission electron microscopy is the method of choice. We came in from the other side, as we were trying to make graphite out of biomass carbon. We have studied catalytic carbonization of wood charcoal using Al-triisopropoxide as a catalyst. In this contribution we report on a typical finding with respect to the fundamental changes in our carbon samples while using TEM analysis.

B/PI.07 C70 AND C60 MONOLAYERS ON Au(111) AT THE LIQUID-SOLID INTERFACE: AN STM STUDY

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The adsorption of C70 and C60 molecules on reconstructed and non-reconstructed Au(111) surfaces has been investigated by using scanning tunneling microscopy (STM) and spectroscopy (STS) at the liquid-solid interface and at room temperature. At low coverage, C60 decorates the step edges, forming two-dimensional islands on the terraces which indicate that the molecules have a high mobility even at room temperature. At higher coverage, the C60 molecules form a close-packed $2\sqrt{3}\sqrt{3}R30^\circ$ structure commensurate with the Au(111) surface. In the same conditions, C70 molecules present a close-packed hexagonal but incommensurate arrangement. Coadsorption experiments of C70 and C60 demonstrate that it is possible to embed one single C70 molecule in a C60 two-dimensional matrix, allowing in particular the comparative study of their electronic properties. Remarkably, the amplitude of the Z modulation for C70 is much higher (about two times) than the C60 modulation. Taking in account the close diameters of these two types of fullerenes, this drastic difference is attributed to their electronic structure rather than to their geometric shape.

B/PI.08 CARBON NANOTUBE FILLED POLYCARBONATE COMPOSITES PRODUCED BY MELT MIXING AND THEIR USE IN BLENDS WITH POLYETHYLENE

Petra Pötschke, Arup R. Bhattacharyya, Department of Polymer Reactions and Blends, Institute of Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany

Carbon nanotubes (CNT) containing polymer composites have attracted much attention due to opportunity to get electrically conductive polymer materials at much lower filler contents as compared to traditionally used conductive fillers, like carbon black. This contribution presents composites of polycarbonate (PC) with varying amounts of multi wall carbon nanotubes (MWNT) which were produced by diluting a masterbatch of PC with 15 wt% MWNT using melt mixing in a DACA-Micro Compounder. During the melt mixing procedure, which is the preferred method of composite formation in many cases, the tendency of MWNT to form aggregates may be minimized by appropriate application of shear. Electrical resistivity measurements indicated percolation of MWNT between 1 and 1.5 wt%. Atomic Force Microscopy showed the state of MWNT dispersion and indicated no preferred orientation in extrusion direction. Eventually, a conductive PC-2 wt% MWNT composite was melt mixed with polyethylene in order to get co-continuous blends exhibiting double percolation. Conductivity of the blends could be achieved in compositions down to 30 vol% filled PC in which the total MWNT content was only 0.48 vol%. These blends exhibited co-continuous structures wherein the nanotubes appear to bridge the phases

- B/PI.09** CURRENT-VOLTAGE MEASUREMENTS ON SINGLE MOLECULES AT LOW TEMPERATURES
Roman Krahne(a), Tali Dadosh(b), Yoav Gordin(a), Amir Yacoby(a), Hadas Shtrikman(a), Diana Mahalu(a), Israel Bar-Joseph(a) and Joseph Sperl(b), (a)Department of Condensed Matter Physics, (b)Organic Chemistry Department, Weizmann Institute of Science, 76100 Rehovot, Israel
 Recently, there is a growing interest in the study of the electrical properties of organic soft matter like molecules. In this work we use gold nanoclusters to chemically bond to benzene-dimethyl-thiol molecules. In the chemical fabrication the concentrations are chosen in such a way, that two gold clusters bind to one molecule, i.e. gold cluster-molecule-gold cluster dimers are obtained. The positioning of the dimers between the electrodes is done using the technique of electrostatic trapping [1]. The electrodes are either fabricated by conventional electron beam lithography, or by a novel method combining optical lithography, selective etching and molecular beam epitaxy (see Ref. [2]). In the latter case the flexibility in MBE growth enables us to incorporate a doped layer that acts as a gate electrode. The transport measurements were performed at low temperatures and we obtain stable current-voltage (IV) responses. The dominant feature we observe in the IV's is a clear gap around 0V, with the gap size in the range of hundreds of mV, varying for different devices. Control experiments on single gold clusters give a Coulomb blockade gap of about 3 mV, roughly two orders of magnitude smaller, so that we can attribute the large gap as a property of the dimer. We demonstrate gating feasibility of our setup on single gold clusters and present gate-dependent data on the dimer structures.
 [1] A. Bezryadin, C. Dekker, and G. Schmid, Appl. Phys. Lett. 71, 1273, 1997
 [2] R. Krahne et al., Appl. Phys. Lett. 81, 730, 2002
- B/PI.10** USE OF SMALL-ANGLE NEUTRON SCATTERING IN STUDIES OF FULLERENE SOLUTIONS
 V.L. Aksenov, M.V. Avdeev, Frank Lab. of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Reg., Russia
 The review covers experimental data obtained by means of small-angle neutron scattering (SANS) from a number of fullerene solutions. SANS is a powerful technique to reveal structural peculiarities at the scale of 1-100 nm, and in some cases can be effectively used for studying the structure of fullerene solutions. For molecular solutions of fullerenes SANS allows one to detect whether the solvation of fullerenes or formation of fullerene clusters take place. Results of SANS experiments on fullerene solutions in carbon disulfide, toluene, chloronaphthalene are discussed. Recent SANS investigations of stable aqueous dispersions of fullerenes are presented. The interest to these systems is connected with their possible medical applications. They are produced by the addition of fullerene solutions in organic solvents to water with simultaneous ultrasound treatment. The SANS contrast variation based on different mixtures of light and heavy water provides us with the information about structural features of the aggregates in addition to complementary techniques such as electron microscopy, UV-Vis spectroscopy, scanning calorimetry and others. Examples of SANS applications in structural investigations of complex fullerene solutions including fullerenes in binary mixtures, as well as solutions of fullerene derivatives are given.
- B/PI.11** CHARACTERISATION OF NANOSTRUCTURED COATINGS BASED ON OXIDES FOR TRIBOLOGICAL APPLICATIONS
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 The aim of the project is to develop single layer nanostructured coatings combining oxidation resistance, temperature stability, and chemical inertia with wear endurance in various environments. In order to reduce the brittleness of ceramic materials, we embedded ZrO₂ nanoparticles in a metallic matrix. Coatings were produced using a reactive magnetron sputtering. The deposition parameters (substrate Bias, pressure) were correlated to the structure and the composition of the coating (phase, topography). The structure was studied by TEM and SEM, the topography by AFM, and the composition by XPS. In order to investigate the homogeneity of the plasma, we determined the ion current and the ion energy by Langmuir probe. The formation of nanoparticles in the plasma was studied by capturing particles in-situ with TEM-grids. Mechanical properties like hardness and brittleness were determined by nanoindentation. Wear resistance in dry and humid environment is presented.
- B/PI.12** TEMPERATURE DEPENDENT ESR OF Li DOPED CHALCOGENIDE NANOTUBES
Denis Arcon(a,b), Andrej Zorko(a), Pavel Cevc(a), Ales Mrzel(a), Maja Remskar(a), Dragan Mihailovic(a), Robert Dominko(c), (a)Institute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia, (b)Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia, (c)Miran Gaberscek National Chemistry Institute, Hajdrihova 19, 1000 Ljubljana, Slovenia
 X-band ESR of lithium doped MoS₂ nanotubes will be reported for temperatures between room temperature and 4 K. Two distinct ESR components were observed in all samples studied: a narrow component with a linewidth of about 4 G and a broad component with a linewidth of more than 800 G. The broad ESR component is attributed to Mo d-orbital-derived conducting band of MoS₂ nanotubes. The large weakly temperature dependent ESR spin susceptibility of charged MoS₂ nanotubes is thought to reflect strong electronic correlations and one-dimensional electronic structure with the presence of van Hove singularities in the density of states. The broad ESR component is discussed in terms of conducting electrons coupled to defects and in terms of random-exchange Mo Heisenberg chain model. The narrow component is suggested to be due to the formation of small spin clusters.
- B/PI.13** DIRECT OBSERVATION OF ENCAPSULATED METAL ATOMS IN METALLOFULLERENE PEAPODS
Kazu Suenaga, T. Okazaki, T. Shimada, R. Taniguchi, H. Shinohara, S. Iijima, AIST and Nagoya University, Higashi 1-1-1, 305-8565 Tsukuba, Japan
 High resolution transmission electron microscopy (HR-TEM) with the single atom sensitivity is able to visualize the intramolecular structure of the metallofullerenes inside single-wall carbon nanotubes. Direct observation of metal atom positions inside each fullerene molecule has led to a successful determination of the molecular symmetry among possible isomers for Sc₂@C₈₄. A giant motion of encapsulated atoms in metallofullerene molecules has been clearly observed in Gd₂@C₉₂ peapods.

Theory, Modeling

Session Chair: István László

- B/PI.14** ASSIGNMENT OF CHIRAL VECTORS IN CARBON NANOTUBES (CNTs)
Ch. Kramberger, R. Pfeiffer, Ch. Schaman, H. Kuzmany, Institut für Materialphysik, Universität Wien, Vienna, Austria
All physical properties of a SWCNT are defined by its chiral vector. The chiral vector is the lattice vector of graphene that becomes the circumference when rolling up a stripe of graphene into a tube. Common single wall CNTs (SWCNTs) have diameters between 1 nm and 3 nm. Double wall carbon nanotubes (DWCNTs) were derived from peapods (C60@CNT) by annealing at 1300 ÅC in an active vacuum ($< 5 \cdot 10^{-7}$ mbar). They are a novel phase of carbon and have raised a major scientific interest recently. The inner NTs can have diameters as small as 0.5 nm. In this contribution we will focus on the radial breathing mode (RBM) with scales with $1/d$. So far the different RBMs of bulk samples could not be resolved because of line broadening and their high density. However the Raman spectra of these DWCNTs show well distinguishable RBM lines of the different inner tubes, besides the usual ones. The former are rather well separated because of their small diameters and more sparse geometrically allowed diameters. We have performed Raman measurements with different laser wavelengths ranging from 325 nm to 1064 nm. The evaluation of these spectra has led to a full assignment of the chiral vectors to the spectroscopic lines. The results will be compared to assignments of chiral vectors obtained by other methods.
- B/PI.15** THEORETICAL STUDY ON JUNCTION OF PORPHYRIN CHAIN FOR NANOSCALE DEVICE
Hiroshi Mizuseki(a), Nobuaki Igarashi(a), Rodion V. Belosludov(a), Amir A. Farajian(a), Chiranjib Majumder(b) and Yoshiyuki Kawazoe(a), (a)Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan, (b)Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Mumbai, India
Recently, molecular electronics has attracted strong attention as a "post-silicone technology" to realize a future nanoscale electronics device. A quarter century ago Aviram and Ratner (1) have first demonstrated how an organic molecule could function as a molecular rectifying diode. A rectifier could be built by combining these two molecular subunits which have acceptor or donor group (2-3). Porphyrin possesses good electron-donating properties due to its large easily ionized π -electron system, and a long molecular wire of fully conjugated porphyrin polymer was reported by Tsuda et al. (4). In this study, we propose rectifier diode can be created by combining two metal porphyrin molecules with different metal atom. To estimate the electron transport through this molecule, we have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), providing a strategy by which the rectifying properties of the porphyrin polymer can be understood. This study was performed through Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.
- B/PI.16** MOLECULAR POLARIZABILITIES OF CARBON NANOTUBE MODELS
Francisco Torrens, Institut de Ciència Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot (Valencia), Spain
The interacting induced dipoles polarization model implemented in our program POLAR is used for the calculation of the dipole-dipole polarizability. The method is tested with single-wall carbon nanotube (SWNT) models as a function of nanotube radius and elliptical deformation. The results for polarizability follow the same trend as reference calculations performed with our version of program PAPID. For the zigzag tubes, the polarizability is found to follow a remarkably simple law, i.e., varies as the inverse of the radius. A dramatic effect is also found with elliptical deformation. It is found that the polarizability and related properties can be modified continuously and reversibly by the external radial deformation. These results suggest an interesting technology in which mechanical deformation can control chemical properties of the carbon nanotubes. POLAR calculations differentiate more effectively than PAPID computations among SWNT models with increasing radial deformation. POLAR calculations discriminate more efficiently than PAPID computations between the effective polarizabilities of the highest and lowest curvature sites. This remarkable and significant tunable polarizability can have important implications for metal coverage of metals on nanotubes and selective adsorption and desorption of foreign atoms and molecules on nanotubes and can lead to a wide variety of technological applications, such as catalysts, hydrogen storage, magnetic tubes, etc.
- B/PI.17** COMPUTER SIMULATION OF SUPPORTED C60 FULLERENES FRAGMENTATION BY ELECTRON BEAM
M.V. Makarets(a), Yuriy I. Prvlutskyy(b), O.V. Ogloblya(b), (a)Kyiv National Shevchenko University, Departments of 1)Physics and (b)Biophysics, Volodymyrska str. 64, Kyiv 01033, Ukraine and P. Scharff, Technical University of Ilmenau, Institute of Physics, 98684 Ilmenau, Germany
Now the particle beam technology is intensively investigated with the purpose of creation and modification of the different electronic nanoscale systems. In particular, the ensembles of supported carbon clusters with extremely low size dispersion and with properties which can be transformed by the variation of the band gap and the density of states near Fermi-level can be used for development of new generation of electronic devices. In the present report the computer simulation of the electron beam induced fragmentation of C60 fullerenes supported by surface and in fullerite film was carried out. In particular, we have developed the Monte-Carlo simulation of the radiation-induced defect generation and its dynamics using the TRIM-package for random targets and MARLOW-code for crystal targets, the simulation of the atomic excitation and ionization processes in the target using the Firsov and Lindhard-Scharff models and semi-empirical approximations. The time dependence and spatial distribution of both the radiation defects in the target, specifically vacancies, interstitial atoms and more complicated defects of crystal structure and the electron excitation and ionization of target atoms along the projectile traces were calculated. This work was supported by INTAS grant (N 2136).
- B/PI.18** LOW-TEMPERATURE SPECIFIC HEAT OF CARBON NANOTUBE SYSTEMS
Valentin N. Popov, Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria
The low-temperature specific heat of isolated single-walled and multiwalled carbon nanotubes as well as finite bundles of single-walled carbon nanotubes is calculated within a valence force field model of the lattice dynamics. It is shown that the q^2 behavior at small wavevectors of the transverse acoustic phonons of the studied systems gives rise to low-temperature phononic specific heat which varies with temperature T as \sqrt{T} . Such a temperature dependence of the phononic specific heat of quasi-one-dimensional systems is predicted for the first time. Recently, this dependence has been confirmed by low-temperature experimental data on finite bundles of single-walled carbon nanotubes.

- B/PI.19** STRUCTURES OF "CUBIC GRAPHITE", CARBENE AND OTHER UNCONVENTIONAL FORMS OF CARBON AND BORON NITRIDE
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 Besides a graphite and diamond the abundance of many other forms of carbon and boron nitride is known many years ago to exist, in particular, so called "cubic graphite", hexagonal a-carbene, etc. However their structure remains to be unresolved until now. Recently "cubic graphite" with 1-5 GPa in hardness and other carbon forms have been synthesized by Carbex, Ltd. on a specially developed gas high-pressure-temperature equipment under $P < 1000$ bar and $T < 1$ GPa [1]. Key to interpret such structures was given in [2], where cubic crystals built from fullerenes B₁₂N₁₂, B₂₄N₂₄ have been suggested, in particular, a "hyperdiamond" with C₂₄ molecules in a diamond lattice, and bcc-fullerite $\sqrt{2}$ -B₁₂N₁₂ and $\sqrt{2}$ -N₂₄ ($\sqrt{2}$ =Li, Be, etc.) with a density $\rho = 4.11$ - 5.28 g/cm³ higher than for diamond. Here structures of above unconventional forms of C and BN is established for the first time. In particular, the agreement between theoretical and experimental values of the lattice constant, density and all lines on Debye X-ray diffraction patterns give us evidence that the "cubic graphite" is a simple cubic fullerite of copolymerized N₂₄ molecules bonded with square faces. Like zeolites all such phases contain 2D lattices of cylindrical nanochannels in their structure resulting to unusual optical, chemical and other properties.
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- B/PI.20** ATOMIC SPONTANEOUS DECAY RATE ENHANCEMENT NEAR A CARBON NANOTUBE
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 Spontaneous decay rate variation of an atom located near media interfaces and/or optical inhomogeneities, the Purcell effect, was formerly investigated for various types of microcavities, optical fibers, photonic crystals, etc.. The effect took on special significance recently in view of rapid progress in physics of low-dimensional nanostructures. We analyze the Purcell effect for an excited atom in the vicinity of a single-wall carbon nanotube (CN). We model the excited atom by a two-level system with an electric dipole transition allowed. CN optical properties are described by effective boundary conditions accounting for CN axial conductivity generated by both intraband and direct interband transitions of pi-electrons. We have calculated the atomic spontaneous decay rate within the framework of the model described. Both weak and strong atom-field coupling regimes were analyzed. In the weak coupling regime, our calculations show the drastic increase of the spontaneous decay rate (by up to 4 - 5 orders of magnitude) compared with that of the same atom in vacuum. Such an increase is physically interpreted as being due to the electromagnetic vacuum renormalization: the density of photonic states near CN effectively increases since, along with ordinary free photons, there appear surface photonic states coupled with CN electronic quasiparticle excitations. These latter ones are responsible for the nonradiative atomic decay (photon emission by the atom with subsequent CN quasiparticle excitation). The drastic increase of the atomic spontaneous decay rate near CN is associated with the nonradiative decay via surface quasiparticle excitations in the nanotube.
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- B/PI.21** SIMULATION OF CARBON NANOTUBE FIELD EMISSION CATHODES USING MEASURED FIELD ENHANCEMENT DISTRIBUTIONS
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 The possibility of using carbon nanotubes as field emission electron sources has attracted a lot of interest in the recent years. The advantage of using carbon nanotube (CNT) cathodes resides in several facts among which the most important are: (i) using CVD methods planar cathodes can be fabricated in simple and cheap processes on large surfaces; (ii) emission can be achieved at low macroscopic fields (of the order of 2 V/mm) due to the large aspect ratio of the CNT and (iii) due to the chemical inertness and mechanical toughness CNT field emitter are very robust. Despite these advantageous properties, achieving high emission site density (above 1 mio. per cm²) and high emission current density (above 1 A per cm²) remains challenging. The related issues here are emission homogeneity, single emitter I-V characteristic and critical emission current per single emitter. We will present how the relevant parameters to characterize planar CNT field emission cathodes can be obtained using scanning anode field emission microscopy (SAFEM) and how these parameters can be introduced in simulations of the global cathodes behavior. We will discuss measurements and mechanisms of emitter degradation and show simulations of the global cathode degradation at high emission current densities. We will further address the issue of using ballast resistors to improve the emission homogeneity.
- B/PI.22** COMPUTER SIMULATIONS OF FLOW IN NANOSCOPIC GEOMETRY
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 Large scale molecular dynamics (MD) computer simulations are used to study the flow of fluids in nanoscopic pores. We discuss in detail the different steps that are required to model such systems in order to gain insight into the microscopic properties of real materials such as carbon nanotubes. An important issue in this context is for instance the model for the fluid-wall interactions: First these interactions may affect the structural and dynamical properties of the fluid (e.g. a possible layering or a slower or faster dynamics near the wall). Second, they determine - apart from the shear rate, of course - the effective hydrodynamic boundary conditions, e.g. in a steady-state Poiseuille flow. Furthermore, if one wants to extract transport coefficients such as the shear viscosity from Non-Equilibrium MD the choice of the thermostat is very important because thermostats always introduce an artificial dynamics. All these issues are addressed by considering two systems, namely silica between "Lennard-Jones" walls and a simple fluid in a carbon nanotube.

- B/PI.23** LITHIUM INTERACTION WITH POLYCYCLIC AROMATIC HYDROCARBONS: A DENSITY FUNCTIONAL THEORY STUDY
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The most common negative electrodes in lithium-ion batteries are made by carbonaceous insertium compounds such as synthetic graphite, carbon fibers, etc. [1]. At ambient temperature, there is a limit to the amount of lithium that can intercalate pure graphite: one lithium per six carbon atoms to form the LiC₆ compound. In addition, in carbonaceous materials containing substantial hydrogen, lithium appears to reversibly bind near hydrogen atoms [1]. The binding mechanism in 'soft' carbon materials, that is in carbonaceous materials containing a considerable amount of hydrogen, has been investigated by several authors by considering small aromatic hydrocarbons [2,3]. In this work we investigate the interaction of lithium with a considerably large polycyclic aromatic hydrocarbon: hexabenzocoronene C₄₂H₁₈. We carried out quantum chemical calculations with the hybrid B3LYP functional and the 6-31G* basis set and investigated the equilibrium geometries of several structures that correspond to different interaction sites for lithium. From the computed equilibrium structures the preferential sites for lithium interaction are identified. It is shown that the most stable structures correspond to lithium bound to the periphery of the hydrocarbon in agreement with previous experimental findings. The structural and energetic characteristics of these compounds will be discussed.
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- B/PI.24** COMPUTING TEMPERATURE-DEPENDENT RELATIVE ST ABILITIES OF HIGHER FULLERENES: C₈₄ AND C₉₄ IPR SET
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The 24 isolated-pentagon-rule (IPR) isomers of C₈₄ are optimized at HF/6-31G* and SAM1 levels of theory. Harmonic vibrational frequencies are calculated by SAM1 method. Energetics is combined with entropy contributions so that a proper Gibbs free energy treatment is possible. Results of temperature-dependent relative stabilities have indicated that not only the two most experimentally prevalent isomers (22:D2 and 23:D2d) are two most populated species with a ratio of about 1.8:1, but also the recently experimentally assigned minor isomers (24:D6h and 19:D3d) were shown with an abundance ratio of 3:2 within a broad temperature area. The HF/6-31G* evaluations of the equilibrium isomeric composition of C₈₄ agree well with the recent experimental data. The similar treatment is further applied to 134 C₉₄ IPR isomers. If temperature effects are considered accordingly, a good agreement with experimental observation can be achieved.
- B/PI.25** METAL CLUSTERS AND POSSIBILITY OF THEIR STABILIZATION IN CRYSTALLINE AND AMORPHOUS MULTIFUNCTIONAL MATERIALS
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Metal clusters retain continuous interest both for basic research and applications in different branches of material science (catalysis, optics, bioactive properties, etc). Nuclearity of clusters is a key factor providing their properties. Applications require to keep clusters as stable species within solid matrices which should stabilize the clusters and admit occurrence of their functional features. A number of materials of the different chemical nature can be used for incorporation of metal clusters, however, the proper size-control is possible when geometric obstacles exist for cluster growth and aggregation. Zeolitic crystal lattices and nanometer-sized pores of amorphous silica materials provide these obstacles and demonstrate stabilization of clusters from silver, copper, gold, platinum, etc. In the present work, we simulate geometry and electronic structure of a series of silver and copper clusters, Ag_n and Cu_n (n<20), with ab initio MOLCAO calculations. A variety of geometrical isomers were calculated by the RHF and UHF methods including configuration interaction at the MP2 level and CIS taking the 19e effective core potential for Ag and all-electronic basis set for Cu. The most stable isomers were selected from the point of view of fitting the size of zeolite cavities (e. g. in the Ag₈ family), and electronic absorption spectra were estimated and compared with observable optical data both for metal-zeolite and metal-silica systems. Energies of the electronic transitions of the clusters with appropriate geometry and nuclearity enter the range corresponding to wavelength less than 350nm that allows us to distinguish them from the plasmon resonance bands due to the larger particles simulated by the another way, with the Mie theory.
- B/PI.26** EXCITON EFFECTS IN CARBON NANOTUBES
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The large binding energy of excitons in one-dimensional semiconductors has important consequences for the optical properties of these materials. Using a variational effective-mass model, the localization and binding of excitons in semiconducting carbon nanotubes can be calculated as a function of diameter and chirality. Results are presented for both zigzag and chiral nanotubes and the dependence on geometrical properties is discussed. The results are compared to available experimental data.

B/PI.27**NANOCARBON MATERIALS OF POLYMERIZED FULLERENES AND NANOTUBES**

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Nanocarbon materials of polymerized fullerenes or/and single-walled nanotubes (SWNT) are considered. Such structures can be produced as a result of different cycloaddition reactions: (2+2), (2+4), (3+3), and their combinations as well between fullerenes as between nanotube surfaces and/or SWNT caps. Geometrical structures and properties of the following forms are reported:

- 1) semiconducting solids - close-packed 2- and 3-dimensional structures based on (D6h)-C36 [1];
 - 2) new semiconducting 3D polymers on the base of C60 formed as a result of several cycloaddition reactions [2]; new ferromagnetic 2D defect C60 polymer structures [3];
 - 3) chain and 3D semiconducting structures describing high-pressure and high-temperature C70 phases [4];
 - 4) semiconducting polymer structures on the base of SWNT including structures of (n, 0) and (n, n) nanotubes [5];
 - 5) crossing polymerized nanotubes [6], and cap-linked SWNT structures. Some of considered polymer structures have good agreement with experiments: C36 [7]), C60 [8] and C70 [4] materials, SWNT polymers [9].
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B/PI.28**STRUCTURAL RESPONSE OF FULLERENES UPON REDUCTION**

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Due to the high molecular point group symmetries of C60 and C70 (Ih and D5h, respectively) their lowest unoccupied molecular orbitals exhibit a high degree of degeneracy. Thus, the reduction of this fullerenes is expected to lead to pronounced structural responses in the resulting fulleride-anions [1]. Therefore we started systematic studies in the synthesis and structural characterization of compounds containing mono- [2] and dianionic [3] C60- and di- and trianionic C70- fullerides [4] prepared by chemical and electrochemical means. The structure-chemistry of these crystalline fullerides exhibits a high diversity. Nevertheless, the results of experimental and quantum-chemical investigations reveal the structural response of fullerenes upon reduction to be of highly localized character.

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Technology, Engineering**Session Chair: Elizabeth Gregan****B/PI.29****CARBON FILAMENTS ROPES FORMATION**

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For the first time the formation of the ropes of carbon filaments via catalytic decomposition of CO on Co catalysts was observed. Reaction of CO decomposition was performed in flowing quartz reactor at 700-900°C in the presence of granulated Co supported on Al2O3. Co catalysts were prepared via magnetron sputtering of Co/Si target in Ar atmosphere on Al2O3 plate and initially consisted of Co particles with 2 nm diameter shared SiO2. Structure of carbon filaments ropes was investigated with use of low and high resolution transmission electron microscopy and scanning electron microscopy. The formation of coiled carbon filaments ropes with diameters about 100-500 nm was observed. The filaments consist of the piles of graphite sheets that are oriented perpendicular to the filament axis ("pack of card" structure) and have a diameter about 10-30 nm. Ropes diameters are comparable with cross-section of catalysts particles. The ropes ordering depends on the reaction temperature. We suggest that carbon filaments ropes formation is conditioned by specific structure of catalyst particles, which formed during sintering of initial Co particles separated by SiO2.

B/PI.30**CHEMICAL MODIFICATION OF SINGLE-WALLED CARBON NANOTUBES**

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The dimensions, graphitic surface chemistry and electronic properties of single walled carbon nanotubes make such materials ideal candidates for new chemical or biochemical sensors. Nanotubes can be non-destructively functionalized along their sidewalls or ends with small molecules, large macromolecules and even proteins. Individual nanotube reaction products are characterized by atomic force microscopy.

- B/PI.31** RECENT ADVANCES IN THE CHEMISTRY OF FILLED SINGLE WALLED CARBON NANOTUBES: THE STRUCTURE OF THE MATERIALS RbI@SWNT AND CoI₂@SWNT. DOES THE FILLING CAUSE DISTORTION OF THE WALLS OF THE SWNT?
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Single walled carbon nanotubes have been filled with nanocrystals of rubidium iodide and cobalt iodide. High resolution transmission electron microscopic examination of filled tubes show that there is continuous filling with crystalline material. Detailed studies of individual filled SWNT show 1) RbI@SWNT, there are twisted rubidium iodide crystals and changes of the tube diameters commensurate with distortions caused by the 2 x 2 RbI encapsulated crystals and 2) the presence of continuous crystals of CoI₂ in which the cobalt has a unique a tetrahedral structure unlike that found in bulk CoI₂.
- B/PI.32** PECVD-GRWOTH OF CARBON NANOTUBES USING MODIFIED TIP-PLATE CONFIGURATION
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We use a modified plasma configuration to create dense DC plasma in which a pointed tip is placed against a plate in a PECVD growth chamber. Carbon nanotubes are grown on silicon or quartz substrates where cobalt or nickel acts as catalyst. A base pressure of 1*10⁻⁶ torr is typically achieved using turbo pump station. Deposition is carried out in a pressure of 1-5 torr. A DC voltage between 400 and 800V can be applied to electrodes. The pointed electrode, connected to positive voltage, stands against the plate electrode. Ethylene is used as the inlet gas, although ethane and CO were also tried. Mixture of N₂/H₂ is used for in-situ surface cleaning of the substrates and to realize nanometer islands. A 2-10nm thick Co or Ni is deposited onto Si wafers or quartz plates using RF sputtering. The growth initiates by exposing the samples to a flow of 12ccm of N₂/H₂ followed by introducing the feed gas. SEM has been used to study the formation of islands and growth of nanotubes. Round islands of Co were formed after heat treatment of Si wafers at 600oC for 10mins. Diameter of islands varies between 50 and 200nm. Study of CNT's by HRTEM is underway. Multiwall nanotubes were grown on isolated islands with a length of 1-2µm. Using Ethane/H₂ and at 800oC, tubes with a length of 5 to 15µm and 20 to 40nm diameter were realized. Effect of plasma power and ethylene/H₂ ratio on the size and growth of tubes were investigated. Under similar circumstances Ni yields CNT diameter 50% more than Co as the catalyst. Dependence of emission characteristics of CNTs and their turn-on electric field on the diameter of tubes as well as the effect of pressure during growth is being studied. This configuration is being used to grow CNT's at pressures more than 50torr.
- B/PI.33** SPUTTERING DEPOSITION OF NICHEL FILMS ON DIFFERENT SUBSTRATE HEAT TREATED AS CATALYST FOR CARBON NANOTUBE
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The growth process for carbon nanotube usually involves the use of fine particles of some transition metal catalyst (Ni, Fe, or Co) on heated substrate exposed to a gaseous carbon source such as methane or ethylene. Conditions to achieve small diameter nanotubes depend upon the size of the metal catalyst particles. In this work films of increasing thickness of nichel (1-3-10 nm) were deposited by radio frequency magnetron sputtering on different substrates. Silicon, silica and SiO₂/Si with thermal oxide and sputtered oxide film were used as substrates. The effect of different substrates and deposition parameters has been studied after the heat treatment of the films in reduced atmosphere. The aim of the reported study was to find the better growing conditions to realize size controlled clusters of nichel as catalyst for nanotube growth. Contact angle measurements of the substrates and scanning electron microscopy, x-ray photoelectron spectroscopy, x-ray diffraction and reflectivity measurements were used to characterize the nichel films and clusters.
- B/PI.34** GROWTH OF CARBON NANOFILAMENTS FROM PALLADIUM SEEDS ON SILICON OXIDE
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Carbon nanofilaments with various microstructures have been grown on silicon oxide by decomposing acetylene on palladium seeds. Combining different experiments we conclude that growth is limited by initial palladium amounts. Palladium was found incorporated inside the filament body in the form of encapsulated nanoparticles and atomic impurities. This contrast with now-classical models of filament growth on transition metals where the catalytic particles are considered as non-evolving entities.
- B/PI.35** EFFECT OF SUBSTITUTIONAL B ON CARBON MWNT OXIDATION IN AIR AND OXYGEN PLASMA
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Carbon oxidation mechanisms between in air and atomic oxygen are quite contrary; oxidation active sites in air are mostly edge sites of carbon: in contrast, atomic oxygen is known to preferentially attack carbon atoms in basal plane. This preferential oxidation is proposed to be due to high pai-electron density between layers. Substitutional B is known to reduce the pai-electron density in carbon due to a less electron. Therefore, it would be interesting to use B-doped carbons to evaluate the proposed preferential oxidation mechanism in atomic oxygen because of a change in pai-electron density. The objectives here are to compare the relative oxidation behavior of carbon multiwalled nanotubes (MWNT) and to evaluate the nature of preferential carbon oxidation in different environment (air and oxygen plasma). MWNT were doped with elemental B at different concentration and heated at 2300 C. The oxidation behavior of MWNT in air was measured by non-isothermal TGA up to 1000 C and found that substitutional B doping increases oxidation inhibition, as expected. Oxygen plasma in a silent discharge system was used to simulate atomic oxygen environment. The relative oxidation inhibition of MWNT in oxygen plasma was similar to in air: the higher the B loading, the higher the oxidation inhibition. It seems to be that a decrease in pai-electron density between layers by substitutional B is beneficial for carbon oxidation in oxygen plasma.

B/PI.36

CARBON NUCLEATION AS A KEY STEP OF CARBON DEPOSITION ON THE METAL CATALYSTS

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An understanding of the formation mechanisms of the carbon deposit is very crucial for the development of controlled production of pure nanocarbon materials. For any type of carbon deposits on metal catalysts (carbon fibres and filaments, multi-wall and single-wall nanotubes) their formation occurs via the common steps including metal-carbon particles formation and carbon nucleation. Due to low self diffusion of carbon in carbon materials up to 1400-1500°C, that results in the stability of carbon deposits below these temperatures, initial products of deposit growth are stable for mutual transformation. Thus nucleation of carbon nanostructures is very important for the formation of specific nanocarbon materials. A variation of carbon nucleation conditions leads the formation of different carbon structures (nanotubes, filaments, carbon shells). We have performed a thermodynamic analysis of the carbon nucleation on metal surfaces to estimate the influence of reaction parameters on the carbon nucleation step. As a result of this analysis a functional dependence between the critical radius of the carbon nucleus (r_{crit}) and reaction parameters such as reaction temperature, carbon supersaturation degree, and parameters which characterize the metal catalyst (metal-carbon bond strength, work of adhesion) was obtained. The analysis of obtained functional dependence of r_{crit} in combination with metal-carbon phase diagram analysis allows: - to formulate the relationship between the size of carbon nucleus and type of carbon deposit; - to lighten the optimization of single-wall nanotubes growth conditions; - to estimate the real carbon supersaturation of metal-carbon particles; - to propose the mechanism of bamboo-like carbon nanotubes formation.

B/PI.37

IN-SITU XRD INVESTIGATIONS ON THE SYNTHESIS OF GRAPHITE NANOFIBERS AND THE ADSORPTION/DESORPTION OF HYDROGEN

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We have been used a special designed X-ray powder diffraction (XRD) cell as reaction vessel to study in situ both, the formation of graphite nanofibers (GNF) and their behaviour during high-temperature activation and hydrogen adsorption experiments up to 5 bar. The experiment begins with the formation of active catalyst species by reduction of the Ni/Cu-Catalyst (98/2 wt.-%) in hydrogen/nitrogen at 350 ÅC. The crystallographic changes that occur during this processes is monitored by x-ray diffraction measurements in the 2Theta-range 15-65Å. Increasing the temperature up to 600 ÅC and switching the gas to ethylene/hydrogen atmosphere the formation of GNF by chemical vapor deposition is monitored. The pristine GNF was treated with hydrogen at 5 bar at temperature in the range from 25 to 600ÅC up and down. We have monitored the (002) reflex to study the lattice expansion in case that hydrogen enters the region between the graphitic sheets under pressure conditions or the relaxation back to the ground state of the lattice in case of decrease of the (002) reflexes by switching from N2 to H2 at 25 Åc (1 bar), rising the pressure from 1 to 5 bar and by rising the temperature from 25 to 600 ÅC at 5 bar. After decompressing the cell to 1 bar and cooling down to 25 ÅC the lattice distance was found to be at the starting level

B/PI.38

SYNTHESIS OF MWCNT-BASED COMPOSITES WITH INORGANIC COATING

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Carbon nanotubes (CNTs) represent due to their tremendous mechanical properties a promising candidate to substitute the carbon fibers as reinforcing elements in composites. Moreover, composites containing CNTs can provide many other applications due to their extraordinary optical and electrical properties. In this contribution, we report on multiwalled carbon nanotube (MWCNTs) with a homogeneous coverage of various inorganic materials, such as alumina, silica and titania. MWCNTs were synthesized by catalytic CVD, purified, and impregnated using organometallic and inorganic compounds as precursors. Our results suggest that an effective interfacial bonding between CNT surface and precursors is the most important issue for the formation of MWCNT-based composites. In particular, the ionic character of the coating material has to be taken into account. A direct, solvent-free impregnation technique turned out to be the most successful for all organometallic compounds and provided homogeneous inorganic cover layer on the surface of purified MWNTs. With ionic coatings such as AlCl3, the adsorbed layer of surfactant promotes the coverage via ionic interaction. The composites were investigated by transmission electron microscopy and their composition was analyzed by EDX and XPS.

B/PI.39

CARBON REDISTRIBUTION PROCESSES

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Here we present results on the processes of carbon atoms redistribution leading to the corrosion of carbon nanostructures with high surface energy and to the formation of large-scale graphitic structures. We have performed TEM study of products produced via nanodiamond and onion-like carbon treatment in the a closed vessels at 1200-2000 K in presence of the controlled quantities of oxygen containing molecules (CO, CO2). Due to the reversible reaction: $\dot{N} + \dot{N} \dot{2} \dot{U} 2\dot{N}$ small carbon particles were corroded. The corrosion of small particles was accompanied the formation of graphitic ribbon structures or polygonized particles. Intermediates of growing structures were characterized with high resolution TEM. The observed growing steps and arched edge planes of graphite crystals were proposed as intermediates. The carbon redistribution processes can be based not only on the reactions with oxygen containing molecules. Analysis of the other possible reactions will be presented. Processes of carbon redistribution must be taken in account as a negative factor that influences the stability of carbon nanostructures. However using seeds of specific form and certain conditions the new graphite or even diamond crystals can be presumably prepared.

B/PI.40**FULLERENE PRODUCTION FROM POWDERED AMORPHOUS CARBON IN PLASMA**

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A new modification of the gas discharge method for fullerene production is developed. Powdered amorphous carbon particles admitted into the flowing plasma of a plasmatron are used as a source of carbon atoms, in distinct from the conventional approach, where this aim is reached through the thermal vaporization of a graphite anode. A physical model for vaporization of a small carbon particle in a weakly ionized plasma is built, which allows one to establish the interconnection between the time taken for vaporization of a particle, its size and the plasma temperature. Estimations based on this interconnection show that the effective vaporization of particles of micron size is reached using He or Ar gas carrier flowing with velocity of about 100 cm/s through the plasmatron channel of about 10 cm in length. The results of preliminary experiments are in agreement with those estimations. Different modification of plasma guns with backwards injection channels as well as different feeders will be presented.

The main advantages of the proposed approach relates to continuous input of carbon feedstock materials into plasma zone and usage of low cost carbon black produced from waste hydrocarbons.

Thursday, June 12, 2003
Jeudi 12 juin 2003

Morning
Matin

Session VII: Fundamental properties 1
Session chair: Hans Kuzmany

- 8:30 **B-VII.1** -Invited- THE RAMAN RESPONSE FROM NANOTUBES@NANOTUBES
P. Knoll(a,b), R. Pfeiffer(a), Ch. Kramberger(a), R. Kaindl(c), H. Kuzmany(a), (a)Institut of Materials Physics, Vienna University, Strudlhofgasse 4, 1090 Vienna, Austria, (b)Institut of Experimental Physics, University Graz, Universitätsplatz 5, 8010 Graz, Austria, (c)Institut of Mineralogy, University Graz, Universitätsplatz 2, 8010 Graz, Austria
Carbon cages have attracted pronounced interest of scientific research the last years. Especially, the inside of carbon nanotubes offer the possibility of a clean nano-room, where chemical reactions take place under conditions not available at other environments. If single wall carbon nanotubes (SWCNT) filled with C₆₀ fullerenes, the so called peapods, are heated up to 1300 ÅC the C₆₀ form a nanotube without catalyst hosted by the outer SWCNT. These carbon nanotubes in the inside of the SWCNT we have studied by resonance Raman spectroscopy with IR to UV laser excitations at several temperatures. The diameters and chiralities of the inner tubes have been determined. The radial breathing modes (RBMs) show a very narrow line width and also the resonance range is limited to a very narrow spectral window. Both observations indicate a rather long vibrational and electronic lifetime for the carbon nanotubes in the inside of the SWCNT. We further discuss new observed features which demonstrate the break down of the simple tight binding approach for small tube diameters.
- 9:10 **B-VII.2** REVERSIBLE AND IRREVERSIBLE THERMAL EFFECTS IN RAMAN SPECTRA OF SINGLE-WALL CARBON NANOTUBES
Elena D. Obratsova, Natural Sciences Center of General Physics Institute, RAS, 38 Vavilov street, 119991, Moscow, Russia
A monitoring of temperature-induced changes in Raman spectra of single-wall carbon nanotubes (SWNT), heated by laser or by furnace, gives useful information about structure and electronic properties of the material. Two types of effects have been observed: the irreversible spectral changes resulted from a partial etching of the material under the elevated temperature; the reversible changes reflected the temperature-induced modification of the material electronic structure. The irreversible changes were most pronounced in the spectra of HipCO nanotubes (containing the tubes with diameters 0.4-2.0 nm). A step-by-step disappearance of the breathing Raman modes for the smallest nanotubes has been interpreted as their selective oxidative etching. (The effect was observed in air only). The etching temperatures, depending on tube diameters, have been estimated by measuring the tangential mode position corresponding to the breathing mode disappearance. The reversible changes were the following: additionally to the Raman signal of nanotubes, satisfying the resonance conditions at room temperature, new breathing modes, corresponding to the smaller tubes, appeared at elevated temperatures. The effect has been observed for SWNT synthesized by different techniques. A mechanism of a temperature-induced broadening and shift of van Hove singularities in one-electron DOS of nanotubes was used to explain the effect. The work is supported by RFBR 01-02-17358, INTAS 00-237, program "Low-dimensional quantum structures".
- 9:30 **B-VII.3** ADVANCES IN SINGLE NANOTUBE SPECTROSCOPY
Ado Jorio, M.A. Pimenta, M.S.S. Dantas, C. Fantini, M. Souza, UFMG, Belo Horizonte, Brazil, A.G. Souza Filho, UFC, Fortaleza, Brazil, Ge.G. Samsonidze, G. Dresselhaus, M.S. Dresselhaus, MIT, Cambridge, USA, R. Saito, UEC, Tokyo, Japan
We present a review of single nanotube spectroscopy followed by new findings on Raman scattering. We discuss the dependence of the resonance Raman spectra on the incident laser energy and we address single vs double resonance mechanisms for Raman spectra on carbon nanotubes, showing the power of making measurements at the single nanotube level. We also present some new results on polarization dependence for the Raman spectra of isolated single wall carbon nanotubes, discussing apparently contradictory results in the literature.
- 09:50 **B-VII.4** RAMAN SPECTROSCOPY OF TEMPLATE GROWN SINGLE WALL CARBON NANOTUBES IN ZEOLITE CRYSTALS
Martin Hulman, Hans Kuzmany, Orest Dubay, Georg Kresse, Institut fuer Materialphysik, Universitaet Wien, Strudlhofgasse 4, 1090 Wien, Austria, Ling Li, Z.K. Tang, Physics Department and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Hong Kong
Single wall carbon nanotubes with diameter 0.4 nm grown in the channels of AlPO₄-5 crystals were studied by Raman spectroscopy. Up to 19 different laser lines were used to characterize vibrational properties. Spectra depend strongly on the energy of the laser line used for excitation. It was found that only two types of nanotubes with different chiralities, (5,0) and (4,2), are responsible for the spectra observed. The frequencies of the radial breathing mode were reliably assigned. It was established that (5,0) is a metallic and (4,2) a semiconducting nanotube from the high energy part of the spectra. A shift of the two components of the G band with A₁ symmetry was found in accordance with the theoretical predictions. A strong response was also observed for frequencies ~ 1250 cm⁻¹. The positions of two peaks assigned to the (5,0) do not depend on the laser energy whereas only one peak was observed for the (4,2) nanotube. Its frequency shifts with the laser energy like the D line of large diameter nanotubes, but the rate of the shift is only a half of the value known for the latter.

10:10 **B-VII.5** CHARACTERIZATION OF CHEMICAL FUNCTIONALIZED SINGLE WALLED CARBON NANOTUBES
J. Abraham, A. Hirsch, R. Graupner, L. Ley, F. Hennrich, M. Kappes, Universitat Erlangen-Nurnberg, Organische Chemie II, Henkestr. 42, 91054 Erlangen, Germany
The chemical functionalization of carbon nanotubes attracted considerable interest since their discovery in the early 80's. In present work we pay attention to the functionalization of single walled carbon nanotubes (SWCNTs) obtained both via laser ablation and HiPCO to work out possible diversities. Derivatization was achieved by utilizing the addition reaction of nitrenes to SWCNTs. This reaction enabled us to attach a variety of functional groups to the sidewall of the SWCNT, ranging from ethyl-, polyethyleneglycol- to crownether-substituents. The compounds were successively characterized using AFM, TEM, UV/Vis-nIR, ¹H NMR, XPS, Raman and TGA. The combination of these various characterization techniques allowed us to show the influence of the addend on the tube and vice versa. Furthermore we determined the solubility of the derivatized SWCNTs.

10:30 **BREAK**

Session VIII: Fundamental Properties 2

Session Chair: Vitaly K. Koltover

10:50 **B-VIII.1-Invited-** WHAT WE KNOW AND WHAT WE DO NOT KNOW ABOUT SEMICONDUCTOR PROPERTIES OF FULLERENE THIN FILMS?

Eugene.A. Katz, Department of Solar Energy and Environmental Physics, J. Blaustein, Institute for Desert Research, Ben-Gurion University of the Negev, Sede Boqer 84990, Israel

Pristine solid C₆₀ is found to exhibit a semiconductor behavior while retaining a molecular character. In spite of the extensive studies of C₆₀ films, a whole set of questions have yet to find satisfactory answers. One of the central issues, that still remain open at the most fundamental level, concerns the effect of crystalline structure, and in particular such structural defects as grain boundaries (GB), on the semiconductor properties of the films. The present paper starts with a review of the published data on this problem which are fragmentary and often contradictory. It is well known that GB in van der Waals molecular crystals do not produce dangling bonds or other defects that generate deep states. If so, do GB really influence semiconductor properties of C₆₀ films? If so, what is a physical mechanism of such an effect? We suggest that a GB diffusion is one possible mechanisms which govern the properties of the material. The experimental evidence for the GB effect on the rate of oxygen and metal diffusion in C₆₀ films is reported. The influence of this phenomenon on the electronic properties of the material is discussed. Finally, we present our recent experimental observation of the strong effect of the crystal structure of C₆₀ films on the temperature dependence of their conductivity and photoconductivity near the orientational disorder/order phase transition.

11:30 **B-VIII.2** FULLERENE-CONTAINING MACROMOLECULES WITH INTRIGUING PROPERTIES

Jean-Francois Nierengarten, Groupe des Materiaux Organiques, Institut de Physique et Chimie des Materiaux de Strasbourg, Université Louis, Pasteur et CNRS, 23 rue du Loess, B.P. 43, 67034 Strasbourg Cedex 2, France

11:50 **B-VIII.3** PHOTOEMISSION RESULTS ON DIFFERENT PHASES OF Rb₁C₆₀ AND Na_xC₆₀

P. Rudolf(a,b), I. Marenne(b), L. Kjeldgaard(c), J. Schiessling(c), P. Brähwiler(c), T. Pichler(d), R. Larciprete(e), A. Goldoni(e), (a)Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, (b)Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, 5000 Namur, Belgium, (c)Department of Physics, Uppsala University, Box 530, 75121 Uppsala, Sweden, (d)Institut für Materialphysik Universität Wien, 1090 Wien, Austria, (e)Elettra Sincrotrone Trieste Area Science Park, 34012 Basovizza, Italy

To gain further insight into the relationship between geometric and electronic structure in alkali fullerides, we have investigated RbC₆₀ and Na_xC₆₀ (0<x<3) films by angular dependent valence band and core-level photoemission spectroscopy.

The vacuum distilled fcc phase of RbC₆₀ obtained at 525 K shows a low spectral density at the Fermi level. By quenching the sample in the monomer phase (50 K), a clear Fermi edge appears, indicative of a 3D metallic character. A small extra component in the Rb 3d lines indicates a 10% of tetrahedral occupation. The intensity at the Fermi edge disappears when the insulating dimer phase is formed by heating to 117 K. Further annealing to 370 K produces the polymer phase, characterized by a very low intensity at the Fermi level.

The analysis of Na_xC₆₀ for average Na concentration x<1 found indications for the formation of a dimer phase corresponding to a stoichiometry x=1 which coexists with a rock salt structure. However, this dimer phase is present prevalently at the surface and disappears when the sample is annealed. At very low doping (around x=0,5), we found also modifications in the photoemission spectra which could be explained with a phase transition from a system where the phases separates to a solid solution behaviour.

This work was performed within the EU-TMR "FULPROP" network, contract n. ERBFMRX-CT97-0155 and the measurements at ELETTRA, Trieste, Italy and MAXlab, Lund, Sweden were supported ‘Access to Research Infrastructure’ action of the improving Human Potential Program (ARI) of the EU.

12:10 **B-VIII.4**

DOPING OF SINGLE WALLED NANOTUBES

R. Czerw(a), J. Liu(a), P.-W. Chiu(b), L. Zheng(a) S. Roth(a), D.L. Carroll(a), (a)School of Materials Science and Engineering, Clemson University, Clemson SC 29634, USA, (b)Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

Significant progress has been made in doping mechanisms of multiwalled carbon nanotubes with boron, and nitrogen. Acceptor and donor states have been theoretically predicted and observed using tunneling spectroscopy. The electronic behavior of these nanotubes is typical for degenerately doped, small bandgap semiconducting materials. Recently, however, these doping schemes have been extended to single walled nanotube growth and the behavior is strikingly different from the multiwalled case. In the case of boron doping, many of the doped single walled nanotubes still exhibit significant bandgaps with modification to the electronic structure far into the valence band, not at the Fermi level. Further, atomic resolution images of these nanotubes exhibit standing wave structure across the tube's surface reminiscent of Friedel oscillations. Nitrogen doped single walled nanotubes, also exhibit bandgaps and a strongly distorted lattice, leading to modifications in both valence and conduction band structure. In this presentation, these results will be presented in the context of interface interactions which clearly indicate changes in the nanotube's workfunction upon doping.

12:30 **B-VIII.5**

ELECTRONIC PROPERTIES OF ENCAPSULATED C₃₆ IN ARMCHAIR CARBON NANOTUBE

Yuanhe Huang, Baohua Yang, Jianguan Huang, Department of chemistry, Beijing normal university, Beijing 100875, China

Recently transmission electron microscopy shows that fullerenes are aligned in a chain and encapsulated in CNT [1]. It has shown that the peapod C₆₀@(10, 10) is a metal with hybrid electronic band, which derives its character from both the nanotube states and the C₆₀ molecular orbitals [2,3]. How about in the case of encapsulated C₃₆ in carbon nanotube? In this work, the stabilities and electronic properties of C₃₆@(n, n) are investigated using SCF-MO and SCF-CO methods. Four models of C₃₆@(6, 6), C₃₆@(7, 7), C₃₆@(8, 8) and C₃₆@(9, 9) are used for the study. The geometrical parameters of the peapods are obtained from HF SCF-MO-321G optimization results with Gaussian 98 program package and the structures of encapsulated C₃₆ in carbon nanotube of limited length. In C₃₆@(6, 6) and C₃₆@(7, 7), both the tubes and the C₃₆ cages are distorted. The tube silhouette itself becomes undulating and the C₃₆ inside are lengthened along the tube axis direction. But the changes is little in C₃₆@(8, 8) and C₃₆@(9, 9). The band structures of these peapods are calculated using ab initio B3LYP-DFT SCF-CO methods at the 3-21G level with the CRYSTAL 98 program. For (n, n) nanotube, the two frontier bands cross with E_f at k=2p/3 of Brillouin zone. These characteristics are still maintained in C₃₆@(8, 8) and C₃₆@(9, 9). Whereas in C₃₆@(6, 6) and C₃₆@(7, 7) the Fermi energy is no longer at level of the cross point of the two bands, and moves up to higher positions.

[1]B.W. Smith et al. Nature 1998,396,323

[2]D.J. Hornbaker et al. Science 2002,295,828

[3]S. Okada et al. Phys. Rev. Lett. 2001,86,3835

12:50

LUNCH

Thursday, June 12, 2003
Jeudi 12 juin 2003

Afternoon
Après-midi

Session IX: Multifunctional applications
Session Chair: Eugenia Buzaneva

14:00 **B-IX.1** -Invited- APPLICATIONS OF CARBON NANOTUBES

John Robertson, Engineering Department, Cambridge University, Cambridge CB2 1PZ, U.K.

Carbon nanotubes are presently famous for their unique and extreme properties, such as high strength, thermal conductivity, ballistic electrical conductivity, etc. However, it is also difficult to manipulate their properties. The talk will review how to control their growth and properties, and then it will review some of their potential applications in field emission, microwave amplifiers, transistors, supercapacitors, conductive composites, hydrogen storage, etc.

14:40 **B-IX.2** TRANSITION METAL CHALCOGENIDE NANOTUBES: CAN THEY REALLY DO EVERYTHING CARBON NANOTUBES CAN DO?

Dragan Mihailovic, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

We review the properties of new transition metal dichalcogenide nanotubes, particularly focussing on the synthesis, structure, electronic, magnetic and mechanical properties of Mo-S based systems. Their chemical characteristics are very different than carbon-based NTs, which makes them complementary in terms of interactions with other molecules and chemical functionalisation. The properties of doped lithium-doped NTs are found to be of interest from a fundamental physics point of view as one-dimensional electronic systems due to their exceptionally small lateral coupling leading to very peculiar properties. On the applications side, MoS₂ nanotubes and related nanostructures appear to be very promising as a new Li-battery electrode materials. Apart from field-emission, where they have also shown to be comparable to carbon-based NTs and use in composites, these materials are also interesting from the point of view of lubricants and, being "soluble" in polar solvents they can be interfaced with organic systems.

15:00 **B-IX.3** C-NANOTUBE REINFORCED MULTI-FUNCTIONAL COMPOSITE MATERIALS

Ben Wang, Richard Liang and Chuck Zhang, Florida Advanced Center for Composite Technologies, Florida A&M University - Florida State University College of Engineering, 2525 Pottsdamer Street, Tallahassee FL 32310-6046, USA, Leslie Kramer, Lockheed Martin Missiles and Fire Control - Orlando 5600 Sand Lake Rd. MP-450, Orlando FL 32819-8907, USA

Many people, fully inspired by the amazing strength property of single wall nanotubes, have attempted to fabricate high performance composite materials reinforced with nanotubes. Most utilized an intuitively straight-forward method where nanotubes are directly mixed with an epoxy matrix materials. Once the mixture suspension is made, composite samples can be injection molded or compression molded with the suspension. So far, the property test results have been less than satisfactory. There are a number of reasons for it, including 1) poor dispersion, 2) low nanotube loading in epoxy, 3) nanotubes' tendency to form bundles, 4) weak interfacial bonding between nanotubes and epoxy matrix, and 5) lack of orientation or alignment necessary to take advantage of the directional properties, i.e., thermal, mechanical and electrical. [...] In our presentation, we will discuss in detail the processes of buckypaper forming, magnetic alignment and composite fabrication. We will also share with the conference participants property test results, including strength, electrical resistivity and thermal conductivity.

15:20 **B-IX.4** CARBON NANOFIBERS FOR COMPOSITE APPLICATIONS

Ernst Hammel, K. Mauthner, X. Tang, M. Trampert VP Electrovac GesmbH, Aufeldgasse 37-39, 3400 Klosterneuburg, Austria, A. Eder, Gabriel Chemie GesmbH, Industriestrasse 1, 2352 Gumpoldskirchen, Austria, P. Potschke, Institute of Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany

Carbon nanofibers and nanotubes are promising to revolutionize several fields in material science and are suggested to open the way into nanotechnology. Further market development will depend on material availability at reasonable prices. We have achieved bulk production capacities of high purity carbon nanofibers (CNFs) at low cost by a catalytic chemical vapor deposition (CCVD) process. Reasonably low temperatures and yields of up to several g/m²min at more than 70% carbon gas-to-fiber conversion rates allow considerable cost reductions. Polymer composites have been prepared by shear mixing of CNFs into polymer matrices and extrusion. In polypropylene the application of less than 10 vol% CNFs reduced the volume resistivity from >10E13 Ohmcm to a value of ~10E5 Ohmcm. Furthermore polycarbonate-CNF composites were prepared using masterbatch compounding. Interactions between the native nanofibers and the polymer matrix have been studied to optimize their mechanical and electrical properties. Different sizings of fibers are normally used for nylon, polycarbonate and other high temperature applications. We are focussing on the development and volume production of a single carbon nanofiber type which can be used in a wide range of systems not restricted to polymer composites.

15:40

BREAK

Session X: Electronics

Session Chair: Ado Jorio

- 16:00 **B-X.1** -Invited- NANOTUBE BASED TRANSISTORS
Siegmar Roth, Max Plank Institut fuer Festkoernertorschunf, 70569 Stuttgart, Germany
The talk will give an overview of the historic development and the state of the art of carbon-based transistors: Generation 1: nanotube over lithographic leads on silicon chip, back gate; Generation 2: lithographic aluminium strip as gate, Al₂O₃ as dielectric, nanotube above, lithographic source and drain; Generation 3: All-Carbon Transistor. Particular attention will be drawn to two aspects of the discussion: a) geometrical changes of nano-objects if charge is applied, b) need of wiring each transistor to an energy reservoir, if amplification is needed. Now remains the question on how you will fill the hole left in place of Po-wen Chiu's talk. Do you want me to look around among my acquaintances to find a substitute who could speak to a specific topic of nanotube electronics?
- 16:40 **B-X.2** HIGH MOBILITY SEMICONDUCTING NANOTUBE TRANSISTORS AND MEMORIES
M.S. Fuhrer, B.M. Kim, T. Brintlinger, Y.F. Chen, T. Durkop, G. Esen, S.A. Getty, Department of Physics and Center for Superconductivity Research, University of Maryland, College Park MD 20742-4111, USA
Recently, exceptionally long (tens of microns), clean semiconducting single-walled nanotubes (SWNTs) have been prepared by chemical vapor deposition. We have studied the electronic properties of devices consisting of individual long semiconducting SWNTs contacted by metal source and drain electrodes, with a conducting silicon back gate. The gate-voltage dependence of the conductance places a lower bound on the hole mobility in these nanotubes of 20,000 cm²/Vs at room temperature[1], rivaling the best known semiconductors. A simple floating-gate memory cell, in which charges are stored in traps in the 500 nm-thick silicon dioxide gate dielectric, has been demonstrated[2]. Memory operation is obtainable with a few volts applied to the gate, and the charge storage is non-volatile. Single electronic charges may be stored and detected at temperatures up to 100 K. The high mobility of these nanotubes also suggests applications to high-speed electronics and to chemical or biological sensors, which are being pursued.
[1] Paul L. McEuen, Michael S. Fuhrer, Hongkun Park, IEEE Transactions on Nanotechnology, 1, 78 (2002).
[2] M. S. Fuhrer, B. M. Kim, T. Dürkop, and T. Brintlinger, Nano Letters 2, 755 (2002).
- 17:00 **B-X.3** ULTRAFast OPERATION, OSCILLATIONS, AND NOISE IN MULTIFUNCTION NANOTUBE TRANSISTOR
Per Hyltdgaard, Department of Applied Physics, Chalmers University of Technology and Goteborg University, 41296 Gothenburg, Sweden
The nanotube resonant-tunneling transistor [SSC 116, 569 (2000)] can be realized either as a nanotube heterostructure or by an external gate control on a (all-semiconducting) nanotube [PRL 88, 258302 (2002)]. Either way, such nanotube transistors comprise a pair of conducting-nanotube leads surrounding a nonconducting barrier and an external gate that controls the energy position or resonant/defect levels trapped in the barrier region. Here I characterize the electrostatic gate control and the resulting electron dynamics to document an ultrafast, robust operation which is limited by the resonant-tunneling times. In addition, I show that the transistor can also exhibit a negative-differential amplification and I discuss possibilities for using this response in realizing fast oscillations. Finally I present nonequilibrium Green function calculations to determine the shot-noise variation with gate bias.
- 17:30 **B-X.4** AMBIPOLAR FIELD-EFFECT TRANSISTOR IN AS-GROWN SINGLE WALL CARBON NANOTUBES
Mahdi Iqbal, Bakir Babic, Christian Schonenberger, Institut für Physik, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland
We use a simultaneous flow of ethylene and hydrogen gases to grow single wall carbon nanotubes by chemical vapor deposition. Strong coupling to the gate is inferred from transport measurements for both metallic and semiconducting tubes. At low-temperatures, our samples act as single-electron transistors where the transport mechanism is mainly governed by Coulomb blockade. The measurements reveal very rich quantized energy level spectra spanning from valence to conduction band. The Coulomb diamonds have similar addition energies on both sides of the semiconducting gap. At intermediate temperature signatures of subbands population have been observed.
- 17:45 **B-X.5** CONTROL OF CARBON NANOTUBE CIRCUITS AND THEIR SENSOR APPLICATIONS
Philip G. Collins, University of California at Irvine and Nanomix Inc, 4129 Frederick Reines Hall, Irvine CA 92697, USA
This talk will review recent progress controlling the properties of carbon nanotube-based nanoelectronics. The potential gains of shrinking conventional devices to nanometer sizes, as well as the possibilities envisioned for novel quantum devices, make this a field filled with opportunity. However, as with any disruptive technology in its early stages, nanoelectronics still faces major challenges from both scientific and technological points of view. Surface effects, interfacial barriers, and material variability all have significant effects on current nanodevices, though we are currently having some success controlling these factors. Furthermore, these surface effects can be advantageous for certain applications such as chemical sensing. Compared to microelectronics, the field of chemical sensing is poorly served by solid state devices at present, making this an area of immediate opportunity for nanoelectronic devices. Prototype nanotube-based chemical sensors are currently being tested for commercialization.

18:00 **B-X.6** INDIVIDUAL SINGLE-WALL CARBON NANOTUBES: PREPARATION AND SELF-ASSEMBLY IN THIN FILM NANOSTRUCTURES
Nina I. Kovtyukhova(a,b), Thomas E. Mallouk(a), (a)The Pennsylvania State University, Department of Chemistry, University Park, PA 16802, USA (b)Institute of Surface Chemistry, N.A.S.U., 03680 Kyiv, Ukraine
The individual single-wall carbon nanotubes (SWNTs), actually one-dimensional fullerene macromolecules, are now available and can be used as unique building blocks in many areas of molecular technology. Here we introduce a synthetic route to individual SWNTs through the complete exfoliation of their ropes by an oxidation technique previously developed for crystalline graphite. The resulting individual nanotubes are 50 to 500 nm long and contain oxygen functions on the ends and walls. The SWNTs graphene cylinders retain in much their aromatic structure and in this are more stable to the oxidation than the graphene sheets of natural graphite. The oxidized SWNTs are water soluble, and readily self-assemble into dense monolayer films on cationic surfaces. The films reveal linear current-voltage behaviour, however they are about 3 orders of magnitude more electrically resistant than starting SWNT material. Examples of layer-by-layer self-assembly of the individual SWNTs into electronically functional films are presented.

18:20 **BREAK**

18:30–19:30 **POSTER SESSION II**

Fundamental Properties 1, 2

Session Chair: Elena Obratsova

- B/PII.01** MECHANICAL PROPERTIES OF ION BEAM DEPOSITED NANOCARBON FILMS
S. Tamulevicius(a), L. Augulis(b), S. Meskinis(a), Vkopustinskas, (a)Institute of Physical Electronics, Kaunas University of Technology, Savanoriu 271, Kaunas 3009, Lithuania, (b)Institute of Materials Science, Kaunas University of Technology, Studentu 50, Kaunas 3031, Lithuania
An article concentrates on the analysis of mechanical properties of diamond like carbon films, carbon nanotubes and hydrogenated amorphous carbon nitride deposited from the direct ion beam on crystalline silicon. The conventional laser interferometry combined with the extra thermal heating as well as electronic speckle pattern interferometry were applied to define intrinsic stress, elasticity modulus in dependence on technological conditions. Raman scattering and ESCA were used to identify phase composition. It is demonstrated that deposition at different temperatures, ion flux composition results in formation of phases with different mechanical properties. Diamond like carbon films can be deposited at room temperature. Increase of the substrate temperature results in formation of polymer-like films. Growth of the nanotubes was observed at temperatures higher than 400C. Synthesis of the carbon films on the substrate coated by micro or nanostructured catalytic Ni films results in formation of the carbon nanotubes. There were revealed that carbon nanofibers, deposited on the thermal SiO₂, have wider diameter and are longer in comparison with the nanofibers deposited onto the native SiO₂. Dimensions of the nanofibers deposited from the acetylene gas (C₂H₂) are larger in comparison with the nanofibers deposited from the hexane-hydrogen vapor (C₆H₁₄+H₂). Decrease of the deposition temperature resulted in the decrease of the diameter of the carbon nanofibers.
- B/PII.02** SECOND-ORDER RAMAN SCATTERING FROM TREATED CARBON NANOTUBES
A. Naumenko, N. Berezovska, I. Dmitruk, Faculty of Physics, Kyiv National Taras Shevchenko University Kyiv, 03680 Kyiv, Ukraine
Carbon nanotubes, annealed at various temperatures in range 900 – 2800 C have been studied by Raman scattering. Spectra were excited by emission of argon ion laser with 514.5 nm and 488.0 nm wavelengths and recorded with DFS-24 double grating spectrometer. The Raman results indicate that increase of the treatment temperature leads to enrichment of the spectra. At the same time low-frequency shift is observed. Changes in frequencies and the intensity redistribution of the Raman modes with the phase content of materials have been detected. Results for first- and second-order Raman spectra are also presented for HOPG, polycrystalline and amorphous samples and show the similar features as in spectra under discussion. The second-order Raman spectra are even more sensitive than the first-order spectra to the heat treatment.
- B/PII.03** ELECTRONIC STRUCTURE OF C₆₀/CuPc AND C₆₀/CuPc NANOPARTICLES AND THIER LAYERS
C. Tsamis, A. Nassiopoulou, Institut of Microelectronics, IMEL/NCSR Demokritos, P.O. Box 60228, 15310 Aghia Paraskevi Attikis, Athens, Greece, I. Lysko, O. Gorchinskiy, E. Buzaneva, Taras Shevchenko Kiev National University of Radiophysical Faculty, The Scientific and Training Center "Physical and Chemical Material Science of Kiev National Taras Shevchenko University and NASU", 64 Vladimirska Str., 01033 Kiev, Ukraine, P.Scharff, K. Risch, Technische Universitat Ilmenau, Fakultat fur Mathematik und Naturwissenschaften, Institut fur Physik / FG Chemie, Postfach 100565, 98684 Ilmenau, Germany
The idea to form CuPc/C₆₀ nanoheterojunctions in the CuPc, C₆₀ nanoparticles mixture under photoexcitation and to detect the electronic structure of these nanoparticles and formed nanoheterojunctions by UV-VIS spectroscopy has been realized. For CuPc, C₆₀ molecular crystals (p- and n- semiconductor, correspondently) dissolved in toluene the bandgaps $E_g = 0.70$ eV (for CuPc nanoparticles from molecules in toluene), $E_g = 0.31$ eV (for CuPc molecular crystals and nanoparticles mixture in toluene) and $E_g = 1.85$ eV (for C₆₀ nanoparticles in toluene) have been evaluated. For CuPc and C₆₀ nanoparticles mixture in toluene and on quartz substrate the band offsets of the edges VB band CuPc and LUMO band C₆₀ are $E = 1.55$ and 1.4 eV, correspondently. These results are evidence of present CuPc/C₆₀ nanoheterojunctions in the solutions and on quartz surface.

- B/PIL.04** SYNTHESIS AND PROPERTIES OF FULLERENE-BASED STARBURST POLYTHIOPHENE-b-POLY (α -CAPROLACTONE)
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 Synthesis and Characterization of novel fullerene-based star polythiophene-b-poly (α -caprolactone) are demonstrated. These well-defined star copolymers essentially can be viewed as "core-shell" nanoparticles. The biocompatible inner core of star was synthesized via the living ring opening polymerization of (α -caprolactone) using polyhydroxylated C60 as initiator. After capping the terminal of each arm with thiophene, the surrounding shell of conductive polythiophene was prepared by oxidative polymerization of thiophene monomer. These unimolecular nanoparticles revealed good solubility in various organic solvents and excellent conductivity after treating with iodine. The potential functions of this nanosystem as chemical sensor have also been investigated by our group. All of these data will be presented in this conference.
- B/PIL.05** POLYMER MORPHOLOGY IN CONJUGATED POLYMER-MULTIWALLED CARBON NANOTUBE COMPOSITES.
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 To date conjugated polymer research has developed applications in areas such as display technologies and LED's while carbon nanotube research shows the potential for material reinforcement or conductivity enhancement. These two fields can be combined to create exciting new composite materials which have new, improved and more useful properties. We have recently developed a composite material using the conjugated polymer PmPV and multiwalled carbon nanotubes providing a purification method to recover multiwalled nanotubes from carbon soot. In this work we investigate the polymer-nanotube interaction present in the purification process. Photoluminescence measurements show that the PL quantum yield decreases linearly with increasing nanotube content. In contrast to this the PL efficiencies measured in the presence of air show a reduction in photo-oxidation which may be attributable to a reordering of polymer strands which protects the vinylene bond on the polymer backbone from singlet oxygen attack. We present a model based on the assumption that the polymer strands adsorb onto the nanotubes in an ordered fashion using the nanotube hexagonal lattice as a template and show that the experimental data agrees well with theoretical predictions. Further evidence for ordering of the polymer chains at the nanotube surface is provided by FTIR and differential scanning calorimetry. Changes in the FTIR fingerprint region verify that the polymer backbone experiences a different vibrational environment due to the presence of nanotubes while the DSC results show a second crystalline region is present in the composite indicating that the carbon nanotubes are promoting crystallization in the composite.
- B/PIL.06** NONCOVALENT FUNCTIONALIZATION OF SWNT: RAMAN SPECTROSCOPY AND AB INITIO CALCULATION OF COUPLING PYRENE MOLECULE WITH SWNT
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 Interactions of pyrene with carbon SWNT have been investigated employing Raman spectroscopy and the correlated level ab-initio quantum-chemical method MP2. Raman spectra of HiPco SWNT (1) and SWNT with pyrene (2) films in the range of 160-1800 1/cm were measured. As a result of noncovalent interaction between SWNT and pyrene the most intensive component G-mode (1590 1/cm) of (2) is shifted to the low frequency (about 2 1/cm) and became narrow (about 3 1/cm), intensity of low-frequency component of G mode (1550 1/cm) is decreasing about 30 %. Structure and interaction energies of the complexes of pyrene and nanotubes of various sizes (from 0.49 to 1.58 nm) are determined. The BSSE-free numerical optimization performed for the pyrene-zigzag (12,0) SWNT was performed and converged to the 1/2 staggered conformation with intermolecular distance of 3.5 Å. The BSSE-free interaction energy in the complex is -30.8 kJ(1/mol). Increasing of the nanotube diameter leads to increasing of the interaction energy till -37.2 kJ(1/mol) in the case of planar carbon surface. For the zigzag (n,0) SWNT with n > 10 the interaction pyrene-nanotube is more preferable than interaction pyrene-pyrene. For nanotubes with n < 10 the interaction energies with pyrene are lower than interaction energies in the pyrene dimers. This work was supported in part by INTAS project N 00-237
- B/PIL.07** THE HEAT TREATMENT INFLUENCE ON STRUCTURAL AND MICROMECHANICAL PROPERTIES OF THE FULLEREN LAYERS
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 The influence of the heat treatment at 523K and the subsequent relaxation during two weeks at 293K on the structural, micromechanical and plastic properties of the C60 layers was investigated. The heat storage at 523K was equal to 3 hours; the layers thickness – about 1-3mm. The magnitude of microhardness (H) was the measure of the strength properties. The load (P) on the Vickers indenter was varied in region from 5 to 30 g, accordingly the indenter penetration depth ranged 1.2 to 1.6mm. In this paper the C60 layers brittleness was studied by the use of a registration method of the acoustic emission signals (AES), arising under microindentation. The load dependence of AES summary account (N) was investigated on the both as-grown and heat treated C60 layers. The investigations at room temperature (293K) were performed. It was established the weak influence of the heat treatment on the microhardness magnitude at all loads: after treated H decreased by about 20%. The H(P) curves for heat treated samples were placed lower in comparison with these for untreated ones. Beside this in both cases the H is increased with P rise. Such dependence shape is perhaps determined by the enhancement of the C60-glass interface line influence at large indenter loads. The different feature of the N(P) dependencies before and after heat treatment was revealed. The AES number is weakly increased with P rise for samples before treatment. Analogous behavior is conserved after treatment too, but in this case the N(P) dependence is became sharply non-monotonous: the pronounced N maximum at 15g is observed.

- B/PIL.08** THE OPTICAL SPECTROSCOPY AND CONDUCTIVITY OF DNA/SWCNT LAYERS ON SUBSTRATES
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For the application of SWCNT in optical systems and to construct simple logic circuits, it is necessary to create their layers. These layers by DNA technology on Au, Si substrates have been created. From UV-VIS-NIR (250-1700 nm) absorption spectra obtained for SWCNT and DNA/SWCNT layers the principal electronic absorption bands have been evaluated (1.24 and 2.57 eV), but the behaviour of absorption curve for DNA/SWCNT layer are determined by ratio of DNA and SWCNT volumes. The band at 1.25-2 eV with minimal absorption has been detected. In the experimental IR-spectra the vibration modes at 360, 450, 650, 820, 1250, 1400, 1440, 1575 cm⁻¹, which have been theoretically predicted for SWCNT with diameter 10-40 nm, we evaluated for DNA/SWCNT composite layer on these substrates. In these spectra the presence of added DNA bases group were identified. The current-voltage characteristics of metal (Pt/Ir) tip - DNA/SWCNT - metal (Pt/Ir) tip have the behaviour of diode type. The value of conductivity are determined by ratio of DNA and SWCNT volumes. These results we used for obtained integrated diodes systems.
- B/PIL.09** OPTICAL CHARACTERIZATION OF FULLERENE FILMS ON FLAT AND MICRORELIEF SEMICONDUCTOR SUBSTRATES
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Comprehensive optical characterization of C60 films on semiconductor substrates has been performed by means of ellipsometry, Raman and photoluminescence spectroscopy. These films have been prepared by the sublimation C60 under vacuum. The morphology of these films and the C60-substrate interaction were investigated by using atomic force microscopy (AFM). Both flat and microrelief wafers of Si, Ge, and InP have been used as substrates. It was found formerly that the stronger interaction occurs between C60 molecules and Si surface; and the C60 films on patterned InP surface grown oriented with their grains arrayed in [011] and [101] perpendicular directions. Initial optical characterization was performed by means of ellipsometry to determine thickness and optical constants of the films. Raman spectra have been measured at room temperature under argon laser excitation. It is shown to be very useful for structural characterization of the films and for stress estimates. Results are compared with XRD data. Observed increase of Raman signal from microrelief samples and its possible connection with surface enhanced Raman scattering effect are under discussion. Raman spectra can also provide information on dimer formation and significant impurities. But low temperature photoluminescence is more suitable for this task. Influence of growth conditions and semiconductor surface on film quality are studied on the number of samples and discussed in the report.
- B/PIL.10** VIBRATION MODES OF CARBONACEOUS MATERIALS IN SEIRA EXPERIMENT
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Vibration states of different graphites - fullerene C60, single and multiwall carbon nanotubes - have been registered on gold nanostructures with FTIR spectroscopy. Here we registered the effect of surface enhanced infrared absorption. The data of SEIRA spectroscopy are compared with conventional IR-spectroscopy and Raman spectroscopy. SEIRA spectroscopy is more sensitive to molecular structure than conventional spectroscopy and it give a possibility to register forbidden bands. We registered additional bands in fullerene C60 [1] and carbon nanotubes. This numerous bands in carbon nanotubes could be assigned to C=C, C-C, C=O, C-O etc molecular groups. Raman spectroscopy is better to use for characterization of structure ordering level.
I.G. V. Andrievsky, V. K. Klochkov, A. B. Bordyuh and G. I. Dovbeshko. Chemical Physics Letters. –2002. –364, 11-2. – P.8-17.
- B/PIL.11** ELECTRONIC STRUCTURE AND ARRANGEMENT OF TREATED HiPCO NANOTUBES
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Arrangement and electronic structure of single-wall carbon nanotubes, produced by HiPCO method, were investigated using X-ray emission, X-ray absorption, and optical absorption spectroscopy. Effect of heating on the diameter distribution of HiPCO tubes was detected in optical experiment. To interpret the spectral changes, tight-binding calculations of carbon tubes differed in diameter and chirality were performed. The change of electronic structure of HiPCO nanotubes in the result of purification was observed by X-ray spectroscopy. X-ray absorption spectrum of nanotubes treated by acids showed an additional peak corresponded to the oxidized state of carbon. X-ray emission spectroscopy revealed a significant change of the valence band of HiPCO tubes, which were purified by thermal oxidation in air and acid treatment. The spectrum of purified nanotubes showed an increase of high-energy maximum compared to that in the spectrum of pristine material. Explanation of experimental data was made on the bases of quantum-chemical calculations of carbon tubes with various size and shape vacancies.
This work was financially supported by the INTAS (Projects 00-237, 01-254).

- B/PII.12** ELECTRONIC STATE OF CARBON PRODUCED BY ANNEALING OF NANODIAMONDS AT DIFFERENT TEMPERATURES
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 The nanodiamonds (ND) annealed at temperatures 1150–2100 K were studied using X-ray fluorescence spectroscopy and field emission measurements. C_{Kα} spectra of materials produced in the temperature range of 1420–1600 K showed that carbon atoms constituting the nanoparticles are at least in three states: diamond-like, graphitic and another state characterized by high electron localization. Comparison between X-ray spectroscopic data and theoretical spectra of models calculated using density functional theory suggested the latter form of carbon would constitute the chains of linked hexagons with armchair boundaries. The chains are likely to be generated at the interface between agglomerated ND particles. C_{Kα} spectrum of onion-like carbon (OLC) formed at 1800 K exhibited strong increase of high-energy maximum that might result from defects in the curved graphitic networks. Quantum-chemical calculations revealed the holed cage is more preferable model to explain experiment. The changes of C_{Kα} spectra measured for annealed ND samples are in correlation with their field emission characteristics.
 This work was financially supported by the INTAS (Projects 00-237, 01-254).
- B/PII.13** ELECTRON-ELECTRON INTERACTION IN NANOCARBON MATERIALS (NANOTUBES) AND GRAPHITE
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 From the time of discovery nanotubes one of the most important problems is the possibility of a superconducting state in them. Superconducting state is determined by electron-electron interaction. On the other hand electron-electron interaction is exhibited in electronic transport properties of conductors in normal state -so-called interaction effects (IE). IE are connected with the correction to density of states of conduction electrons in a result of quantum interferences of electrons at their diffuse motion in random conductors. IE contribute to diamagnetic susceptibility χ . The χ of arc-produced sample of multiwall carbon nanotubes (MWNTs), brominated ones, and graphite (G) was measured from 4.5 to 400 K. An additional contribution $\Delta\chi(T)$ to $\chi(T)$ was found at $T < 50$ K for all samples. It is shown that $\Delta\chi(T)$ is dominated by IE correction to χ . The IE shows a crossover from two-dimensional to three-dimensional behavior at $B = 5.5$ T for MWNTs and three-dimensional behavior for G at B from 0.01 up to 5.5 T. The effective interaction between electrons for interior layers are repulsion and the electron-electron interaction $\lambda_{c,c}$ was estimated to be $\lambda_{c,c} \sim 0.26$ for MWNTs and $\lambda_{c,c} \sim 0.1$ for G
- B/PII.14** SYNTHESIS AND CHARACTERIZATION OF SUPERHARD C60 POLYMERIC PHASE AROUND 830K AND 13 GPa.
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 Extensive investigation of C₆₀ polymerization at high pressure high temperature (HPHT) conditions was performed. Unlike to most of previous works done in this field, we performed studies using in situ methods. The progress was achieved due to special design of the externally heated diamond anvil cells (DAC). This design allowed us to perform in situ Raman study of C₆₀ P-T diagram in the broad temperature and pressure range up to 27 GPa and 900K. In the most interesting P-T region around 13 GPa and 830 K we also performed in situ X-ray diffraction study using synchrotron radiation at ESRF. The in situ study in this P-T region was also enforced by extensive study of the bulk sample synthesized using multi-anvil press at 830 K and 13 GPa. This sample was studied using Raman spectroscopy, High Resolution TEM, X-ray diffraction. Compressibility study up to 26 GPa allowed to calculate bulk modulus of the synthesized phase. Hardness of this sample was found only about 35 GPa, which is much less compared to “harder than diamond” phases reported in literature. It is shown that only control of pressure and temperature conditions is not enough for reproducible synthesis of superhard phases. Other factors such as stress and P-T pathway must be taken into account as well.
- B/PII.15** SUPERHARD 3D POLYMERS OF CARBON NANOCCLUSERS
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 New superhard phase of single wall carbon nanotube (SP-SWNT) has been compared experimentally with 3D polymeric phases of analogous carbon cluster - fullerene C₆₀ (both SWNT and C₆₀ composed from curved graphene sheets). Mechanical properties of material composed from the polymerized clusters are determined by properties of the cluster. The 3D carbon nanocluster polymers were studied both in situ under pressure in a shear diamond anvil cell and after pressure release. Information about bulk modulus was derived from the pressure dependence for the mode in high-energy range of the Raman spectra (i.e. the band 1594 cm⁻¹ for SP-SWNT and 1570 cm⁻¹ for 3D polymer of C₆₀). This is bond-stretching mode of pair of carbon sp² atoms, it is building bond for the clusters and in general it does not require the presence of graphitic structure and lies in the range 1500-1630 cm⁻¹. In present study the Grüneisen parameter for 3D fullerite polymer was estimated experimentally using available experimental and theoretical data for bulk modulus of ultrahard fullerite (540 to 800 GPa depending on structure and synthesis conditions). The reasonable value for the fullerite Grüneisen parameter is the same as for the graphene sheet (1.1). The same value was used for the present estimation of bulk modulus of SP-SWNT (465 GPa). The value is close to diamond and consistent with theoretical calculations 420 GPa (L.A. Chernozatonskii et al. JETP Letters, 74, 467 (2001)). In addition to high bulk modulus SP-SWNT reveals superhard properties: its hardness (62 to 150 GPa) belongs to the range between cubic BN and diamond.

- B/PIL.16** GAS EXPOSURE AND THERMAL ANNEALING EFFECTS ON CARBYNOID STRUCTURES IN NANOSTRUCTURED CARBON FILMS INVESTIGATED BY IN SITU RAMAN SPECTROSCOPY
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 The presence of a large amount of stable carbynoic structures in nanostructured carbon films produced from supersonic cluster beams [1] has been recently disclosed by in situ Raman spectroscopy [2]. The formation of sp linear chains is revealed by a large structured band with the main peak at nearly 2100 cm⁻¹ and a shoulder at 1980 cm⁻¹, assigned to polyynes and polycumulene moieties respectively. The temporal evolution of the carbyne peak has been analysed for films exposed to several gases (He, N₂, H₂, dry air) at the pressure of 500 mbar. In oxygen-rich environment the carbynic species appear to be very reactive whereas the effects of the other gases are less destructive and substantially equivalent. Ex situ infrared absorption measurements have confirmed the role of oxygen in the carbyne stability. The thermal stability in UHV has been studied up to 200 centigrade degrees. We observe different decay kinetics as a function of annealing temperature, showing a threshold in the carbyne stability.
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 [2] L. Ravagnan, F. Siviero, C. Lenardi, P. Piseri, E. Barborini, and P. Milani, C. S. Casari, A. Li Bassi, and C. E. Bottani, Phys. Rev. Lett. 89,
- B/PIL.17** RAMAN SPECTROSCOPY STUDIES OF CARBON NANOTUBES PREPARED BY ELECTRIC ARC DISCHARGE
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 Carbon Nanotubes were prepared by the arc discharge of graphite in Ar atmosphere. Two kind of samples were processed. One, sample S1, using conventional catalysts (Fe, Ni, Co and FeS) and another, sample S2, using the same catalysts and an additional commercial glue. The Raman spectrum of each sample shows additional peaks to the well known characteristics of carbon nanotubes. In both cases band D (1369 cm⁻¹) and G (1590 cm⁻¹) are present. Different features in the low wavenumber (< 300 cm⁻¹) region are present for each sample. A comparison of both spectra allow us to confirm the role of the commercial glue in the carbon nanotubes processing. Additional structural analysis for the determination of the kind and size of the nanotubes was also carried out.
- B/PIL.18** ENHANCEMENT OF THE MECHANICAL PROPERTIES OF THE CARBON NITRIDE THIN FILMS BY DOPING
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 Due to the failure of synthesizing predicted superhard crystalline carbon nitride thin films, lot of efforts have been generated towards amorphous or nano-crystalline carbon nitride (CN_x) or related material. The drawbacks of the carbon nitride films like high build up stress and less amount of nitrogen incorporation into the films limits its application. Growing the carbon nitride films with doping may enhance the performance. In the present investigations CN_x thin films were synthesized by hotfilament plasma enhanced chemical vapor deposition (HF-PECVD) technique using acetylene (C₂H₂), ammonia (NH₃) and hydrogen (H₂) as feedstock gases at different substrate temperature. The films were doped with Si by using silane (SiH₄) gas. Nano-indentation, AFM, FTIR, and RBS techniques were employed to characterize the deposited Si doped CN_x films. Nano-indentation reveals that the films are very hard. The maximum hardness of the film achieved is 30 GPa without the film delamination from the substrate. Substrate temperature influenced the mechanical properties of the deposited film. With the increase of substrate temperature from 500°C to 650°C, the hardness of the films increases about 3 times. FTIR observation correlates this measurement. The role of Si is thus described as catalyzer. The Si doping percentage also influences the hardness of the films. RBS measurement reveals that a high amount of nitrogen is incorporated into the film. The typical value of the nitrogen is about 45 at %.
- B/PIL.19** COMPARATIVE STUDIES OF THE CARBON NANOTUBES GROWN BY SIMPLE TECHNIQUE
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 Carbon nanotube is a novel material system whose unique properties offer intriguing possibilities for the wide range of applications. Carbon nanotubes were grown on metallic wire by a very simple technique called as Cold Plasma Chemical Vapor Deposition (CP-CVD). In this technique carbon nanotubes were grown directly over the catalyst-supported wire by resistive heating in hydrocarbon atmosphere at about 700°C. The localized dissociation of the hydrocarbon gas over metallic wire allows one to get well control nanotubes. In this process the nanotube grows very rapidly. We have made the comparative studies of the properties of the nanotube by varying different parameters like: growth time, process gas, growth temperature, growth pressure, catalyst and its concentrations. The effect of plasma created by applying additional bias is also the matter of discussion. The growth time has the influence on the density of the nanotube films but the length and diameter of the nanotubes also changes at low growth time region (up to 1 min). Methane does not promote to grown nanotube at particular time and temperature in compare to acetylene gas. Use of dimethylamine gas allowed to grow thin and short length nanotubes. With the increase of growth temperature nanotube diameter and periodicity of the spiral nanotube increases. The growth pressure and catalyst concentrations have only influence on the density of the nanotube. Additional plasma creations around the wire by applying bias align the nanotubes and also produce very long self-supporting nanotube (about 45 mm). This kind of nanotube has direct implementation in the field of luminescent devices, but still more applications to come. SEM and TEM were employed for characterization.

- B/PII.20** STUDY OF STRUCTURE AND MORPHOLOGY OF LANGMUIR-BLODGETT SWCNT/BEHENIC ACID MULTILAYERS BY X-RAY SCATTERING TECHNIQUES
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 Langmuir-Blodgett (LB) technique is a powerful method to organise organic films as complex structures. It allows the realization of a molecular architecture of different molecules with high control and reproducibility over the number of repeated layers and their thickness. The resulting structure, in optimised process condition, is well ordered with a preferential orientation. On the other hand, the realisation of ordered structures containing single wall Carbon Nanotubes (SWCNTs) is one of the main requirements for their numerous applications. The goal of this work was to achieve an ordered structure consisting of SWCNTs alternated with behenic acid layers in order to study the effects of the inclusion of carbon nanotubes in LB systems and verify the formation of an organised structure. A structure consisting of SWCNTs embedded in LB layers of behenic acid was built spreading SWCNT and behenic acid at the air/water interface and depositing them on Si(100) at a surface pressure of 35 mN/m and 27 mN/m respectively. The structural ordering, multilayer periodicity and interface configuration of the LB films were characterised by X-ray specular reflectivity (XSR) and X-ray diffuse scattering. The surface morphology was investigated by scanning probe microscopy (STM/AFM) and scanning electron microscopy (SEM). Low-angle x-ray measurements exhibit distinct satellite peaks demonstrating that the periodicity of 55Å of the LB behenic acid reference sample was still conserved when SWCNT layers were inserted between the behenic acid layers. Moreover, no relevant structural and morphological in-plane asymmetry could be revealed. The morphological properties measured by X-ray scattering were compared with results of AFM and SEM analyses.
- B/PII.21** ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF HETERONANOTUBES: MWBNNT AND B-DOPED SWCNT
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 We present a study of multiwalled boron nitride nanotubes (MWBNNT) and boron doped single walled carbon nanotubes (B-doped SWCNT) which have been produced by substitution reaction from SWCNT templates. The morphology and crystal structure of the samples have been characterized by transmission electron microscopy (TEM), electron diffraction and electron energy-loss spectroscopy (EELS). Pure MWBNNT with a 1:1 BN atomic ratio as well as clean SWCNT with B-substitution levels up to 15% have been produced. The electronic structure, the optical properties and their characteristic active vibration modes reveal strong significant changes with respect to pristine SWCNTs and in good agreement with state of the art ab initio calculations. This shows the potential of this doping technique as a basic element for molecular electronic devices.
 Work supported by DFG and the EU research and training network COMELCAN.
- B/PII.22** GISAXS STUDY OF THE ALIGNMENT OF ORIENTED CARBON NANOTUBES GROWN ON PLAIN SiO₂/Si(100) SUBSTRATES BY A CATALYTICALLY ENHANCED CVD PROCESS
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 Despite the importance in the alignment of carbon nanotubes films to provide quite accurate emission centers for field emission, there are to our knowledge no quantitative study of the degree of alignment of CNTs films in the literature. Indeed SEM images provide a valuable qualitative impression of alignment in many reports but i) the images are only qualitative; ii) this is a local probe that can induce some misinterpretation about the true uniformity of the sample. Grazing Incidence Small Angle X-Ray Scattering (GISAXS) is well suited to get important structural information on the alignment and the correlation between nanostructures. In addition, we also investigate the alignment of CNTs by angular measurements of Auger electrons (C KVV transitions sensitive to the p electrons). In both cases the strong 1D anisotropic character of p electrons in oriented CNTs is spectroscopically probed. We have performed GISAXS experiments to get structural (orientation of the alignment mainly, but also size distribution and density) and correlation information (mutual alignment, presence of defects in the orientation) on nanostructures grown on plain SiO₂ (thickness 2-8 nm)/Si(100) substrates after dispersion of a metallic catalytic islands. It is expected to get a sharp GISAXS signal if the nanotubes are perfectly aligned normal to the surface. The degree of the alignment of CNTs was studied according to growth parameters (substrate temperature, NH₃ concentration, gas activation parameters, nature of the metal).
- B/PII.23** EPR STUDIES OF THE CEMENTITE NANOPARTICLES IN A CARBON MATRIX
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 Three samples with different concentration of iron carbide (Fe₃C, cementite) in a carbon matrix have been synthesised by carburisation of nanocrystalline iron with methane. The samples have been characterised by XRD and SEM methods. The mean crystallite size of the obtained iron carbide has been found to be in the range from 41 to 67 nm. The electron paramagnetic resonance (EPR) measurements have been done at room temperature. Very intense EPR spectra have been recorded for all samples. The resonance field strongly depends on the concentration of cementite. The EPR spectra have been fitted by at least two Lorentzian-shape lines, centered at low (0,1 T) and high (over 0,2 T) magnetic field. The linewidth strongly depends on the Fe₃C/C ratio. The EPR signal arise probably from the agglomerates of Fe₃C. The EPR line components depend on the degree of graphitization. The shift of the resonance field is connected with a strong ferromagnetic interaction between the aggregates.

- B/PII.24** NANOINDENTATION STUDIES OF MULTILAYER AMORPHOUS CARBON FILMS
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The mechanical properties of multilayered amorphous carbon (a-C) thin films, developed by rf magnetron sputtering on (100) c-Si substrates, with sp³ (hard) and sp²-rich (soft) sequential layers, were investigated by nanoindentation. The total (~100nm) and bilayer thickness (between 14 and 45nm), as well as the sp³ and sp² carbon bonded content were determined by spectroscopic ellipsometry in the 1.5-5.5 eV energy region. The Continuous Stiffness Measurements (CSM) technique was used to measure hardness, (H), and elastic modulus, (E), as a function of depth. The Bhattacharya - Nix equation, which is the result of the simulation with the finite elements method to a nanoindentation experiment and takes into account the substrate effect on the measured values of (H), was applied afterwards in order to extract the real values of thin films' hardness (Hf). The dependence of (Hf) on the nanostructure properties, like the percentage of sp³ content and the bilayer thickness, was studied. The (Hf) was found to relate linearly with the sp³ bonded carbon. In addition, the multilayer structure affects Hf and specifically results in films' strengthening with a corresponding reduction of the bilayer thickness, which is in agreement with the Koeler's model, that can be generally applied in crystalline multilayered structures, consisting of a hard and a soft material. Finally taking advantage of the variation of the sp²- rich layer thickness, we extend the previous model conclusions, proposing the thickness reduction of the soft layer to achieve final functional properties (i.e. hardness enhancement).
- B/PII.25** PREPARATION AND PROPERTIES OF "PURE" N@C₆₀
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Since endohedral fullerenes became available as macroscopic quantities in the last decade, many efforts were made to explore the specific properties of these new materials. In our opinion, endohedral fullerenes based on encapsulated group V elements are most promising because of their exceptional spin relaxation properties in combination with chemical stability. One major obstacle of broader use is still the preparation of samples containing significantly more than 100 ppm of "cage" material. I will discuss recent progress made in our laboratory towards developing a reliable and reproducible method resulting finally in a "chemically" pure N@C₆₀ sample.
- B/PII.26** NANOSTRUCTURING OF C[sub 60] (FULLERENE) THIN FILMS
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Highly ordered films of C[sub 60] were produced on mica and HOPG (highly ordered pyrolytic graphite) substrates by vapor deposition. It was shown earlier that they can be stabilised by charge injection [1]. Nanostructuring by different electrochemical procedures (potentiodynamic and galvanostatic conditions) was realized. The influence of film thickness and counterions on electrochemical doping in aqueous solutions and ionic liquids was investigated by ex situ STM and AFM, optical, vibrational and mass spectroscopy as well as by in situ Raman spectroelectrochemistry. The main products of electrochemical reduction in aqueous solutions, which is irreversible and completely changes the structure of the film, are hydrogen C[sub 60] oligomers and containing C[sub 60] derivatives. The films were stable under ambient conditions over weeks. One application of such nanostructured fullerene layers is the use in electronic devices. We developed a fabrication process for fullerene containing organic field effect transistors.
- B/PII.27** INVESTIGATE OF STRUCTURE OF C60 BY ANNAELING PROCESS
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The effect of thermal annealing on C60 thin films deposited by vacuum evaporation was investigated. Aluminium was coated on some films before annealing. The properties of films were studied in terms of annealing temperature for bare C60 films and Aluminium coated C60 films. The crystallinity and physical properties of C60 films were changed by annealing temperature as low as 100 oC. The X-ray diffraction and Raman spectroscopy indicated that the films have C60 structure below 300 oC for annealing time as long as 3 hours. Higher temperature annealing results in formation of microcrystalline graphite. Dependence of surface roughness and electrical properties of these films were also investigated. In this study, we could demonstrate that properties can be improved and the surface roughness can be improved by annealing of C60 after coating of Aluminium.
- B/PII.28** SYNTHESIS AND CHARACTERIZATION OF CARBON NANOTUBES-TIO2 NANOCOMPOSITES
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TiO₂ based nanocomposites are interesting nanomaterials for photocatalytic reactions, due to the semi-conducting properties of TiO₂ which band gap of energy is 3.2 eV. In the present study, carbon multi-walled nanotubes (MWNTs) produced by catalytic decomposition of acetylene at 600oC on a CoxMg(1-x)O solid solution were covered by a thin layer of TiO₂. The MWNTs coating was performed by a sol-gel method using classical alkoxides as Ti(OEt)₄ and Ti(OPr)₄ and by hydrothermal hydrolysis of TiOSO₄ in sulphuric acid under pressure at 180°C. In order to compare the two different ways, the corresponding nanocomposites were characterised by various techniques as: x-ray diffraction, IR and XPS spectroscopy, thermal analysis, gas adsorption, SEM and TEM. The activity of the nanocomposite materials was evaluated in the photocatalytic decomposition of aromatic pollutants in aqueous solution under UV irradiation.

B/PII.29**DIFFUSION COEFFICIENT OF AZOBENZENE DRIVEN POLYMERS**

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Thin films of azobenzene containing polymers display interesting properties for optical storage. When exposed to near UV or green light they undergo topographic deformations, at an intensity (a few mW per cm²) far under the one necessary to increase the film temperature. We investigated spin-coated azopolymer films on which an amplitude modulated grating (~ 1000 grooves/cm) has been inscribed prior to the experiment. We studied the disappearing of the amplitude grating under uniform UV illumination. The topographic measurements were made by using an AFM coupled with an optical microscope. Hence, we studied the progressive homogenization of the topography, for different states of light polarization, versus time and related it to a diffusion parameter which requires a model to make sense. It is now understood that irradiated azomolecules isomerization goes along with a motion. To describe it we resort to an improved random walk model which takes into account the gradient of the light intensity times the concentration as a driving force and to which is attributed a diffusion parameter. Then this diffusion term is added to a Edwards-Wilkinson type equation which describes a surface evolution through the medium of a Laplacian of the interface height that accounts for the smoothing surface tension. By confronting experimental results with the model we evaluated the diffusion parameter and related it to microscopic phenomena.

B/PI.30**MECHANICAL PROPERTIES OF HYBRID POLYMER NANOTUBE SYSTEMS INCLUDING SUPER TOUGH COMPOSITE FIBRES**

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In this work, mechanical properties of hybrid materials fabricated from nanotubes and commercially available polymers were investigated. It was found that, by adding various concentrations of arc discharge multiwall nanotubes, both Young's modulus and hardness increased by factors of 1.8 and 1.6 at 1wt% in PVA and 2.8 and 2.0 at 8wt% in PVK, in reasonable agreement with the Halpin-Tsai theory. Furthermore, the presence of the nanotubes was found to nucleate crystallization of the PVA. This crystal growth is thought to enhance matrix-nanotube stress transfer. In addition, microscopy studies suggest extremely strong interfacial bonding in the PVA-based composite. This is manifested by the fracture of the polymer rather than the polymer-nanotube interface. The dependence of the polymer nanotube interfacial interaction on host polymer was studied by intercalating various polymers (PVA, PVP and PS) into single wall nanotube buckypaper. Even for short soak times, significant polymer intercalation into existing free volume was observed. Depending on the polymer and the level of intercalation tensile tests on intercalated sheets showed that the Young's modulus, strength and toughness increased by factors of 3, 9 and 28, respectively. This indicates that the intercalated polymer enhances load transmission between nanotubes due to the significant stress transfer. The level of stress transfer was observed to scale with polymer hydrophobicity as expected. In addition super tough polymer-nanotube fibers were produced from a continuous flow coagulation spinning method. This procedure allowed extremely long (>20m) fibres to be produced and dried very rapidly. These materials displayed extremely high Young's Modulus, tensile strength and toughness of >100GPa, >1GPa and 500J/g.

Multifunctional Applications&Electronics

Session Chair: Jens H. Walther

B/PII.31**CARBON NANOTUBE SHEETS FOR THE USE AS ARTIFICIAL MUSCLES**

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Besides a lot of outstanding properties of carbon nanotubes, like the high current carrying capacity, the high field emission, the tensile strength, etc. the expansion under applied low voltage (1-5V) predestinated those material for special fields of applications. The electromechanical properties of bucky paper can be used for actuators or artificial muscles. Nevertheless, since the first observation of this effect by Baughman (R.H. Baughman et al. Science 284 (1999) 1340-1344) less is known about the macroscopic properties of bucky papers.

To develop an actuator which fits to industrial requirements, the production and the quality of bucky paper must be optimized and the material must be tested as well as adapted to a prototype actor.

To analyze the electromechanical properties, we developed an experimental setup to measure the maximum forces or the elongation of the bucky papers. The characterized buck papers are distinguished e.g. in their thickness, purity, different raw materials or composition. Morphological or chemical properties of the used material were characterized among others by FE-REM, EDX and XPS. The analysis of adsorption/desorption isotherms gives additional information about the BET-surface area as well as the pore size distribution with varies e.g. in dependence of the purification steps.

The properties like response time, maximum displacement and force as well as the switching frequency could be improved compared to the first materials under investigation.

B/PII.32**MEASUREMENT OF THE NANOFRICTION OF ATOMICALLY THIN FILMS ON METALLIC SUBSTRATES AND FUTURE APPLICATION TO NANOTRIBOLOGY OF CARBON NANOTUBES**

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Using a quartz-crystal microbalance we perform measurements of nanofriction of simple atoms or molecules sliding on a surface [1]. We have already used this technique to study the tribological interaction of noble gas films physisorbed on metallic substrates, finding very interesting non-linear and hysteretic phenomena [2]. Our work is the first observation, in the field of nanotribology, of the well-known dynamical phase transition called depinning transition. Now we are setting-up a new UHV apparatus in order to improve our experimental conditions. In particular, our purpose is to perform nanofriction measurements of simple molecules physisorbed on carbon nanotubes, thanks to financial support of 2003 "Carbon-based microstructures and nanostructures" FIRB.

[1] L. Bruschi and G. Mistura: Phys. Rev B 63, 235411 (2001)

[2] L. Bruschi, A. Carlin and G. Mistura: Phys. Rev. Lett. 88, 046105 (2002)

- B/PIL.33** SELECTED NANOSYSTEMS AS AN ACTIVE ELECTRODE MATERIAL FOR LI-ION BATTERIES
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In order to improve the energy density and cycleability of batteries, nanostructured solid state materials are presently the focus of intense research. Selective synthesis of new materials with fullerene-like structure and one-dimensional nanoarray structure is a promising route for further development of new electrode materials used in Li-ion batteries. A possible choice is an active material based on carbon SWNT, where lithium is inserted into the space between tubes in the SWNT bundle. Recently, we have synthesized a new material, i.e. single-wall nMoS₂ nanotubes, which is capable of reversible lithium insertion. Another alternative are one-dimensional arrays of transition metals dichalcogenides. Comparing their properties with layered, quasi-two-dimensional transition metals dichalcogenides and with graphite, a standard electrode material, the new materials show promising improvements. The overall characteristics of the selected nanosystems indicate that they may be considered as viable electrode materials for Li-ion batteries.
- B/PIL.34** CARBON NANOTUBES ARRAY AS CHARGE COLLECTOR OF A HIGH RESOLUTION RADIATION SENSOR
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We propose the fabrication and characterisation of a Carbon NanoTubes (CNTs) array as the main building block of a radiation detector, for use in sub-nuclear and high energy Physics experiments and in nuclear medicine and exploitable for space environment. The CNTs array will be located between the active medium and the read-out electronics. The total charge produced in the active medium traversed by a particle will be driven via the carbon nanotubes to the read-out electronics. Multi-wall CNTs, with 10 - 100 nm diameter, having metal or semiconductor electrical properties, will enable a deep sub-micron resolution in the analysis of the spatial distribution of charge. A highly needed major breakthrough in the CNTs technology for nanoelectronics is the development of a fabrication method capable of producing uniform CNTs with well-defined and reproducible electronic properties. In the case of the detector of the present project, CNTs highly uniform in size and spacing and electrically insulated from each other are required for the optimisation of the charge collection. In this work a template based CVD method for the synthesis of an array of CNTs has been investigated. Highly ordered, parallel, and perpendicular to the surface, nanochannels in alumina foil of hundreds square millimeters area have been formed by anodic oxidation of aluminium. Pore size and pitch in the range of 10 – 200 nm and 100 to 400 nm, respectively, has been obtained for alumina thickness up to 0.1 mm. A metal catalyst such as Co and/or Ni has been deposited inside the alumina nanochannels for the subsequent selective cracking of the carbon feedstock species. Preliminary results on the CVD synthesis of CNT in a proper designed reactor will be presented.
- B/PIL.35** A NOVEL APPROACH TO ASSEMBLY OF CARBON NANOTUBES AND QUANTUM DOTS FOR NANODEVICE APPLICATIONS
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Carbon nanotubes have attracted much attention in the fabrication of nanoscale devices including transistors and sensors. The challenge has been the ordered placement and manipulation of the nanotubes. Conventional fabrication techniques must be augmented by new approaches to take the advantage of the quantum nature of the nanoscale devices, involving the assembly of atom-like nanostructures into 2-D and 3-D units. Here, we demonstrate a novel approach for forming nanoassemblies of carbon nanotubes and quantum dots using the EDC coupling procedure. We present FTIR and Raman spectroscopy of the chemical conjugation procedure and transmission electron microscopy of the nanoscale building blocks. Potential future applications of our methodology include the fabrication of novel electronic and photonic devices.
- B/PIL.36** ELECTRON FIELD EMISSION FROM MULTI-WALLED CARBON NANOTUBES
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Films of aligned multi-walled carbon nanotubes are produced by two different methods, thermal chemical vapour deposition (CVD) and plasma chemical vapour deposition. The field emission measurements show that films from the thermal CVD have higher emission current than the plasma CVD. In the thermal CVD the result shows that the current density as a function of applied electric field (on multiple cycles) is reproducible up to a value around 1 mA/cm². Exceeding this value leads to light emission and irreversible changes occur in the nanotube film. Spectral measurements of this light show a purely blackbody radiation effect with a temperature around 1550 K for the onset current density, but temperatures over 2000 K are also seen for higher current densities. The onset of the light emission also occurs at approximately the same value as a noticeable change in the slope of the Fowler-Nordheim plot, indicating a structural change of the nanotube film. Investigation of the emission properties of as-produced individual multi-walled carbon nanotubes is carried out using a combined transmission electron microscope (TEM) and a scanning tunnelling microscope (STM). This gives the unique possibility to observe the carbon nanotube while the field emission measurements are performed, revealing structural changes of the tube at high emission current. The observation and results from the individual nanotubes will be correlated to the results obtained from the macroscopic measurements.

- B/PIL.37** GAS SEPARATION PROPERTIES OF MOLECULAR SIEVING CARBON MEMBRANES WITH NANOPORE CHANNELS
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Molecular sieving carbon membranes (MSCM) have characteristic properties in gas permeation, which are attributable to the interaction between gas molecules and carbon surface in very narrow nano-channels. The gas separation properties and the adsorption-diffusion mechanism in permeation were investigated for the MSCM which has nano-channels with the diameter of about 0.3 nm. The permeability study using MSCM prepared from polyimide films gave some parameters of adsorption and diffusion in the nano-channels. Adsorption amount of H₂ estimated by the permeation technique was in good agreement with the result of adsorption measurement using a typical volumetric method. The agreement experimentally supports the surface diffusion mechanism in nanopore channels even at ambient temperatures. The activation energy of H₂ diffusion was 3-6 times higher than that on graphite surface, sensitively depending on the diameter of pore channels. The MSCM showed quite high H₂/CO permselectivity which can achieve the reduction of CO content in reformed gas from 1 % to 5-6 ppm. The MSCM will be a promising material for the application to hydrogen purification system in fuel cell vehicles with on-board reformer using methanol or gasoline as an energy source.
- B/PIL.38** FIELD EMISSION OF CARBON NANOTUBES ARRAY GROWN ON SUBSTRATES PATTERNED BY A SEQUENCE OF LITHOGRAPHIC PROCESS
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Field emission on carbon nanotubes array grown on substrates patterned by combined lithographic techniques. Field emission is one of the most promising potential applications of carbon nanotubes (CNTs). These nanostructures combine positively a geometrical effect (local exhalation of the electric field due to a strong curvature radius) and an electronic effect (weak work function) as well as they display strong chemical inertness and thermal conductivity, which open the way to the realization of convenient electron sources for vacuum electronics such as flat panels, cold cathodes. Field emission measurements obtained on CNTs grown on SiO₂/Si(100) substrates by the DC HF CCVD process where a dispersion of metallic catalytic transition metal (Co, Ni) particles was previously performed, showed that the thresholds of emission were strongly dependent on the nature of the material. Therefore they were within the range 1-4 V/μm for CNTs. By contrast they ranged above 10 V/μm either for carbon nanofibers or nanocones. However the current densities were quite variable and often reached a rapid saturation both due to screening of the field by the high density of CNTs and to conductivity limitations of the substrate. Therefore we used patterned surfaces to grow array of CNTs emitters. Patterned surfaces were obtained by controlled deposition of metallic spots by a combination of lithographic techniques, using either photons, electrons or ions beams. Array of particle islands of Co or Ni were obtained in the range 5-100 nm. Under proper CVD conditions we could grow subsequently one CNT by metallic island if the size of the metallic island did not exceed 60 nm.
- B/PIL.39** IN SITU XRD INVESTIGATION OF THE CCVD SYNTHESIS OF GRAPHITIC NANOFIBERS AND THE ADSORPTION/DESORPTION OF HYDROGEN
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In recent years graphitic nanofibers (GNF) have been proposed as sorbent for hydrogen storage and as cathodic material for Li ion batteries. In the present work the GNF were synthesized by catalytic chemical vapour deposition (CCVD). The applied NiO/CuO catalyst (98/2 wt.-%) was prepared by coprecipitation of the carbonates from the respective metal nitrates followed by calcination in air at 400 °C. As a powerful tool to study the synthesis of GNF we have been using a specially designed X-ray reaction chamber (XRC). The XRC allows to characterize in situ both, the activation of the catalyst and hydrogen adsorption experiments in different atmospheres up to 900 °C and 10 bar. The reduction of the catalyst and the formation of Ni and Cu metal at 350 °C is finished after 2 hours. GNF is synthesized by CCVD at 600 °C in a C₂H₄/H₂ gas stream. Following the working hypothesis that hydrogen molecules occupy interplanar sites between (002) planes in the graphite lattice, the d₀₀₂-value was monitored in dependence on the hydrogen uptake. The pristine GNF was treated in H₂ at 5 bar at temperatures from 25 to 600 °C up and down. We detected in creases of the d₀₀₂-value up to 0.045 Å. d₀₀₂-value changes occurred only under in situ conditions, i.e. without contact of the fibers with air. Additional SEM and TDS/MS measurements confirmed the XRC results.

Magnetism of Nanosystems

Session Chair: Tatiana Makarova

- B/PIL.40** REFRACTIVE INDEX OF FERROMAGNETIC SEMICONDUCTORS WITH LASER-INDUCED NANOSTRUCTURED GRATINGS
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The influence of intensive laser radiation (coherent light beams (CLB)) on a refractive index of the ferromagnetic semiconductor (FMSC) is studied. Is considered FMSC, which external surface $z=0$ is illuminated by two CLB with identical frequencies ω , which satisfy to a condition $\hbar\omega < E_g$ (E_g is the average energy of the carrier, a is the width of a forbidden region). In this case CLB interfere both on a surface and in volume of FMSC the interference picture - spatially-periodic alternation of light and dark areas (maximums and minimums of an electric intensity) is formed. Under its activity the conduction electrons will move from light areas and to be accumulated in dark, reserving area of a positive charge. Between areas of a positive and negative charge there will be an electric field. Under its activity the crystalline lattice of FMSC will be deformed. Its strain will give that through one area light will transit faster, and through other - more slowly. Thus we shall receive spatially-periodic structure - lattice of a refractive index. We design change of a refractive index of FMSC in a field of CLB and the parameters formed nanostructure - lattice of an index of refraction are appreciated.

- B/PIL.41** DENSITY MATRIX APPROACH TO MAGNETOTRANSPORT IN CARBON NANOTUBES
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For density matrix the Liouville equation in effective mass approximation is solved in an arbitrary magnetic field for deformation acoustic scattering. Using density matrix off-diagonal components the nanotube conductivity is calculated. If nanotube considered as effective conducting media it is shown that electron transport depends strongly on a ratio between nanotube diameter and magnetic length. For multi-wall nanotube in a strong magnetic field this ratio can be much more than unity. In this case magnetic quantization determines electron transport parameters and the electron mobility determines sign of magnetoresistance. It is positive for high mobility and is negative for low mobility. In the last case magnetoresistance depends linearly on a weak magnetic field. For intermediate mobility magnetoresistance can change sign depending on magnetic field magnitude. If ratio is less than unity the size quantization is very significant and magnetic field can be considered as perturbation. In this case magnetoresistance is always positive. Band gap value determines its dependence on a magnetic field. For wide gap nanotube magnetoresistance depends approximately quadratic on a weak magnetic field. For narrow gap nanotube the spin-orbital interaction is very strong. It leads to the linear dependence on a weak magnetic field. Our results show that in nanotube the negative magnetoresistance can be described, at least partially, without theory of weak localization.
- B/PIL.42** MAGNETIC AND OPTICAL PROPERTIES OF Fe-FILLED CARBON NANOTUBES
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Nanotubes are promising objects for nanoelectronics. Additional filling of the tubes by ferromagnetic conductor as e.g. Fe gives rise to a lot of new possibilities as for applications as for fundamentals. We report studying of magnetic, optical, transport properties of Fe-filled multi-walled carbon nanotubes grown by chemical vapour deposition on Si substrates. Surface distribution of magnetization have been measured with magnetoresistive sensor magnetometer as well as magneto-optically by contact printing methods. The revealed inhomogeneous distribution of magnetization correlate with the local deviation of the nanotubes axes from a perpendicular to the film plane.
Interpretation of the optical reflectance and transmission spectra allows to evaluate electronic structure of the filled nanotubes. As the tubes were aligned perpendicular to the film plane they manifested magnetic anisotropy with the easy axis along the tubes [1]. We have shown that a difference in coercivity in the longitudinal and transverse directions can be simply inferred from calculations of magnetic anisotropy in the fixed magnetostatic conditions. Changing of Fe content as well as a temperature cause correspondent changes both in local and total magnetization.
[1]. T.Muhl et. al. Journ. of Appl. Phys. 93 (2003) (accepted).
- B/PIL.43** SOL-GEL TEMPLATE AIDED FABRICATION OF NANOWIRES OF COLOSSAL MAGNETORESISTIVE OXIDE
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We have fabricated linear array of nanowires of technologically important colossal magneto resistive oxide lanthanum calcium manganite, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) using anodized alumina (AAO) membranes with pore diameters 20 nm and 100 nm as templates. We will discuss the novel polymeric sol-gel process using metal nitrates in aqueous solution and employing ethylene glycol as the polymerizing agent, developed by us as a general method for the fabrication of nanowires and nano powders of advanced multicomponent oxides. X-ray powder diffraction, energy dispersive x-ray analysis (EDAX) and selected area electron diffraction (SAED) studies indicated that single phase polycrystalline nanowires could be prepared by heat treating to temperatures as low as 500°C and that the nanowires stabilize in distorted cubic phase. The morphology of the nanowires were studied by scanning electron microscopy on the array of nanowires embedded in the alumina matrix and also transmission electron microscopy on the nanowires freed from the membranes. We will also present the interesting magnetic properties exhibited by these nanowires. The AC susceptibility data indicated a drop at 220 K corresponding to the transition from the ferro-paramagnetic phase and also a sharp fall at low temperatures indicating that the ferromagnetic phase may not be stable below 100 K. Our findings demonstrate that nanowires of manganites could be a new medium for studying intricate physics in these fascinating materials.
- B/PIL.44** ORDERED MAGNETIC METAL NANOWIRES IN THE MESOPOROUS SILICA MATRIX
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One of the most important challenges in material science is the preparation of nanostructures with the controlled properties and creation of the functional nanomaterials. However, the use of the nanostructures as materials is strongly restricted because of their low stability. The approach to solve this problem is the preparation of the so-called nanocomposite materials. This enables one to avoid aggregation of nanoparticles and protect them from external influences (e.g., from oxidation in air), which simplifies application of such materials. Here we report the synthesis of magnetic nanocomposites using mesoporous silica as a host material. Iron nanoparticles were incorporated into the pores of mesoporous silica. During the synthesis, a hydrophobic metal complex was introduced into the hydrophobic part of the as-prepared meso-SiO₂/surfactant composite. Thus prepared nanocomposites were characterized by TEM, ED, SAXS, SANS and magnetic measurements. It was showed that particles shape and size are in good agreement with the shape and size of the pores. Particles are uniform and well ordered in the silica matrix. Thus, mesoporous silica serves as nanoreactor for the formation of Fe-nanoparticles. This approach leads to functional materials with nanosized active elements in amorphous silica matrix, which could find application as high-density data storage devices.
This work is supported by RFBR (03-03-32182) and INTAS (01-204).

Nanosystems for biomedical applications

Session Chair: Silke Krol

- B/PIL.45** THIN CARBON LAYERS ON NANOSTRUCTURED SILICON FOR BIOMEDICAL APPLICATIONS
Anca Angelescu, Irina Kleps, Mihaela Miu, Monica Simion, Adina Bragaru, National Institute for Research and Development in Microtechnologies (IMT), P.O.Box 38-160, Bucharest, Romania
Adhesion of cells to biomaterials is fundamental in many tissue engineering and biotechnological processes. Biocompatibility is controlled mainly by the interface between a biomaterial surface and living tissue cells. One way to change the surface properties is by preparing a suitable coating. The carbon material as a thin surface layer is an attractive material for coating implants, e.g., in orthopaedic and dental surgery. The present study examined the technological parameters-structure-property relationships of carbon thin layers on nanostructured silicon samples with respect to the living cell adhesion. Different thin carbon layers were deposited on porous silicon (PS) layers with 35-50% porosity: (i) polycrystalline SiC films were prepared by PECVD method, by hexamethyldisilane decomposition ($T = 600^\circ\text{C}$; $t_{\text{dep}} = 1\text{h}$; $P = 0\text{ Torr}$; $D_{\text{precursor}} = 0.8\text{ ml/h}$; $H_2 = 2-3\text{ l/min}$; $P_i = 2-2.5\text{ Torr}$); (ii) the DLC layers were obtained by PECVD method from methane or methanol precursor at the following working parameters: $T = 600^\circ\text{C}$; $t_{\text{dep}} = 8\text{h}$; $P_{\text{uO}} = 0\text{ W}$, $D_{\text{CH}_3\text{OH}}$ or $D_{\text{CH}_4} = 0.015\text{ l/min}$, $H_2 = 6-13\text{ l/min}$, $P_i = 0\text{ Torr}$; (iii) a-SiC layers, 30-40nm thick, were obtained by electron gun evaporator. All the experimental layers were investigated by AFM, XPS, FTIR and RAMAN measurements. On these structures, three cellular lines: B 16; CHO; MDBK were grown. Our studies indicate that the interaction at the interface is specifically controlled by the surface morphology, especially by surface roughness, and by the chemical state of the surface which is given mainly by the material and by the method of surface preparation. The results indicate that the cell attachment on the surface of carbon coatings can be controlled by deposition parameters during the technological process.
- B/PIL.46** CATALYTIC FILAMENTOUS CARBONS (CFC) AND CFC-COATED CERAMICS FOR IMMOBILIZATION OF BIOLOGICALLY ACTIVE SUBSTANCES
G.A. Kovalenko, D.G. Kuvshinov, O.V. Komova, A.V. Simakov, N.A. Rudina, Boreskov Institute of Catalysis, Novosibirsk 630090, Russia
The problem to develop the effective adsorbents for immobilization of biologically active substances, including microorganisms, is still relevant because of its importance for medical applications, and for biotechnology and pharmaceutical industry. Obviously, such adsorbents-supports must meet certain criteria. First, they must have sufficient adsorption capacity with respect to biologically active substances (BAS) and firmly hold them on the surface. Second, they must retain and stabilize the biological activity of immobilized BAS at a relatively high level. Third, they must possess high mechanical strength and resistance to biological and chemical degradation. Finally, their cost should be relatively low. Adsorption properties of supports based on bulk catalytic filamentous carbons (CFC) have been studied with respect to different substances of biological origin – amino acid (L-tyrosine), protein (bovine serum albumin), enzyme (glucoamylase) and non-growing cells of microorganisms (E.coli, Bacillus subtilis, Rhodococcus sp.). The factors influencing the adsorption efficiency have been investigated. The main conclusion is that the value of accessible surface area is of crucial importance in the adsorption of the studied adsorbates of biological origin on bulk CFC-based adsorbents. A comparison of three independent methods for the calculations of the values of accessible surface area lead to conclusion that comparative method is a universal technique reflecting the physical meaning of the observed phenomena.
- B/PIL.47** C60/DNA/HYDROXYAPATITE NANOCOMPOSITES AS NOVEL NANOMATERIALS FOR BIOMEDICAL APPLICATIONS
O. Lysko, A. Veligura, A. Gorchinskiy, Y. Prylutskiy, S. Prylutska, E. Buzaneva, Taras Shevchenko National University of Kiev, Radiophysical and Biological Faculties, The Scientific and Training Center "Physical and Chemical Material Science of Kiev National Taras Shevchenko University and NASU", 64 Vladimirska Str., 01033 Kiev, Ukraine, V. Dubok, Institute for Problems of Material Science NANU, Kiev, Ukraine, P. Scharff, K. Risch, TU Ilmenau, Institut für Physik / FG Chemie Postfach 100565, 98684 Ilmenau, Germany
The creation of fullerene bone active drugs containing polyfluorobisphospho fullerenes and adaptation C60 water-soluble and DNA for biological use as and use these C60 solutions for the modification of hydroxyapatite nanoparticles in vitro [1,2] stimulated our study DNA nanotechnology and properties of C60/DNA/Hydroxyapatite composites with several C60 contents. C60 in water solution with C60 aggregates derivatized with (OH)_n groups have been used. The hydroxyapatite nanopowder was prepared by chemical precipitation from solution of calcium nitrate and two-substituted ammonium phosphate. The gel with hydroxyapatite nanopowder and C60 in water solution with DNA gel adding have been used for composite preparing. From UV-VIS and IR spectra of composites revealed distinct changes in the components due to their interaction controlled by C60 concentration in composites: C60 forms bonds with part of OH groups in hydroxyapatite, and bond with DNA thymine and some others DNA basis pairs.
[1] Lon J. Wilson, Interface 1999, p 24.;
[2] Wilson, S. R. "Biological Aspects of Fullerenes," in Fullerenes: Chemistry, Physics, and Technology, Kadish, K. M.; Ruoff, R. S. (eds), John Wiley & Sons, New York (2000).

- B/PIL.48** EFFECT OF X-RAY AND UV IRRADIATED C₆₀ FULLERENE AQUEOUS SOLUTION IN THE BIOLOGICAL SAMPLES
P. Scharff, L. Carta-Abelmann, K. Risch, Technical University of Ilmenau, Institute of Physics, 98684 Ilmenau, Germany, Yu.I. Prylutskyy(a), V.M. Yashchuk(b), K.M. Kushnir(b), O.P. Matyshevska(c), S.V. Prylutska(c), T.V. Koval(c), O.A. Golub(d), Kyiv National Shevchenko University, Departments of (a)Biophysics, (b)Physics, (c)Biochemistry and (d)Chemistry, Volodymyrska Str. 64, 01033 Kyiv, Ukraine
The fullerenes and their derivatives exhibit high biological activity in vitro and in vivo. The biological effects of these carbon materials depend considerably on their chemical modification and light treatment. The obtaining recently C₆₀ fullerene aqueous solutions (C₆₀FAS) with different stable C₆₀ aggregates (both hydrated molecules and clusters and microcrystallites) opens the prospect for their use for biological studies. Thus, the purpose of this work was to investigate the bioactivity of the C₆₀FAS in the biological medium (the suspension of thymocytes, isolated from Wistar rat thymus) in dependence on the low energy UV and X-ray irradiation. In particular, the results of our experiments show that under the influence of UV and X-ray irradiation an increase of the pro-oxidant properties of the C₆₀FAS at the low concentration of C₆₀ fullerene (10⁻⁵ M) and the damage of the DNA structures in the thymocytes suspension take place. The revealed pro-oxidant effect of the C₆₀FAS may be used in the bionanotechnology, for example, for the photodynamic therapy of transformed cells.
This work was supported by BMBF grant (Ukr 02-007).
- B/PIL.49** STRUCTURE OF C₆₀ FULLERENE IN WATER: SPECTROSCOPIC DATA,
P. Scharff, K. Risch, L. Carta-Abelmann, Technical University of Ilmenau, Institute of Physics, D-98684 Ilmenau, Germany, I.M. Dmytruk(a), M.M. Bilyi(a), O.A. Golub(b), À.V. Khavryuchenko(b), E.V. Buzaneva(c), Yu.I. Prylutskyy(c), S.S. Durov(a), Kyiv National Shevchenko University, Departments of (a)Physics, (b)Chemistry, (c)Radiophysics, (d)Biophysics, Volodymyrska Str., 64, Kyiv 01033, Ukraine, V.L. Aksenov, M.V. Avdeev, Joint Institute for Nuclear Research, 141980 Dubna, Russian
Fullerenes are widely investigated currently and have potential for various technical applications. In particular, for biomedical testing, water-soluble forms of fullerenes are undoubtedly of great interest [1]. The samples of C₆₀ fullerene aqueous solution (C₆₀FAS) were prepared with different concentration of C₆₀ fullerene in water: from 0.1 to 2.8 mg/ml (for comparison, the solubility of C₆₀ fullerene in toluene is 2.9 mg/ml). The results of complex experimental investigations of C₆₀FAS structure, including the UV-VIS, Raman, IR and small-angle neutron scattering (SANS) spectroscopy, are presented. All methods indicate to the simultaneous presence in the solutions of spherical C₆₀ aggregates and solid C₆₀ composed of a hydrated single C₆₀ molecules. Both the size of these aggregates and presence of the crystalline phase increase with C₆₀ fullerene concentration in water. The obtained experimental results were confirmed by theoretical quantum-chemical calculations of C₆₀ fullerene structure in water.
[1] Jensen AW, Wilson SR, Schuster DI. Bioorg. Med. Chem 1996; 4: 767-771.
- B/PIL.50** STUDY OF COLLOIDAL SOLUTIONS OF C₆₀ FULLERENES IN WATER BY SMALL-ANGLE NEUTRON SCATTERING
M.V. Avdeev(a), V.L. Aksenov(a), G.V. Andrievsky(b), L.I. Derevyanchenko(b), V.K. Klochkov(b), A.A. Khokhryakov(a,c), (a)Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia, (b)Institute for Therapy of Ukrainian AMS, Postyshev ave. 2-a, 61039 Kharkov, Ukraine, (c)Kyiv Taras Shevchenko National University, Volodymyrska str. 64, 01033 Kyiv, Ukraine
Fullerenes as strong antioxidants manifest a significant therapeutic effect in living organisms. However, the use of antioxidant properties of fullerenes faces difficulties connecting with the fact of low fullerene solubility in polar solvents, in particular, water. In recent years the production of dispersions of fullerenes in water was developed and is of current interest from medical point of view. In the present work the small-angle neutron scattering (SANS) is applied to study colloidal solutions of fullerenes (C₆₀) in water obtained by transferring of the fullerenes from an organic solution (benzene) into aqueous phase with the help of ultrasonic treatment followed by the extraction of the organic solvent. The obtained dispersions (concentration 0.002 ÷ 0.2 mM) are stable and according to preliminary tests may be used in medical applications. The SANS experiments showed that these systems are highly polydisperse in a wide interval of sizes up to 50 nm, which testifies the electron microscopy data. The contrast variation based on different mixtures of light and heavy water points to the presence of a component in the aggregates, which is different from fullerenes. This component is assumed to be responsible for stabilization of the dispersions. A number of hypotheses about its origin, in particular the formation of special hydration shells around the fullerenes, are discussed.
- B/PIL.51** INTERACTION OF NUCLEIC ACID WITH SINGLE-WALLED CARBON NANOTUBES: SEIRA EXPERIMENT AND MODEL
G.I. Dovbeshko(a), O.P. Repnyzka(a), E. Obratsova(b), Ya. Shtogun(c), (a)Institute of Physics of National Academy of Sciences of Ukraine, Prospect Nauki 46, Kiev-03039, Ukraine, (b)P.N.Lebedev Physics Institute, Russian Academy of Sciences, 53 Leninsky pr., Moscow 117924, Russia, (c)The Faculty of Radiophysics of National Taras Shevchenko University, 64 Volodymyrska Str., Kyiv-01033 Ukraine
Nowadays a study of single-walled carbon nanotubes (SWCNT) is of great scientific and applied interest due to their wonderful mechanical and electrical properties [1]. However, due to their not good solubility to any solvents, it is very difficult isolate one SWCNT from another. It is known some polymers and nucleic acids that one tries to use for it [2]. However, the mechanism of the DNA interaction with SWCNT is important for application and fundamental knowledge, however until now it is not clear. Structural characterisation of graphite and SWCNT has been done with Raman and FTIR spectroscopy. Interaction of nucleic acids with graphite powder and SWCNT was studied with SEIRA spectroscopy [3]. Analysis of DNA-SWCNT complex vibration modes has shown the structural changes in DNA: sugar and bases conformations, changes in phosphate vibrations and could be interpreted as A-B conformation transition and stabilisation of structure in some DNA fragments. We have proposed the model of DNA interaction with SWCNT based on wrapping of nucleic acid molecules around SWCNT.
[1] Z. Guo, P.J. Sadler, and S.C. Tsang, Adv. Mater. 10 (1998) 701.
[2] M.J. O'Connell, P. Boul, L.M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K.D. Ausman, R.E. Smalley, Chem. Phys. Lett. 342 (2001) 265 – 271.
[3] G.I. Dovbeshko, V.I. Chegel, N.Y. Gridina, O.P. Repnytska, Y.M. Shirshov, V.P. Tryndiak, I.M. Todor, G.I. Solyanik, Biospectroscopy, 67 (6) (2002) 470-487.

B/PIL.52 THERMOBIOSENSORS OF GENERATIVE TYPE: DEVELOPMENT AND INVESTIGATION OF SOME PHYSICAL AND BIOLOGICAL CHARACTERISTICS

Nickolaj F. Starodub(a), Alexandra N. Shmyr'ova(b) , (a)A.V. Palladin Institute of Biochemistry UNAS, 9 Leontovicha Str., 01030 Kiev-30, Ukraine, (b)National Technical University "Kiev Polytechnical Institute", Ukraine

The main purpose of this work was obtaining of thin films from such new type of solid electrolytes (SE) as α -Al₂O₃ and LaLiTiO₃ and creation on their basis of thermobiosensors. At the high temperature the conductivity of SE films was caused by thermal activated transitions from the dip levels in suppressed zone, at the low temperature – by change of carrier mobility of charge at the dispersion on the implants. In the dependence on regimes of the evaporation of LaLiTiO₃ films their thermal sensitivity changed. The character of temperature dependence of resistance was similar as in semiconductors (exponential dependence with negative temperature coefficient). It allows considering that the SE films are as semiconductors with combined electron-ionic conductivity. Alumina films have practically linear dependence with negative temperature coefficient in the range -60 - +80 °C. It is caused by synchronous action of several mechanisms. Maximal thermoelectromotive for LaLiTiO₃ films was higher in 6-8 times than for semiconductor thermal elements in the similar conditions. At the response time 1-2 min the range of the determined concentrations of glucose and urease were 5-100 and 10-200 mmol/L, respectively. In report it will be demonstrated the use of these transducers at the creation of multi-parametrical biosensor included enzymes, antibodies and bacterial cells and intended for control of total and individual toxicity of environmental.

B/PIL.53 FLUID DYNAMICS IN THE MULTI-WALLED CARBON NANOTUBE

D.A. Gavryushenko(a), V.M. Sysoev(a), L.Yu. Matzui(a), Yu.I. Prylutskyy(b), Kyiv National Shevchenko University, Departments of (a)Physics and (b)Biophysics, Volodymyrska Str. 64, 01033 Kyiv, Ukraine and Yu. Gogotsi, Drexel University, Department of Materials Engineering, Philadelphia PA 19104, USA

The understanding fluid behavior in nanochannels is important for the proper design and efficient operation of micro- or nanofluidic devices. A natural complication under the study of fluid dynamics in the multi-walled hollow carbon nanotubes (MWCNT) is the underlying fundamental question of whether fluids behave as continua at these ultrafine length scales, typically down to a nanometer or less. In the present report the internal pressure and density profile of water, located in the MWCNT were calculated in the wide interval of the variation in the thermodynamic variables, including critical point, by use of the solution of isoperimetrical problem about the minimization of free energy of system in the limited volume under the condition of the constancy of the number of particles. It was found that far from the critical point a substantial change in the density occurs only in the wall layer, whereas near the critical point a significant change of the density in entire volume of system takes place. It is shown that during the calculation of the pressure of water in the MWCNT it is necessary to consider the Tolman correction.

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Friday, June 13, 2003
Vendredi 13 juin 2003

Morning
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Session XI: Magnetism of Nanosystems
Session Chair: Nina I. Kovtyukhova

- 8:50 **B-XI.1** -Invited- **MAGNETIC ORDERING IN POLYMERIZED FULLERENES**
Tatiana. L. Makarova(a,b), B. Sundqvist(a), P. Esquinazi(c), R. Hohne(c), K.-N. Han(c), Y. Kopelevich(d), (a)Umea University, 90187 Umea, Sweden, (b)Ioffe PTI, 194021 St. Petersburg, Russia, (c)University of Leipzig, Linnestr. 5, 04103 Leipzig, Germany, (d)Instituto de Fisica, Unicamp, 13083-970 Campinas, Sao Paulo, Brazil
An observation of a room-temperature magnetically ordered state in fullerenes polymerized at certain pressure and temperature conditions has been repeated and confirmed by several groups. Experimental evidence exists for ferromagnetic behavior in other carbon structures: photopolymerised fullerenes, pyrolytic carbon and bulk graphite. The explanations of the phenomena vary from intrinsic magnetism in either an ideal, or a defect-containing carbon structure to the model of magnetic proximity effects, where the presence of impurities triggers the magnetic ordering in carbon. Our recent observation of ferromagnetic domains in large impurity-free areas of polymerized C60 gives a strong argument in favor of an intrinsic nature of fullerene ferromagnetism. A comparative study of fullerenes polymerized at different pressures and temperatures, as well as photopolymerized fullerenes allows us to formulate some conditions necessary for observation of magnetic ordering in fullerene solids.
- 9:30 **B-XI.2** **JAHN-TELLER EFFECT IN ORGANIC FERROMAGNET TDAE-C60**
D. Arcon, R. Blinc, P. Jeglic, T. Apih, A. Omerzu, Institute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia
Only few purely organic ferromagnets have been discovered so far and the corresponding transition temperatures TC are very low. In view of that it is rather remarkable that the C60 based purely organic 1:1 charge transfer compound TDAE-C60 (TDAE=tetrakis-dimethyl-aminoethylene) exhibits a ferromagnetic transition at TC = 10 K. In this paper we'll report on the recent 13C NMR study of TDAE-C60. The observed huge increase in the width of the 13C NMR spectra of TDAE-C60 in the middle of the ferromagnetic phase at 10 K is due to a Jahn-Teller distortion of the C60 ions which becomes visible in view of the resulting changes in the Fermi contact electron-13C NMR shifts. The shape of the 13C spectra allows for a direct determination of the belt-like redistribution of the unpaired electron spin density on the C60 ions, which is responsible for the relatively high ferromagnetic transition temperature in this purely organic system.
- 09:50 **B-XI.3** **MAGNETIC PROPERTIES OF ANISOTROPIC CO PARTICLES ENCAPSULATED AT THE TIP OF ALIGNED CARBON NANOTUBES**
CS. Cojocaru, C. Meny, A. Derory and F. Le Normand, IPCMS, UMR 7504 CNRS, PO Box 43, Bat 69, 23 rue du Loess 67034 Strasbourg Cedex, France
The next generation of materials for magnetic recording media will require i) the design of regular arrays of ferromagnetic nanoparticles with well controlled morphology and behaviour and ii) to physically separate these particles, either by vacuum or by a nonmagnetic material to fully discriminate the bits of information. Other requirements are the chemical stability, the obtention of a definite direction for magnetization, the mechanical stiffness... The growth of carbon nanotubes by a catalytic CVD process requires the presence of nanoscaled transition metals particles (Fe, Co, Ni), which are ferromagnetic. These particles are encapsulated after growth on the top of the nanotubes. Moreover in appropriate deposition conditions they took a very anisotropic shape, and the particle fills the nanotube which is a nonmagnetic material. The magnetic properties of these arrays of Co nanoparticles encapsulated into carbon were investigated by SQUID and MFM. Different magnetic behaviour were evidenced -Superparamagnetic behaviour for small particles (5 ÷ 8 nm) encapsulated into non oriented nanotubes Strong magnetic anisotropy perpendicular to the plan of the substrate of metallic nanowires (diameter~25 nm and aspect ratio from 1/4 to 1/10), induced by the cork-like shape of the nanoparticles. In this case the coercitive field (750 Oe), the magnetic anisotropy combined with high density (1010particles/cm2) and the weak dipolar interactions evidenced by MFM are very attractive for dense storage media.
- 10:10 **B-XI.4** **SPIN-LEAKAGE OF THE FULLERENE CAGE OF ENDOMETALLOFULLERENES: EPR, ENDOR AND NMR EVIDENCES**
Vitaly K. Koltover, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia
The goal of this project was to answer the question, whether the area of localization of the unpaired electron in paramagnetic endometallofullerenes (EMF) is restricted by the fullerene shell, or a spin-leakage beyond the fullerene cage is also possible. The EPR signals of La@C82 and Y@C82 with unusually small hyperfine splitting constants aLa and aY were revealed in dimethylformamide (Koltover et al, 2000). The intense matrix 1H-ENDOR signal for La@C82 in the polycarbonate film was revealed. Since La@C82 does not contain hydrogen atoms, it testifies the hyperfine interaction of the unpaired electron of La@C82 with hydrogen atoms of the polymer (Koltover et al, 2002). For La@C82 in the hexamethylphosphoramide (HMPA) solution it was shown that the 31P NMR signal of HMPA is shifted from 22.900 ppm in the neat HMPA to 23.048 ppm in the presence of La@C82. The paramagnetic nature of the shift indicates a partial localization of the electron spin density on the HMPA phosphorus atoms (Koltover et al., 2003, in press). Solid powders of complexes of La@C82 and Y@C82 with HMPA were studied by EPR and magic angle spinning NMR. The 31P measurements revealed considerable chemical shifts of the 31P NMR lines relative to pure HMPA. Moreover, these paramagnetic EMF form clusters, in which the quenching of their electron spins takes place (Koltover et al., 2003, in press). Thus, the data of EPR, ENDOR and NMR experiments testify the partial runoff of the unpaired electron beyond the fullerene cage, shall it be a direct electron transfer or a spin-polarization mechanism. The spin-leakage of the fullerene shell may serve the important factor for applying EMF in magnetoelectronics.

The work was supported by Russian Foundation for Basic Research(project #01-03-32945).

10:30

BREAK

Session XII: Nanosystems for biomedical applications

Session Chair: Yury Gogotsi

- 10:50 **B-XII.1** -Invited- **NANOCAPSULES – AN INNOVATIVE TOOL FOR MEDICINE AND SCIENCE**
Silke Krol(a), Alberto Diaspro(a), Ornella Cavalleri(a), Daniela Silvano(b), Alessandra Gliozzi(a), (a)INFM, Department of Physics, University of Genoa, Genoa, Italy, (b)Ecole Polytechnique Fédérale de Lausanne, Laboratoire Chimie Physique de Polymères et Membranes, 1015 Lausanne, Switzerland
A new generation of capsules with a dimension of a few nanometres up to several millimetres was achieved by alternating deposition of polyions with opposite charge, so-called Layer-by-Layer technique and allows the coverage of charged cores. Depending on the chosen application the capsules can be hollow, for example in the case of capsules for drug delivery or solid with still the core inside, in the case of protected living cells or tissue. Unique to these capsules is the possibility to widely influence the permeability and properties of the capsule walls. The pore size in the walls as well as the layer thickness is tuneable by pH, ionic strength, or choice of polyelectrolyte. By tuning the pH or ionic strength it is possible to control the opening and closing of pores or cavities in the walls: the pH dependent wall permeability can be exploited letting charged proteins and molecules enter. A wide variation of cores is used inducing the size and shape of the capsules. The aim of our study is the development of hollow capsules templated on non-toxic and easy-to-remove calcium carbonates cores. The core removal process is a crucial step in capsule preparation: in some cases capsule breakage can occur during core dissolution or large amount of template material can remain inside. Furthermore we showed that living yeast cells survive the encapsulation procedure and live for at least 2 days in such a good condition that they duplicate by breaking the capsule.
- 11:30 **B-XII.2** **CARBON NANOTUBES AS BIOSENSORS - A MOLECULAR DYNAMICS STUDY**
J.H. Walther(a), R.L. Jaffe(b), T. Werder(a), P. Koumoutsakos(a), (a)ICoS, ETH Zurich, 8092 Zurich, Switzerland, (b)NASA Ames Research Center, CA 94035, USA
Prospective applications of carbon nanotubes (CNTs) in biological systems include biosensors and DNA sieves. The design of these nano-scale systems relies on our understanding on the structural properties of the device and its interaction with the surrounding fluids - most prominently the behaviour in water, due to the ubiquitous presence of water in biological systems. The design and modelling of these nano-fluidic systems may be conducted using molecular dynamics (MD) simulations techniques, or traditional Navier-Stokes calculations provided the complex interactions at the fluid-solid interface may find a suitable macroscopic form. In particular, water at dense hydrophobic surfaces is known to exhibit a slip velocity as demonstrated in the early experiments by Helmholtz and von Piotrowsky (1860). The present study involves non-equilibrium molecular dynamics simulations of water in a planar Couette and Poiseuille flow, and water flowing past an array of CNTs. While the planar flow configurations exhibit a significant slip, with slip lengths of 15 - 60 nm, the flow past the CNTs appears to satisfy the no-slip condition. The fluid forces acting on the array are furthermore found in good agreement with the macro-scale Stokes-Oseen solution for the flow past an array of circular cylinders.
- 12:00 **B-XII.3** **IN VITRO ASSAY OF SINGLET OXYGEN GENERATION IN THE PRESENCE OF WATER-SOLUBLE DERIVATIVES OF C60**
B. Vileno, LNNME-IPMC-FSB-EPFL 1015 Lausanne Suisse, A.Sienkiewicz, Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland, L. Forro, LNNME-IPMC-FSB-EPFL 1015 Lausanne, Suisse. Switzerland
Singlet molecular oxygen is well-known to be an efficient intermediate in photooxygenation reactions. It reacts with numerous biomolecular targets, including phospholipids, amino acids, nucleic acids and other oxidizable species. Photo-induced generation of singlet oxygen has found numerous applications in many fields. In particular, medical applications of singlet oxygen for selective eradication of tumors in Photodynamic Therapy (PDT) require efficient photosensitizers of singlet oxygen. Due to their high triplet quantum yield that is near unity, fullerenes (C60 and C70) dissolved in organic solvents have been found to be excellent photosensitizers for generation of singlet oxygen. In this study we used the ESR technique to monitor the yield of singlet oxygen generation by water-soluble derivatives of C60 and we compared it to the photosensitizing efficiency of protoporphyrin IX-based chromophore that is currently clinically tested for PDT applications. Our ESR results point to the excellent photophysical properties of water-soluble derivatives of C60, which conserve their ability to generate singlet oxygen at high yields, even upon functionalization. Additional ESR experiments on spin-labeled proteins and AFM assay on healthy and cancerous cells confirmed the strength of the photo-oxidative stress generated in the presence of water-soluble derivatives of C60.
- 12:15 **B-XII.4** **NANOPOROUS CARBONS FOR SEPSIS TREATMENT**
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Gram-negative sepsis, in which the release of lipopolysaccharide (LPS) from bacteria results in a systemic inflammatory response, causes many patients to develop multi-organ failure. These patients have a poor prognosis with 90% mortality when three or more organs fail. Release of LPS into the bloodstream also triggers an inflammatory response with inflammatory cytokines further deteriorating the situation. Adsorbents may provide a novel therapy for sepsis by removing LPS and inflammatory cytokines from the circulation. Common adsorbents with narrow pores in the range of 0.4-2 nm are not efficient in removing large molecules of cytokines or LPS. Activated carbons with bimodal pore size distribution, in the range of 0.4-2 nm and 10-50 nm, have been produced from porous polymer precursors. Adsorption of LPS and TNF has been studied from model solutions and human

blood serum. It has been shown that activated carbons with bimodal pore size distribution adsorb these substrates more efficiently than conventional carbons. Uncoated polymer pyrolysed carbons have shown good haemocompatibility comparable or better than that of commercial coated activated carbon Adsorba 300C. It has been concluded that extracorporeal adsorption using bimodal activated carbons could be efficient in sepsis treatment.

12:30 B-XII.5

BIOLOGICAL MOLECULE CONFORMATIONS PROBED AND ENHANCED BY METAL AND CARBON NANOSTRUCTURES: SEIRA, AFM AND SPR DATA

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The effect of surface enhanced optical vibrations near curved metal surface consists in essential increase (by factor 10- 10⁹) of the intensities of some bands of the molecules adsorbed on metal surfaces in Raman scattering, luminescence, infrared absorption [1]. Here we present data on conformation detection of nucleic acids, lipids and proteins on metal or carbon nanostructures with surface enhanced infrared spectroscopy (SEIRA). Earlier we obtained the enhancement of the IR signal of nucleic acids and lipids on the rough metal surface about 3-10 times in the experiment in FTIR reflectance mode [2]. We have registered clear resolution of the forbidden bands in the SE (surface enhanced) experiments. However, the detection of conformations of protein is much better in the experiment with gold surface than the same for DNA. Application of the metal substrate gives a possibility to do modeling of different possible conformations of proteins and its state as isolated molecule or molecule in gas phase [3]. It is experimentally shown that carbon nanotubes could be used as optical enhancers too.

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Concluding Remarks