

International Conference
on
NANOMATERIALS AND NANOTECHNOLOGIES
(NN 2003)

Crete, Greece
August 30, 2003 – September 6, 2003

A B S T R A C T S

International Conference
on
NANOMATERIALS AND NANOTECHNOLOGIES
(NN 2003)

ABSTRACTS

Location: The Creta Maris Hotel, Hersonessos, Crete, Greece

Dates: August 30, 2003 – September 6, 2003

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NANOMATERIALS AND NANOTECHNOLOGIES (NN 2003),
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The objective of this Conference is to highlight current and future multidisciplinary research on nanostructured materials and development of nanotechnologies with the primary focus on reinforce of connection between the fundamental science, engineering and commercialization of nanostructures; between universities, governmental laboratories, academic institutions, private research sector and industry. This Conference aims to assess the current status and to identify future priority directions of fabrication, research, design and applications of nanocomposites, carbon nanotubes, self-assembled supramolecules, nanostructured bulk solids, films and coatings, quantum dots and wires. Particular emphasis will be placed on developing close interactions among scientists and engineers from Asia, Europe, and North America and fostering future transdisciplinary and multi-institutional collaboration in this new and rapidly growing area.

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Location: Creta Maris Hotel, de-luxe (five-star) hotel situated on the north coast of Crete, 25 km east of Heraklion airport on its own golden beach.

NN 2003 Proceedings will be published in **Reviews on Advanced Materials Science** (RAMS) Journal. RAMS web-sites:
<http://www.ipme.ru/e-journals/RAMS/>
and
<http://www.ipme.nw.ru/e-journals/RAMS/>

DEGRADATION OF NANOPARTICULATE-COATED AND UNCOATED SULFIDE-BASED CATHODOLUMINESCENT PHOSPHORS

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Changes in the cathodoluminescent (CL) brightness and in the surface chemistry of nanoparticulate SiO₂-coated and uncoated ZnS:Ag,Cl powder phosphor have been investigated using a PHI 545 scanning Auger electron spectrometer (AES), an Oriol optical spectrometer and a JEOL 6400 scanning electron microscope (SEM). The data were collected in a stainless steel UHV chamber with residual gas pressures between 1x10⁻⁸ and 1x10⁻⁶ as measured by a Dycor LC residual gas analyzer (RGA). The primary electron current density was 272 $\mu\text{A}/\text{cm}^2$, while the primary beam energy was varied between 2 and 5 keV. In the presence of a 2keV primary electron beam in 1x10⁻⁶ Torr of water for both the SiO₂-coated and the uncoated cases, the amounts of C and S on the surface decreased, that of O increased and the CL intensity decreased with electron dose. This surface chemistry change lead to the development of a surface dead layer and is explained by the electron beam stimulated surface chemical reaction model (ESSCR). The penetration range of the impinging low energy primary electrons is on the order of 10-100 nm creating a reaction region very close to the surface. The ESSCR takes this into account postulating that primary and secondary electrons dissociate physisorbed molecules to form reactive atomic species. These atomic species remove surface S as volatile SO_x or H₂S. In the case of an oxidizing ambient (i.e. high partial pressure of water), a non-luminescent ZnO layer is formed. This oxide layer has been measured to be on the order of 3-30 nm. In the case where the vacuum of 1x10⁻⁸ Torr was dominated by hydrogen and had a low water content, there was a small increase in the S signal, no rise in the O Auger signal, but the CL intensity still decreased. This is explained by the ESSCR whereby H removes S as H₂S leaving elemental Zn, which evaporates due to a high vapor pressure. In the case of ZnS:Ag,Cl coated with SiO₂, morphological changes were observed on the surface after extended electron beam exposure. Erosion of ZnS occurs more dramatically at an accelerating voltage of 5kV even at the same current density. Uncoated ZnS:Ag,Cl phosphors exhibited similar surface chemical changes to that of SiO₂-coated ZnS:Ag,Cl but did not degrade to the same extent. Also, no change in the surface morphology was observed. These SEM images as well as reaction rate data suggest that these nanometer sized SiO₂ particles acted as a catalyst for decomposition of the ZnS especially in a reducing ambient (i.e. high hydrogen partial pressure). In order to reduce CL degradation of these and other phosphors, protective coatings were pulse laser deposited onto the phosphor surface. The effectiveness of these coatings was dependent upon both the thickness and the uniformity. Thicknesses of these coatings ranged from 1-5 nm and were uniform as determined using profilometry and TEM.

Recent Advances in Microwave Processing of Nanomaterials

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Implementation of nanomaterials for commercial applications has been plagued by the lack of a near net shape forming technique that is conducive to processing nanopowders. Conventional sintering of nanopowder compacts in a thermal furnace leads to shrinkage cracks and excessive grain growth, and often poor sintering. In the last two decades microwave processing has proved itself to provide rapid and uniform sintering of variety of materials including metal powders. Microwave processing is one of the few near net shape sintering techniques that involves volumetric heating. Powdered samples can be sintered to near full density in a microwave field without using any pressure during sintering. The soaking times in a microwave field are shorter by as much as 50% as compared to conventional heating processes. We have developed microwave sintering methods for a number of difficult to process nanophase materials, including phase pure tungsten (i.e. without any liquid phase forming additives), transparent magnesium oxide, aluminum oxide – titanium oxide, and WC/Co nanocomposites. The focus of the presentation will be on microstructural evolution in the above mentioned material systems during various stages of sintering, and a study of the microwave-nanopowder interaction.

Microstructure and magnetic properties of Zinc ferrite nanoparticles synthesized from hydroxide carbonate precursors.

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Zinc ferrite has normal spinel structure with zinc ions in the tetrahedral sites. However, recent researches on ultrafine zinc ferrite prepared by coprecipitation technique has showed defect crystal structures and abnormal magnetic properties. Zinc iron hydroxide carbonate complexes were synthesized using the reverse microemulsion process. To get ferrite particles, the carbonate complex particles had been calcined at 330°C for 6 hrs. The powder samples have been studied and characterized by means of powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Mossbauer spectroscopy and a superconducting quantum interference device (SQUID) magnetometer. The zinc ferrite particles having an inversion parameter of about 0.28 were synthesized. The magnetic hysteresis loops observed at 5 K were caused by a result of the relatively strong coupling between A and B sites. The powders were found to have a relatively high inversion parameter compared to normal zinc ferrite.

Continuum Nanomechanics

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The structure of an extended continuum thermomechanics framework for describing deformation, diffusion and heat flow at the nanoscale is discussed. Applications to capturing the stability of deformation and defects in nanocrystals, as well as the diffusion in nanopolycrystalline materials are discussed.

Nanocrystalline MCrAlY Alloys for Thermal Barrier Coatings Applications

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This work describes recent progress in improving the oxidation behavior of the bond coat using HVOF and LPPS nanostructured MCrAlY coatings. NiCrAlY and CoNiCrAlY powders were cryomilled and sprayed onto a Ni-based alloy. Oxidation and thermal cycling experiments were performed on the coating in order to analyse the formation of the oxide phases (morphology and composition) at the bond coat/top coat (YSZ) interface. The nanostructured characteristic of the coating and the presence of Al₂O₃ within the cryomilled powders enhance the nucleation of the TGO alumina layer which protects the coating from further oxidation. The cryomilling process of the MCrAlY powders has shown to be effective in improving the oxidation behavior of the coatings used in turbine engine applications.

Modification of metal nanoparticles in SiO₂ by thermal oxidation

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High-flux negative-ion implantation is one of the promising methods to fabricate elemental nanoparticles (NP) in insulators, e.g., Cu NP in SiO₂, without surface charging accumulation. One way to extend this method to fabrication of compound NP, e.g., GaAs NP in SiO₂, is sequential ion implantation. However, in some cases, the secondary implantation of the sequence induces too enhanced diffusion of the primarily implanted atoms, and prevents the compound formation. Even succeeding in the formation, the nanoparticles contain a lot of defects. In this paper, another method, which is only applicable to oxide compounds, but generates less defects, i.e., oxidation of element nanoparticles in insulators, is examined. The examples include oxidation of nickel NP and copper NP in SiO₂, which are investigated using optical absorption, RBS, femto-seconds transient absorption and TEM. Collaboration between nanotechnology and a conventional technology is stressed.

POROUS SILICON MATRIX FOR APPLICATIONS IN BIOLOGY

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Different porous silicon (PS) layers, with an average pore size distribution of 10 nm were realised on p+Si(111), and p+Si(100), by partial electrochemical dissolution in hydrofluoric acid based solutions. Various treatments for structure surface modification/stabilisation were made in order to ensure the PS biocompatibility. Some of these treatments are: thermal treatment in N₂ at 300⁰C for 60 min, and at 800⁰C for 30 min; 30 nm deposited carbon layer; deposited carbon monolayer; hexametildisilazane treatment for 20 min in a temperature domain 90-150⁰C; 50 nm a-SiC deposited by hexametildisilane.

On these structures, three cellular lines, B 16; CHO; MDBK were grown, in order to evaluate the use of functionalised PS as test-support for cell growth.

The test structures were characterised by SEM, TEM and AFM, and the cells viability was emphasized by imunofluorescence microscopy measurements.

Carbon Nanotube Electronics and Electro-Optics

Phaedon Avouris

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Carbon nanotubes are nearly ideal, one-dimensional nanostructures with unique properties that recommend them for applications in nanoelectronics. I will discuss the electronic structure and electrical properties of semiconducting carbon nanotubes and the fabrication and performance of nanotube devices. Results of transport experiments and theoretical modeling will be used in addressing such issues as the nature of the switching in nanotube transistors, the nanotube-metal electrode interaction, the resulting charge transfer and the role of co-adsorption and the ambient environment on the transport properties. I will then discuss how these findings can be utilized to produce high performance p-type, n-type and ambipolar nanotube field-effect transistors and intra-nanotube logic circuits. The 1D character of carbon nanotubes also has important implications for the electro-optical properties of nanotubes, an aspect that has not received proper attention. I will present experimental results that demonstrate the potential of carbon nanotubes in this area. I will close by discussing the technological prospects of nanotubes in electronic and photonic applications.

REINFORCED SILICON NITRIDE NANOCOMPOSITES

Cs. Balazsi et al

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Novel carbon nanotube reinforced silicon nitride ceramics matrix composites have been prepared. As carbon nanotubes present exceptional mechanical, superior thermal and electrical properties (thermal stability up to 2800! C in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [1]) in general, there are high expectations for improvement of quality of carbon nanotube nano/microcomposites. Despite of this, only modest improvements were reported related to properties of carbon nanotube silicon carbide, polymer, metal oxide matrix composites. In the use of nanotubes to form advanced composites a critical issue was identified that needs to be further clarified, namely the interfacial bonding of the nanotubes to different matrices. Addressing to this critical issue, in this work an attempt has been made to improve the mechanical and thermal properties of silicon nitride matrix with the help of carbon nanotube addition. [1] E. T. Thostenson, Z. Ren, T-W. Chou, *Composite Science and Technology* 61 (2001) 1899-1912.[2] K-T. Lau, D. Hui, *Carbon* 40 (2002) 1597-1617. Dr. Csaba Balázsi thanks for OTKA Postdoctoral Research Grant (D38478) and János Bolyai Research Grant.

EXAMINATION OF CARBON NANOTUBE REINFORCED SILICON NITRIDE NANOCOMPOSITES

Cs. Balazsi, Z. Konya, F. Weber, L. P. Biro, P. Arato

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Novel carbon nanotube reinforced silicon nitride ceramics matrix composites have been prepared. As carbon nanotubes present exceptional mechanical, superior thermal and electrical properties (thermal stability up to 2800! C in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [1,2]) in general, there are high expectations for improvement of quality of carbon nanotube nano/microcomposites. Despite of this, only modest improvements were reported related to properties of carbon nanotube silicon carbide, polymer, metal oxide matrix composites. In the use of nanotubes to form advanced composites a critical issue was identified that needs to be further clarified, namely the interfacial bonding of the nanotubes to different matrices. Addressing to this critical issue, in this work an attempt has been made to improve the properties of silicon nitride matrix with the help of carbon nanotube addition. [1] E. T. Thostenson, Z. Ren, T-W. Chou, Composite Science and Technology 61 (2001) 1899-1912. [2] K-T. Lau, D. Hui, Carbon 40 (2002) 1597-1617. Dr. Csaba Balázsi thanks for OTKA Postdoctoral Research Grant (D38478) and János Bolyai Research Grant.

SYNTHESIS AND CHARACTERIZATION OF SILICON NITRIDE BASED COMPOSITES CONTAINING DIFFERENT CARBON NANOSPECIES

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The synthesis of new materials with extreme technological properties is of great fundamental interest. Ceramics based on silicon nitride are well-known as low density materials with high strength and toughness. With these combination of properties silicon nitride based ceramics are an ideal candidate for several structural applications, even at high temperatures. As an alternative way to improve the mechanical and thermal properties of silicon nitride matrix, we performed the preparation and examination of carbon nanospecies added silicon nitride ceramic matrix composites. Nanoparticles of carbon black and graphite have been added to silicon nitride starting powder and sintering additives (Al₂O₃ and Y₂O₃). These mixtures were mechanochemically activated several hours in a planetary type alumina ball-mill in order to achieve a homogenous mass. As an alternative to nanograins, carbon fibres and carbon nanotubes have been added to carbon free silicon nitride batches. Sinter-HIP has been applied to rectangular bars which were earlier dry pressed. Structural and morphological analysis were performed on as-prepared samples. Bending strength and elastic modulus have been found to be influenced by amount of carbon species introduced in silicon nitride matrix. A desintering process was observed. During pressureless sintering step the structure retained the α-Si₃N₄ phase, after second sintering step new phase(s) appeared.

Hybrid Materials Based on Single-Walled Carbon Nanotubes and Tetraazamacrocyclic Compounds

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We studied (experimentally and theoretically) interaction of a series of aromatic tetraazamacrocyclic ligands [tetraazaannulene (H2TAA), tetramethyltetraazaannulene (H2TMTAA), and meso-tetraphenylporphine (H2TPP)] and their transition metal complexes [e.g., of Ni(II) and Cu(II)] with single-walled carbon nanotubes (SWNTs). In particular, SWNTs strongly adsorb NiTMTAA and CuTMTAA from ethanol solutions, with SWNT:complex mass ratio of ca. 5:4. According to the results of molecular mechanics (MM) modeling, this corresponds to a dense monolayer coverage. A saddle-shaped conformation of the macrocyclic complexes helps their better accommodation on the cylindrical nanotube walls, resulting in a highly ordered chess-like molecular assembly. Theoretical MM studies of other macrocyclic compounds (H2TAA and H2TPP) interacting with SWNT sidewalls revealed types of molecular arrangement different from that for the TMTAA complexes. The materials synthesized were characterized by IR, UV-Vis and EPR spectroscopy, as well as electron microscopic methods.

Amidation and Esterification of Terminal Carboxylic Groups of Single-Walled Carbon Nanotubes: Theoretical Studies

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Theoretical approaches are a useful way to study chemical properties of carbon nanotubes. Our experimental studies deal with the chemical modification of oxidized nanotube tips by using the reaction of their terminal carboxylic groups with vaporous aliphatic amines and alcohols. One could expect that reactivity of the carboxylic groups depends on whether the nanotubes have an armchair or zigzag structure, since this changes spatial orientation of the terminal groups. To verify whether this might cause substantial differences in geometric and energetic parameters, we studied theoretically the reactions of monocarboxy-derivatized fragments of zigzag and armchair SWNTs with the simplest aliphatic amine, methylamine, and the simplest aliphatic alcohol, methanol. We employed a two-level ONIOM approach (B3LYP:UFF). The amide and ester formation are more energetically preferable for the armchair nanotubes. Differences in the geometry of reaction complexes, transition states and products are discussed, as well as the influence of the model SWNT diameter on the parameters calculated.

THERMOSET AND THERMOPLASTIC COMPOSITES USING POLYMER WRAPPED SWNTs AS REINFORCEMENT

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We are developing a method for incorporating Single Walled Carbon Nanotubes (SWNT) into thermosets and thermoplastics to act as reinforcement. The helical structure of poly (m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) encourages this polymer to wind itself around both individual SWNTs and multiple SWNT ropes. This forms a polymer/nanotube mixture in which the polymer is mechanically anchored to the nanotube but is not chemically bound to it. Because interaction between the PmPV and SWNTs is purely mechanical, no incursion into the bond structure of the SWNTs occurs. Placing various functional groups on the side chains of the PmPV polymer will make covalent bonding possible between this PmPV derivative and the epoxy matrix in the final composite. This will provide optimal strength in the final composites by maximizing the load transfer properties of the derivative. How well this final composite is capable of conveying the extraordinary strength and durability of the carbon nanotubes to the final PmPV/SWNT/matrix composite as a whole will depend on the PmPV derivative's ability to transfer the applied load from the composite's matrix to the SWNTs.

NANOCRYSTALLINE HYDROGEN ABSORBING MAGNESIUM-NICKEL ALLOYS

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Magnesium-nickel alloys are attractive hydrogen storage materials because of their volumetrically plentiful hydrogen capacity. However, the hydriding-dehydriding reaction takes place at elevated temperature and is relatively slow. The aim of this study was to show the effect of nanometer-scale structure on the hydriding properties of Mg-Ni alloys. The Mg-Ni alloys with nanocrystalline structure were successively synthesised by mechanical alloying. The microstructure of ball milled powders were characterized by X-ray diffraction analysis, scanning electron microscopy and X-ray energy dispersive spectroscopy. The rate of hydriding was determined using a Sieverts apparatus at various temperatures. The nanocrystalline materials show much better hydrogen sorption characteristics than their polycrystalline counterparts.

AEROSOLS-An opportunity for nanotechnology-surface treatment, also on large scale

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Due to the ability of being able to create the smallest drops ($\ll 1\mu\text{m}$), technology is available that can produce a large-area, thin film on various substrates. By selecting the substrates that is required and the aerosol solution to be used, various profile characteristics can be produced for surface areas. In combination with a corona treatment, suitable adhesion mechanisms have been produced that can even be used on nonpolar plastic surfaces. Production examples and applications of nanocoatings for use are shown.

CATALYTIC EFFECT OF NANOMETER SIZED ADDITIVES ON HYDROGEN SORPTION IN NANOCRYSTALLINE MAGNESIUM-NICKEL ALLOY

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Magnesium-nickel alloys are well known by their high hydrogen storage capacity. However, difficult activation and poor absorption/desorption properties prevent their use as hydrogen storage material. The aim of this study was to show the influence of nanometer sized catalysts on the surface activity of nanocrystalline Mg-Ni alloy. Nanocrystalline Mg-Ni-based powders were fabricated from pre-alloyed powders by milling in a Fritsch planetary ball mill. Modification of the surface of the Mg-Ni powders was carried out by introducing small amount of nanometer sized catalysts to the powders in the course of the ball-milling process. The microstructure of ball milled powders were characterized by X-ray diffraction analysis, scanning electron microscopy, X-ray energy dispersive spectroscopy and differential scanning calorimetry. The hydrogen storage properties of the nanocrystalline powders with nanometer sized catalysts were characterized. Hydriding properties of the processed powders are strongly affected by their nanometer-scale structures.

ADVANCES IN THE SYNTHESIS AND CHARACTERIZATION OF BORON NITRIDE NANOTUBES

R.Czerw 1, S.M.C. Vieira 2, S. Webster 1, D.L. Carroll 1

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Boron Nitride (BN) nanotubes represent a significant potential in nano-mechanical device applications. Recent work on the synthesis and processing of pure boron nitride nanotubes has allowed detailed studies of purified materials. Using non-resonant Raman Spectroscopy, a number of active vibrational modes of the BN - nanotube lattice have been identified with very few surprises. Scanning tunneling microscopy and spectroscopy results are intriguing however. In most cases, a bandgap of 4.5 eV on multiwalled nanotubes has been obtained. In contrast, 10% of the tubes studied exhibit a larger, 5.0 eV bandgap, and show clear evidence of negative differential conductivity. This can be interpreted in terms of ballistic transport models from the tip of the STM into the substrate below and may be related to a piezo-response of the nanotube.

ENHANCEMENTS TO CONJUGATED POLYMER DEVICES VIA THE INCORPORATION OF CARBON NANOTUBES

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Conjugated polymers are reaching commercial viability as the active layer in organic light emitting diodes (OLEDs) and solar cells, but their commercial application is hindered by shorter than desired reliabilities and lifetimes. A primary degradation mechanism of electroluminescent polymers used in organic light emitting diodes (OLEDs) over time is photo-oxidation. We have been able to reduce photo-oxidation in conjugated polymer films and solutions by the incorporation of single walled nanotubes (SWNTs). The mechanism is thought to be a suppression of the triplet state in the polymer and consequently a reduction in singlet oxygen formation. Incorporation of the SWNTs into OLEDs has shown similar benefits with regard to photo-oxidation of the polymer and also by preventing degradation of the polymer-metal interface. The benefits of SWNT to organic photovoltaics (OPV) is less clear. In some materials, such as poly(3-octylthiophene) (P3OT), the incorporation of nanotubes improves the efficiency of the OPV through modification of the transport, but does not appreciably improve the donor-acceptor interface. This is not surprising, since as grown SWNTs are a mixture of semiconducting and metallic tubes with a variety of bandgaps. For commercially realizable OPVs and to fully exploit the high aspect ratio, we must tailor the nanotube bandgaps through doping. Progress in doping SWNTs will be presented.

PYROELECTRIC AND PIEZOELECTRIC CHARACTERISTICS OF CARBON NANOTUBE - POLYMER NANOCOMPOSITES

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Recent work on carbon nanotube v poly (vinylidene di fluoride) (PVDF) blends has shown some exciting enhancements in both the pyroelectric and piezoelectric coefficients of the poled polymer. For piezo-phenomena, the poling vs. response curve of transduction clearly indicates that enhanced properties are only observed when the matrix is poled over specific voltages. This optimum poling voltage for enhancement is strongly dependent on the copolymer of PVDF used as a host indicating the existence of some steric effect related to the nanotubes. Further, quite different pyro- and piezo- electric behaviors are obtained as a function of polymerization route, copolymerization, and processing. In each case, it is evident that single walled nanotubes within the matrix act as heterogeneous nucleation sites for polymer phase formation, greatly enhancing specific phases at the expense of others. These results suggest a greatly expanded role for the application of organically based electro-active polymer actuation may be possible.

Production of Cobalt-Ferrite Compound Nanoparticles Using Reverse Micellar System

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In the recent years, metal particles of nanometer dimensions have been investigated because of their present applications and perspectives of their various fields of science, technology and pharmaceutical. For example, in the electric industry; semiconductors resulted in the transition from the vacuum tubes to diodes and transistors and eventually to miniature chips. This process is limited by the capacity of information storage devices, which in most cases work on the magnetic recording principle. Increasing the storage density requires more strict control over morphology of the magnetic material and strong reduction of its dimensions, down to the sizes of single domain [1-3]. A lot of methods of manufacturing nanocrystalline by inorganic materials is happen but micro-emulsion systems and reverse micelle systems are mostly used than another methods. Because of it is no need expensive devices and particles dimensions and formations are under control with this method [2, 3]. In this study, we demonstrate the versatility of the reverse micelle method of synthesis of cobalt-ferrite compound. In addition, there is two different surfactant (sodium diisooctylsulfocinate (AOT) and cetyltrimethylammonium bromide (CTAB)) were used to prepare the reverse micelle system in isooctane, separately. Desired amount of cobalt-ferrite compound in the aqueous phase was mixed with the reverse micelle phase with orbital shaker during 2 hours. After that isopropanol was mixed the reverse micelle solutions and centrifuged to separate the cobalt-ferrite particles. Cobalt-ferrite particles were washed with water three times and dried in air. Analyses of the nanoparticles were achieved with scanning electron microscope (SEM) and Physical Properties Measurement System (PPMS). The experiments showed that particle morphologies have changed depending on reverse micelles system. The nanoparticles physical properties and particles size, which prepared by AOT, were compared with the another particles prepared by CTAB. References 1. Egorova, E.M., Revina, A. A., 2000, Synthesis of Metallic Nanoparticles in Reverse Micelles in the Presence of Quercetin, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 168, 87-96. 2. Carpenter, E.E., 2001, Iron Nanoparticles and Potential Magnetic Carriers, Journal of Magnetism and Magnetic Materials, 225, 17-20. 3. O'Connor, C.J., Kolesnichenko, V., Carpenter, E., Sangregorio, C., Zhou W., Kumbhar, A., Sims, J., Agnoli, F., 2001, Fabrication and Properties of Magnetic Particles with Nanometer Dimensions, Synthetic Metals, 122, 547-557.

Structures and properties of the crystalline Si-C-N films using additional Si-source and Co-catalyst

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Si-C-N films were synthesized on Si substrates by microwave plasma chemical vapor deposition (MPCVD) with a mixture of CH₄ and N₂ as gaseous sources, and Co-coated Si columns to act as a catalyst and an additional Si source. Two conditions, conditions 1 and 2, were implemented by varying the time at which the solid sources were introduced. Under condition 1, the solid sources were applied “before” film deposition. Under condition 2, the solid sources were applied both “before and during” film depositions. Analytical results indicate, although that both conditions yield crystalline Si-C-N films, the time at which the solid sources are applied is critically affects the films’ structures and properties. Synthesizing Si-C-N films under condition 1 yields crystals with more re-nucleation, a structure closer to a pseudo T-Si₃N₄ structure, a higher C content, detectable Si(2p)-C bonding, lower nano-hardness and better field emission properties. Synthesis of film under condition 2 yields, crystals with more facets, a structure closer to pseudo ? -Si₃N₄, and an additional thin layer under the crystalline layer. SEM, TEM, XPS, XRD, nanoindentor and field emission were used to characterize the film’ structures and properties.

Growth models of carbon nanotubes assisted with Co-based catalysts

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Carbon nanotubes (CNTs) were synthesized on Si and SiO₂ coated Si substrates by a microwave plasma chemical vapor deposition (MPCVD) system, with CH₄ and N₂ as source gases. Three catalyst films, specified as conditions 1, 2 and 3, were employed as catalysts to grow carbon nanotubes. Conditions were, 1: Co film on Si substrate; 2: Co film/SiO₂ film on Si substrate, 3: Co film on Si substrate with rapid thermal annealing (RTP). The catalyst films were proven to be equivalent to Co-Si-O or Co-Si catalysts in CNTs growth. SEM, TEM+EDS, HRTEM and Raman spectroscopy were employed to characterize CNTs microstructures, morphologies and catalyst compositions. The results show that the bamboo-like CNTs using the Co-Si catalyst (conditions 1 and 3) were governed by the base-growth mechanism due to strong chemical bonding between the CoSi_x phases and Si substrate. Both bamboo-like and the hollow CNTs, using the Co-Si-O catalyst (condition 2), were dominated by the tip growth mechanisms. The effect of nitrogen on the growth mechanism of the bamboo-like CNTs is proposed.

Improvement of diffusion barrier behavior of Ti-related nitride thin films using multilayered design

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Small-angle X-ray diffractometry, transmission electron microscopy, and electrical measurement were employed to examine the effectiveness of TiN, TiAlN, and multilayered TiN/TiAlN diffusion barriers (all having a total thickness of 40 nm) against copper penetration toward silicon. Failure of the TiN barrier upon annealing is caused by the diffusion of copper through the barrier's grain boundaries, forming pyramid-shaped Cu₃Si precipitates. The Si/TiN/Cu loses electrical integrity at a threshold temperature (T_e) of ~500°. The TiAlN barrier containing slight amount of aluminum (< 2 at%) exhibits an improved capability by delaying the formation of Cu₃Si precipitates, and Si/TiAlN/Cu thus yields an elevated T_e of 600°. The performance of the multilayered TiAlN (adjacent to Si)/TiN equates to that of TiAlN. However, the multilayered film with an inverted design (i.e., TiN adjacent to Si) is the most effective barrier by yielding a T_e of ~700° for Si/TiN-TiAlN/Cu. Failure mechanisms of these barriers are currently under investigation.

Magnetic Field-induced Growth of Single-crystalline Fe₃O₄ Nanowires

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Single-crystal nanowires of Fe₃O₄ with diameters of 35~100 nm and lengths of about 0.48~2.7 μm have been successfully synthesized in a hydrothermal cell with a 0.25T magnetic field applied. The growth behavior of Fe₃O₄ nanoparticles under an extra magnetic field was compared with that under zero magnetic fields. The XRD patterns indicate that both of the two processes result in the formation of pure Fe₃O₄. However, the morphology of the particles was changed significantly, TEM observations show the morphology of the particles changed from quadrangle and hexagon in zero magnetic field into nanowires in a finite magnetic field. HRTEM image further reveals that the nanowires are single crystal grown along [110] direction, one of the easy magnetization axes of Fe₃O₄, confirmed by electron diffraction studies. Magnetic measurements show that the as-prepared sample exhibited saturation magnetization lower than the sample from the synthesis route under zero magnetic fields, which was discussed in terms of the magnetic domain pinning in one-dimensional nanostructures due to spatial confinement.

CATALYTIC OXIDATION OF CARBON MONOXIDE OVER COBALT OXIDES

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Catalysts of nanoCoO_x and Au/CoO_x (x is an atomic ratio between 1.00 and 1.33) were prepared to study their catalytic activity toward the CO oxidation. The oxidation state of cobalt ions in the prepared catalysts was characterized with the TPR (temperature programmed reduction) technique. Two consecutively reductive steps, i.e., CoO_x into CoO at 570 K and CoO to metallic Co at 650 K, were found to proceed in TPR on raising the sample temperature. The relative peak-area observed from the two steps in each TPR trace was used to determine the ratio x in freshly prepared catalysts. Their catalytic activities were further tested in a fixed bed flow reactor. The measured activity increased with the ratio x in catalysts. A mechanism is proposed to interpret for the variation in activity.

Molecular Dynamics Study of the Temperature Dependence of the Critical Size of Silicon Nucleation

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We adopt molecular dynamics simulation to study the temperature dependence of the critical size of silicon nucleation. The critical size is a divide. In a corresponding amorphous matrix, an embedded crystal with a size larger than the critical size will grow, while one sized smaller will melt. For a nano-crystal, the critical size has strong temperature dependence. To study the above phenomenon at the atomic level, we employ Stillinger-Weber- s three-body potential to modify the parallel molecular dynamics program DL_POLY so that it is capable of handling systems containing silicon atoms. The computational model is a spherical silicon crystal embedded in a corresponding amorphous matrix. Periodic boundary conditions and the NPT ensemble are set. The crystal radius is set at several different values for each distinct temperature level. Finally, it is found that the critical size decreases when the temperature is reduced, which is consistent with existing thermodynamics models.

Preparation and Characterization of Magnetic Fe, Fe/C and Fe/N Nanoparticles Synthesized by Chemical Vapor Condensation Process

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Magnetic Fe, Fe/C and Fe/N nanoparticles were synthesized by Chemical Vapor Condensation (CVC) Process using the precursor of Fe(CO)₅ under Ar, CO and NH₃ atmosphere. We investigated the microstructures, magnetic properties of the nanoparticles and their surface characteristics systematically by means of HRTEM, DTA-TGA, Mössbauer spectroscopy and magnetization measurement. The temperature of synthesis of nanoparticles was varied in the interval of 400 v 1100°C. The spherical nanoparticles of the mean diameter of 6-50nm comprise of the metal core and shell. To form composite nanoparticles of Fe/C and Fe/N, CO and NH₃ gas were flowed to a chamber with a precursor vapor of Fe under the control of other processing parameters. The effect of CVC parameters on the microstructure and surface characteristics had been investigated. * Presenter Author's DetailsName : Dr. Chul-Jin ChoiCompany/Organization : Korea Institute of Machinery and MaterialsAddress : 66, Sangam-Dong, Changwon, Kyungnam, South-KoreaTelephone : 82-551-280-3532Fax : 82-551-280-3599E-mail : cjchoi@kmail.kimm.re.kr

Superparamagnetic Relaxation in cobalt ferrite nanoparticles synthesized from hydroxide carbonate precursors

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Cobalt ferrite nanoparticles synthesized from cobalt iron hydroxide carbonate complexes prepared by a reverse microemulsion method. The particles have been studied by X-ray diffractometry, transmission electron microscopy, SQUID magnetometry and Mössbauer spectroscopy. All peaks of X-ray diffraction patterns can be attributed to a cubic spinel structure with the lattice constant = 8.39 Å. The average size of the particles, determined by transmission electron microscopy, is 7.8 nm. Superparamagnetic behavior of the particles is confirmed by the coincidence of the magnetization versus plots for different temperatures. As the temperature increases toward the Néel temperature, line broadening and a pronounced central doublet appear, suggesting superparamagnetic relaxation. As the temperature increases, the relaxation rate increases rapidly with a seventh power of the absolute temperature.

Study on magnetic nanoparticles-biodegradable polymer composite

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Magnetic carriers, including magnetic nanoparticles and biodegradable polymer, may find promising application in targeted drug delivery systems. Using a localized magnetic field and selective catheter, magnetic carrier-drug complex is targeted to the tumor. The carrier in our study is composed of poly (D, L-lactide) (PLA) and nickel ferrite nanoparticles. The nickel ferrite nanoparticles were synthesized by two methods, i.e. polyol process and ball milling. It was found that the ball milled nickel ferrite with average size of 10nm could only adsorb to the surface of PLA spherical particles. If the ball milled nickel ferrite nanoparticles were modified by the double surfactants (oleic acid and tri-octylphosphine (TOP)), they could be covered by PLA via the surfactants. The polyol process can produce the surfactants modified nickel ferrite particles in a single step. Because of more effective adsorption of surfactants, the magnetic particles synthesized by polyol process are more surface-active when blending with PLA.

Nanoscale Electronics for Chemical Sensing

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The recent progress in fabricating nanoscale electronics from novel materials like carbon nanotubes has enjoyed significant attention. 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, technological, and economical points of view. For example, it may be many years before nanoelectronic elements can compete commercially with conventional digital electronics. On the other hand, the field of chemical sensing is poorly served by solid state devices at present, making this an area of immediate opportunity for nanoelectronic devices to gain a foothold. This talk will survey our recent progress using novel molecular wires like carbon nanotubes in chemical and biological sensors. These molecular wires are exquisitely sensitive to certain gases, and by incorporating them as the active components of nanoelectronic devices we have demonstrated concept prototype sensors. Scientifically, the devices are interesting because they allow a novel electronic probe of molecular interactions at the single-molecule scale. Technologically, the sensors are mechanically robust, require extremely small amounts of power, and have been integrated into a silicon-based platform which is manufacturable in large quantities and at low cost.

Application of Image Processing to the Characterization of Nanostructures

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The inspection and characterization of nano materials and structures should be performed extensively and whenever possible in a non-invasive way. During recent years a major development of image acquisition and digitalization systems was achieved, as well as in what concerns image analysis and processing. Those techniques are now being frequently used in metrology and characterization laboratories including in the fields of nanomaterials and systems. On this communication we will review the most relevant image acquisition and processing systems and techniques pointing out recent developments. Reference will be made to the work being performed at the Microtopography Laboratory and at the Functional Coatings Group of the University of Minho.

SINTERING BEHAVIOR OF TITANIUM-TITANIUM NITRIDE NANO-NANOCOMPOSITE POWDERS.

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Present investigation attempts to study the sintering behavior of titanium-titanium nitride nano-nanocomposite powders. Nanosize titanium powders of average particle size of about 65nm were produced through the high-energy attrition milling of micron size titanium powders. The nanosize titanium powders were mixed with 8 wt% and 15 wt% nanosize titanium nitride powders (~50nm) to give two compositions of the nano-nanocomposites. Sintering experiments were carried out using high sensitivity vertical dilatometry at various temperatures in the range of 400! C to 1250! C in ultra high purity argon atmosphere. The nano sized titanium powders and titanium-titanium nitride nano-nanocomposite powders showed distinct sintering behavior in both; α -Ti range and β -Ti range in terms of the shrinkage and apparent activation energy for sintering. Shrinkage was found to be higher in the β -Ti range than in the α -Ti range irrespective of TiN addition. The addition of TiN caused a significant increase in the activation energy in the alpha phase where as in the beta phase it resulted in lower activation energy.

Synthesis of Precursor-Derived TiC-Ni based Nanocomposites by Direct Reduction & Carburization Processing

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Precursor-derived TiC-Ni based nanocomposites were synthesized by direct reduction and carburization processing. The process has proven very versatile as a wider range of compositions can be produced. Their phase structure, morphological and chemical features were characterized by XRD, SEM and TEM. Results show that the interfacial bonding between TiC and Ni was found to be of a good quality. The TiC reinforcement was in situ formed instead of being added to the matrix. The formation mechanism of the TiC-Ni based nanocomposites was discussed.

ENHANCED APPROACH TO SYNTHESIZE CARBON ALLOTROPES BY ARC PLASMA

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This approach allows to produce carbon vapor in plasma from traditional graphite electrodes and amorphous carbon particulates under influence of a buffer Nobel gas flow supplied into plasma zone. Carbon vapor is evacuated from hot plasma zone by efficiently organized radial exhaust inert gas stream. Model of small carbon particle vaporization is build. This model allows to establish interconnection between time taken for vaporization of carbon particle, its size and plasma temperature. The results of performed experiments are in good agreement with estimations. Study of influence of inert gas flow dynamics differently supplied to hot plasma zone during fullerenes synthesis was performed and interconnections between time taken for vaporization of carbon particle, its size and plasma temperature were defined. It was established relationship between different methods of gas introduction in plasma zone, different configurations of gas stream, gas flow rates, reactor internal gas pressure, applied power, diameters of used electrodes and fullerenes productivity, concentration, and yield. Our approach allows to apply big currents without significant reduction of fullerenes content in soot; to reduce cathode deposits and in some cases eliminate it at all; and to use big electrodes. Fullerene yield was analyzed by HPLC-UV(Vis) and HPLC-MS methods. Proposed method allows significantly increase fullerenes productivity at much low cost.

Characterization and Properties of Electrodeposited Nanocrystalline FCC Ni-Fe Alloys

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Nanocrystalline FCC (face-centered-cubic) nickel-iron alloys with compositions in the range of 5 to 60 wt% Fe were produced by electrodeposition techniques. The thermal stability of the Ni-21%Fe alloy was investigated by annealing experiments. The structure and composition of these deposits were characterized using electron microscopy and x-ray techniques. Microhardness and tensile tests were employed for evaluating the mechanical properties of the as-deposited and annealed samples. In this paper, the effects of composition and heat treatment on deformation and fracture of nanocrystalline Ni-Fe alloys are discussed.

Metallic and Intermetallic Nanoparticles, Filaments and Tree-like Assemblies Prepared By Laser Vaporization Controlled Condensation

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Nanoparticles exhibit interesting properties that are usually different from the bulk materials properties. The evolution of the nanoscale properties is largely dependent on the size, shape and assembly of the nanoparticles. In this work, we present a method to synthesize size-selected nanoparticles of a variety of materials by coupling the laser vaporization controlled condensation (LVCC) technique with a differential mobility analyzer (DMA). The LVCC method is based on using pulsed laser vaporization within well-defined conditions of temperature and pressure in a thermal diffusion cloud chamber. The coupling of LVCC and DMA is applied to synthesize metallic Al, Fe, Ni, Ti, and intermetallic FeAl, Ti₃Al and NiAl nanoparticles of selected sizes. The LVCC method can be coupled to plasma and ionic polymerization techniques, thus allowing the incorporation of the metallic nanoparticles within the polymer films. We will present the application of the LVCC method for the catalysis of gas phase polymerization of several olefin monomers. The effect of electrical charging of the nanoparticles by ions and free electrons generated by the laser vaporization process has been investigated. Enormous electrostatic aggregation due to dipole forces is observed between nanoparticles to form chain aggregates, and between the chain aggregates to form tree-like filaments. The assemblies display stretch and contraction properties depending on the strength of the applied field. These observations have significant implications for the ductility and the plastic behavior of the materials formed from consolidated nanoparticle assemblies. Finally, the preparation and catalytic activity of metal / metal oxide nanoparticles for the oxidation of CO will be presented. The results indicate that the nanoparticle catalysts exhibit significantly enhanced low temperature activity for the CO oxidation as compared to the bulk powder catalysts.

Developing XAFS method designed to characterize materials containing nanostructures

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Our research is devoted to development of X-ray absorption spectroscopy techniques allowing to determine spatial and electronic structure parameters of materials containing semiconductor heterostructures. The experimental procedures developed are used for characterization of extended well-ordered surface self-assembled heteroepitaxial structures containing Ge-nanoislands on Si(001) or Si(111) and InAs-nanoislands on AlAs. These structures revealing quantum dots (QD) properties [1] were deposited on substrates via molecular beam epitaxy (MBE).

Surface sensitive EXAFS (Extended X-ray Absorption Fine Structure)è XANES (X-ray Absorption Near Edge Structure) spectroscopy based on total electron yield and fluorescence yield detection modes [2] are used: 1) for the determining of local structure parameters (interatomic distances (± 0.01 Å), partial coordination numbers, symmetry of various atoms environment) for systems on surface, 2) for study of local structure parameters of heterosystem after interface diffusion, 3) for extracting information concerning the energy structure of the QDs free states. It was established that local microstructure parameters are linked to nanostructure morphology and adequate models are suggested and discussed.

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Crystallization and failure behaviors of Ta-Co nanostructured/amorphous diffusion barriers for copper metallization

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Sputter-deposited polycrystalline tantalum (Ta) and tantalum nitride (TaN) thin films are currently used as diffusion barriers for global copper interconnects in commercial integrated circuits. Their grain boundaries, however, tend to act as the main diffusion paths for copper atoms to penetrate the diffusion barrier, causing the failure of silicon/copper interfaces or generating deep-level recombination centers in dielectrics. Amorphous thin films thus are potentially more promising than Ta and TaN as they lack grain boundaries. Therefore, this work examines the thin-film properties and diffusion barrier behaviors of thin Ta-Co co-sputtered films, aiming at depositing highly crystallization-resistant and highly conductive diffusion barriers for copper metallization. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) indicate that the deposited Ta-Co films indeed have a glassy structure and are free from highly resistive intermetallic compounds, thus giving a resistivity as low as under 50 $\mu\Omega$ -cm. Examining Si/Ta-Co/Cu stacked samples by using 4-point probes, XRD and cross-sectional TEM reveals that thermally induced failure of amorphous Ta-Co barriers are triggered by the barrier's crystallization at temperatures just under 500°C. Nonetheless, as the crystallization temperature of Ta-Co can be increased markedly to ~ 700°C by adequately controlling the deposition parameters, the effectiveness of the nanostructure/amorphous Ta-Co thin film thus can be substantially enhanced by effectively blocking diffusion of copper towards the underlying silicon.

Effects of different hybridizations on transport through severely deformed carbon nanotubes

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The main purpose of the present work is to establishing a correspondence between mechanical deformation and transport properties, which is presumably useful in nano-sensor applications. As a byproduct of this study, the potential differences in the mechanical behavior of armchair and zigzag tubes, as well as that of armchair-zigzag junctions, are also revealed. We use a tight-binding model to describe the nanotubes. For various semiconducting and metallic nanotubes, the relaxed structures under severe deformations, both elastic and plastic, are obtained. After obtaining the relaxed structures, the Green's function approach is employed in order to obtain the conductance of the systems under consideration. The current-voltage characteristics are then determined using the Landauer-Buttiker formalism. It is concluded that a large change in conductance usually is accompanied by severe deformations. The effects of various orbital hybridizations resulting from different levels of deformation are investigated. It is observed that I-V characteristics indeed depend on the deformation, hence the possibility of usage as nano-sensor.

Synthesis and characterization of phosphors nanosized Y_2O_3 doped Eu^{3+}

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Yttrium oxide nanoparticles with luminescent properties were produced at low temperature for direct oxide precipitation. Europium doped yttrium oxide ($Eu^{3+}: Y_2O_3$) particles with size < 5 nm were synthesized in colloidal solution, followed of controlled precipitation was obtained fine powders sub-micronic. We report the structural and luminescent evolution for different concentration of europium. X-ray diffraction (DRX) was used to determine the crystalline structure for samples annealing in air. The size of the nanoparticles was in the range 5 to 100 nm showed a good distribution, excellent morphology and high crystallinity with the temperature evolution. High resolution transmission electron microscopy (HRTEM) showed that the powder is crystallized immediately after of the synthesis. Promising nanophosphors with excellent luminescence intensity were analyzed by emission spectroscopy.

Why Alkali Metal Doped Carbon Nanotubes Poses High Hydrogen Uptake? A Mixed QM/MM Study

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A mixed Quantum Mechanics / Molecular Mechanics (QM/MM) model is used for investigating the nature of the molecular hydrogen adsorption in pure and alkali metal doped single-walled carbon nanotubes (SWNTs). For the QM part the DFT with B3LYP functional is used while for the MM we employ the universal force field (UFF). This mixed theoretical model was tested also by MP2 single point energy calculations. Our results demonstrate that the charge transfer from the alkali metal to the tube polarizes the H₂ molecule and this charge induced dipole interaction is responsible for the higher hydrogen uptake of the doped tube.

Position and size controlled fabrication of nano-metals and vsemiconductors with fine focused electron beam

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We have discovered that Si nanocrystals can be formed in a SiO₂ thin film under irradiation of an electron beam at high temperature. The acceleration voltage of the beam was 100 kV in order to reduce sputtering for Si atoms. When the high-intensity electron beam was focused on the amorphized SiO₂ thin film at 850 K, crystalline Si nanoparticles were emerged at the irradiated area. The diameter of the nanoparticles was as large as the beam diameter (several nm). The typical electron beam current density was 4×10^8 C/m². The exposure time was 5 sec. An array of the Si nanocrystal dots was also fabricated using this method. Similarly, when decomposeable gases with electron beams, such as W(CO)₆ were introduced at the beam irradiated areas, nan-metal islands can be formed depending upon the beam diameter. The combination of these methods indicates the possibility of position and size controlled fabrication of materials.

Novel Supramolecular Architectures with Carbon Nanotubes

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Substantial efforts have been devoted recently to the development and technology of carbon nanotubes due to their outstanding properties and application potential. Primarily based on the extension of classical organic concepts, only a few derivatives of carbon nanotubes have been developed in order to produce functionalized and/or soluble carbon nanotubes. In this study, a general survey of the concepts for the derivatization of carbon nanotubes is presented and the different types of reactions and syntheses are highlighted. Supramolecular approaches presented are based on the use of single- and multi-wall carbon nanotubes as building blocks for supramolecular constructs. The use of carbon nanotubes as synthons follows a general strategy, in which multifunctional molecules are connected to the carbon building blocks. Thus, several model systems have been studied and examples of interaction products of carbon nanotubes with organic macrocycles, hydrophilic polymers, and biomacromolecules such as DNA are given. The novel carbon nanotubes-based hybrid architectures are expected to have an application potential in many areas such as the biomedical and electronic areas due to their hydrophilicity and conducting properties as well as building blocks for molecular machines and robotics.

Nano-finger electrodes for the electro-optical generation and tuning of gratings at several wavelengths

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The electro-optical generation of gratings has been introduced as early as 1971 (J. M. Hammer) for modulators and logics and has since this time been reported extensively where the finger spacing was in the μm range. Most recently modern control concepts have been introduced by the author where reflections (i) are switched on and off and tuned electro-optically and (ii) switching between several wavelengths is optional. This should be possible by (iii) sequentially arranged gratings with different spacings and (iv) multiple finger electrodes at several vertically stacked layers. The composition of finger electrodes for multiple gratings requires finger widths and spacing in the nano range (500 nm to 200 nm and less). The voltage adjustment at the multi-nano finger electrodes, in order to modulate the refractive index of electro-optical active grating material, is assumed to cause many problems (the upper electrode layer, closed to the material is slowing down the propagating waves and the electrical fields at the subsequent lower electrode layers superpose). The modulated shape of the refractive index changes are searched for examples of multi-nano finger electrodes in order to allow the calculation/computation of the reflection coefficients which are the matrix elements in the photonic controller matrix. Another goal is the proper designarrangements of the electrodes and insulation between the layers. The work concentrates on multiple grating for two wavelengths which may also be useful for several other purposes (add-and drop, routing).

Formation, Reactivity, and Phase Transformations in Silicon/Silica, Tin Oxide, and Titanium Oxide Based Nanostructures

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A series of experiments has been undertaken to generate and characterize native and doped silicon/silica, tin oxide, and titanium oxide nanostructures. Silicon/silica nanospheres are found to display unusual catalytic support and reactive properties. These structures can be agglomerated to wire-like configurations subsequently providing a means to grow silica nanotubes and to produce silica nanofiber arrays from silicon seeds in an oxidative flow. The silica nanotubes may fill an existing need for the catalytic conversion of high molecular weight hydrocarbons (MW - 1000). Two unique syntheses have been used to generate SnO_{2-x} nanowires, nanoribbons, and nanotubes. Crystalline nanowires which display both a rutile and orthorhombic structure are formed from high temperature synthesis with SnO/SnO and Sn/SnO mixtures. Several of the wires display a phase transformation between rutile and orthorhombic crystal structures normally observed at pressures in excess of 150 kbar in the bulk. Similarly, under somewhat different experimental conditions nanoribbons and nanotubular structures can be formed which display combined rutile and orthorhombic structures. A single step mixed SiO/Si/SiO₂ synthesis has been used to form silica nanospheres decorated with SnO_x nanocrystals. Partially agglomerated SiO₂ nanospheres of diameter - 45 nm have been used as nanosupports (substrates) for SnO_x crystallites of diameter 3-6 nm. Unique reactivity and ready phase transformation is found to accompany the nitriding of TiO₂ nanoparticles, efficiently producing TiO_{2-x}N_x nanoparticles which represent photocatalytically active quantum dots absorbing light well into the visible. Taking advantage of the fact that nanoparticles may have a significantly enhanced interaction-reaction probability, we have successfully accomplished the conversion of TiO₂ to TiO_{2-x}N_x at room temperature on a time frame of seconds. Here, TiO₂ nanoparticles are treated chemically in solution to provide the source of nitrogen in forming TiO_{2-x}N_x. Thi

s solution phase conversion process represents a much simpler, faster, and higher yield process than that of Ashai et al 1 in the gas phase to produce an effective photocatalyst absorbing in the visible. In distinct contrast, the similar treatment of either rutile or anatase TiO₂ submicron powders does not produce the conversion to the oxynitride at room temperature. A ready reactivity for TiO₂ operative only at the nanoscale regime, is accompanied also by the palladium induced phase transformation of TiO_{2-x}N_x.1. R. Ashai et al., Science 293, 269 (2001).

Nanostructured oxides and bio-composites for advanced chemical sensors: An assessment of microstructure-sensing property relationships

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Semiconducting oxides are typically used as sensing element for conductimetric gas sensing devices. The use of nanofabrication techniques for processing oxides favors the formation of metastable polymorphic phases due to the small physical size of the nanomaterials. The high surface areas associated with nanoparticles or nanowires promote the adsorption of gaseous molecules to the oxide's structure and thus are expected to increase gas sensitivity. Selectivity, on the other hand, has been recently shown to depend strongly on the oxide's crystal structure. Therefore, it is important to assess the relative importance of crystallographic and morphological features of nanostructured oxides to the sensing response of these materials to a given analyte so as to be able to fabricate materials with controlled properties. This work presents a study of nanostructured MoO₃ and WO₃ that are used as sensing elements for the detection of gaseous ammonia or amines. The sensing responses obtained are of the order of a few seconds and the gas sensitivity levels below the ppm range. A p-n type transition in the sensing response of these oxides was observed, which is related to polymorphic phase transitions occurring during sensing. Furthermore, nano-composite oxides (doped with enzymes) have also been produced and characterized structurally. Emphasis is given on analyzing the biomolecule-oxide interactions. The sensing properties of the nanocomposites are currently being evaluated.

Nanostructured bulk solids by field activated sintering

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Structural nanomaterials are distinguished by unusually high strength, fatigue resistance, hardness, wear resistance, fracture toughness, and extensive high temperature formability. However, commercial applications have only begun to tap the potential of high strength parts (e. g., GIGAS nano-Al alloys or high strength nano-SiC springs). More commonly they are used as thermal barrier coatings or in friction and wear resistant rotating parts (e.g. sleeves or bearings). Wider application of these materials will require more reliable mechanical properties at the nanoscale and a more aggressive shift from basic science studies to the design and processing of optimum parts with unique properties. Field activated sintering is a recently developed process, which dramatically shortens the processing time for powder densification, thereby making it a good candidate for sintering nanostructured materials. The application of an external electrical field activates the particle surfaces, enhances sintering and minimizes grain growth upon densification. The process has been successfully applied for the densification of a variety of materials, electrically conductive, superconductors or insulators, monolithic and functionally graded materials, regular size or nanocrystalline. The emphasis of current studies is to understand the electrical field effects during powder consolidation. This talk will overview modeling and experimental studies of electrical field effects on sintering nanosize particles.

Synthesis and organization of metallic, semiconductor and oxide inorganic nanostructures in planar molecular nanoreactors

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Monomolecular layers at the gas-liquid interface and multilayer Langmuir-Blodgett (LB) films were used as molecular nanoreactors for generation and organization of inorganic and composite nanostructures. Gold and palladium metallic nanoparticles and nanowires were generated two-dimensionally via the chemical decomposition of precursor molecules in a mixed Langmuir monolayer at the gas/aqueous borohydride solution interface with amphiphilic polymeric and monomeric surfactants. Nickel oxide and iron oxide nanoparticles were synthesized in the nickel arachidate and ferric arachidate LB films via incubation of the films in the sodium borohydride solution at ambient conditions. The effects of time-dependent self-organization of nanoparticles in the film matrix were observed. Semiconductor CdS nanoparticles were formed via hydrogen sulfide treatment of cadmium arachidate LB films. Polymeric quasi-crystalline planar monomolecular structures and nanoscale-ordered nano-composite planar polymeric films with incorporated ligand-stabilized metal clusters, iron oxide and semiconductor nanoparticles were fabricated successfully. The obtained nanostructures were characterized by transmission electron microscopy.

**METAL-CONTAINING NANOPARTICLES ON THE SURFACE OF NANOGRANULES OF
ULTRADISPERSED POLYTETRAFLUOROETHYLENE**

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A universal method of stabilization of metal-containing nanoparticles on the surface of polytetrafluoroethylene matrix has been developed. The chemical aspect of this process involves the formation of nanoparticles upon the thermodestruction of metal-containing compounds. The polytetrafluoroethylene matrix is very interesting because this polymer is very inert. Firstly metalcontaining (Fe, Co, Fe₂O₃, CdS, Cu, Pd) nanoparticles (3-7 nm) was obtained on the surface of nanogranules ultradispersed (150-300 nm) polytetrafluoroethylene. The size and structure of nanoparticles was determined by TEM, EXAFS, X-ray emission and Mossbauer spectroscopy. Nanoparticles on the surface of nanogranules have a rather narrow size distribution. As a result magnetic polytetrafluoroethylene with high coercive force (~ 600 Oe) was fabricated. High catalytic activity Pd-containing nanoparticles in hydrogenation was showed.

Hybrid organic-inorganic polymers with nanoscale building blocks: Precursors, processing, properties and applications

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Hybrid inorganic-organic polymers (IOP, ORMOCERs) are composites with inorganic and organic nanobuilding blocks linked via stable covalent bonds. Precursors are mainly organically modified silicon alkoxides and/or functionalized organic oligomers/polymers. The modified heteropolysiloxane network as basic structural element is synthesized via sol-gel-processing. A method often used is the formation of the inorganic network by polycondensation reactions (e.g. Si-O-Si bond formation) in a first step, followed by the organic crosslinking (thermal curing at 80-180 °C or UV-processing). Another type uses the silanization of organic polymers in a first step, with subsequent hydrolysis and polycondensation reactions of the silanized units. This process leads to room temperature/self-curing materials, without need for thermal or UV-curing. The presentation focuses on the selection of precursors for various applications and the chemistry involved in processing. Basic properties and the application potential of ORMOCERs as coatings, fibers and composites are presented. Optical transparency and hardness with ease of functionalization by organic groups combined with polymer like processing, are some of the main advantages of these hybrid materials. Property/composition relationships are shown for mechanical, optical and permeation/barrier properties. Some examples for industrial implementation of this technology are given.

An NSF Perspective on International Cooperation in Materials Research

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The fundamental properties of materials frequently define the capabilities, potential, reliability and limitations of technology. Advances in materials research enable progress across a broad range of science, engineering and technology with dramatic impacts on society. Continued progress in materials science and engineering is increasingly dependent upon collaborative efforts across disciplines, as well as closer coordination among funding agencies and effective partnerships involving universities, industry and government laboratories. Partnerships are important not just at the national level but increasingly at an international level as well. In this talk I will outline NSF activities in support of materials research and nanoscale science and engineering, focusing on opportunities for international cooperation and collaboration. I will describe recent efforts by NSF and its counterpart agencies in other countries and regions of the world to develop an international materials network. I will include examples of international partnerships established in this context, and describe current opportunities for obtaining NSF support for the US side of international collaborations in materials.

Nano-catalytic Tin Oxide Particles Synthesized by Low Temperature Aqueous Mixing and Doping (LTAMD)

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In this work, ultra-nanocrystalline catalytic tin oxide particles were synthesized by newly developed low temperature aqueous mixing and doping (LTAMD) method. The LTAMD is the one time synthesis of the tin oxide particles with the Pd-Pt composite catalysts using Sn butoxide, Pd and Pt acetylacetonate. Differed from the current method, the combination of the doping process to the synthesis of the tin oxide nanoparticle simultaneously without chloride below 300oC. Those reagents were mixed uniformly in isopropylacohol and dried by evaporating the solvent at room temperature. The remained particles were then heat-treated at 100 ^oC to remove the organic component thoroughly. As a result, the ultra-nanocrystalline tin oxide particles doped with Pd-Pt composite could be synthesized with the particles size and specific surface area of 1 nm and 442 m²/g, respectively. Also, applying the particles, nanocrystalline gas sensor with high sensing properties could be fabricated.

Novel Synthesizing Process for Nanocrystalline Indium Tin Oxide particles by Low-temperature One-time Mixing and Oxidation (LOMO)

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Recently, nanocrystalline indium tin oxide (ITO) particle is increasingly used for information displays industry. However, the size cannot be decreased to 35 nm because of the bottleneck in current technology using the high temperature synthetic process above 700oC, which is required to remove the chloride. TG-DTA results showed that the temperature above 700oC is required for the removal of the chloride. The chloride causes the high fabrication cost and environmental pollution. So, in order to overcome the drawback and synthesize the more ultrafine nanocrystalline ITO particles, we developed a new clean method of low-temperature one-time mixing and oxidation (LOMO). The process temperature does not exceed 300oC by the excluding the chloride ions from the synthetic materials. Applying the LOMO method, nanocrystalline indium-tin-oxide particles were successfully synthesized. HRTEM, XRD and BET analysis revealed that the synthesized nanocrystalline particles were with ultrafine size below 3 nm and ultrahigh specific surface area above 117 m²/g. So, the good quality nanocrystalline ITO particles could be synthesized with our own LOMO method.

Local variation of magnetization in nanocrystalline ultra-soft magnetic films investigated with Lorentz transmission electron microscopy and electron holography

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For quite some time it is known that in nanocrystalline soft magnetic films with an induced uniaxial anisotropy, the direction of the magnetization wiggles around the easy axis producing a so-called micromagnetic ripple. The local variation of the magnetic field in a thin film influences the out-of-focus image in the transmission electron microscopy (TEM) via variation of the Lorentz force that acts perpendicular to directions of the electron beam and to the magnetic induction. Consequently, in Lorentz transmission electron microscopy (LTEM) the quasi-periodic oscillation of the transversal component of the local magnetization leads to almost parallel (1D) fringes in under- or over-focused images. It will be shown that from the spacing between the fringes the wavelength and the amplitude of the angular spread of the magnetization direction can be estimated, using a simplified relation. In addition, besides ripple fringes in the LTEM image, there appears also a dotted contrast along the ripple fringes. A theory of LTEM images for films with 1D- and 2D periodical topographies, in combination with the micromagnetic oscillations of the magnetization, is presented. The theory predicts the 2D-pattern in LTEM in agreement with experimental observations.

The nanocrystalline Fe-Zr-N films have been prepared by DC magnetron reactive sputtering with a thickness between 50 and 1000 nm. The films have been deposited on glass or silicon substrates at several temperatures between room temperature and 200 °C. Polymer or Cu substrates were used to float the film on a grid for TEM investigation. The deposition conditions were chosen to obtain a composition $(\text{Fe}_{99}\text{Zr}_1)_{1-x}\text{N}_x$, where the concentration of nitrogen was in the range $x \leq 25$ at%. A 64 kA/m magnetic field was applied in the plane of the samples during deposition to induce uniaxial anisotropy of up to 1.6 kA/m). Electron holography and LTEM studies were performed, using JEOL 2010F transmission electron microscope equipped with a post-column energy filter.

Formation and field-emission properties of carbon nanofibers by a simplified thermal growth

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Field emission properties from a carbon nanofibers (CNFs) film prepared by a simplified thermal growth were investigated. Using a special phenolic solution as precursor, a high-density CNF network was grown on Ni-based film at 700C under Ar atmosphere (1 atm). Characterization analyses indicated that the single CNF with ~100 nm has a length in range of 10v20 ì m and high fiber density ~108/cm². Field emission tests showed that the turn-on voltage of CNFs is at 6 MV/m, and the thresholds voltage at 1 mA/cm² is at 7 MV/m. Typical current-field data in Fowler-Nordheim model can estimated the work function of the CNFs in range of 0.8v3.5 eV.

Phase Contrast Microradiography?Examining Matters Deeper with Higher Precision

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One hundred years after the discovery of X-ray, radiography has reached a new level of sophistication and power. With higher coherence of the X-ray source produced by synchrotron, phase difference is added to the absorption as another, yet much improved, contrast mechanism. Together with the improvement in the detecting system, we can now look deep inside into matters with unprecedented precision and speed. Sub- μm resolution radiograph can now be obtained with ease and fast phenomenon can be observed in a real time fashion. The application of this new tool has already helped researches in materials science, biology and medicine. Ongoing developments in the instrumentation and reconstruction algorithms have generated even higher excitement with the recent demonstration of nanometer scale resolution in 3D. It is anticipated that with the new installation of X-ray free electron laser, X-rays can be used to 'image' a single protein molecule with atomic resolution in the near future and to continue the legacy started by Röntgen. Review of this advent of this technology, its application to various domains in science, the relevance to the nano-science and -technology, and the future potential will be presented.

Borazine-siloxane organic/inorganic hybrid polymer (Synthesis, Properties and Applications)

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Borazine-siloxane polymer that is organic/inorganic hybrid polymer having both borazine and siloxane structures alternatively can be synthesized by hydrosilylation polymerization of B,B',B''-triethynyl-N,N',N''-trimethyl-borazine with tetramethylcyclsiloxane. Polymerization under diluted conditions gave a homogenous solution of the linear polymer and thin homogeneous films can be made on a silicon wafer by spin-coating and further this linear polymer became to be network structure by annealing. The thin film consisted of this novel network polymer has low dielectric constant below 2.5 without pore, excellent thermal and mechanical properties, and moreover Cu diffusion barrier properties. The application of this polymer thin film as hardmask for the low-k organic polymer interlayer dielectric can result in the total interlayer insulator with the effective dielectric constant which is the required value for ULSI at 70nm scale. Fortunately, an environmentally friendly semiconductor process can be realized, because this thin film can be etched without use of any PFC gases which cause global warming.

Comparison of different support types for the preparation of nanostructured catalytic membranes

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Different nanostructured catalytic membranes have been prepared by platinum deposition (evaporation and ionic impregnation) within the porous framework of different tubular porous supports of a few nanometer pore size. The aim of the work is to investigate the influence of preparation methods and the influence of the type of support on the properties of the obtained catalytic membranes. Some parameters of the preparation procedure, controlling the deposition performance, have been explored. The platinum deposition was carried out using different techniques. Various types of supports made of different types of oxides and carbon with different layer distribution and pore diameters have been investigated. The catalytic membranes have then been characterized by hydrodynamic measurements as well as scanning and transmission electron microscopy. The distribution of platinum within the thickness of the membrane wall has been correlated to the preparation parameters and material of the support.

Synthesis of High Performance Electrolyte Cell with Nano Ordered CeO₂ Thin Electrolyte Film

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In order to develop new energy conversion technique, electric power and hydrogen multi generation system by partial oxidation reaction of methane source using thermo nuclear power, Plasma coating technique was employed to make nano ordered thin solid electrolyte film of Ce_{0.8}Sm_{0.2}O_{1.9}, which shows high ion conductivity of 1.4 S cm⁻¹ at 1273K and low loss of self-electric resistivity in the temperature range of 173-1273K. The solid electrolyte cell with the Ce_{0.8}Sm_{0.2}O_{1.9} thin film and both of porous positive and negative electrodes by plasma spray technique. This paper will report new possessing technique of nano thin film onto the porous electrodes and fundamental properties of the cell.

PROPERTIES OF YSZ AND CeGdO NANOPOWDERS PREPARED BY TARGET EVAPORATION WITH A PULSE-REPETITIVE CO₂-LASER

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The design and characteristics of a setup for producing oxide nanopowders are reported. Y₂O₃ v stabilized ZrO₂ (YSZ), Al₂O₃+YSZ and CeGdO nanopowders are prepared by target evaporation with a pulse-periodic CO₂-laser, followed by vapor condensation in air stream. Average laser radiation power is 600 W, pulse power ~ 10 kW. The output rates of YSZ and Al₂O₃+YSZ nanopowders are 15-20g/h, and CeGdO nanopowder - 55-60g/h. The grain mean size in the powders is 15nm. Data for the powder characteristics, as well as results of X-ray phase and structure analysis, are reported. The reasons of higher CeGdO output rate are discussed.

Single crystal SBN:Yb /Opal matrix (SiO₂):Er composite as a nanophotonic structure

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Thin layer of opal matrix on SBN:Yb (001) crystal substrate was prepared via sedimentation method and post-growth annealing treatment .

The film thickness of cubic package of SiO₂ nanospheres (240 nm in diameter) was of 25 monolayers. Erbium oxide (Er₂O₃) was introduced into the interspherical space of opal matrix using the sol-gel method (about 35 – 40 % relative to the pore volume). The nanophotonic structure obtained was used to study Er³⁺ ion photoluminescence at around 1.55 μm (third communications window). The possibilities of Er³⁺ cascade excitation by the Yb³⁺ ions were studied, what leads to strong increasing of pump efficiency and broadening of absorption band. The specific features of photoluminescence in such nanocomposites will be discussed.

Structural ordering of metal-containing amorphous carbon thin films induced by low-energy electron beam projection

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Localized ordering and crystallization behavior of sputter deposited amorphous carbon (a-C) films with a small amount of metal additives were investigated using transmission electron microscopy, low-energy electron energy-loss spectroscopy and temperature dependent conductivity measurement. Electrons accelerated with 30kV-60kV were irradiated to 100nm-thick a-C films deposited on Si substrates through a 3-micron-thick Si window. After the electron beam projection, dispersed clusters with a stack of 10-15 layers of graphite c-plane were observed in the a-C films containing 15at%-Co, and structural ordering was detected in the a-C films containing Y, Rh or W up to 1at%. Significant change in conductivity mechanism which can be attributed to the structural ordering was detected in the temperature range from 15 K to RT. The effects of metal catalysis and the low-energy electron beam irradiation on the localized structural ordering will be discussed.

An industrial method for nanoparticle synthesis with wide range of compositions

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A flame-based method (called DND, Direct Nanoparticle Deposition) has been developed originally mainly for manufacturing of rare earth doped amplifying fibers (used e.g. in EDFA). Main advantages of the method are: 1) avoiding of harmful phase separation of rare earth, 2) wide range of concentration of various dopants and co-dopants and 3) good repeatability. The key factors of the method are: 1) Possibility to feed the precursors into the flame alternatively as liquid solution and/or gas mixture. 2) Hot hydrogen-oxygen flame ensuring the vaporization of low-vapour-pressure precursors. 3) Flame properties leading to extremely rapid particle formation and small primary particle size (10-100 nm). Also the cooling rate of the multicomponent particles after formation may be high, preventing phase separations due to the lack of time to reach the equilibrium conditions. Due to the flexibility to several possible particle composition, research has been carried out on applicability for synthesis of other materials than doped glass, in order to generate: single/ multicomponent oxide particles and/or single and multicomponent noble-metal particles. The paper discusses the application and results of silica-alumina-erbium, silver, and silver-palladium particles generated by this method. / S. Tammela et al., Direct Nanoparticle Deposition process for manufacturing very short high gain Er-doped silica glass fibers, Proceedings of ECOC 2002, September 8-12, Copenhagen.

Interfacial structures of GaN/sapphire and Co/Si using synchrotron x-rays

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We investigated the interfacial nanostructures in metal/semiconductor thin films using synchrotron x-ray scattering. In GaN nucleation layers, the existence of tensile-strained, aligned, interfacial domains is attributed to a 6/7 matched interfacial structure, where 6-Ga atomic distances in GaN match to 7-Al atomic distances in sapphire. The tensile state of the interfacial domains is preserved during annealing to 1100°C, while the stacking sequence changes from cubic to hexagonal order. Similar 6/7 matched interfacial structure is also observed in compressively strained, interfacial domains of Pd/GaN, where 6-Ga atomic distances match to 7-Pd atomic distances. In the interfacial nanostructure of Co/Si system, we find a layerwise consumption of silicon substrate during the deposition of Co monolayers. The interfacial silicide layer formed in the initial stage of growth is a commensurate phase of pseudohexagonal Co₂Si with a long-range order and large strain imposed by Si substrate.

Analysis of the behavior of single wall carbon nanotubes under tensile stress by direct HRTEM observation

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The remarkable mechanical properties of Single Wall Carbon Nanotubes (SWCNT) make them excellent candidates for high strength composite materials. The mechanical properties of SWCNT have been extensively studied theoretically, and many interesting properties have been shown. On the experimental approach, the studies of mechanical properties have been less frequent. In the present paper we describe a method that allows high-resolution transmission electron microscopy studies of SWCNT being elongated until their rupture. We used the intense beam of a field emission electron microscope to mold a carbon fiber between two holes on an amorphous carbon film. When a few atomic layers are left the fiber becomes a SWCNT of 0.9 nm. Subsequent irradiation is used to open the holes, fact that result in a force that pulls out the fiber under tensile stress. At this point if the tensile stress continues the SWCNT deforms until failure occurs. Three mechanisms of failure, determined by the symmetry and initial diameter of the tube, were identified: a) brittle fracture; b) plastic deformation followed by: i) production of a smaller SWCNT at the center of the tube (necking); and ii) formation of a linear chain of carbon atoms bridging the two sides. It was found a Young's modulus of 1.2 TPa for the brittle SWCNT and a value between 120 to 530 GPa for the ductile SWCNT. In the case of the plastically deformed tubes we found that a SWCNT of 0.57 nm in diameter is spontaneously formed at the neck of the fiber, as the pulling out force keeps on acting on the tube, a narrower tube of 0.34 nm is formed. This produces a (7,0) (4,0) (7,0) heterojunction in a controlled way. In addition, there have been recorded, for the first time, images of the linear carbon chains; a remarkable fact is the stability of those chains which remain under tensile stress for about 15 to 20 s. From theoretical calculations performed on the formation of linear chains we have concluded that the bonding was cummulene type, the chain contained between 8 to 9 atoms with a bond distance between 1.27-1.34 Å. The force constant of the observed constrained chain is 3.15 eV/Å² in contrast with the value for a free chain (7.4 eV/Å²).

On the nanothermodynamics of bimetallic nanoparticles

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A nanoparticle characterizes as a organizational feature at the intermediate scale between individual molecules and about 100 nm; it is seen as a building block of new materials or devices. Its properties are novel and very different from bulk solids, because principally to its large surface area, and the confinement effects. Then, the study of the properties of nanoparticles is very relevant in the new emerging technology for the 21st century. In particular the thermodynamic functions differ from that of the macroscopic system, and consequently nanoparticles will show a phase diagram very different from that of the bulk. In the present work we study nanoparticles of the bimetallic system Au-Pd. The morphology and microstructure of the nanoparticles were analyzed using high-resolution transmission electron microscopy images and extensive simulations by molecular dynamics. We have obtained the total energy of the particles as a function of their structure and size. It is found that the total energy of particles constituted by a eutectic like alloy was lower than that of a solid solution. We show that the composition of the particles have an important effect on their morphology and microstructure. Results of the molecular dynamics calculations have been compared with experimental data.

Dynamical structural disorder and charge transport in a DNA model

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An interacting carrier-lattice model is presented for studying charge transport in DNA. Using the Peyrard-Bishop nonlinear model we investigate the effects of intrinsic dynamical structural disorder, resulting from thermal fluctuations, to the propagation of an electron, or a hole, through the stacking orbitals of a double-stranded DNA. We use semiclassical Langevin molecular dynamics simulations to mimic finite temperature. Different kinds of charge-lattice couplings have been used affecting either the on-site energy of the charge carrier, or its hopping integral through neighboring base-pairs.

Control of DNA-metal nanostructure self-assembly using the tools of molecular biology.

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There is currently great interest in the development of new tools to control the self-assembly of novel nanostructure materials, due to the important potential applications of such materials in catalysis, biology, electronics and medicine. The groups of Mirkin and Alivisatos introduced one-step self-assembly of gold nanoparticles using the hybridisation properties of thiol-modified DNA ligands. Here, we describe the application of the techniques of molecular biology to extend the control available over the assembly of such DNA-metal nanostructures. We have used restriction endonuclease enzymes to cleave DNA ligands of gold nanoparticles at specific sites. The cohesive ends formed after cleavage may be used to create specific links between particles by hybridisation and enzymatic ligation. This method of revealing latent reactive sites within DNA ligands is analogous to the use of protecting groups in organic synthesis and provides the potential for multi-step synthesis and manipulation of nanostructures.

Some peculiarities of two-pulse transmission and reflection of laser radiation by thin semiconductor films

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The theoretical investigation deals with effects of the nonlinear steady state and nonstationary transmission and reflection of laser radiation by a thin semiconductor film in two-beam regime taking into account the processes of two-photon biexciton generation from the ground state of the crystal and optical exciton-biexciton conversion. We have obtained the system of nonlinear differential equations, which have described the time evolution of the amplitudes of excitons, biexcitons and fields of transmitted and reflected pulses under the action of two incident pulses with different frequencies, amplitudes and envelopes. We have proved the possibility of efficient controlling by the transmission of one of the pulses by change of the shape, intensity and time delay of the second pulse. For the short pulses of the rectangular shape we have predicted the nonstationary regimes of the total reflection of the incident pulse, of the total bleaching, of the transformation of a short pulse into the train of supershort pulses, of the generation of solitary supershort pulse, the width of which is of some orders less, than the width of the incident pulse. We have obtained the regions on the bifurcation plane depending on the amplitudes of the incident pulses, which correspond to the total reflection and self-pulsations. We have found the dependence of the self-pulsing of transmitted pulses on the amplitudes of incident pulses. The change of the time delay between pulses is the flexible and perspective controlling method of the film transmittivity. We predicted the possibility of the high-speed thin film response far off on the front tale of the incident pulse. The maximum of the generated pulse appears earlier than the maximum of the incident pulse, which is due to the inversion throwing-off in the system created by the first pulse.

Theory of nonlinear waveguiding due to exciton–biexciton conversion in the nanosemiconductors

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Theory of nonlinear planar three–layer waveguide, consisting of a linear plate, imbedded into two nonlinear non–Kerr semiinfinite media. The dispersion and nonlinearity of which are due to the processes of exciton–photon interaction and optical exciton–biexciton conversion is presented. We assume that TE–polarized electromagnetic wave stationary propagates along the waveguide. The theoretical investigation was carried out semiclassically using the material equations for the amplitudes of exciton and biexciton waves and the system of Maxwell equations for the field. From the material equations we obtained the expression for the dielectric function of the crystal. We have found the exact analytical solutions of equations and obtained the expressions for the spatial profiles of the surface and guided modes and the transmitted power. It was shown, that for the same type of mode profile in the plate two types of profile exist in nonlinear medium, namely monotonous and nonmonotonous ones. These modes exist in different ranges of spectrum and transmit different powers. The monotonous modes have the linear solutions as their counterpart, while the nonmonotonous modes have no the linear counterparts at all. If the level of excitation increases, every mode changes its profile and dispersion law. This can lead mode to push out of the guide or to pull it in the guide. Effective refractive index of nonmonotonous profiles has the particular dependence on the power and it is excited at the powers, which exceed the critical one.

Two-beam self-reflection phenomenon in semiconductors

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New nonlinear-optical effect – the self-reflection phenomenon in the system of excitons and biexcitons in semiconductors was studied. We have established that the backward propagating wave appears in the optical homogeneous semiinfinite nonlinear medium on the field induced by the forward propagating wave the sharp gradients of the refractive index and extinction coefficient of medium. We assume that two electromagnetic waves with different frequencies and field amplitudes propagate in the medium. We have obtained the system of two nonlinear second order wave equations, which describe the steady-state propagation of the both waves. The numerical integration of these equations was carried out beyond the slowly varying envelopes approximation. We showed that the spatial field profiles along the direction of propagation of the every wave consists two domains: the exponentially decreasing tails inside the crystal, where the only forward propagating wave exist, and the nonlinear nonexponential parts including the crystal interface, in the range of which the forward and backward propagating waves exist. These results evidence that the optical homogeneous nonlinear medium converts into the medium with the spatial distributed feedback in the presence of the strong laser radiation, which is the set of the field induced Fabry-Perot quasicavities with different reflection coefficient. We showed that in the neighborhood of any point of the crystal the optical functions changed abruptly. We investigated the inherent spatially distributed refractive indices, extinction coefficients and interior reflectivity. The reflection coefficients of the front face of the crystal depending on the incident field amplitudes are characterized by the strong multistable behavior.

Synthesis and morphology of Carbon and Boron Nanostructures via Microwave Heating

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This work is devoted to microwave heating of sucrose, boron, and graphite for studying the processing of nanoparticles and carbon nanotubes (CNTs) by vaporization. We have applied heating by microwaves (MW) (power 800W, frequency 2.45 GHz) in air at 30-60 min. The condensed material was collected on a fused silica target. After deposition, the morphology of carbon nanotubes was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM). The samples were found to contain nanotubes, nanoparticles and fibers which appeared to be highly graphitized. A possible growth mechanism will be discussed.

X-ray investigations of nanostructured CP Ti processed by severe plastic deformation

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Different techniques of the X-ray analysis were applied to investigation of microstructure peculiarities of CP Ti, processed by severe plastic deformation, namely by high pressure torsion (ÈÈÈ). Dependences of crystallite sizes, elastic microdistortions of the crystal lattice, dislocation density on the applied pressure and on the deformation degree were analyzed. A formation of basic texture components during HPT process shear in the HCP lattice was investigated. Temperature dependences of the lattice parameters and the coefficient of linear expansion in an interval from 80 È to 295 È were studied. There were determined the characterizing Debye temperature, the Debye-Waller factor, values of static and dynamic atomic shifting in nanostructured ÈÈTi in frames of the Einstein-Debye quasiharmonical approaching. A formation of w-phase of high pressure was revealed. There were also determined conditions of phase alpha-omega transition with the impact of the applied pressures (~5-7 GPa). Structure characteristics of the mentioned phases and a subsequent thermal stability of the obtained high-pressure w-phase were studied.

Vanadium oxide nanofibers by electrospinning

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Nanostructural material which are considerable intermediates between classical molecular scale and microsized entities, constitute a rapidly growing field of scientific interest and industrial applications. Such materials are very interesting in many respects particularly for the production of highly functional finely dispersable and resource saving base materials for nanodevices because of the chemical reactivity and physical properties in the nano region are strongly dependent on the size of the structures. The shape of the nanoparticle plays a large role in determining the basic properties, for example, isotropic or anisotropic behavior and region dependent surface reactivity. In this work, vanadium oxide nanoparticles have been prepared by electrospinning, which is a technique used to prepare nanofibers with large surface area to volume ratio. Scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) methods are used to characterize the fibers. The results indicated that the vanadium oxide fibers are unstable at higher temperature.

Preparation and morphology of Niobium oxide fiber

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Mesoporous transition metal oxides are important due to its behavior as catalysts, electronic materials and battery electrodes. Particularly, niobium oxide finds a variety of applications in modern technology in different components ranging from capacitors, to wave guides, oxygen sensors and as corrosion resistant materials. Because of the relatively large number of applications and interesting properties, the niobium oxide has been prepared in the form of fiber by electrospinning process. The obtained fibers have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and infrared spectroscopy (IR) methods. The SEM photos showed the porous like surface of the fiber calcined at 700°. The XRD data confirmed the crystalline nature of the fiber. The IR spectra gave further evidence for the formation of the niobium oxide fiber.

Preparation and photoluminescence property of germanium dioxide nano fiber

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Germanium dioxide nano fibers have been prepared by electrospinning method using germanium oxide sol and poly(vinyl acetate). The poly(vinyl acetate) has been removed by heat treatment (calcinations). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images showed that the fiber nature is stable upto 700 °C and beyond this temperature, the fiber nature is changed. X-ray diffraction studies confirmed the crystallinity of the fiber. The photoluminescence spectra of the fiber indicated that the fibers may have potential applications in one-dimensional optoelectronic nanodevices.

Growth control of Ga and In nanodots via photochemical reactions for applications to group III nitrides-based nanophotonic devices

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We present the growth control of gallium (Ga) and indium (In) nanodots in the photochemical reactions of metallorganic reagents for applications to group III nitrides-based nanophotonic devices. Ga and In nanodots less than 30 nm in the typical size were fabricated on a substrate via the photodissociation of Ga(CH₃)₃ (trimethyl gallium) and In(CH₃)₃ (trimethyl indium) using 5th harmonic generation ($\lambda = 213$ nm) of a Nd:YAG pulse laser. In addition, we have controlled the arrangement of the nanodots, i.e., array and square loops, by selecting substrate material and varying growth conditions. In this paper, we will discuss the nanofabrication and characterization for the group III nitrides using the advanced nanotechnology including optical near fields technique.

Sintering of Iron Nanopowders

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Sintering behavior of iron nanopowders was studied. Iron nanopowders were produced by chemical vapor condensation process. The mean particle size of the powders was 20nm and the powders were thinly coated with iron oxide to prevent powder oxidation. Iron nanopowder was cold pressed and then sintered at temperature up to 1200°C in hydrogen atmosphere. Iron oxide on the powder surface can be removed by control the heating schedule during sintering. Sintered density was mainly depended on the green density, sintering temperature and oxide content in the powder. High sintered density can get at low sintering temperature. Microstructures of the sintered bodies were greatly influenced by the sintering conditions. Uniform and fine-grained structure can get at low sintering temperature.

InO_x Nanostructured Thin Films

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The structural, electrical and sensitivity response characteristics of indium oxide, prepared by dc sputtering, are reviewed in this work. The electrical conductivity (σ) of these films is compared to those obtained from other deposition techniques, and found to depend upon the synthesis technique and the deposition parameters. The structural characteristics are directly related to the substrate and growth parameters. Our sputtered-InO_x films exhibit conductivity changes of about seven orders of magnitudes during the processes of photoreduction and oxidation. A conductivity value of $1.5 \times 10^2 \text{ } \Omega^{-1}\text{cm}^{-1}$ has been found at room temperature, which provides the possibility to use this material as interconnect in IC's and as a sensor at ambient conditions without additional heating. Furthermore, the sensing properties towards ozone, NO and CO₂ of these films are presented. Optimum operating temperatures have been found where the response to ozone of InO_x is greater and stable. The optimum sensitivity of our films is demonstrated in the low temperature range of 200 C° to RT, and is of the order of a few ppb. These characteristics promote indium oxide as a candidate material in gas sensor devices for toxic gases operating with low power requirements.

FUNCTIONAL POLYMER v CARBON NANOCOMPOSITES FOR MECHANICAL STRAIN SENSING

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Electrically conductive polymer composite (ECPC) are obtained when particles of good conductors (carbon black, graphite powder, carbon fibre, micro-particles of metals) are implanted into an insulating polymer matrix. Most often ECPC are used as the so-called thermodynamic inactive materials in electric heating elements and resistors. Recently efforts have been made [1-3] to obtain active ECPC the conductivity of which would be strongly dependent on external thermodynamic parameters v pressure, temperature, and other. Such materials might set up basis for a new generation of cheap large-size sensors. Irreversible dependence of electrical resistance on deformation at stretch or pressure has been found in case of microsize particles [1]. New interesting properties are expected in case the composite contains dispersed nano-size conducting particles [2-3]. In our earlier studies composites containing conductive carbon black nano-particles in a polyisoprene matrix [3] reversible change of electric conductivity by many orders has been revealed at stretch deformation. In other words, a giant and reversible tenso-resistance effect is observed in the electrically conductive polymer nanocomposite (ECPNC). The main task of the present study has been to investigate the electrical resistivity of ECPNC vs tensile strain and pressure near the percolation threshold to obtain the best composition for sensor applications. A conductive-tip atomic force microscope was used for mapping of carbon black conductive network into an insulating matrix to elaborate a nanostructure model of the extremely strong reversible tenso-resistance effect. REFERENCES[1]. J.N. Aneli, G.E. Zaikov, I.M. Khananashvili. Effect of mechanical deformations on the structurization and electric conductivity of electric conducting polymer composites. Journal Applied Polymer Science, 74 (1999) 601- 621.[2]. L.Flandin, A.Chang, S.Nazarenko, A.Hiltner, E.Baer. Effect of strain on the properties of an ethilene-octene elastomer with conductive carbon fillers . Journal of Applied Polymer Science, 76 (2000) 894-905. [3]. M.Knite, V.Teteris, B.Polyakov, D.Erts. Electric and elastic properties of conductive polymeric nanocomposites on macro- and nanoscales, Materials Science & Engineering C, 19 (2002) 15-19.

Growth front roughening and structure of deposited nanocluster films

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The growth of thin films by direct deposition of nanoclusters has attracted considerable interest, both from a fundamental and a technological point of view. The advantage of the method is that well-adhered metallic films can be produced on a wide variety of substrates. To the best of our knowledge, so far none of the previous studies have considered scaling aspects of the surface morphology explicitly. This is the topic of this contribution, in which the surface morphology of metallic nanocluster films has been explored as a function of deposition time and film thickness. Analyses of the height-difference correlation function with atomic force microscopy and X-ray reflectivity measurements yield for Cu nanoclusters a roughness exponents H of 0.45 ± 0.05 . The rms roughness amplitude w evolves with deposition time as a power law, $w \propto t^{\beta}$ ($\beta = 0.62 \pm 0.07$), leading also to a power law increase of the local surface slope ρ . These scaling exponents, in combination with an asymmetrical height distribution, points at a complex non-linear roughening mechanism. The film growth mode has similarities with the Kardar-Parisi-Zhang scenario. Further, transmission electron microscopy was employed for investigating the structural stability of nano-sized iron clusters as deposited and after in-situ annealing treatments under high vacuum conditions. The thin iron oxide shell that is formed around the iron clusters (upon air exposure) is of the order of 2 nm surrounding a 5 nm core of bcc iron. The oxide shell breaks down upon annealing at relatively low temperatures ($\sim 500^{\circ}\text{C}$).

The Verwey transition in magnetite nanoparticles stabilized in polymer thin films

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Magnetic nanoparticles dispersed in polymer matrices are very interesting and technology important objects of studying. The magnetite are known as magnetic material since antiquity, but even at present its properties are intriguing. For example, the nature of the Verwey transition has not been yet fully understood. In the bulk magnetite this transition takes place near 120 K and results in sharp anomalies of the electrical conductivity, the magnetization, the thermal expansion and other characteristics. The study of nanoparticles allows to find an effect of a sample size on material's properties. To our best knowledge, just a few systematic investigations of the Verwey transition in nanosystems were still performed. It is interesting also how small should be nanoparticles to demonstrate the Verwey anomalies. We have investigated the structure and magnetic properties of magnetite nanoparticles stabilized in polyvinyl-alcohol thin films. The nanoparticle synthesis method is based on in situ reactions taking place in the volume of the polymer matrices which undergo swelling in water. The films have a thickness of about 100 nm and contain magnetite nanoparticles of concentration from 0.6% (vol.) up to 5.7% (vol.). The transmission electron microscopy (TEM), the x-ray diffraction (XRD) were used for characterization of the nanostructures. The magnetite nanoparticles were characterized by the distinct bimodal size distribution and well-defined crystallinity. The TEM pictures show that the nanoparticles are distinctly divided in two groups: rather small (below 10 nm) and relatively large (about 70-80 nm). XRD peaks correspond to the structure of the bulk magnetite. The diffraction peaks are visibly broadening due to the smallness of the crystallites. The average size of crystallites, according to the XRD data, is equal to 5-7 nm. That is, in our samples the small (less than 10 nm) particles dominated. No traces of other oxide iron phases have been observed by XRD in the samples. The EPR spectra for all samples studied are typical for iron-based nanoparticles. The EPR singlet is like to be a superposition of two lines with significantly different linewidths. The temperature dependencies of the EPR resonance field and the peak-to-peak linewidth demonstrate in coordination the unusual behaviour below approximately 150 K. Starting from this temperature, the resonance field markedly decreases and the linewidth significantly increases. The shift of the resonance field points to growing of the film magnetization (or changing of magnetocrystalline anisotropy). The sharp broadening of the EPR signal is typical of the EPR behavior near the phase transition point. It is interesting that for the thin films of bulk magnetite the significant increasing of the magnetic resonance linewidth was observed at about 90 K. As for the magnetization, its behaviour in thin films and in nanoparticles near the Verwey point can be different depending on various factors, especially, on stoichiometry. Since the characteristic temperature of anomalies does not change with increasing particle concentration it is unlikely probably that we have to do with some collective effect. The increasing of the Verwey temperature in nanoparticles in comparison with the bulk material is very interesting result, since usually a phase transition temperature in nanoparticle system is lower than in the bulk counterpart. Probably, some ionic or electron structure reordering, which results in the Verwey transition, can occur at higher temperatures if the magnetite particle is sufficiently small.

Comparison of Fe/Al₂O₃ and Fe,Co/Al₂O₃ catalysts used for production of carbon nanotubes from acetylene by CCVD

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Among other methods, catalytic chemical vapor deposition (CCVD) has been proven a simple and productive technique for producing both single and multi wall carbon nanotubes. In most cases acetylene is used to produce multi-wall nanotubes (MWNT) in CCVD procedures. It has been demonstrated that supported transition metals (in particular iron, cobalt and nickel) are excellent catalysts in this process. Impregnated silica, alumina or zeolite- and clay-derived supports are used frequently. Iron-base catalysts usually produce carbonaceous tubes with high efficiency. However, as high resolution electron microscopy studies reveal, the MWNTs may be covered with amorphous carbon in significant extents, i.e. the product is not always pure MWNT. To improve the catalyst performances, supported bimetallic systems composed from Fe, Co and Ni (2.5 wt % each) were also prepared and evaluated. Fe-Co systems were found to produce MWNTs with superior quality and yields on various supports (alumina, 13X and ZSM-5 zeolites), or on mixtures of them (silica-aluminas). For interpreting the advantageous effect of alloying with Co, Fe-Co alloy formation is suggested. To obtain more direct confirmation on the alloy formation, application of Mössbauer spectroscopy seems also promising. In the present study a report is given on the characterization of the alumina supported fresh and spent Fe, and Fe,Co catalysts. Samples were analyzed by Mössbauer- and infrared (IR) spectroscopies and X-ray diffraction (XRD). The formed carbonaceous products were characterized by TEM and TG techniques, as well.

Mobility in Organic Semiconductor Thin Films

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Abstract: A number of papers have appeared recently reporting the evaluation of carrier transport parameters in organic semiconductors with the objective of improving the understanding of the luminescent and current conduction properties. Of the different transport parameters evaluated, carrier mobility stands out to be particularly intriguing in view of its "unusual" dependence on electric field and temperature. The most common reason put forward to explain such dependence is the inherent disorder found in these solids, and in many instances, the fact that carrier transport in organic semiconductors frequently involves trap states. Methods such as time of flight measurement and impedance spectroscopy have been used to minimize effects such as dispersion, and most results pointed to a conduction mechanism linked to space charge limited current at low bias. At moderate field strength, trap-related carrier transport had been proposed and this was correlated to the exponential square-root (electric) field dependence. Models have also been put forward to compute parameters such as: the density of states function in the presence of traps. Such computations however were rather cumbersome and it was difficult to extract accurately unknown physical parameters appearing in the model equations]. This work re-examined mobility data recently reported in [1,2] and analyzed them based on two known physical models: one related to barrier height modulation and the other to trapping. Interesting enough, the mathematical expressions resulting from applying these models appeared to be similar in form. To a good extent, one could even correlate the physics. In addition, an analysis was made on the projection of the carrier mobility limit for these materials at very low field and suggestions were made as to how improvements could be achieved beyond the currently observed values.¹ B.J. Chen, W.Y. Lai, Z.Q. Gao, C.S. Lee, S.T. Lee and W.A. Gambling, *Appl. Phys. Lett.*, 75, 4010 (1999)² 9. H.C.F. Martens, H.B. Blom, J.N. Huiberts, and H.F.M. Schoo, *Phys. Rev. B*, 61, 7489 (2000).

In-situ synthesis of porous Al₂O₃-ZrO₂ composite by sol-gel process

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Al₂O₃-ZrO₂ composite has been widely used wear parts and tool materials because of having high mechanical properties and high fracture toughness. The composites also have a great potential in the application of environmental materials because of their intrinsic properties such as high chemical resistance and high oxidation resistance. For the application of environmental ceramic filters, the improvement of fracture strength is an important factor as well as the control of microstructure such as porosity, pore size and morphology. Therefore, in order to improve the fracture strength of porous Al₂O₃-ZrO₂ sintered bodies. We successfully made the porous body having nano-framed structure by sol-gel process. In this work, we will report on the characterization of microstructure, crystal structure and morphology of in-situ synthesized Al₂O₃-ZrO₂ powders as well as those of sintered porous bodies using by TG, DTA, XRD, FE-SEM and TEM techniques.

TEM Microstructure of nano sized iron nitrides fabricated by CVC

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Iron nitride offers a number of useful properties including corrosion resistance, magnetism and working ability etc. Many researches have focused on further improvement of its properties, and nano-technology becomes a promising route. There is a growing interest in using chemical vapor condensation (CVC) for the fabrication of nano-particles, although some conventional processes such as arc discharge, mechanical alloying and inert gas condensation have been frequently used. The CVC has advantages in high productivity and availability of precursor in wide range over the conventional methods.

In the present work, iron nitride powders existed with nano size were fabricated by CVC process and their microstructure and crystal structure were investigated by Fe-SRM, XRD and HRTEM techniques which depend on the function of decomposition temperature and flow rate of carrier gas.

Fabrication of fibrous monolithic Al₂O₃/ZrO₂ nano-composites

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ZrO₂ toughened Al₂O₃ composites, which are considered to be subject to a phase transformation toughening mechanism, were wide candidate materials for bio-ceramic as well as wear parts and cutting tool materials because of their improved mechanical properties. Especially, there have been a lot of research works to improve the fracture toughness, but still under the development. To prevent the intrinsically catastrophic failure of ceramics, the fibrous monolithic (FM) process is newly introduced to realize the fibrous microstructure control of ceramic materials. This is one of multi-pass extrusion technique using the mixtures of nano-ceramic powders and polymers. Using this technique, we can successfully obtained the sound fibrous monolithic Al₂O₃/ZrO₂ nano-composites. In the presentation, we will report the relationship between microstructures and mechanical properties of fibrous monolithic Al₂O₃/ZrO₂ nano-composites.

Nanobionics and the constructor for nanobionics systems

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Nanobionics is the science about construction of artificial nanomachines. Because the carbon is main material for producing nanomachines, nanobionics is science about carbon structures and compounds. The program "NanoBionic Constructor" has been elaborated for the of atoms' coordinates generation in the carbon nanoclusters of different types: diamond, graphite, tubulene (carbon-nanotube), fullerene, diamond-en, diamond-in and diamond-ar. Diamond-en, diamond-in and diamond-ar are new forms of carbon clusters that we suggested in the work [S. V. Kozyrev, et al., Ph. of Sol.St. V. 43, No 5, 2001, pp. 963-966]. "NanoBionic Constructor" can design nanoclusters of above types into electronic and mechanical devices.

CONDENSATIONAL GROWTH OF NANOPARTICLES AND IMPURITY MOLECULE TRAPPING

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The problem of the impurity molecule trapping in the condensational growth of nanoparticles is studied theoretically. The equation for the trapping coefficient of impurity molecules (including non-condensable components) taking into account the particle size and the parameters characterizing the interaction of gas molecules with the particle surface has been obtained. It is shown that the trapping coefficient as a function of the particle size can have a maximum. The possibility to control the nanoparticle composition by the resonance (e.g., laser) radiation due to the excitation of impurity molecules is discussed. The effect of the resonance radiation on the growth rate and the critical (equilibrium) radius of the nanoparticle is considered. It is shown in particular that in the case, when the excitation of vapor molecules leads to the decrease of the condensation coefficient, the critical radius of the particle increases. This work was supported by GA AS CR, project number IAA4072205.

Structure control and its influence on photoactivity and phase transformation of TiO₂ nano-particle

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Nanocrystalline titania (TiO₂) has received great attention in recent years due to its unique dielectric, optical, catalytic properties and potential applications in many fields. Properties influencing the photocatalytic activity of TiO₂ particles have been suggested to include the surface area, crystallinity, crystallite size and crystal structure. In our study, it has been demonstrated that the properties of titania are strongly dependent on its thermal history and processing parameters. This paper shows our results on the structure manipulation and hence the phase transformation and photoactivity of nanocrystalline TiO₂ powders which were synthesized by a sol-gel method. HRTEM, XRD retrieved refinement, FTIR, and UV-Vis spectrometer were used to carefully characterize the structure, crystallite size, chemical composition and photoactivity of TiO₂ powder. Quantum size effect was observed in the control-sized nanocrystalline TiO₂ particles.

LiMn_{2-y}Cr_yO₄ nanopowders synthesized by the microwave-induced combustion method and their electrochemical properties

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Spinel LiMn_{2-y}Cr_yO₄ nanopowder was successfully prepared by the microwave-induced combustion method from lithium nitrate, manganese nitrate, chromium nitrate, and urea. Firstly, the microwave-heated LiMn_{2-y}Cr_yO₄ nanopowder was studied by TG/DTA, XRD, and SEM. Secondly, the microwave-heated LiMn_{2-y}Cr_yO₄ powder was thermal treatment from 600°C to 800°C for 8-hrs. Finally, The charge and discharge characteristics of LiMn_{2-y}Cr_yO₄ cathode were examined in laboratory cells. The cells were composed of a LiMn_{2-y}Cr_yO₄ cathode and a lithium metal anode separated by a polypropylene separator and a glass mat. The electrolyte solution was 1M LiPF₆/ethylene carbonate(EC) and dimethylcarbonate(DMC). The cells were typically cycled in the voltage range of 3.0-4.3 V at a constant current density of 55mA/cm²(40mA/g). The result shown that the both capacity and cycle life of the cell in which LiMn_{2-y}Cr_yO₄ prepared by the combustion method are better than those by the traditional solid-state sintering method.

Examined the Gas Absorption Properties of Single Wall Carbon Nanotube Bundles by X-ray Absorption Techniques

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Carbon nanotubes (CNTs) have a large specific surface area and a nano-scale structure that provides plenty sites at which gases can react. They therefore exhibit very good adsorption properties that lead to many applications. For example, a CNT gas sensor can work by altering the electric properties of the CNTs by adsorbing the gaseous molecule on the surface of the CNTs. The use of CNTs to store hydrogen, given their capacity for adsorption, has also been widely investigated. Utilization of these properties has led to applications of ensembles of nanotubes as gas sensor, scanning probes, and nanoelectronic devices. X-ray Absorption Near-Edge Structure (XANES) usually extends to energy of the order of 50 eV above the edge that includes the unoccupied part of band structure just above the Fermi level. Thus, certain aspects of the electronic structure of detected element can be revealed. By inverting these data, the location of the first few atoms surrounding the absorbing atom can be obtained. In this study, CO and NO₂ gases absorbed on the single wall carbon nanotubes (SWCNT) are examined by XANES techniques with Synchrotron Radiation sources in Taiwan. The C and O K-edges of x-ray absorption have been used to examine the absorption properties of CO and NO₂ gases. Gas molecules adsorb weakly on SWCNTs and change donors or acceptors to the nanotubes. Charge transfer and gas-induced charge fluctuation might significantly offer the transport properties of SWCNTs. The results indicate the absorption of O K-edge have the obviously shift at around 520eV for CO and NO₂ absorption (40ppm) comparing to that of vacuum condition. The vacant orbital and electronics configuration of the CO and NO₂ absorption is derived from XANES spectrum and will provide the information to study the gas sensing properties of SWCNTs.

The Small-Angle X-ray Scattering Studies on the Synthesis of Silver Nanoparticles

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Small-angle X-ray scattering (SAXS) was employed to investigate the size and shape of the silver nanoparticles synthesized by wet chemical reduction method. The silver nanoparticles were synthesized by mixing 10 ml 0.5 mM AgNO₃, 10 ml 0.5 mM trisodium citrate, and 0.6 ml 10 mM NaBH₄ at room temperature. Right after mixing, the solution turned gold color indicating that silver nanoparticles were formed. The SAXS data from the solution containing the synthesized silver nanoparticles can be well fitted with monodisperse rodlike particle model. The analysis shows that these as-produced silver nanoparticles have a rodlike shape with 4 nm in radius and 20 nm in length. It was discovered accidentally that the produced silver nanoparticles change color from gold to red-brown by laser irradiation during dynamic light scattering measurement (with Argon laser, wavelength 488 nm). By SAXS analysis, it was found that the silver nanoparticles change from smaller rodlike structure to a larger structure with 5.8 nm radius and 25 nm length after 3 hour laser irradiation. Our study showed that smaller silver nanorods could be transformed into slightly larger nanorods by laser irradiation, accompanied by a color change. Further studies will be conducted to elucidate the mechanism of such transformations. This research is supported by the Ministry of Education, ROC, through the Program for Promoting University Academic Excellence, grant no. 91-I0037-J4.

Surface and bulk effects of non-depositing energetic species during growth of Boron Nitride and Carbon films

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Boron Nitride (BN) and amorphous Carbon (a-C) are two of the most widely studied diamond related materials the last few years. The films development and their exceptional properties have met not only growing scientific and research interest, but also technological and commercial interest for various applications (for example, in computer hard disks, lenses, mechanical and surgical tools, protective coatings on optical devices against wear and on solar cells for space, as a lubrical and a material with adjustable mechanical strength).

It is generally accepted that similar growth mechanisms exist for sp^3 -bonded a-C (diamond-like) and cubic BN (c-BN) films. In addition, research on BN and a-C growth has been focused mostly on bulk processes, like the subplantation and densification (SD) mechanisms, which are due to the depositing energetic species (such as inert gas ions: B^+ , N^+ , C^+). However, in sputter deposited c-BN and sp^3 -bonded a-C films the incorporation of non-depositing energetic species enhances the surface effects during growth, on which have not given much attention so far.

In this work, we review the field and carry out an experimental and computational study of the effect of Ar^+ irradiation during the growth of c-BN and a-C by sputter deposition. We have found that the sputter deposition of BN and a-C does not follow exactly the same overall trends that are described in the literature.

Thus, for BN it was found that the dominant effects for the c-BN growth are the subplantation of N^+ and B^+ species, which follow very well the SD model for ion energies below the threshold of Ar^+ subplantation into BN. However, combined Spectroscopic Ellipsometry (SE) / X-Ray Reflectivity and X-Ray Photoelectron Spectroscopy (XPS) analysis does not confirm the existence of an sp^2 -bonded (h-BN) overlayer on the film surface, as it is expected in the SD mechanism. The absence of such sp^2 -bonded overlayer is attributed to the surface etching by non-penetrating, heavy Ar^+ ions. The film stress follows the prediction of the SD model for films with stress higher than a stress threshold of 5 GPa. Thus, we attribute the c-BN growth to a combined SD/stress mechanism. For energies higher than the threshold for Ar^+ subplantation, the Ar^+ penetrate into BN and disrupts the B-N bonds resulting to defective BN structures, stress relief and enhancement of h-BN. Finally, there is a very narrow window of ion energy (<40 eV) for the successful growth of c-BN films.

In a-C films sp^3 -bonded C is formed in a wider window of Ar^+ ion energy (80-100 eV) due to the combination of the SD mechanism and surface activated sp^3 formation. XPS valence band spectra provided the electron density of states in the a-C films' valence band. The characteristic broad p band of diamond was prominent in most of the films. The valence band structure of the films was correlated with their optical response measured by SE. In a-C growth by sputter deposition we observed the formation of an sp^3 -bonded surface and a close correlation of the Ar impurities with the sp^3 -content in a-C. It was found a considerable increase of sp^3 content in films deposited with high-energy ion irradiation, which suggests that Ar impurities promote the transformation of sp^2 bonds to sp^3 , in contrast with the BN growth, where the penetrating Ar disrupts the c-BN.

Electrical Properties and Device Applications of Ag(TCNQ) Nanowires

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We will present our recent research results on the electrical property characterization of Ag(TCNQ) nanowires and their application for ultra high density data storage. Ag(TCNQ) is an organometallic material. It is synthesized using the vacuum saturated vapor reactive method. The nanowires form a highly ordered array of uniform spacing and diameter. We have studied their electrical bistability property (high resistance and low resistance, respectively) and one dimensional conductive characteristics using both scanning tunneling spectroscopy and electrical transport measurements. Electronic devices has been made with a single molecule of Ag(TCNQ). And we will demonstrate their nanometer-scale electrical storage properties such as writing, reading and erasing functions.

Nanostructured High Strength Mg-5%Al-x%Nd Alloys Prepared by Mechanical Alloying

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Nanostructured Mg-5%Al-x%Nd ($x = 0.5, 1$ and 5 wt.%) alloys were prepared by mechanical alloying. Microstructural characterisation revealed average crystalline size to be about 30 nm after mechanical alloying while it increased to about 90 nm after sintering and extrusion. Mechanical properties showed increases in 0.2% yield stress, ultimate tensile strength and ductility after 20 h of mechanical alloying. The increase in yield stress and ultimate tensile strength was attributed to reduction in grain size as well as to the enhanced diffusion after mechanical activation. Although ultra high yield stress was observed from the specimen with 5%Nd, its ductility was reduced to about 1.6%.

Plasmachemical fluorination of single walled carbon nanotubes

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The commercially available single walled carbon nanotubes (SWNTs) from CNI, USA synthesized by the HiPCO-method have been fluorinated by exposing them to CF₄ and SF₆ plasma atmospheres under r.f. conditions. Prior to functionalization the SWNTs were purified to remove amorphous carbon and the metallic catalyst by oxidation in air and washings in mineral acid. The success of the purification procedure was proved by TGA and TEM. The fluor content was varied by the plasma parameters and the treatment time. Element contents were determined by XPS. Furthermore the preservation of the fine structure after the functionalization was documented by TEM. The plasmachemical treatment has shown to be a mild and good controllable method for the fluorination of SWNTs and offers an alternative approach to the reaction with elemental fluorine.

Thermal plasma CVD of carbon nitride films on steel

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Carbon nitride films have been synthesized by an inductively coupled thermal RF plasma (ICP) on steel substrates placed on a water-cooled substrate holder. Deposition was carried out at nominal frequency of 4 MHz, plate power in the range of 2 kW to 20 kW, and pressure between 0.004 and 0.1 MPa. ICP was of standard design. The carbon source was a graphite rod (diameter 5 mm) which was installed in the axis of the plasma; Ar and N₂ were used as plasma gas. The carbon nitride films were analyzed by EDX, XPS, XRD, FTIR, Raman spectroscopy, and SEM. The synthesized films are found to be amorphous or sometimes crystalline with a cubic structure. The N/C atomic ratio of the as-produced films was measured to be in the range of 0.3 to 0.8. The different types of C-N bonds were detected including sp³ bonded carbon phase.

Effects of heat treatment on the structure of thermal plasma synthesized SiCN composite nanopowders

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SiCN composite nanopowders were synthesized by the RF induction plasma at atmospheric pressure. The chemical composition as well as the morphology of the SiCN composite powders can be controlled by the precursor and plasma processing. Mean particle size of the powders is in the order of 10 to 60 nm with a narrow distribution. Frequently the as-produced powders exhibit a high degree of chemical disorder or structural defects. Because the composition and the structure of starting powders have a great influence on the properties of composite ceramics, the change of chemical composition, crystallization, and morphology of the as-produced powders during heat treatment (600 to 1500 °C) were investigated. The recovery behaviour of the disorder of the solid under the recrystallization temperatures permits to draw conclusions from the structural defects and the thermal stability of the as-produced powders.

Synthesis of tailored SiC and SiCN nanopowders by a thermal RF induction plasma

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SiC and SiCN nanopowders were synthesized from commercially available precursors by a thermal RF induction plasma at atmospheric pressure. The frequency of the used power supply was 4 MHz and its maximum plate power was 5 kW. The maximum powder yield was about 200 g/h. The quenching is an important process-step in the plasmachemical synthesis for producing tailored powders that are needed for the development of advanced materials. Therefore the influence of the quenching rates on the physical and chemical powder properties were investigated. The nanopowders were analyzed by EDX, XPS, XRD, FTIR, BET, and TEM. The dependence of the particle properties such as particle size, morphology, crystallinity, and chemical and phase composition on the quenching conditions are discussed in detail.

Molecular Mobility and Gas Transport Properties of Polycarbonate-Based Nanocomposites

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Plasma synthesized SiC nanopowders are dispersed in dichloromethane/bisphenol A polycarbonate (PC) solution by high power ultrasonification. The nanoparticle dispersion is stabilized during film casting under well adapted preparation conditions. The influence of the SiC nanoparticles on the molecular mobility of the PC are studied by dielectric relaxation spectroscopy using films of about 50 μ m thickness. No influence on the cooperative segmental mobility (glass transition) is detected. The relaxation region corresponding to local movements of molecular groups are strongly broadened and the activation energy is reduced with increasing nanoparticle concentration. The most significant change is observed in the so called α' - and α'' -relaxation region due to the extremely large surface to volume ratio of the nanoparticles. Gas transport properties of these nanocomposite films are characterized in terms of permeability, diffusivity and solubility as well as corresponding activation energies. Concentration dependent CO₂ permeation experiments reveal in comparison to pure PC films a significant reduction of plasticization effects.

Absorption Band Control Induced by *Pi*-conjugated Nano-Columnar of Aromatic Polyacetylenes Prepared with a Rh Complex Catalyst

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We have reported that highly stereoregular polymerization of para alkoxy phenylacetylenes is induced by a Rh complex catalyst: [Rh(norbornadiene)Cl]₂ when EtOH or triethylamine was used as the polymerization solvent to selectively produce cis-transoid polymers in high yields. These polymers were found to produce pseudo-hexagonal structure called a columnar. The columnar is considered as self-assembly in which helical main chain polymers were packed tightly to create nanometer holes. In this report we show a novel poly(p-alkoxyphenylacetylene)s having a normal or branched alkyl chain which were prepared by the Rh complex catalyst together with influences of the alkoxy chains with respect to not only the diameter and the columnar content but also the color of the resulting polymers.

Robust nano cluster layers for structural amplified fluorescence biochips

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In previous studies we demonstrated that structural enhanced fluorescence (SEF) enables us to amplify fluorescent signals 200 fold in comparison to standard glass chips. SEF is based on a locally enhanced field, created by a nanocluster layer driven by a laser beam and tuned by a waveguide interlayer to a specific wavelength. The novel signal-boosting phenomenon is ideally suited for application in ultrasensitive biochips. DNA biochips based on hybridisation analysis need to cope with chemical and thermal stress significantly more severe than protein recognition assays. Therefore a stable multilayer set up was introduced and a chemically active surface layer was applied. The nanometric multilayer is based on a palladium layer introducing chemical stability as well as the necessary chemical compatibility for the SEF technique. The nano-granular structure of a silver nano-cluster layer enables the excitation of surface waves, localised - as well as surface-plasmons within the metal cluster films driven by laser excitation. Sandwich layers of metallic glass deposited on the Ag-cluster film function as a waveguide and establish the proper distance to the fluorophores, thereby enabling energy transfer by adjusting the local phase. A covalently reactive coating allows simple and straightforward one-step immobilisation and prevents the leakage of DNA even under stringent conditions. Divinylsulfone and epoxy-silane based chemistry enables covalent coupling of DNA, RNA and even proteins. The chips are compatible with standard procedures of DNA-biochips and withstand several hybridisation cycles at high temperature and even stripping in boiling water.

Properties and Applications for Electrodeposited Nanocrystalline Fe-Ni Alloys

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Iron-Nickel alloys are of great commercial interest as a result of their soft magnetic and thermal expansion properties. A proprietary, high efficiency electrodeposition process has been developed to produce the full range of Fe-Ni alloys (Ni: 0-100%) as fully dense freestanding nanocrystalline material, with average grain sizes in the range of 10-15nm. The Fe-Ni alloys can be produced in the form of either net shape components or continuous foil (5-250 μ m thickness). In this presentation, the physical properties of the nanocrystalline Fe-Ni alloys will be presented and compared with their conventional counterparts to demonstrate performance improvement obtained through extreme grain refinement. Properties that will be addressed include: hardness, ductility, thermal expansion, ferromagnetism (maximum induction, permeability, coercivity), electrical resistivity and thermal stability. Potential industrial/commercial applications for these nanocrystalline Fe-Ni alloys will be discussed, with particular emphasis on emerging applications in the electronics industry and in magnetic shielding and power generation/transmission.

Surface Properties of Nanocrystalline Alloys Characterised by Mössbauer Spectrometry

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Nanocrystalline alloys prepared by controlled annealing of amorphous precursors feature interesting magnetic properties which envisage promising technological applications. Mössbauer spectrometry enables to reveal correlation between the microstructure and macroscopic behaviour by providing simultaneous information on both structural characteristics and magnetic interactions. In addition, comparison of surface and bulk properties is also possible. Microstructure and magnetic arrangement is reviewed for the surface regions down to the depth of about 100 nm and for the bulk of the investigated specimens adopting conversion electron Mössbauer spectroscopy (CEMS) and transmission Mössbauer spectroscopy (TMS), respectively. NANOPERM-type nanocrystalline alloys are of special interest. They are inspected under different experimental conditions (temperature, amount of nanocrystalline grains) for as-prepared samples as well as for samples with their surface being modified by laser irradiation and ion bombardment. This work is supported by the grants 1/8305/01 and DAAD 17/2002.

Crystalline fullerene thin films prepared at room temperature by Synchrotron radiation ablation

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Crystalline Fullerene Thin Films Prepared at Room Temperature by Synchrotron Radiation Ablation

H. Miki, H. Nakanishi and S. Imai Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan M. Sasaki The Industrial Research Center of Shiga Prefecture, Ritto, Shiga 520-3004, Japan Fullerenes have become one of the most interesting materials for use in advanced nanodevices. Synchrotron radiation ablation (SRA) reactions enable the preparation of fullerene thin films at room temperature. Deposition of fullerene thin films was carried out on a Si substrate at room temperature using the powder-state fullerene targets installed in the compact synchrotron light source of Ritsumeikan University. The powder fullerene raw material was prepared by the arc discharge method. The deposited films were characterized by X-ray diffraction, Raman spectroscopy, and Fourier-transform infrared spectroscopy. The composition of deposited fullerene film is the same as that of the fullerene target. The film deposited by SRA showed better crystalline quality than that of a film deposited by vacuum evaporation. The annealing effects on the fullerene film by SRA were investigated. Significant degradation of fullerene films began at 300 degrees centigrade in air. Keywords: Fullerenes, Synchrotron radiation ablation, Thin films

GRAIN BOUNDARY DIFFUSION IN METALS

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This paper presents an overview of grain boundary diffusion in metals and its possible role in deformation processes in nano-grained materials. Experimental results published over the recent years are briefly reviewed, including the effects of segregation, pressure, and grain misorientation on grain boundary diffusion. Recent progress in the atomistic modeling of diffusion mechanisms in grain boundaries is discussed. The atomic mechanisms of point defect formation and migration in grain boundaries are remarkably different from those in the regular lattice. Such mechanisms can include collective atomic jumps involving several atoms, ring process, and similar phenomena. The results of atomistic modeling can explain many features of grain boundary diffusion observed experimentally. The rates of grain boundary diffusion at low temperatures are evaluated and compared with characteristic rates of other processes in nanostructured materials. The role of non-equilibrium grain boundary structure on diffusion coefficients is also analyzed.

INORGANIC v ORGANIC CRYSTALS GROWN BY SELF-ARRANGMENT OF FULLERENES

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The chemical transport reaction is a standard method for growing plate-like crystals of transition metal dichalcogenides and also enable to grow multiwall MoS₂ and WS₂ nanotubes [1,2]. Recently was discovered a new catalyzed transport reaction involving fullerene C₆₀ which has been shown to produce macroscopic quantities of subnanometer MoS₂ nanotubes [3]. The composite materials of transition metal dichalcogenides and fullerenes are potentially useful for solar cells, provided fullerene as electron acceptor molecules, could be intercalated into the layered structure to act as acceptors [5,6] and facilitate more efficient separation of electrons and holes in a solar cell. So far what has been achieved is only fullerene evaporation onto the surface of MoS₂ crystals [7]. We report on the first evidence of C₆₀-MoS₂ and C₇₀-MoS₂ composite layered crystals synthesized by chemical transport reaction. Strong undulations of the crystals are typical for the composite material and the formation of the highly dissociated dislocation loops evidence a lattice strain incorporated in the thin crystal flakes. Based on electron diffraction, mass spectroscopy and x-ray data, we propose a model structure consisting of hexagonal stacked MoS₂ molecular layers alternating with the C₆₀ or C₇₀ monolayers.. The structure of the transported material was studied using 300 keV Philips CM300 Jeol JEM v 2010F and Philips XL 30 FEG electron microscopes. The new composite materials are attractive for a doping of two-dimensionally ordered fullerenes with alkali metals and organic electron donors to create the charge transfer complexes with potentially interesting physical properties. The new synthetic route open also possibility for preparation a new composite layered crystals from others dichalcogenide transition metals. These new compounds are potentially useful for solar cells, provided fullerene intercalated into the structure to act as acceptors and facilitate more efficient separation of electrons and holes in a solar cell.[1] M. Remskar, Z. Skraba, F. Cleton, R. Sajines, F. Levy, *Appl. phys. lett.*, 69, (1996) 351 [2] M. Remskar, Z. Skraba, M. Regula, C. Ballif, R. Sanjines, F. Levy, *Adv. mater.* 10, (1998) 246[3] M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Èeh, J. Demsar P. Sadelmann, F. Levy, D. Mihailovic, *Science*, 292, (2001) 479[4] V.I. Zubov, N.P. Tretiakov, J. F. Sanchez-Ortiz, J.N.T. Rabelo, J.B.M Barrio, *Mol.Cryst.and Liq.Cryst.* 10, (1998) 51[5] Q. Xie, E. Peres-Cordero, L. Echegoyen, *J. Am. Chem. Soc.*, 114, (1992) 3978[6] D. Dubois, K.M. Kadish, S. Flangan, R. E. Haufler, L. P. Chibante, L. J. Wilson, *J. Am. Chem. Soc.*, 113, (1991) 4364[7] M. Sakurai, H. Tada, K. Saiki, A. Koma, H. Unasaka, Y. Kishimoto, *Chem. Phys. Lett.*, 208, (1993) 425

Single-wall carbon nanohorn assembly as a potential applicant for hydrogen and methane storage

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Single-wall carbon nanotubes (SWNTs) are expected for having potential for clean energy gas storage, especially methane and hydrogen. The mechanism of hydrogen and methane storage on SWNT is not well understood, although many researchers have studied the storage of these gases using SWNTs. We examined both experimentally and theoretically the adsorption mechanism of methane and hydrogen on single-wall carbon nanohorn (SWNH) assemblies, a highly pure and SWNT-related material. The heat of adsorption of hydrogen on internal SWNH nanospaces was estimated to be 5-6 kJ/mol that is about 4 kJ/mol larger than the enthalpy change of vaporization of hydrogen; nanospaces of SWNHs stabilize hydrogen molecules. On the other hand, the density of methane in nanospaces of SWNHs achieved liquid-like density even at 303 K above critical temperature, which is caused by enhanced methane-methane interaction in nanospaces of SWNHs. We will discuss adsorption mechanism for these gases and the possibility of the storage potential of SWNHs.

Surface spin disorder and exchange bias in La_{0.7}Ca_{0.3}MnO₃ nanoparticles synthesised by mechanochemical processing

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Nanoparticles of La_{0.7}Ca_{0.3}MnO₃ have been synthesised via the chemical reaction $0.7\text{LaCl}_3 + 0.3\text{CaCl}_2 + \text{MnCl}_2 + 2.35\text{Na}_2\text{CO}_3 + 0.325\text{O}_2 \rightarrow \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + 4.7\text{NaCl} + 2.35\text{CO}_2$ effected by high-energy ball milling and subsequent heat treatment. Single-phase La_{0.7}Ca_{0.3}MnO₃ particles having crystallite sizes ranging between 24 nanometres and 1 micrometre were obtained after removing the NaCl by-product phase by washing. Magnetic measurements showed that the spontaneous magnetisation decreased with decreasing crystallite size; that the coercivity increased with decreasing temperature; and that below about 50 K field-cooled hysteresis loops for the smallest particles were wider than the corresponding zero-field-cooled ones and shifted towards the negative field. These observations are discussed in terms of a model in which it is assumed that each crystallite consists of a ferromagnetic core and a spin-glass shell that are exchange-coupled.

Calcium phosphates and hydroxylapatite thin films processing by assisted ultraviolet pulsed laser deposition

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Calcium phosphate (CaP) including hydroxylapatite (HA) films were intensively studied in order to optimize the fabrication technologies of bone prostheses. Actual drawback in CaP and HA films processing is their poor mechanical characteristics and adherence. We present a hybrid pulsed laser deposition (PLD) method for growth of high quality CaP films. We used a KrF excimer laser and apply an in-situ ultraviolet irradiation emitted by a low pressure Hg lamp, which assists the deposition. The depositions were made onto Si and Ti alloys substrates in low ambient oxygen at pressures of 10⁻² to 10⁻¹ Pa with substrates heated at 500-600° C. The films were investigated by scanning electron microscopy, transmission electron microscopy and grazing incidence X-ray diffraction. Berkovich nanoindentation tests with both normal load and scratch tests options were performed for films mechanical characterization. Crystalline CaP films were obtained with different morphologies and stoichiometries depending on the deposition conditions. The films exhibit excellent mechanical properties, with values of hardness and Young modulus of 7-8 GPa and 160-170 GPa, respectively. All films withstand to scratch wear and no delamination or film destruction was observed. The ultraviolet lamp irradiation enhanced the gas reactivity and atoms mobility during processing, while the tensile strength between the film's grains and the bonding at the CaP film-substrate interface were increased.

Preparation and characterization of carbon nanotube-epoxy composites

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These days various applications of carbon nanotubes come to the front increasingly besides the different preparation and characterization techniques. Within this wide range of use, more and more researches are connected to the composite materials reinforced by carbon nanotubes instead of carbon nanofibers, following from their more favorable mechanical properties (high aspect ratio, high modulus, stiffness, flexibility and strength). In this work, a simple method of the preparation of epoxy/nanotube composite materials is reported. The main focus of this article is to present the importance of the quality of the reinforcing tubes we used in the experiments. We compare three kind of material containing purified, chemically modified and ball milled carbon nanotubes. From the TEM investigations and the conductance measurements, it seems that both the dispersion and the orientation of the tubes change depending on the pre-treatment of the tubes. The results show that using chemically functionalized nanotubes (acid treated followed by a reaction with diamino-propane) we can reach a good dispersion and almost parallel, straight running tubes in the samples, resulting conductive properties to the basically insulator epoxy matrices.

Low-Energy Electron Beam Assisted Growth and Nanopatterning: Spatial Control via Interference Effects

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The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for electron-beam induced processes in materials growth, etching, and lithography. We have recently demonstrated experimentally and theoretically that the total ESD yield of Cl⁺ from Cl-terminated Si(111) is a function of incident electron-beam direction [1,2]. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). DESD is due to quantum-mechanical scattering and interference of the incident electron to form a surface standing wave in the initial state of the desorption process. This electron standing wave exhibits spatially localized maxima and minima in the electron density and can lead to spatial control of the defect production probability. These defects can then act as seeds for controlled growth of nanostructures and nanoparticles. Results using this low-energy electron beam technique for the controlled growth of metal clusters on a semiconductor and metal-oxide single crystal surfaces will be discussed. Our initial results indicate that this low-energy electron-beam based approach, which does not rely upon serial processing, could be a viable and inexpensive form of nanolithography. 1.) M. T. Sieger, G. Schenter and T. M. Orlando, Phys. Rev. Lett. 82, 3348 (1999). 2.) M. T. Sieger and T. M. Orlando, Surf. Sci. 451, 31 (2000).

Structural Applications for Electroformed Nanocrystalline Metals, Alloys and Metal-Matrix Composites

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From the first engineering structural application for nanocrystalline materials (the Electrosleeve process for nuclear component repair), electroforming has remained one of the most simple and cost-effective methods for commercial-scale production of bulk, fully-consolidated, nanostructures (metals, alloys, metal-matrix composites). In this paper, an overview is provided of production methods and properties for nanocrystalline product forms such as sheet/foil, wire, fabrics/weaves, open-celled foams, coatings, and complex free-standing structures. Previous and emerging structural applications for these nanostructured products/materials (e.g., power plant components, military armour, wear-& corrosion-resistant coatings, medical implants, sporting goods, micromachines etc.) will be presented and discussed in the light of significant commercialization challenges such as time to market (regulatory issues, market acceptance) and production cost / relative performance criteria.

Tight-binding simulations of the various polytypes of silicon carbide.

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Tight-binding calculations for SiC in a variety of polytype structures (3C, 2H, 4H, 6H, 8H, and 9R) are reported using the NRL nonorthogonal tight-binding (TB) model with parameters selected to fit accurately first-principles results. These parameters predict zinc blende (3C) to be the stable crystal structure and wurtzite (2H) the most unstable, with the energies of all the other allotropes falling in between. We have calculated electronic properties (band structure and density of states) and elastic constants. For the 3C SiC we find excellent agreement with previous calculations and experiment. We will also present molecular dynamics simulations using the NRL-TB model.

A new MEMS-based resonant probe for scanning probe microscopy for studies of conductive and non-conductive materials

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We have developed a new micro-electro-mechanical systems (MEMS) probe for scanning probe microscopy. The probe, working in the oscillation regime at a resonance frequency, is a three-terminal device comprising a metal cantilever and two electrodes. One electrode is used to adjust and control the gap between the cantilever and another electrode used for measuring the tunneling current. A computer program has been designed for measurement of the resonance frequency of MEMS-probe and for control of the electronics system. Three feedback mechanisms are used to obtain surface topography: (1) the tunneling current readings between the cantilever and the measurement electrode, (2) tunneling current between the cantilever and the surface of the sample and (3) the shift of the resonance frequency of the cantilever. The first and third feedback mechanisms can be used for characterization of non-conductive materials as well. An advantage in comparison with traditional scanning probe microscopy is that the control of the height is established independently from the piezo-element. The feedback control of the surface height is made fully within the MEMS-probe when the gap between the cantilever and the control electrode can be automatically adjusted using the control voltage in the probe. The piezo-element is used for scanning over the surface only. In addition, our MEMS-probe enables spectroscopic measurements of the energy structure and surface potential on atomic scale.

Numerical Investigation of Equal Channel Angular Extrusion for Bulk Nanostructured Materials Formation

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Bulk nanostructured materials processed by Equal Channel Angular Extrusion (ECAE) is receiving growing attention in recent years due to the cross-section of the workpiece being kept unchanged after deformation. In the ECAE process, knowledge of the plastic deformation behavior of the workpiece is very important to optimize the process conditions such as die design, extrusion speed, temperature, friction, etc. In this paper, the numerical analysis has been used to study the metal flow, plastic deformation, strain/stress fields, and temperature fields during ECAE. Various die designs with different die angles and multiple channels were investigated. The strain rate sensitivity of the materials was considered. The deformation inhomogeneous in the workpiece was addressed. The corner gap formation between the die and the workpiece during the ECAE process was investigated.

Modeling and Analysis of the Strain/Stress Fields and Vertical Correlations in Quantum Dot Nanostructures

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In this paper, the strain and stress fields in quantum dot nanostructures were analyzed with a three-dimensional finite element method for an array of dots. The influence of quantum dot shape, cap layer thickness, and anisotropy ratio of the materials on the strain, stress and strain energy density distributions was studied in much detail. It is found that the elastic anisotropy has strong influence on the strain and stress fields in the quantum dot nanostructures. It is also found that both the elastic interaction among quantum dots and the elastic anisotropy of the materials have strong influence on the strain energy density distribution at the cap layer surface. With the different elastic anisotropy ratios and the cap layer thicknesses, substantially different distributions of strain energy density minima on the cap layer surface are obtained, which may result in various quantum dot ordering phenomena such as fully vertical alignment, partial alignment or complete misalignment.

Visible light emission of Si nanoparticles

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Silicon nanoparticles with average diameters ranging from 5 to 50 nm were fabricated by thermal evaporation. The nanoparticles had a crystalline core covered by an oxide shell, and there are oxygen and a small quantity of hydrogen absorbed on the surface. When excited with a He-Cd laser, the nanoparticles showed visible light emission from 500 nm to 900 nm, with a peak intensity at 800 nm. The intensity of photoluminescence (PL) increased with decreasing the particle size. Moreover, the PL observed in vacuum could be quenched by air and hydrogen, and reappeared after the sample chamber was evacuated. An oxygen-related surface state mechanism is proposed to account for the luminescence of the Si nanoparticles.

In addition, oxygen-containing Si nanoparticles (OCSNs) with different oxygen contents were also fabricated. A blue shift of the absorption edge is observed in the transmission spectra when the oxygen content is increased. The OCSNs exhibit an intense blue-green PL with two primary bands. The peak position of the high energy band (HEB) with a stronger PL intensity is at 520 nm, while the low energy band (LEB) has a peak at 800 nm. The PL intensity increases with increasing the oxygen content of the OCSNs, and is very sensitive to the ambient atmosphere. A mechanism of oxygen-induced luminescent center is proposed to be responsible for the blue-green PL.

Polymer Nanocomposites as Flame Retardant: Effect of Filler Types

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A new approach to address the ever-increasing demand for higher performance flame retarded products has recently focused on utilizing different inorganic additives (OC-MMT, silatrane and alumatrane). The metalatranes were synthesized via the Oxide One Pot Synthesis process, in which alumatrane and silatrane were synthesized directly from aluminum hydroxide ($\text{Al}(\text{OH})_3$) with triisopropanolamine (TRIS) and silicone dioxide (SiO_2) with triethanolamine (TEA), respectively. The main product of alumatrane was pentamer plus one morpholine (m/e 1250), and silatrane was dimer plus one EG (m/e 409). All of composite systems entail using above inorganic materials as flame retardant additives to commodity polymers, such as Nylon 12 and PVC. These nanocomposites were prepared from melt blending process, which had exfoliated structure. The WAXD spectra were correlated with TEM and SEM results showing the incorporation between inorganic additives and polymer matrix. However, the aggregation of silicate layers or silatrane agglomerate at high content loading indicated partially intercalated structure in our system. The gross heat calorific value was reduced while LOI value was increased. This not only increased efficiency of flame retardant additive, but also improved mechanical properties, increasing the tensile strength and modulus as well as elongation.

Hydrothermal synthesis of ceramic NANOpowders. Modelling and experimental verification.

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The paper presents a review of some thermodynamic models proposed to study the high temperature/pressure influence on the equilibrium composition and kinetics of crystallization. A new simple model is proposed to describe the evolution of crystallite sizes and crystallization degree vs. hydrothermal temperature and time. Results obtained in the synthesis of zirconia by conventional hydrothermal synthesis and microwave-hydrothermal synthesis are presented. The crystallization degree, mean crystallite sizes and activation energy for the two methods calculated from experimental data are finally compared with the calculated values. A good agreement was observed at low temperatures and times in the absence of particle growth and agglomeration.

DIRECTLY PATTERNED MAGNETIC MEDIA FOR ULTRA-DENSE DATA STORAGE

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A novel effective technique is presented for patterning regular arrays of magnetic nano-entities. The approach is based on laser-induced onset of ferromagnetic order in granular (superparamagnetic) films of kind of Fe-Cr and Co-C [1,2]. To localize the regions with modified magnetic properties, we employ interference annealing of the films by means of pulsed (~10 ns) UV-laser beams. Atomic force microscopy imaging reveals the formation of crater-like entities and mounds on Fe-Cr and Co-C surface, respectively. It is striking that these entities exhibit a pronounced magnetic force microscopy response whose behavior is dependent on the entity's environment. If the environment has a relatively high permeability ($\mu \sim 10$), the entities are single domain in remanent states, irrespective of their prior magnetization direction. The obtained results are believed to be important for future information storage with ultra-high densities.

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MAGNETIC IMAGING OF NANO-ENTITIES BY NONMAGNETIC PROBES OF ATOMIC FORCE MICROSCOPE

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We present an approach to visualization of small magnetic entities using nonmagnetic tips of atomic force microscope (AFM). The usage of nonmagnetic probes is highly desirable for imaging of magnetic nanocomposites and other small structures, in order to avoid the disturbance of magnetic structure under study by the stray fields of the tip. Using probe's scanning in the contact mode and applying ac magnetic field in situ with the frequency ω in the kHz-range, we have revealed the pronounced response of magnetic nano-entities on 2ω , which was fitted to the resonance frequency of the cantilever. As the subject of our studies, we have chosen the ring-shaped magnets directly patterned on a surface of Fe-Cr films. As found, the dynamic response strongly depends on the orientation of the ac field with respect to the magnetization of the entities. The observed dynamic response and its behavior can be interpreted in terms of magnetostriction and a related quantity, ac susceptibility.

The work has been supported by RFBR (#01-02-16445) and the Royal Swedish Academy of Sciences under the bilateral program for cooperation with researchers from the former Soviet Union.

LASER-PATTERNED NANOSTRUCTURES IN THIN Co-Sm FILMS

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Properties of the nanostructures in high-coercivity magnetic films are of great interest in the context of possible applications for magnetic recording and permanent magnets. It here is essential to produce the composite media of alternating regions that have different coercivities. We present our studies of nanostripe arrays directly patterned in Co-Sm films by means of laser beams with nanosecond duration. A two-time reduction of the coercivity of the 40-nm thick films on silicon substrates has been disclosed after their irradiation by one uniform pulse with fluences of 200-300 mJ/cm². Using a laser interference technique, we have patterned the films with submicron periodicities. Atomic force microscopy studies of the patterns reveal that these consist of the stripes of a solidified phase in a reference matrix. Some indication for the formation of a two-phase material, is also obtained by Kerr magnetometry.

The Enhanced Magnetocaloric Effect of Magnetic Nanocomposites

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Upon the removal of a magnetic field from a magnetic material, the resulting reduction in magnetic spin alignment represents an increase in the material's spin entropy (ΔS). If the field reduction is performed adiabatically so that the total entropy change is zero, then the increased spin entropy is offset by an equal decrease in lattice entropy, as reflected by a decrease in the temperature of the material. This ΔT is called the magnetocaloric effect, and it is a property of the material and its magnetic state. The magnetocaloric effect, upon which the technology of magnetic refrigeration is based, may be enhanced within some ranges of magnetic field and temperature by finely dividing and grouping the ferromagnetic species in a nonmagnetic or weakly magnetic matrix*, thus constituting a magnetic nanocomposite. In this lecture the basis of a magnetic nanocomposite will be reviewed and experimental data, measured on several magnetic nanocomposites will be presented that confirm the earlier predictions for a significantly enhanced magnetocaloric effect in this class of magnetic nanocomposite materials. In particular, experimental verification of cluster calculations will be provided by experimental data for a new magnetic nanocomposite, $(\text{Gd})_3(\text{Ga})_{5-x}(\text{Fe})_x(\text{O})_{12}$ (GGIG), that is superparamagnetic and possesses magnetocaloric effects 3-4 times larger than those of the presently preferred low-temperature paramagnetic refrigerant, i.e., gadolinium gallium garnet (GGG). This new material possesses the potential for both increasing the operating temperature of magnetic refrigerators as well as lowering the magnetic fields required for their operation. If the principle magnetic nanocomposite can be successfully be translated into practice, then magnetic refrigerators could be substantially reduced in size, made much more efficient, and enable cooling at much higher temperatures.

PROCESSING AND PROPERTIES OF NANOCRYSTALLINE FeAl INTERMETALLICS

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Many intermetallics exhibit an entire spectrum of superior mechanical, physical and chemical properties, which make them very attractive candidates for applications in severe environments (e.g. elevated temperatures, corrosive environment etc.). Unfortunately, almost all of them suffer from low ductility and fracture toughness at ambient temperature. Substantial grain refinement is commonly considered as being beneficial for an improvement of ductility and fracture toughness of metallic materials and could possibly be employed for intermetallics. The present work is a comprehensive overview of efforts to produce nanostructured powder and bulk FeAl intermetallics. Ball milled powders of cubic FeAl intermetallic, were successfully consolidated into nearly porous - free bulk compacts by various combinations of shock wave (explosive) loading or high-current impulses. Changes of microstructure during processing and mechanical properties of nanostructured bulk compacts are shown and discussed.

Vertical transport in semiconductor superlattices: control by the disorder in layer parameters.

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Electron transport in semiconductor superlattices is very important for various practical applications. In the present work we model the transport properties of superlattices with a disorder introduced into the layer parameters. We consider both, resonant and sequential tunneling in vertical direction, for a finite voltage applied to a disordered system. The transmission coefficients are found by the transfer matrix method and are used for the further calculations of I-V curves. Electron redistribution among the quantum wells and well bottom energies are calculated. The disorder-induced shift of the energies of resonant states leads to significant changes in the tunneling probabilities, and thus, in the transport through the whole system. The effect of various types and degrees of the disorder on the superlattice properties is discussed.

The Story of Manganese: From Clusters to Crystals

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Among all the 3d transition metal elements, manganese is unique as an atom, cluster, crystal, or impurity in wide band-gap semiconductors. As an atom, it has a half-filled 3d shell and filled 4s shell with a large gap separating the two orbitals. Consequently these atoms interact weakly with each other. As a matter of fact, manganese dimer is a weakly bonded van der Waals system with the largest bond length in the 3d series and its bulk has the lowest cohesive energy. Small clusters of manganese are ferromagnetic while the bulk Mn is antiferromagnetic. As clusters grow, ferrimagnetism sets in and the total moment of the cluster decreases sharply with the increase of size. When doped into GaN semiconductors, the manganese atoms couple ferromagnetically although the measured Curie temperature varies from 10 K to 940 K depending on growth conditions. The talk will present results from first principles calculations explaining various aspects of these interesting entities.

PROCESSING OF NANOPOWDERS

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Laboratory and industrial processes for production of nanopowders of metals, ceramics and composites are presented. Productions of powders using atomization, mechanical and chemical processes for powder production are discussed. A special discussion is made on the production of metals, ceramics and composites nanopowders using thermal plasma processes. The reactive metals, ceramics and composites are produced in the laboratory at the University of Alabama. Processes parameters are optimized based on the reaction thermodynamic and transport calculations. The powders are characterized using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), Energy-dispersive X-ray spectrometer (EDS) and X-ray diffraction analysis (XRD). Challenges in producing a close particle size distribution in the nanosize range without agglomeration are discussed.

Polymer-Layer Silicate Nanocomposites in Solution: Linear PEO and Highly Branched Dendrimer for Organic Wastewater Treatment

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Base on the concept of organic matter adsorption from aqueous system, the highly active site species was come into expected. Poly(amidoamine) (PAMAM) dendrimer, the highly branched structure that emanate from a central core was used in cooperative with Montmorillonite (MMT), smectite clay which has high surface area in nanocomposite form to be an effective adsorbent in organic wastewater treatment application. Due to the inorganic character of MMT, the organic adsorption ability of MMT was improved by replacing the inorganic exchangeable cations via an ion-exchange reaction with octadecylamine and di(hydrogenated tallow)dimethylammonium chloride. These modifying agents are different in their chemical structure. The PAMAM/MMTs nanocomposites were prepared by solution technique comparing with PEO/MMTs, the nanocomposite of linear molecules polymer, which were prepared by melt technique. All nanocomposites were characterized by WAXS, TGA and FT-IR. The behavior of nanocomposites in aqueous solution was studied in term of viscosity of the solution. The ability to remove organic contaminants based on different molecular structure of organically modified clay, PAMAM/MMTs and linear PEO/MMTs nanocomposites were evaluated by using UV/VIS spectroscopy.

GIANT MAGNETO-RESISTANCE OF THE NEW MAGNETIC SEMICONDUCTORS CONTAINING $\text{CuCr}_{1.5}\text{Sb}_{0.5}\text{S}_4$ WITH Co.

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Magnetic and galvanomagnetic properties of the system $x\text{CoCr}_2\text{S}_4 - (1-x)\text{CuCr}_{1.5}\text{Sb}_{0.5}\text{S}_4$ are considered. This system is a solid solution of two semiconducting compounds with a spinel structure: a recently discovered mineral florensovit and ferromagnetic (FIM) CoCr_2S_4 . A giant negative magneto-resistance (MR) $\Delta\rho/\rho$ was observed in both compounds. The temperature dependence of the magneto-resistance $\sim 16\%$, in a field $H = 27$ kOe for the compound with $x = 0.25$. The maximum modulus of the magneto-resistance is observed near 25 K. The temperature dependence $\Delta\rho/\rho(T) = 0.24$ in a field of 30 kO, at $T = 7$ K for the compound with $x = 0.5$. In this field, which is the maximum at which the measurements were carried out, the MR isotherms are still far from saturation. In florensovit and CoCr_2S_4 , on the other hand, there is essentially no MR within the error of these measurements, 0.01%. According to the data of other investigators, described in Ref. [3], MR for CoCr_2S_4 does not exceed 2%. The giant negative magneto-resistance in composition can be explained on the basis that this compound contains afmons- quasiparticles predicted theoretically by Nagaev.

Single crystal SBN:Yb /Opal matrix (SiO₂):Er composite as a nanophotonic structure

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Thin layer of opal matrix on SBN:Yb (001) crystal substrate was prepared via sedimentation method and post-growth annealing treatment. The film thickness of cubic package of SiO₂ nanospheres (240 nm in diameter) was of 25 monolayers. Erbium oxide (Er₂O₃) was introduced into the interspherical space of opal matrix using the sol-gel method (about 35 v 40 % relative to the pore volume). The nanophotonic structure obtained was used to study Er³⁺ ion photoluminescence at around 1.55 μm (third communications window). The possibilities of Er³⁺ cascade excitation by the Yb³⁺ ions were studied, what leads to strong increasing of pump efficiency and broadening of absorption band. The specific features of photoluminescence in such nanocomposites will be discussed.

Optical Films Based on Poly(p-phenylene vinylene) (PPV) and Its Nanocomposites

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A new nanocomposite enhanced the lifetime of poly(p-phenylene vinylene) (PPV) was studied. The natural sodium-montmorillonite was cation exchanged with bis(hydrogenated tallowalkyl) dimethyl quaternary ammonium chloride. These polymer/layered silicate nanocomposites have been synthesized consisting of different organically modified clay loading proven by TGA, WAXD, FTIR, and TEM. Barrier property and color tunability were improved with increasing organophilic clay content. The rate of photoluminescence decay in polymer-clay nanocomposites was drastically reduced compared to that of the pristine polymer. Organic light-emitting diodes based on PPV and its nanocomposites fabricated by spin-coating method have demonstrated good operating stability. The results showed important implications on the enhancement of lifetime in polymer-clay nanocomposites based optoelectronic devices.

Use Sericin as an Antioxidant and Antimicrobial for Polluted Air Treatment

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The aim of this study was to enhance the air filter properties by coating with silk sericin, which is mostly discarded in silk processing wastewater. The antioxidant activities against hydroxyl radical (OHI), the antimicrobial activities and the fiber coated surface were studied in silk sericin from different race of waste cocoon; Polyvoltine waste cocoon Nang Noi Race, Polyvoltine x Bivoltine waste cocoon Dok Bua Race, and Bivoltine waste cocoon Jul Race. The concentration of sericin solution was range from 10 to 20% in distilled water. Among the different race of waste cocoon, Jul race had the highest antioxidant capacity inhibition of OHI, while Dok Bua Race was second and Nang Noi Race had the lowest inhibition activity. For antifungus activity, Dok Bua Race had the highest capacity, while Jul Race was second and Nang Noi Race had the lowest capacity. The inhibition activity in Micrococcus type of bacteria was found that Dok Bua Race had the highest capacity, while Nang Noi Race was second and Jul race had the lowest capacity. The coated surface of sericin on Nylon fiber and PET fiber was smooth along with the fiber. This study therefore demonstrates that sericin from Dok Bua Race had the best properties for coating on the air filter

Transparent films for electromagnetic shielding of plastics

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The interest in the development of lightweight transparent electromagnetic (EM) shields for the radio frequency range has been growing up in the last years together with the expansion of the electronic market and the increasing use of plastics. Example of industrial applications are video displays of electrical and electronic apparatus, of electromedical devices, of portable electronic equipment. Applications in the aerospace sector are also very attractive, such as in protecting the electronic systems of aircrafts from the high-intensity electromagnetic fields (HIRF) emitted by radio emitters, TV, radars and telecommunication systems. Moreover, the recent limits of radio frequency electromagnetic fields suggest the use of transparent shields for building windows. Thin films can provide an effective solution in EM shielding of plastic substrates or enclosures. In particular, the use of 1-D photonic band gap structures named as 'transparent metals' has been recently investigated and tested for EM shielding applications in the radiofrequency range, by using physical vapor deposition technique. In this work, the design method and the technological issues concerning the realization and electromagnetic testing of the shields will be described. Some recent results will be presented, and the perspectives and the limits of the proposed technique will be discussed and compared with other solutions.

Preparation and characterization of Various Nano-metal oxides using Hydrazine hydrate in solution combustion method

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In this paper, We described a simple method to prepare nanosized-Metal-oxides such as alfa iron oxide, gamma-iron oxide, titania, alumina and others using a solution combustion process. In this method, aliquots of the aqueous salts solutions of ferric chloride, aluminum sulfate and other salts are mixed in an optimized ratio of 4:1 with hydrazine hydrate (80% w/v) solution using magnetic stirrer at the highest speed. Immediately after mixing, vigorous reaction started, and lead to the boiling of solution without supply of external heat. The temperature remained high for almost half an hour and then cooled down slowly to room temperature. Beakers containing reaction mixtures are kept in the water bath to sink the heat fast. N₂ and NH₄ gases were evolved during this solution combustion process. At the end of process, the powder obtained was washed thoroughly with dilute (10mM) HCl followed by nano-pure water and dried in the electric oven at 100 degree C. Dry powders of different metal hydrous oxides were redispersed in the de-ionized water by vigorous shaking and with mild ultrasonication for 5 minutes prior size and shape examination using dynamic and static light scattering methods. The diameter of particles was in the range of 30nm-600nm depending on the concentration of the salt precursors. The size can be controlled using controlling the concentration of salts. The phases of nano-metal oxides (such as alfa and gamma) were identified using X-ray diffraction and Mossbauer spectroscopy. The mechanism of the formation of the nano-particles in this process is the fast quenching and sinking of heat evolved during process which avoids the sintering of particles. The quenching is occurred due to evolving gases like ammonia and nitrogen whereas the reaction medium which act as a sink to the heat. Advantages of this method are: Easy and fast process, high yields (85-90%), possible to scale up to industrial grade, highly pure, lesser combustion nature of reaction and hence safe as compared to that of solid state combustion method of hydrazine complexes of metal salts.

Band-gap Widening of 1-10nm Q-Cds in Various Surfactant Self-assemblies: Tight Binding and Effective Mass Models

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In this paper, we utilized tight binding (TB) and the effective mass approximation (EMA) models to deduced the nano-sized of Q-CdS semiconductor. The UV-vis spectra of various sizes of CdS are simulated using tight binding approach. Different surfactant self-assemblies used are: micelle of sodiumdodecyl sulfate (SDS), CTAB in water and monoethylene glycol (MEG) and microemulsions of Aerosol OT/heptane/water. SDS and CTAB are known to formed weak micelle in the nonpolar solvents such as MEG. These different nano-reactors of surfactant self-assemblies affect the formation of CdS and hence the optical properties. The aggregation of CdS are created insitu nano-reactor of the microemulsion system by increasing the concentration of salts of Cd and S ions and analyzed using TB model. The advantages and drawbacks of these two models are to be discussed. Acknowledgement: Department of atomic energy of India gave research scholarship to P. D. Sawant to complete this work.

FERROELECTRIC NANOTUBES

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We report the invention of ferroelectric nanotubes. Details are given for strontium bismuth tantalate (SBT) although barium titanate and lead zirconate-titanate (PZT) can also be made by the same process. The tubes are in the form of fully registered free-standing arrays with each nanotube ca. 80 microns long and of uniform wall thickness d , where d can be adjusted within the range $40 \text{ nm} < d < 140 \text{ nm}$. Nanotube spacing in the hexagonal array can be varied from a few microns to submicron, and inside tube diameter from 0.4 - 4.0 microns. A sacrificial Si substrate is used, and deposition is via "misted" liquid source of charged precursor droplets 0.1-0.3 microns in diameter. Each droplet has an average charge $-5e$, so that the system behaves like the original Millikan oil-drop experiment [R. Millikan, *Science* (1910)]. The charge on the droplets draws them down the nanotubes to uniformly coat the walls; this electrostatic mechanism is not possible with conventional CVD processing. Deposition rate is rapid enough for commercial processing of devices. These nanotubes are piezoelectric insulators. Therefore they provide three new device applications: (1) ink-jet printers. The state of the art ink-jet printer from Seiko-Epson will deliver a 1.0 picoliter droplet and write a 1.0 micron line, permitting lithography-free printing of memory devices and low-density integrated circuits. The new ferroelectric nanotubes should deliver $\times 10$ smaller droplets. (2) A typical state of the art DRAM trench (e.g., Infineon) has a 0.1 micron diameter and is 6.0 microns deep (aspect ratio of 60:1). Our ferroelectric nanotubes can be 0.1 micron diameter by 60 microns deep, for an aspect ratio of 600:1 with perfect step coverage (uniform wall thickness). (3) Drug delivery systems in the body and ultra-thin syringes for medical purposes (e.g., injections into the heart).

Sintering of Nanocrystalline WC-Co Composite Powders

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The aim of this work is to investigate the mechanism of densification of WC-Co nanocomposite at temperatures about the liquid-solid boundary. The processing method of spray thermal decomposition - continuous reduction & carburization was used to produce the nanocrystalline WC-Co composite powders. They were sintered in vacuum with HIP or with SIP treatment, or by the spark plasma system. Density, hardness, tensile rupture strength and coercive force were measured. The microstructures of the sintered composites were studied by SEM and HREM. Results show that the chemical-uniformly dispersed particles and the formation of liquid phase at lower temperatures play a crucial role in low temperature consolidation.

Mechanical Behavior of Ceramic Coatings Reinforced with Carbon Nanotubes

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Carbon nanotube (CNT) reinforced composites have been touted to possess superb mechanical properties due to the unique structure and properties of carbon nanotubes, but no such materials have been fabricated or reliably tested to date. Here, we present the first results on the mechanical properties of highly-ordered CNT-reinforced ceramic matrix composites. The nanocomposites were produced by the template approach, in which CNT are deposited into a porous alumina matrix formed by anodization of aluminum, and are in the form of 20-100 micron thick coatings on an aluminum substrate. Nanoindentation tests were performed on surfaces both parallel and perpendicular to the longitudinal CNT axis. Indentation marks and associated damage were observed by SEM. Indentation parallel to the CNT axis induced cracks that intersect and deflect at the matrix/CNT interface, indicating interfacial debonding. Indentation perpendicular to the CNT axis induced cracks that show direct evidence of nanotube bridging. Indentation at high loads to cause chipping exposed fracture surfaces that exhibit CNT pullout. All of these phenomena indicate that these nanotube composites may function as tough materials. Nanocomposite modulus data obtained from indentation unloading curves were used along with analytic and finite element models to derive the Young's modulus of the porous Al₂O₃ matrix (150 GPa) and the CNT (300 GPa) parallel to the nanotube axis; the latter values are lower than typical estimates of CNT stiffness.

Microbially synthesized bioactive nanoparticle and their formulation active against human pathogenic fungi.

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Lichen fungi have diverse range of chemicals and produces some characteristic metabolites during artificial culture in synthetic medium. During artificial culture of some lichens fungi in synthetic medium for metabolite synthesis, the lichen fungi of *Usnea longissima* (ascomycetes fungi) found to be synthesized bioactive nanoparticle in specified medium under additional conditions. The size of the nanoparticle of almost uniform in size, with a diameter of around 5-40 nanometer across. Such a narrow size distribution is characteristic of microbially synthesized nanoparticle. The nanoparticle become trapped both on the surface of the cell wall and on the cytoplasmic membrane. The controlled synthesis of nanoparticles of well-defined dimensions over a range of chemical compositions is an important aspect of nanomaterials engineering. Biological process are inherently accurate, and synthesis of all the particles takes place during a specific period of cell growth, most of the particle synthesized are of the same size-they have a very narrow size distribution. There is an ever-growing need to develop cleaner, non-toxic and environmentally friendly procedures for synthesizing the nanoparticles. So the research turned to biological systems for inspiration. This is first ever report of microbially synthesis of bioactive nanoparticle from lichen biomass (mycobiont) through in vitro culture. After almost exhaustion of medium after 7-8 days nanoparticles were isolated from medium through various methods before being purified. We were used Bio nanoemulsion technology for in vitro bioactivity testing of formulated nanoparticles from lichen metabolites. Detail in vitro analysis of nanoparticles was carried out against human pathogenic fungi, *Trichophyton rubrum*, *T. mentagrophytes*, *Epidermophyton floccosum*, *Microsporum gypseum*, *M. audouini*, causing fungal infection in humans and animals. Bioactive nanoemulsion was also found broad antifungal spectrum killing some other fungi, *Candida albicans*, *Aspergillus flavus*, *Microsporum nanum*. For clinical investigation, we have formulated bioactive nanoemulsion, before specific analysis. Bioactive nanoemulsion was found to be stable upto two year, during this period no agglutination was observed as specific natural surface protectant was added. Nanoemulsion was found to be extremely safe and effective for controlling dermatophytoses during in vivo investigation. Thus, our study will definitely provide an effective natural nanomedicine (bio-nanoantifungal) active against dermatophytoses; in near future after successful clinical trial, which is our next step. So, in this way we can exploit the lichen biomass (mycobionts) as nanofactories for the production of raw material for nanodrugs.

Plasma Coating of Nanoparticles and Nanotubes

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Ultrathin polymer films have been deposited on both single- and multi-wall carbon nanotubes using a plasma polymerization treatment. HRTEM experiments showed that an extremely thin film of the pyrrole layer (2-7 nm) was uniformly deposited on the surfaces of the nanotubes including inner wall surfaces of the multi-wall nanotubes. Time-of-Flight Secondary ion mass spectroscopy (TOFSIMS) experiments confirmed the nanosurface deposition of polymer thin films on the nanotubes. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

Studies On Reactive Sintering Behavior Of Milled Nano Mo/Si₃N₄ Powder Mixture

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Si₃N₄ - MoSi₂ composites are commercially fabricated by hot pressing or hot isostatic pressing of powders of molybdenum disilicide and silicon nitride. In the present investigation attempts are made to fabricate Si₃N₄ - MoSi₂ in situ composites by reactive sintering of milled nano Mo and Si₃N₄ powder mixtures. The Molybdenum and silicon nitride powders in the molar ratio of 1:3 were milled with a WC grinding media in toluene having a charge ratio of 15:1, for different length of time up to 104 hours. The milled powder was characterized by XRD, TEM, SEM, EDS, DTA, and IR spectroscopy. The present investigation indicates that up to even 104 hours of milling does not lead to the formation of MoSi₂ phase. Size of molybdenum was found to be below 10nm after 40 hours and converted to amorphous phase after 70 hours of milling. SEM v EDS spot analysis of samples showed the presence of WC contamination as high as 10%. IR spectroscopy showed the presence of Si₃N₄ bond only. DTA analysis of milled samples in argon shows the presence two peaks at 440oC and 670oC. The milled sample was subjected to pyrolysis in the temperatures range of 1000-14000C both in commercial argon and vacuum. The percentage of MgO as the sintering aid for Si₃N₄ was varied from 5 to 10 wt%. The sintering studies of samples after different hours of milling were carried out as a function of milling period, contamination, heating rate, temperature, holding time, amount of densification aid, reaction temperature, size of MoSi₂ and Si₃N₄ phases formed. For short dwell time Mo₅Si₃ formed as major phase after reaction in the temperature range of 1400-1600oC. Large dwell time was required to form the ultimate silicide phase MoSi₂. It is interesting to note that reaction temperature of both nano and micron size powder is 1400C. During reaction sintering of nano size powder, MoSi₂ and Si₃N₄ phases were obtained but in case of micron size powder presence of Mo₅Si₃ was also observed. SEM analysis of reacted samples after every 10 hours of milling up to 104 hours shows uniform distribution of MoSi₂ and Si₃N₄. The reacted samples of higher hour of milling also shows the presence of SiC phase. The glassy phase of magnesium silicate was obtained around the grain boundary after sintering.

Nanostructured Conjugated Polymeric Systems for Photovoltaic Applications

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Of crucial importance to the fabrication of polymeric based solar cells is the requirement of a bicontinuous partition of the donor and acceptor phases to allow effective charge separation and transport to the electrodes. Block copolymers are extremely attractive as candidates for photovoltaic applications as they phase separate in the 50-200 nm scale and allow the possibility of fine tuning the donor acceptor energy levels. We used two techniques based on nanoimprint lithography for phase alignment in a block copolymer blend polyfluorene/polyaniline (PF/PANI), polyfluorene being the donor and polyaniline - the acceptor phase. In the first technique, metallic nanostructures induce a phase separation in the polymer layer, whereas in the second technique, the PF/PANI is directly patterned with a stamp. The electrical and photoelectrical properties of the polymeric systems were studied and the phase alignment was characterized by AFM.

LIPOSOME STABILITY VERIFICATION BY ATOMIC FORCE MICROSCOPY

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The observation of liposomes made up of phospholipides by atomic force microscopy has enabled direct visualization of their structure. Liposome/substrate interaction forces were modified by using various surface treatment processes. The images of liposomes supported on mica in air display multiple and single vesicles and also flat bilayers. Molecularly resolved force versus distance curves of the liposomes supported on silanized mica in water display the organization of hydrocarbon chains and corroborate the presence of distinct adsorbed structures. The liposomes respond elastically to small stress but undergo plastic deformation when stresses are severe. The rupture force necessary to perforate the top bilayer of the liposome is ~0.1 nN and the one corresponding to the adsorbed bilayer on the mica is ~0.35 nN. Multiple vesicle liposomes adsorbed on mica and observed within liquids and air show the same average diameter as the ones measured by photon correlation spectroscopy, indicating that their size was unchanged during the drying process. The as prepared liposomes are formed by smaller vesicles that aggregate to give the ~200 nm diameter vesicles.

Progress in the MBE Growth of GaN and its Alloys

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Throughout much of the 1990s, state-of-the-art MOCVD-grown GaN materials and devices were markedly better than those grown by MBE. At the time, this was attributed to the relatively low growth temperature of MBE for nitrides (~600 – 800°C) in comparison with MOCVD (1000 – 1100°C) and the immaturity of the nitrogen sources for MBE. In this talk, we review the Santa Barbara work on MBE of GaN and demonstrate the viability of the technique and current challenges and opportunities.

Currently, the nitride MBE growth is carried out in a dedicated arsenic-free system with recent generation rf plasma nitrogen sources. To avoid issues associated with nucleation on a chemically dissimilar, lattice mismatched substrate (e.g., sapphire), MBE growths are commonly carried out on MOCVD GaN/sapphire ‘templates’. The microstructure, morphology, and physical properties critically depend on V/III ratio and substrate temperature. Threading dislocations, from the underlying MOCVD layer, play a critical role in the morphology evolution. There is a strong interplay between V/III ratio and dislocation-mediated morphologies. Optimal growth conditions are achieved for group III-rich (metal-rich) conditions with complete coverage of a metal ‘wetting layer’ on the surface. In the case of GaN growth, a stable Ga bilayer exists on the surface. The metal-rich growth leads to challenges in minimizing Ga condensation on the substrate surface. By careful flux control, we have now achieved record mobilities both for two-dimensional electron gases (2DEGs) in the AlGaN/GaN system and bulk n-type GaN.

The nature and control of the metal wetting layer remains a focus of much of our work. We present recent work on the growth of InGaN, GaN quantum dots, and AlN on SiC. In the case of InGaN, Ga will incorporate into the growing crystal in preference to In, thus the growths are carried out under an In wetting layer. The nature of the In wetting layer facilitates dramatically increased impurity incorporation into the alloy (or GaN) in comparison with a Ga wetting layer. Control of the nature and evolution of the metal wetting layer is essential for the growth of GaN quantum dots on relaxed AlN layers. The GaN QDs form during growth interrupts that allow evaporation of the metal wetting layer. For the case of AlN growth, we present recent results on growth under Ga and Al wetting layers.

STUDIES OF SORPTION PROPERTIES, TOTAL HETEROGENEITY AND FRACTAL DIMENSIONS OF CARBON NANOTUBES

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Carbon nanotubes are used in many branches of science, industry and technology as e.g. novel components of mechanically strong composites. Adsorption and heterogeneous properties, in particular the fractal dimensions, are necessary for understanding unique physicochemical properties of nanotubes, e.g. surface layers, porosity, semiconducting or metallic behaviour depending on their geometrical parameters and structure. The calculation of the fractal dimensions may be obtained from measurements of adsorption, sorptometry, mercury porosimetry, scanning electron microscopy, small-angle X-ray scattering and nuclear magnetic relaxation methods. Sophisticated measuring techniques and disturbances e.g. by multilayer condensation complicate the necessary investigations. So far, only few studies of those items are available.

For that reason, in this paper possibilities to study physicochemical properties of nanotubes by means of thermal analysis and sorptometry techniques are discussed. We examined carbon nanotube samples which were grown in a horizontal quartz tube reactor placed in a furnace by reaction technique using xylene-ferrocene mixture. Thickness of the adsorbed liquid layers on the surface can be assessed by means of immersion of the solid samples. Adsorption of non-polar (benzene and n-octane) and polar (water and n-butanol) liquid layers were measured using the Derivatograph Q-1500 D (MOM, Hungary). The Q-TG mass loss and Q-DTG differential mass loss curves were measured under the quasi-isothermal conditions in the temperature range 20-250 °C at a heating rate of 6 °/min. Porosity properties e.g. specific surface areas, pore size distribution and pore volume were calculated from low-temperature nitrogen adsorption-desorption isotherms measured by means of the Sorptomat ASAP 2405 V1.01 (Micrometrics Co., USA).

A numerical and analytical procedure for the evaluation of total heterogeneity properties (desorption energy distribution and pore-size distribution functions) using sorptometry and thermodesorption of liquids from nanotube surfaces under the quasi-equilibrium conditions is presented. We also discussed special applications of thermal analysis for investigation of adsorbed liquid layers and surface porosity parameters used for the quantitative characterisation of the total (energetic and structural) heterogeneities of nanotubes. The new method for determination of the fractal dimension of nanotube surfaces using Q-TG technique is presented and discussed. It is in good agreement with results from low-temperature adsorption-desorption isotherms. The presented results show that above method for determination of the fractal dimensions on the basis data thermodesorption of liquids in quasi-isothermal conditions is reliable, simple and practicable.

Nonlinear optical properties of Cu nanoparticles synthesized in silica by ion implantation

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Metal nanoparticles contained in the dielectric matrixes are of great interest due to their possible application in the different fields of nonlinear optics (optical limiting, optical switching etc). The considerable interest to such composites was recently focused on investigation of their properties at the wavelengths corresponded to the surface plasmon resonance of metal nanoparticles. These investigations covered almost all visible spectrum range, but in practice there is a problem to develop composite materials which are suitable for operation at the specific IR wavelengths of the industrial lasers. This report results of nonlinear optical study of Cu nanoparticles implanted in glass matrixes applying the Z-scan method at the wavelength of Nd:YAG laser radiation (1064 nm, 35 ps). As basis dielectric substrates containing nanoparticles soda-lime silicate glass and silica were used. The thickness of all composite layers used was 0,4 mm. The Z-scan scheme with an open and closed aperture allowed to determined nonlinear refractive indices, third order nonlinear susceptibilities and nonlinear absorption coefficients of the synthesized materials. The effect of nonlinear absorption was detected in present samples. It was observed for the first time to my knowledge, that a two-photon absorption may be connected to the surface plasmon resonance of Cu nanoparticles. The two-photon absorption coefficients were determined to be $1,08 \times 10^{-6}$ and $4,1 \times 10^{-7}$ cm W⁻¹ for Cu in soda-lime glass and silica, respectively.

Computational studies of SWCNTs capped by hemispheres of C60 fullerene, based on semi-empirical methods

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The computations were performed with the AM1, PM3, MNDO, and MINDO/3 semi-empirical quantum-chemical methods. Optimized bond distances, effective charge values, total energy, heats of formation and core-core interactions were calculated for zig-zag type SWCNTs with maximum stoichiometry C240 and for arm-chair type SWCNTs with maximum stoichiometry C160. For C60 and C70 fullerenes, STO-3G ab-initio calculations were additionally performed, allowing us to compare all the computed results with the experimental ones. On the basis of optimized geometries of the SWCNTs presented here, singlet electronic states were calculated.

Comparative Study of Different Methods of CNT CVD Deposition by OES

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Comparison of the carbon nanotubes (CNT) deposition conditions in different chemical vapor deposition (CVD) methods (such as microwave plasma assisted CVD and direct-current discharge CVD), using the optical emission spectroscopy (OES) of plasma was performed. The significant difference in the OES spectra under similar deposition conditions (working gas mixture, gas pressure, substrate temperature, substrate nucleation method and so on) was found. The distinction in the relative intensities of the spectral lines of the C₂, CH and H_γ in different methods was studied. Effect of pulse mode plasma excitation [1] in both methods was also considered. Features of plasma assisted and plasma-free (hot-filament CVD and thermal decomposition CVD) deposition methods were discussed.

[1]. Y.A. Mankelevich, A.T. Rakhimov, N.V. Suetin, S.V. Kostyuk, *Diam. and Relat. Mat.*, 5 (1996) 964-967

Atomic ordering, nanocrystal nucleation and grain size effects in soft-magnetic rapidly quenched systems

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Metallic alloy systems with outstanding properties exploit advantageously the enhancement of properties and of special phenomena through decreasing the size of structural units present in the matter. An exemplary case of such systems are nanocrystalline alloys obtained by crystallization from amorphous rapidly quenched state; the size of crystalline grains is typically few nanometers or few tens of nanometers. The influence of nanocrystal dimensions and their overall volume content on thermodynamic parameters, e. g. heat capacity, thermal conductivity or diffusion coefficient and different physical properties is well known. Further effects are related to the amount of interfaces between nanocrystals and the surrounding (usually amorphous) matrix, i. e. nanocrystal surface-to-volume ratio. Another factor worth of consideration is the size distribution of nanocrystals. An ideal case would be represented by a monodisperse system containing nanocrystals of one size only, providing thus a convenient model system for physical investigations of size-property relationships and property enhancement. In real systems obtained by rapid quenching of the melt, however, the nanocrystal size distribution is given by a complex interplay of the processes of nucleation and grain growth from disordered amorphous or undercooled state with local atomic ordering on the scale of nanometers. It will be shown that the type of this ordering in amorphous state is crucial for stability, phase selection and micromechanisms of formation of crystalline phases.

We shall demonstrate the impact of different types of nucleation regimes on the process of transformation from amorphous to nanocrystalline state and on the grain size distribution in these systems. Fundamental knowledge of thermodynamics of nucleation and growth processes will be shown to provide a method for control of grain size distribution by suitable time-temperature regime of the transformation. Application of this approach will be presented on selected iron and cobalt based systems with excellent soft magnetic properties as well as on systems prepared by computer simulation. Establishment of convenient size distributions of nanocrystalline grains via a specific time-temperature treatment derived from information on transition thermodynamics will be correlated with enhancement of magnetic properties in these systems.

Sintering and grain growth in bulk oxidic ceramics

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A relation between particle size and structure of bulk nanoceramics based on alumina or zirconia was studied. The main attention was devoted to the relations between sintering conditions and grain growth. It was established, among others, that in dependence on the technology of preparation the grain size in bulk ceramics was as much as one order larger than the grain size of the initial ceramic powder. Also studied was the influence of ceramic powder particle agglomeration on the final structure of bulk product.

Electrochemical Properties of the Multi Wall Carbon Nanotube Electrode for Secondary Lithium-ion Battery

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In this study, multi wall carbon nanotubes (MWNTs) were synthesis by the chemical vapor deposition (CVD) process, various chemical compounds such as benzene, xylene, cyclohexane, and n-hexane were used for carbon precursor, and ferrocene and thiophene were adopted as catalyst and promoter, respectively. Various microstructures of the MWNTs were obtained. Microstructure of the as grown MWNTs was examined by Raman, HRTEM and FESEM. The MWNTs then mixed with commercial carbon powder were adopted as the electrode of the secondary-ion battery. Cone type half-cell secondary-ion battery was fabricated, and the electrochemical properties of the cell were measured. The influences of the MWNTs synthesized by different precursors and the amount of MWNTs introduced in the electrode on the electrochemical property will be investigated.

Magnetofection: A novel method to enhance retroviral vector gene transduction with magnetic nanoparticles

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Magnetofection is a term to describe an enhancement of gene transfer by magnetic nanoparticle. In this technique, magnetic nanoparticles are first combined with a coating material, which is biologically compatible with retroviral vectors and targeted cells. Then, the coated magnetic nanoparticles are mixed with viral vectors. During the viral transduction, a magnetic field will apply to the vector and targeted cells. The magnetic field can bring the vector to the targeted cells and significantly increase the viral concentration at the targeted site. Subsequently, it could increase the transduction efficiency. We synthesized magnetic nanoparticles of gamma ferric oxide, Fe₂O₃, through a high-yield reduction-oxidation lyothermal method at high temperature under argon gas. Iron pentacarbonyl precursors were reduced to form iron nanoparticles and subsequently oxidized by trimethylamine. We observed a narrow distribution of particle size, 4±0.8 nm by high-resolution transmission electron microscopy (HRTEM) analysis. Following the synthesis of magnetic nanoparticles, we coated the particles with polyethyleneimine (PEI) via sonication. The size of PEI coated particles were between 100 to 200 nm as determined by HRTEM. Finally, we combined the PEI coated particles with Moloney leukemia virus based retroviral vector to form a retroviral vector with magnetic nanoparticles. The correlation of physical properties and biological activities of magnetic nanoparticle coated retroviral vectors will be presented.

Characterization of noble metal alloy nanoparticles prepared by ultrasound irradiation

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Colloidal bimetallic nanoparticles were made from solutions containing two kinds of noble metal ions by ultrasound irradiation (200kHz, 4.2W/cm²), which is a novel technique to prepare nanostructured metal materials being applicable to various industrial fields. In this study, argon-saturated aqueous solutions including Au³⁺/Pd²⁺ and Au³⁺/Pt⁴⁺ ions were sonochemically reduced in the presence of surfactants (SDS or PEG-MS). The obtained nanoparticles were examined by UV-vis spectra, XRD, TEM, HRTEM, EDX and ¹⁹⁷Au Moessbauer spectroscopy. It was found that the prepared nanoparticles assumed three-types of morphologies which were a core-shell structure, a random alloy structure and a mixture of monometallic nanoparticles with changing additives of the surfactants. The ¹⁹⁷Au Moessbauer spectroscopy clearly indicated different electronic structures of Au atoms of the alloy nanoparticles from the bulk, which accounted for a specific character of the nanoparticles.

Mechanical properties of ZrO₂-Al₂O₃ nanostructured PVD coatings evaluated by nanoindentation

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ZrO₂-Al₂O₃ thin nanostructured coatings and stabilised ZrO₂-Y₂O₃ coatings have been deposited by magnetron sputtering in rotating mode with two metallic targets in order to stabilise at room temperature the high temperature phases of zirconia. The structural studies were made by X-Ray Diffraction (XRD) and for coatings with a content of 2wt% of Al₂O₃ the tetragonal phase can't be stabilised. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to characterise the coatings morphology and microstructure. The mechanical behavior of ZrO₂-Al₂O₃ thin films under point loading conditions was studied by nanoindentation using Berkovich indenter with 130 nm tip radius. Low load tests were used to study the effect of the deposition parameters on the hardness and elastic modulus of coatings. High peak load tests were used to estimate the film adhesion to steel substrates. The hardness of the films reaches 15.3 GPa for a ZrO₂-Al₂O₃ nanostructured coating with higher thickness bilayer period. No delamination of the films from substrate was observed for 120 mN peak load. The residual stresses were also determined using the Stoney equation and the highest compressive residual stress found was about -3 GPa for the sample that has the highest hardness.

Design of PVD ceramic coatings using nanostructure concept

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Advanced nanocomposite and multilayered ceramic coatings are commonly used as mechanical, protective, decorative and optical coatings in several industrial applications. The functionality and reliability of functional coated components are strongly related to the thermo-mechanical and physical properties as well residual stresses in the thin films and coatings. Nanostructures concepts and nanoscaled coating architecture would be a unique way of tailoring novel coating properties. As the grain size decreases to the nanometer range, there is a significant increase in the volume fraction of grain boundaries or interfaces. A nanostructured crystalline material is one in which the spacing between lattice defects approaches inter-atomic distances. These characteristics strongly influence the chemical and physical properties of the material. Physical Vapor Deposition (PVD) techniques, in particular reactive magnetron sputtering are suitable technologies to deposit multilayered coatings using nanostructured approaches (the coating is composed of several bilayers with individual thicknesses of a few nanometers). The paper will discuss a brief overview of nanolayers concepts and nanoscaled coating architecture, properties of ceramic coatings, structural stability study of zirconia coatings, properties of solar selective layers and graded approach for achieving high spectral selectivity. Some examples will be discussed in this contribution, namely ZrO₂-based nanostructured coatings, Ti-TiNyOx and Cr-Cr₂O₃ nano-graded thin films used in energy systems. These films were deposited by DC reactive magnetron sputtering technique. Zirconia-Alumina (ZrO₂/Al₂O₃) nanolayered thin coatings are a new method to stabilize the zirconia high temperature tetragonal phase at room temperature. ZrO₂/Al₂O₃ transformation-toughening nanolaminates were prepared by reactive magnetron sputtering. In this contribution we study the structural properties of ZrO₂/Al₂O₃ nanolayered coatings. Ti-TiNyOx and Cr-Cr₂O₃ films deposited as graded nanolayers

present good, durable and reproducible selective solar absorber surfaces, for high efficiency photothermal conversion.. The films were prepared with a decreased gradient of metal concentration, from the substrate to the surface. For films based on Chromium, the optimum film selectivity achieved was a solar absorptance of 94% and a thermal emittance of 6%, at 82 degrees. For Titanium based films, the best selectivity achieved was a solar absorptance of 91% and a thermal emittance of 4%. The microstructure and thickness of the produced coatings were studied by scanning electron microscopy (SEM). The surface microtopography was analysed by atomic force microscopy (A.F.M.). The X-ray diffraction measurements were used to characterize the film crystallographic structure and to study the influence of nanolayer thicknesses on the phase stabilization.

Mechanical properties of ZrO₂-Al₂O₃ nanostructured PVD coatings evaluated by nanoindentation

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ZrO₂-Al₂O₃ thin nanostructured coatings and stabilised ZrO₂-Y₂O₃ coatings have been deposited by magnetron sputtering in rotating mode with two metallic targets in order to stabilise at room temperature the high temperature phases of zirconia.

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The residual stresses were also determined using the Stoney equation and the highest compressive residual stress found was about -3 GPa for the sample that has the highest hardness.

Low temperature Heat-Treatment of Magnetic Iron-Based Nanoparticles Produced by Chemical Vapor Condensation

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In recent years, much attention has been paid to synthesize and investigate nanoparticles, because of wide range of their potential applications. Magnetic nanoparticles have special characteristic of exhibiting single-domain magnetism and can be used in magnetic tapes, ferrofluid, magnetic refrigerants, etc. In this study, we synthesized iron nanoparticles by CVC process using iron pentacarbonyl as a precursor under Ar or He atmosphere. The spherical nanoparticles of the mean diameter of 6-25nm comprise of the metal core and oxide shell. Average particle size increases and size distribution becomes wider and more asymmetric with increasing the decomposition temperature of precursor. Particles produced by CVC have larger size if argon as carrier gas was used. The measured values of lattice constant for as-prepared nanoparticles are larger than that of pure iron and increase with decreasing particle size. Such dependence of lattice constant on average particle size can be explained by the epitaxial growth of oxide shells with a lattice misfit of about 3%, which leads to compressive stresses induced in oxide shell and tensile stresses in metallic core, and causes increasing lattice constant in oxide-coated nanoparticles. To achieve a slow growth of oxide shells, the low temperature heat treatment was carried out in a flow atmosphere of argon contained about 0.0001 vol.% of oxygen. During low temperature heat treatment of iron nanoparticles the drastic decreasing of lattice constant of iron and the increasing saturation magnetization of nanoparticles are observed. The main reasons for those phenomena are the formation of defect structure in the oxide-metal phase interface by oxide film growth, and relaxation of internal stresses. So, the low-temperature heat treatment can be the way to improve magnetic properties of oxide-coated iron nanoparticles.

Research on Nanosciences and Nanotechnologies within the European Union's 6th Framework Programme

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The European Union's 6th Framework Programme for Research and Technological Development (FP6) gives particular emphasis to exploring the “nano-world”. The FP6 area “Nanotechnologies and nanosciences, knowledge-based multifunctional materials and new production processes and devices” will host most of the research, that however may well be carried out also within other FP6 funding chapters in view of the multi-disciplinarity required, the great potential and the many challenges. Funding will be allocated through open calls for proposals, announced also on the web.

Support to “nano-research” was already granted in previous framework programmes, but with much less intensity. In the 4th Framework Programme (1994-1998), some 80 projects involving nanotechnology were funded. With the 5th Framework Programme, (1998-2002) the estimated funding level was about 45 M[€]/year and the European Commission counts today a significant portfolio of nanoscience and nanotechnology projects. This overall project portfolio is very wide in scope, encompassing for example nano-electronic devices, giant magneto-resistance, carbon nanotubes, bio-sensors, molecular diagnostics, nano-composite materials, atomic force microscopes, etc.

The importance of the command at the nano-scale has meanwhile raised and its great potential is more and more evident. A twofold transition is aimed at: a knowledge-based society and a sustainable development. New paradigms of production and new concepts of product-services are demanded. There is a need to move from resource-based approaches towards more knowledge-based ones, from quantity to quality, and from mass produced single-use products to higher added value, eco-efficient and customer-oriented products, processes and services. Nanotechnology is a very powerful tool for these purposes.

Long-term, ambitious research is needed. Universities as well as research centres are called to play a new, often leading role in collaboration with industries. In particular, there is a strong demand for further helping small and medium enterprises to implement new technologies throughout the value-chain.

Integrated research activities with structuring and longer-lasting effects are key factors to support transformation of the European industry in order to cope with the Union's objectives such as those formulated in Lisbon, Goteborg and Barcelona, and in view of the accession of the Candidate Countries in the European Union.

This text does not represent any commitment on behalf of the European Commission. Please refer to official documents. See, e.g.: <http://www.cordis.lu/fp6>; http://europa.eu.int/comm/research/fp6/index_en.html; <http://www.cordis.lu/nanotechnology>

Assembly & Engineering of Nano-Particles for Functional Nanocomposites

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Nanoparticles are most common building blocks in several applications of Nanotechnology. Beside, the enormous increase of their surface area, the high surface to volume ratio of the nanoparticles results in extraordinary high reactivity, and unusual physical properties (optical, magnetic, etc.). Several types of nano-structures (nanoparticles, nano-wires and nano-rods) can be fabricated. Dispersed nanoparticles are used in several important applications, e.g., catalysis, biomedical applications, nanocoatings and nanocomposites. Nanostructured materials, prepared by consolidating nanoparticles with a very high density of grain boundary, have shown to have dramatically improved mechanical and physical properties. More recently, other nano particulates (nanowires, nano-rods, and nano-tubes) have been synthesized. First generations nanoparticles consisted of mostly spherical morphology with complex yet often homogeneous composition and structure. Next generation nanoparticles with distinct core-shell structure can be fabricated with different core and shell composition, e.g., metallic core and oxide shell or the reverse. The selection of the composition and structure of the shell layer allows different chemistries to be conducted at the surfaces, e.g., inducing biocompatibility, enhanced electrical conductivity, or chemical reactivity. Template assisted synthesis allows the engineering and fabrication of several types of nano-structures. Different nano structures can be used for the fabrication of high hierarchical structures through self-assembly. These structures can be made of composites with controlled composition. Careful control of the chemistries at the surfaces of the particles and substrate makes it possible to achieve a spontaneous self-positional organization of the particles on the substrate to form stable 2D and 3D structures and nanocomposites. A short presentation of some recent results from our studies on these systems will be given. Examples include PMMA nanocomposites for radar absorption, magnetic nanoparticles for biomedical applications, nanocomposite light structural applications, advanced nanoceramic coatings for deformation, damage and environmental resistance.

Construction and Characterization of the Multilayer Assembly of Gold Nanoclusters Covered with Functional self-assembled Monolayers

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Multilayers of Gold Nanoclusters (GNCs), which were covered with self-assembled Monolayers of functional alkylthiols, were constructed on various substrates including gold and ITO by wet processes. Several techniques were employed for the multilayer construction. For example, gold nanoclusters covered with the SAM of carboxylate group can be deposited by utilizing electrostatic interaction with cationic polymer. Optical and electrochemical properties of these multilayers were investigated. The multilayers of the GNCs covered with SAM of ferrocene group, which is a one electron redox species, showed all the ferrocene groups within the multilayer were electroactive, showing electrons are transferred through GNC core. Possible application of this system will be described.

Building and Characterization of Organized Architectures of Carbon Nanotubes

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After one decade of extensive investigation carbon nanotubes and the nano- and micro-structures tailored from them still remain one of the most interesting and challenging structures in nanotechnology. This fact is a consequence of the lack of full knowledge of the physical and chemical properties of these systems, and the lack of well-defined macroscale samples. In this talk I will talk about our efforts and results on directed assembly of multiwalled carbon nanotubes on planar substrates into highly organized structures that include vertically and horizontally oriented arrays, ordered fibers and porous membranes. The concept of growing such architectures is based on growth selectivity on certain surfaces compared to others. Growth of nanotubes is achieved by chemical vapor deposition (CVD) using hydrocarbon precursors and vapor phase catalyst delivery. The new technique allows flexibility in building a large number of complex structures based on nanotube building units. I will also discuss various recent efforts of us in creating controllably specific nanotube structures for pores, junctions and other predefined shapes showing the feasibility towards some for the proposed applications. In the second part of the talk I will summarize our results on characterization of the transport properties of carbon nanotubes, namely electro-migration tests, potential mapping of horizontal and vertical nanotube interconnects, current (distribution) measurements on horizontal and vertical nanotube structures, heat conductivity measurements on bulk nanotube samples, and electronic noise characteristics.

Superhard and Functional Nanocomposites Formed by Self-Organization in comparison with Hardening of Coatings by Energetic Ion Bombardment During their Deposition.

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Since the publication of our generic concept for the design of novel superhard nanocomposites [1,2] the preparation and properties of a number of superhard and functional nanocomposites of a different composition were prepared and investigated. The nc-(Ti_{1-x}Al_x)N/a-Si₃N₄ nanocomposite coatings for wear protection of machining tools for dry and fast cutting as well as the new coating technology needed for their large scale industrial production were successfully developed and introduced on the market [3]. A variety of hard functional nanocomposites with a low coefficient of friction were prepared and tested for various applications, such as lubricant-free bearings and others. I shall briefly summarize the present state-of-the art of this field on the basis of results published by several groups.

The second part of the talk will deal with the present status of our understanding of the formation of such thermally very stable ($\geq 1100^\circ\text{C}$), hard and superhard nanostructures by self-organization as a result of thermodynamically driven spinodal phase segregation. I shall also discuss the recent progress in the understanding of the extraordinary combination of their mechanical properties, such as high hardness of 40-100 GPa combined with a high elastic recovery of 80-95 % and a high resistance against brittle failure by catastrophic crack initiation and propagation [4]. The tensile strength of the super- and ultrahard nanocomposites prepared in this way reaches 10-40 GPa, i. e. it is approaching the ideal cohesive strength of strong solids [6]. These properties can be relatively easily understood in terms of conventional fracture physics scaled down to crystallite size of few nanometers and accounting for the critical activation volume needed for the initiation of plastic deformation and structural transitions.

The last part of my talk will be devoted to the so called "nanocomposites" consisting of a hard transition metal nitride and a soft, ductile metal which does not form any stable nitride, e. g. ZrN/Ni, Cr₂N/Ni, ZrN/Cu, TiN/Cu and many others [7]. It was shown recently [8] that the hardness enhancement in such coatings is due to the energetic ion bombardment during their deposition as found and reported for a number of ordinary hard coatings in the past (for the relevant references see [2,9]) and not to any nanostructure effect. This limits the stability of their hardness to 400-600°C although no recrystallization or other structural reconstructions are observed upon such annealing.

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Structural and optical properties of Eu³⁺:HfO₂ nanothick sol-gel waveguiding films

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HfO₂ is a high index, low absorption material used in particular for coatings in the near UV to IR regions. Moreover, hafnium dioxide presents a high crystalline density (9.68) that makes it attractive for host lattice activated by rare earths for applications as scintillating materials [1]. Eu³⁺ doped HfO₂ films are elaborated using sol gel process. Chemical and physical procedures are described to obtain low attenuation and nanothick waveguides. The chemical precursors are hafnium tetra-ethoxide and europium nitrate pentahydrate. The spectroscopic and optical properties of the films strongly depend on structure of the material. This presentation is devoted to the study of the nanostructural evolutions of the layers with annealing temperature and doping concentration. The nanostructural features are investigated mainly by waveguide Raman spectroscopy [2] and transmission electron microscopy. Waveguide Raman spectroscopy is also used to know the nanocrystalites size of films in the very low frequency range [2]. Optogeometric properties are investigated by m-lines microscopy. The results of luminescence studies are finally presented. [1] Van Eijk C W E, Nucl. Instrum. Methods A 460 (2001) 1-14. [2] Le Luyer-Urlacher C., Mugnier J., Recent Res. Devel. Raman Spectroscopy, 1 (2002) 65-81.

Nanotube-Reinforced Composite Materials for Multi-Functional Applications

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The objective of this program is to design, develop and characterize multi-functional composites reinforced with single wall carbon nanotubes. Carbon nanotubes are known for their intriguing mechanical, electrical and thermal properties. However, many researchers have tried directly mixing nanotubes in epoxy without much success in achieving the expected properties, due to weak interfacial bonding, difficulty in uniform dispersion, roping of nanotubes in epoxy. We take a different approach where nanotubes are processed to create buckypapers, which are then used as preforms in making composites. In addition, we have succeeded in aligning nanotubes in suspension under magnetic forces before the buckypaper is formed. The initial results are encouraging: 1) storage modulus has increased by 430%, and 2) buckypapers of aligned nanotubes showed a 5:1 anisotropy ratio. In our presentation, we will discuss the processing steps of buckypapers and magnetic alignment of nanotubes. Potential applications will also be discussed.

New amino-modified silica coated magnetic nanoparticles for efficient gene delivery

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We have developed a novel method for efficient gene delivery using amino-modified silica coated magnetic nanoparticles. The positively charged amino-modified silica coated magnetic nanoparticles have been directly prepared using the synchronous hydrolysis of tetraethoxysilane and N-(α -aminoethyl)- α -aminopropyltriethoxysilane in water-in-oil microemulsion after the synthesis of aqueous magnetic ferrofluid with the precipitation of the chloride mixture with the base. Plasmid DNA can be easily combined onto the positively charged nanoparticle surface to form Nanoparticles-plasmid DNA complexes. The combined plasmid DNA was effectively protected from enzymatic digestion of DNaseI. And the nanoparticles-plasmid DNA complexes can successfully cross various systemic barriers to COS-7 cells as well as mediate high expression of Green Fluorescence Protein (GFP) gene in cells by use of this new amino-modified silica coated magnetic nanoparticles as gene delivery. In comparison with the liposome gene carrier, it shows high transfection efficiency. It would provide a new technology and measure for gene expression, function research and gene therapy.

Adsorption Properties of Oxygen, Nitrogen, and Argon on Single-Walled Carbon Nanotube Bundles

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Carbon nanotubes (CNTs) have nanostructured size and large surface area that can provide excellent absorption behaviors to gases. In this study, adsorption properties of O₂, N₂ and Ar on HiPco Single-walled carbon nanotube bundles (SWCNTs) were investigated by using piezoelectric quartz crystal microbalance (PQCM) and temperature programmed desorption (TPD). A SWCNTs-coated PQCM was used to measure the adsorption isotherms for these gases on SWCNTs at temperatures between 300 and 343 K. From these adsorption isotherms, the isosteric heat of adsorption (q_{st}) was determined and, from this quantity, the binding energy was obtained. To reveal the adsorption activation energies (E_d) of these gases on SWCNTs, TPD tests were also conducted at heating rates between 10 oC /min to 30 oC /min from room temperature to 500oC. Results of PQCM tests show that the binding energies of O₂, N₂ and Ar on SWCNTs obtained were 155, 147 and 141meV, respectively, which are larger by approximately 41-52% on the SWCNTs samples than the values found for the same adsorbents on planar graphite. TPD tests revealed that the larger heating rate, the higher temperature at which maximum desorption rate occurred. These temperatures of maximum desorption for all the tests are below 200 oC. In addition, according to the relation of these temperatures and heating rates, the value of E_d could be obtained. The E_d of O₂, N₂ and Ar on SWCNTs obtained are 209, 192, and 190meV, respectively. These values are very close to the q_{st} obtained from PQCM tests, which are 210, 203, and 197 meV for O₂, N₂ and Ar, respectively. This indicates the adsorption phenomenon of SWCNTs to these gases is categorized in physical adsorption.

Synthesis of Si-B alloy nanowire junctions

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Control of doping level in semiconducting nanowire/nanojunctions is highly demanded for nanoelectronic, photovoltaic, and thermoelectric device applications. One of candidate materials for the applications is boron-silicon alloy due to its thermal and electrical properties, depending on doping level. It is highly conducting, has a high carrier mobility and high microhardness, and is readily oxidized to form a highly insulating compound without using acids or other exotic oxidizing agents. In a recent research, we have grown nanowire junctions of boron-silicon alloys in two different configurations. One is to fuse two nanowires together during their growth and the other, to evaporate SiO_x beads on the nanowires placed nearby or cross each other. We will present a possible growth mechanism of these nanowire junctions and characterization of their physical properties using many techniques including SEM/EDS, XRD, TEM, SPM, and electrical transport measurement.

The relation of the magnetoresistance and magnetic frustration among ferromagnetic clusters in $\text{La}(\text{Mn}_{1-x}\text{Ni}_x)\text{O}_3$

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Colossal magnetoresistance (CMR) properties of $\text{La}(\text{Mn}_{1-x}\text{Ni}_x)\text{O}_3$ ($0 < x < 0.1$) is investigated. The partial replacement of Mn^{3+} by Ni^{2+} causes the conversion of Mn^{3+} to Mn^{4+} . However, the CMR effect of the manganites with excess oxygen decreases as the Ni amount is increased. The samples were prepared both in air and in oxygen atmosphere in order to change the Mn^{4+} ratio. The concentration of Mn^{4+} was determined quantitatively by iodometric titration. We measured the temperature dependence of magnetization after cooling the sample in zero field (ZFC) or in the field (FC). According to the temperature dependence of coercive field and thermoremanent magnetization, a cluster glass like transition is presumed. We propose that the frustration of the interaction among ferromagnetic clusters introduced by substituting Ni for Mn causes the decrease and increase of the magnetoresistance.

Lattice Dynamics of Silicon bulk and Nanowire

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The lattice dynamics of Si bulk and nanowires is investigated using molecular dynamics simulations in a temperature range from 100K to 1000K. The simulations show that the surface scattering in nanowires causes the heat flux autocorrelation to decay dramatically faster compared to that of bulk, and thus significantly decreases the conductivity. The predicted thermal conductivity as a function of materials dimension and temperature is consistent with the experimental result. Interestingly, the simple thermal conductivity function derived from the classical gas kinetic theory holds for nanowires within the simulation framework. That is, change in thermal conductivity with varied materials dimension can be attributed to change in the phonon collision relaxation time and the size effect remarkably overplays temperature effect while the phonon speed remains constant.

An investigation of local structure of alumina-zirconia solid solution via XAFS and HRTEM

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According to the phase diagram of alumina-zirconia system, the largest solid solubility of alumina in zirconia is lower than 7 mol % even if it is annealed at high-temperature. However, our previous research showed that alumina-zirconia solid solution containing 33 mol % alumina can be synthesized by laser ablation. In this paper, the effects of composition and particle size on local structure of alumina doped zirconia will be reported. XRD and TEM were employed to measure phase composition and particle morphology, HRTEM was used to obtain microstructural information and Zr-K edge XAFS spectra were used to obtain the information of local structure like coordination numbers and interatomic distances of Zr-O and Zr-Zr coordination pairs.

Highly Ordered Semiconductor Nanodot Arrays on Silicon using Ultra-thin Alumina Membranes as Masks

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Highly ordered semiconductor nanodot arrays, such as cadmium sulphide (CdS) and cadmium selenide (CdSe), have been successfully fabricated on silicon substrates with and without an overlying oxide layer. The nanodot arrays were prepared using ultra-thin porous alumina membranes as masks in the evaporation process. The size of the nanoparticles can be adjusted from about 10 nm to 200 nm while the spacing between adjacent particles can also be adjusted from several nanometers to about twice the size of the nanodots. The density of the nanodots can be varied from about 10^8 to 10^{11} cm⁻². In addition to controlling the size and the density, the shape of the nanodots can also be freely adjusted by changing the aspect ratio (i.e., diameter of the pore versus the height of the pore) of the apertures of the ultra-thin alumina masks, and the amount of material deposited through the alumina masks. Semiconductor nanodisc arrays, nanohemisphere arrays, nanoellipsoid arrays, and nanopyramid arrays were successfully obtained. Photoluminescence and Raman measurements indicate good optical properties of the CdS and CdSe nanodot arrays. Due to the high regularity of the nanodot arrays and good controllability of the sizes and shapes of the nanodots, the proposed approach can generally be applied for the fabrication of different nanoparticles with controllable shape, size and density. The effects of the shape and size on the optical properties of the CdS and CdSe nanodot arrays are currently under investigation.

Temperature effects on nucleation mechanisms of boron nanowires

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Boron and boron-rich borides have numerous technological applications, particularly where a hard and light material is required. In addition, recent discovery of MgB₂ superconductor is gearing up the miniaturization of boron. In order to scale down the material the nanowires should be synthesized in a controllable way. To date, however, it is not readily applicable to synthesize well-aligned single crystalline boron nanowires. A transition of nucleation mechanism in the formation of boron nanowires has been observed, as the processing temperature varied. A hybrid of the conventional vapor-liquid-solid (VLS) and oxide-assisted (OA) growth mode has been found at high temperatures in the synthesis of boron nanowires when a mixture of boron and boron oxide was used as a vapor source. On the other hand, OA nucleation mechanism was dominated at relatively low temperatures. The single-type boron nanowires were aligned normal to Si substrate at low temperatures, while the aligned bundle-type boron nanowires were formed at high temperatures. Interestingly, Au does not play a catalytic metal, but as a guiding post for aligning each boron nanowire at low temperatures. We report a transition of nucleation mechanism by systematic studies.

Effect of Work of Adhesion on Nanoindentation

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Extended summary Because a large surface-to-volume ratio is a distinctive attribute of a microdynamical structure, adhesion in both microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) has caused great concerns in both scientific and industrial communities. Therefore, a different mechanics, which can be called micro/nano mechanics, is introduced, and micro/nano contact mechanics is one of the main components of this new field. Though continuum adhesion contact mechanics is comparatively clear, a systematic framework for micro/nano contact mechanics is still lacking. Surface effect is very important at micro/nano scales. As a result, it is of importance to consider the effect of work of adhesion between indenter and the tested material on nanoindentation test, since nanohardness is a basic material parameter for the design of MEMS or NEMS. It is noted that a systematic study is still lacking on the effect of work adhesion on nanoindentation test with other kinds of tip shapes (such as Berkovich, cube corner, etc.). This paper analyzes the influence of adhesion energy on the nanoindentation test, and also validates the importance of the adhesion energy through comparison of the JKR (Johnson, Kendall and Roberts), DMT (Derjaguin, Muller and Toporov) and MD (Maugis-Dugdale) models with the Hertz model. With a small applied load, the adhesion energy plays a key role in the contacts and is surely indispensable. The difference between the JKR and DMT models is also discussed and the essence of the difference is brought forward. It is showed that both the JKR and DMT models are the special cases of the MD model: actually, they are each the upper limit and lower limit of the MD model, respectively.

Pseudopotential Theory of Semiconductor Quantum Dots, Wires, and Films

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The electronic structure of nanostructures has almost universally addressed by the "standard model" of effective-mass k - p envelope function approach. While eminently successful for quantum wells, this model breaks down for small structures, in particular, for small dots and wires [1]-[2]. Until recently, it was impractical to test the "standard model" against more general approaches that allow many-band (X - L) coupling. However, it is now possible, due to special tricks [3]-[4], to apply to all-band pseudopotential method to 10³-10⁶ atom nanostructures. This shows (i) how the "standard model" fails, for thin superlattices [2], (ii) how size effect lead to band gaps that differ from what is expected in effective-mass theory (5), (iii) that small dots of III-V materials have an indirect gap that converts to direct above a critical size (6), (iv) how the spectra of CdSe dots evolve from the bulk and how the spectra of dots of Si, GaAs, InP and CdSe compare with experiment, and how the use of pseudopotential wavefunctions leads to very different electron-hole coulomb and exchange energies relative to the "standard model" (7), (vii) how theory predicts the charging spectra and fine-structure of self-assembled InAs/GaAs quantum dots (8). [1.] L.W. Wang, A.J. Williamson, A. Zunger, H. Jiang and J. Singh, "Comparison of the k - p and Direct Diagonalization Approaches to the Electronic Structure of InAs/GaAs Quantum Dots," *App. Phys. Lett.* 76, 339-341 (2000). [2.] Alex Zunger, "On the Farsightedness (hyperopia) of the Standard k - p Model," *Phys. Stat. Solidi* 190(a), 467-475 (2002). [3.] Alex Zunger, "Pseudopotential Theory of Semiconductor Quantum-Dots," *Phys. Stat. Sol.* 224, 727-734 (2001). [4.] A. Zunger, "Electronic Structure Theory of Semiconductor Quantum Dots," *MRS Bulletin Special Issue* 23, 35 (1998). [5.] L.W. Wang and A. Zunger, "High Energy Excitonic Transitions in CdSe Quantum Dots," *J. Phys. Chem. (Letter section)* 102 6449 (1998). [6.] A. Franceschetti and A. Zunger, "Quantum Confinement-induced X transition in GaAs/GaAlAs quantum films, wires and dots," *Phys. Rev. B.* 52, 14,664 (1995). A. Franceschetti and A. Zunger, "Free-standing vs. AlAs-embedded GaAs quantum dots, wires and films: the emergence of zero confinement state," *Appl. Phys. Lett.* 68, 3455--3458 (1996). [7.] A. Franceschetti and A. Zunger, "Direct Pseudopotential Calculation of Exciton Coulomb and Exchange Energies in Semiconductor Quantum Dots," *Physical Review Letters* 78, 915-918 (1997). [8.] S.H. Wei, S.B. Zhang and A. Zunger, "The effects of Ga addition to CuInSe₂ on its electronic, structural and defect properties," *Appl. Phys. Lett.* 72, 3199 (1998). S.H. Wei, A. Zunger, I.H. Choi and P.Y. Yu, "Trends in band gap pressure coefficients in chalcopyrite semiconductors," *Phys. Rev. B. Rapid Communications* 58, R1710 (1998).

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