

# SYMPOSIUM F

## Nanophase and Nanocomposite Materials III

November 29 – December 2, 1999

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\* Invited paper

**8:30 AM \*F1.1**

**SUCCESSFUL STRATEGIES FOR FINDING NICHES FOR THE RARE USEFUL NANOCOMPOSITES: CUTTING TOOLS AND NITRIDE POWDER SYNTHESIS.** Rustum Roy, Evan Pugh  
Professor of the Solid State Emeritus, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

As the earliest champion of nanocomposites one is disappointed that few major developments of materials with radically improved properties have resulted in well over a decade. This paper will examine the relevance of the existence of nanocomposites in nature (specific minerals in special forms) or in technology (many glasses and the entire glass-ceramic industry) to guiding research in finding useful nanocomposites. One key strategy for making useful nanocomposites is the use of microwave radiation for reaction and sintering. Two examples will be described utilizing nanocomposites in the use of microwave radiation for reaction and sintering: (1) by reducing the reaction time by one order of magnitude in WC-Co cutting tools (Agrawal et al.); and (2) by utilizing exothermic reactions in a unique configuration using the Penn State microwave process to make nanophase AlN, TiN, VN etc. (Baidyanathan et al.).

**9:00 AM F1.2**

**MAGNETIC ENTROPY CHANGE OF NANOCOMPOSITES COMPOSED OF A SILVER MATRIX AND GRAINS OF IRON-OXIDE OR -NITRIDE.** T. A. Yamamoto, M. Tanaka, K. Nishimaki, K. Shiomi, T. Nakagawa, M. Katsura, T. Nakayama and K. Nihara, Osaka Univ, Osaka, JAPAN.

Magnetocaloric effect of superparamagnetic nanocomposites composed of iron-oxide or iron-nitride grains dispersed in a silver matrix was studied by calculating magnetic entropy change  $\Delta S$  induced by a change in magnetic field  $H$  applied to the material. These nanocomposites were synthesized by the inert gas condensation technique and nitridation by heat treatment in an ammonia gas stream. Average sizes of the iron-containing grains were 10-30 nm. Magnetic phases in the materials were  $Fe_3O_4$  or  $\gamma-Fe_2O_3$  for the oxide-composites and  $\gamma-Fe_4N$  or  $\epsilon-Fe_3N$  for the nitride-composites. The superparamagnetism was confirmed typically in a temperature range from room temperature to 150 K. Values of the  $\Delta S$  were obtained by applying a thermodynamic Maxwell's relation,  $(\partial S/\partial H)_T = (\partial M/\partial T)_H$ , to data set of magnetization  $M$  measured at various temperatures  $T$ . These results clearly indicated significant enhancement due to the nanostructure as predicted. The values of the  $\Delta S$  were investigated by comparing their dependencies on temperature and magnetic field with those given by the Langevin's superparamagnetism, which showed a fair agreement in a nanocomposite with 9%-Fe while a considerable disagreement in another one with 50%-Fe.

**9:15 AM F1.3**

**NEW OPPORTUNITIES FOR NANOCOMPOSITES.** Amit Singhal, Ganesh Skandan, Nanopowder Enterprises Inc., Piscataway, NJ; Harald Eifert, Don Kupp, Fraunhofer Resource Center Delaware, Newark, DE; Glenn Amatucci, Telcordia Technologies, Red Bank, NJ; Bernard Kear, Rutgers-The State University of New Jersey, Piscataway, NJ.

With the growing interest in nanopowders and nanostructured materials, established technologies are beginning to use nanopowders instead of coarser particles, and new applications are evolving that exploit the unique properties of nanocrystalline materials. In particular, novel applications are emerging for the use of nanoparticle dispersions as a second phase. The matrix containing the nanoparticles can be either a liquid, polymer, metal or a ceramic. However, the morphology of the dispersed phase is not the same in different applications. For example, in the area of chemical mechanical polishing, the 'aggregate' particle size in the liquid medium has to be tailored into the nanoscale. On the other hand, for intrinsic electrical conductivity in polymers and in Li-ion rechargeable battery electrodes, the primary nanoparticles need to be processed so as to deliberately form micron size aggregates with an open structure (fractal morphology). The aggregated nanoparticles are then dispersed in a polymer matrix. Processing issues in the applications mentioned above, and the corresponding properties and performance of these 'novel' nanocomposites will be discussed.

**9:30 AM F1.4**

**INFLUENCE OF PARTICLE POSITION AND THERMAL RESIDUAL STRESSES ON ABRASIVE WEAR OF ALUMINA/SiC NANOCOMPOSITES.** J.L. Ortiz Merino, R.I. Todd, University of Oxford, Department of Materials, Oxford, UNITED KINGDOM; A.J.

Winn, Manchester Materials Science Centre, Manchester, UNITED KINGDOM.

Alumina/SiC nanocomposites consist of alumina grains of conventional size (a few  $\mu m$ ), containing a dispersion of SiC 'nanoparticles' (<300nm). The nanocomposites have improved mechanical and tribological properties compared to unreinforced alumina. This paper shows that the abrasive wear rate of alumina-based nanocomposites can be reduced by a factor of three or more compared to unreinforced alumina of the same grain size. The improvements were the result of the suppression of surface grain pullout on the addition of the nanoparticles. Correlation of the response to abrasion with systematic changes in microstructure and thermal residual stress showed that it was the nanoparticles situated on the alumina grain boundaries which were responsible for reduction of grain pullout, and that the effect was most pronounced for systems in which the thermal residual stresses were highly compressive in the particles. These conclusions were supported by modelling of the fracture process, which showed that the compressive radial stresses around the nanoparticles could cause significant local toughening of the grain boundaries.

**9:45 AM F1.5**

**RESIDUAL STRESS AND SUBSURFACE MICROSTRUCTURE INVESTIGATION FOR GROUND AND POLISHED ALUMINA/SILICON CARBIDE NANOCOMPOSITE AND MONOLITHIC ALUMINA CERAMICS.** H.Z. Wu, S.G. Roberts, Department of Materials, University of Oxford, Oxford, UK; A.J. Winn, B. Derby, Manchester Materials Science Centre, UMIST, Manchester, UK.

Surface residual stresses induced by grinding and polishing in alumina/silicon carbide nanocomposite and monolithic alumina have been investigated by Hertzian indentation and fluorescence spectroscopy. Specimens were ground and then polished with diamond slurry with grit size ranging between 8  $\mu m$  and 1  $\mu m$ . The results show that the surface residual stress state in the nanocomposites is more sensitive to surface treatment than that in the monolithic alumina. Surfaces of both ceramics were examined in cross-section by TEM so as to make direct observation of the plastic deformation induced by the surface treatments. There is a change in the predominant deformation micromechanism from twinning in the alumina to dislocation generation in the nanocomposites.

**10:30 AM \*F1.6**

**PREPARATION AND FUNCTIONALITY OF NANOCOMPOSITE FILMS COMPOSED OF COBALT OXIDE ULTRAFINE PARTICLES.** Naoto Koshizaki, Takeshi Sasaki, Quan Li, Nat. Inst. Mater. Chem. Res., Tsukuba, JAPAN.

Nanocomposites that consist of oxide nanoparticles dispersed in other oxide matrices would have a great potential for a new type of functional materials, because various kinds of functional oxides can be combined to create novel functionalities. One of the examples for such functional nanocomposites is a CoO/SiO<sub>2</sub> nanocomposite that has been developed in our group. The nanocomposite structure plays an important role in the reversible optical transmittance change observed by gas atmospheric change from air to nitrogen oxide. However, most of combinations for oxide/oxide composites are easy to form compounds or solid solutions, which resulted in the unavailability of various nanocomposite structures and the difficulty in controlling their nanostructure, as in the CoO/SiO<sub>2</sub> nanocomposite system. In this paper, the ArF excimer laser ablation technique to obtain mono-dispersive crystalline oxide nanoparticles not under island structure formation scheme at the initial stage of film growth but under inert gas condensation scheme is discussed. The effects of preparation condition on the size, morphology and crystallinity of nanoparticles and nanoparticle-aggregated films were extensively studied mainly for cobalt oxide. Utilizing the suitable nanoparticle preparation conditions, we can obtain nanoparticle-aggregated films that can be crystallized at comparably lower temperature than those obtained by the conventional method. The preparation of nanocomposite films with the material combinations that cannot be obtained by simultaneous deposition method becomes also possible by alternate deposition technique. The structural characterization of these films in comparison with nanoparticle preparation conditions will be described.

**11:00 AM F1.7**

**THERMITE REACTIONS IN Al/CuO<sub>x</sub> NANOLAMINATE FOILS.** Kerri J. Blobaum, Michael E. Reiss, Tim P. Weihs, The Johns Hopkins Univ., Dept. of Materials Science & Eng., Baltimore, MD.

In a typical thermite reaction, Al powder is used to reduce Fe<sub>2</sub>O<sub>3</sub> powder and the heat released during the reaction is sufficient to melt the resulting Fe product. This reaction has been used to join materials for nearly 100 years, but it is not yet well understood. Here,

we consider a similar reaction between Al and  $\text{CuO}_x$  in nanolaminate foils which provide a unique opportunity to study thermite reactions in a simple and controlled sample geometry. The foils are sputter deposited at ambient temperature and they contain many alternating nanoscale layers of Al and  $\text{CuO}_x$ ; the total foil thickness is on the order of tens of microns. The thermite reactions are easily ignited at room temperature and self-propagate very rapidly down the foils. We will present reaction velocities measured using an optical technique and heats of reaction quantified using differential scanning calorimetry (DSC). We will also isolate and identify intermediate reaction phases with quenching experiments and X-ray diffraction and transmission electron microscopy. Based on these measurements, we will present insights into the diffusion mechanisms and reaction kinetics of thermite reactions in these nanostructured materials. We will also highlight potential applications, including the joining of microscale circuit board components that are too small to facilitate the use of powders.

#### 11:15 AM F1.8

**PULSED LASER DEPOSITION OF GALLIUM ARSENIDE NANOSTRUCTURES AND THIN FILMS BY A COPPER-VAPOR LASER.** Long Dinh, S. Hayes, C. Saw, W. McLean II, M. Balooch, Lawrence Livermore National Laboratory, Livermore, CA; J.A. Reimer, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA.

The properties of GaAs nanoclusters and films deposited on substrates by a Cu-vapor laser were investigated. Nanoclusters of GaAs were produced by laser ablating a GaAs target in an Ar background gas. X-ray diffraction and transmission electron microscopy revealed that these GaAs nanoclusters had randomly oriented crystalline cores and As rich amorphous oxide outer shells. These clusters assembled, upon vacuum annealing, along step edges and at defects on substrates to form wire like structures. Our results also showed that GaAs films deposited in vacuum were not crystalline and rich in As. Post-deposition annealing in vacuum to between 400C and 500C drove off the excess As. The stoichiometry of the films was confirmed by both Auger electron spectroscopy and x-ray photoelectron spectroscopy.

#### 11:30 AM F1.9

**THE MICROSTRUCTURE AND PROPERTIES OF FRAMEWORK ZIRCONIUM PHOSPHATES BASED NANOCOMPOSITES-CATALYSTS OF ALKANES ISOMERIZATION.**

Vladislav A. Sadykov, S.N. Pavlova, G.V. Zabolotnaya, R.I. Maximovskaya, S.V. Tsybulya, D.I. Kochubei, V.V. Kriventsov, N.M. Ostrovskii, V.K. Duplyakin, V.I. Zaikovskii, E.A. Paukshits, E.B. Burgina, A.M. Volodin, Boreskov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA; M.V. Chaikina, Institute of Solid State Chemistry SB RAS, Novosibirsk, RUSSIA; N.N. Kuznetsova, V.V. Lunin, Lomonosov Moscow State Univ, Moscow, RUSSIA; R. Roy, D.K. Agrawal, Materials Research Lab, The Penn State Univ, University Park, PA.

Nanocomposites comprised of highly dispersed zirconia loaded with tungsta and platinum are known to be among the most promising catalysts of C5-C7 alkanes isomerization. However, their properties strongly depend upon the starting compound -amorphous hydrated zirconia preparation procedure, thus making performance irreproducible. In this work, as alternative to zirconia, nanosized crystalline framework zirconium phosphates synthesized via sol-gel route or mechanochemical activation of the mixture of solid starting salts followed by hydrothermal treatment in the presence of polyethyleneoxide were used. Acid properties of zirconium phosphates were tuned by incorporation of substituting cations (La, Al, B, W) or anions (F) into the lattice at the preparation stage. Nanoparticles/clusters of  $\text{WO}_x$  were introduced either during mechanochemical activation stage or via traditional impregnation route followed by calcination, Pt (up to 0.3%) was supported from hexachloroplatinum solution. XRD, TEM, 31P MAS NMR, EXAFS, UV-VIS, FTIRS, XPS, TPR were used to characterize the nanocomposites structure/microstructure and surface properties. The density of Lewis and Bronsted acid centers and their strength were evaluated using FTIRS of surface hydroxyls and adsorbed CO along with ESR spectroscopy of adsorbed TEMPO nitroxide molecule. Nanocomposites performance in the reactions of pentane and hexane hydroisomerization were characterized both in pulse and flow regimes, and for some systems good performance was demonstrated, while cracking was effectively suppressed. Catalytic properties of nanocomposites were analyzed from the microstructural and mechanistic point of view taking into account distribution of carbocations generation/isomerization and hydrogen transfer functions between spatially separated components. This work is in part supported by the University of Russia Program under Grant No 3514.

#### 11:45 AM F1.10

**MAGNETOPHORETIC ELECTROCHEMICAL DEPOSITION OF**

**NANOCOMPOSITE THIN FILMS.** J.L. Katz and Y. Xing, Department of Chemical Engineering, Johns Hopkins University, Johns Hopkins University, Baltimore, MD; R.C. Cammarata, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD.

A novel magnetophoresis electrochemical deposition method employing a magnetic field gradient during electrodeposition to produce nanocomposites composed of magnetic nanoparticles in a thin films matrix will be discussed. Magnetic iron oxide nanoparticles with a mean size of less than 50 nm are dispersed in an electrolyte solution containing copper sulfate and sulfuric acid. When subjected to a magnetic field gradient, these particles are embedded into a copper thin film as it is being electrodeposited, forming a nanoparticulate composite. With this technique, films containing a large density of nanoparticles have been fabricated with up to 50% particle volume fraction. These nanocomposite films, with inorganic magnetic particles in a conductive metal matrix, are expected to have unusual mechanical, electrical and magnetic properties.

#### SESSION F2: NANOPHASE CERAMICS

Chairs: Horst Hahn and Richard W. Siegel

Monday Afternoon, November 29, 1999

Salon F (M)

#### 1:30 PM \*F2.1

**SYNTHESIS AND CHARACTERIZATION OF NANO-CRYSTALLINE CERAMICS.** Markus Winterer, Thin Films Division, Materials Science Department, Darmstadt University of Technology, Darmstadt, GERMANY.

Nanocrystalline materials are characterized by a large fraction of atoms located in interfaces, i.e. surfaces or grain boundaries. This particular microstructure is the source for heterogeneous disorder and novel properties of these materials. The influence of synthesis methods and parameters on the structure of nanocrystalline zirconia will be presented. EXAFS spectroscopy provides structural information independent of the degree of disorder. Partial pair distribution functions can be extracted by Reverse Monte Carlo Modelling. This is supplemented by complementary methods, XRD, NDP, SEM and TEM providing a consistent picture on crystallinity, crystallographic structure and distribution of dopands in these materials. Structure and microstructure of nanocrystalline ceramics are correlated to the synthesis procedures.

#### 2:00 PM \*F2.2

**THE SYNTHESIS OF NANOCRYSTALLINE CERAMICS BY A NOVEL ELECTROSTATIC SPRAY ASSISTED VAPOR DEPOSITION METHOD** Kwang-Leong Choy, Imperial College of Science, Technology & Medicine, Department of Materials, London, UNITED KINGDOM.

This contribution presents an overview of an emerging cost-effective Electrostatic Spray Assisted Vapor Deposition (ESAVD) process for the synthesis of nanocrystalline oxide and non-oxide ceramics. This process involves spraying atomised charged precursor droplets across an electric field in an open atmosphere to initiate either homogeneous or heterogeneous chemical reactions for the synthesis of either continuous solid films or powder particles. The composition of the material can be controlled by tailoring the chemistry of the precursors. This atomistic deposition method can operate at low processing temperatures and provide high purity materials with structural control at the nanometer scale level. The versatility of ESAVD has led to the deposition of films and powders for a wide range of applications, including electrical, optoelectronics, magnetic, catalytic, structural and functional applications. A comparison between the ESAVD and other conventional vapour processing techniques such as Physical Vapour Deposition and Chemical Vapour Deposition will be made. The application of ESAVD to the production of nanocrystalline ceramics will be reviewed and the benefits of ESAVD will be addressed. The scientific and technological significant of the ESAVD method will be presented. The fundamental aspects of ESAVD including process principle, deposition mechanism, reaction chemistry, thermodynamics/kinetics, and transport phenomena of chemical precursors will be presented. The experimental set up of ESAVD and the influence of various process parameters (e.g. deposition temperature, field strength, chemistry of the precursor, flow rate, deposition time etc) on the structure and properties of the materials will be reviewed. The paper will also include the recent development work of ESAVD technologies based on different heating and aerosol generation methods. The technical viability of this process to be scaled up for large area and large scale production of nanocrystalline films and powder particles will be addressed.

**2:30 PM F2.3**

UNUSUAL PREPARATION OF NANOPHASIC MATERIALS BASED ON STANNIC OXIDE. Georges Denes, Arnaud Gueune, Eva Laou, Stephane Le Huerou, Abdualhafeed Muntasar and Frederic Nicolas, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

Nanophasic stannic oxide SnO<sub>2</sub> is usually prepared by rapid hydrolysis of a tin(IV) salt or an organotin(IV). Tin(IV) oxide is a well known semiconductor with numerous applications. We have identified and studied a novel method for preparing nanocrystalline SnO<sub>2</sub>, and in some cases nanocomposites containing SnO<sub>2</sub> and tin(II) and/or other tin(IV) species. The novelty of the method lies in the fact that it is prepared using a divalent tin material, namely tin(II) fluoride SnF<sub>2</sub>, upon oxidation with a limited amount of hydrogen peroxide. The material obtained contains nanoparticles of SnO<sub>2</sub>·nH<sub>2</sub>O (n = ca. 2), which can be easily dehydrated at moderately high temperature without particle growth, to form a nanoceramic. Particle growth and recrystallization to rutile type SnO<sub>2</sub> is obtained upon heating at higher temperature, to give microceramics. Depending on the H<sub>2</sub>O<sub>2</sub>/SnF<sub>2</sub> ratio in the reaction mixture, nanocomposites of SnO<sub>2</sub> containing divalent and/or tetravalent tin oxide/fluoride are obtained. The preparation and results will be presented.

**2:45 PM F2.4**

A NOVEL METHOD FOR SINTERING NANOPHASE CERAMICS WITHOUT GRAIN GROWTH. I-Wei Chen, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

While very fine powders may initially have a better sinterability, particle coarsening and grain growth usually prevail to prevent obtaining fine grain sizes in the fully dense bodies. Indeed, according to the sintering paradigm established over the last forty years, grain growth is inevitable during final stage sintering, defined as the stage when the density exceeds 90%. To circumvent this problem, high pressure has often been used to promote densification without grain growth. We show here a novel two-step pressureless sintering method which allows complete densification without any grain growth. As a result, fully dense yttrium oxide bodies with a grain size of 60 nm have been obtained. The processing window and the kinetics of growthless sintering suggest important mechanisms that differentiate grain boundary diffusion and grain boundary migration. Evidence for a threshold process for grain boundary diffusion is also manifest. This method has been applied to a number of oxides resulting in nanophase materials.

**3:30 PM \*F2.5**

PREPARATION METHODS AND SUPERPLASTIC PROPERTIES OF FINE-GRAINED SILICA OR ALUMINA DOPED TETRAGONAL ZIRCONIA. Yoshio Sakka, Thoru S. Suzuki, Tetsuo Uchikoshi, Koji Morita and Keijiro Hiraga, National Research Institute for Metals, Tsukuba, JAPAN.

Preliminary studies of fine-grained yttria doped tetragonal zirconia (Y-TZ) and its composites have shown that certain requirements must be met to achieve superplasticity: fine grain size, homogeneous microstructure and the inhibition of grain growth during high-temperature deformation. These requirements are being met both through advances in powder preparation and through novel developments in powder processing, such as colloidal processing. Particle dispersion control is the most important factor in colloidal processing. The dispersion of particles in aqueous suspensions can be stabilized by electrostatic repulsion or electrosteric repulsion. Slurries of tetragonal zirconia, silica-zirconia and alumina-zirconia fine particles were prepared by adjusting the pH value or adding appropriate amounts of polyelectrolyte. Their dense bodies were obtained through colloidal filtration, followed by cold "isostatic" pressing (CIP) and low-temperature sintering. Excellent superplastic properties were observed for Y-TZ, Alumina-doped TZ and Silica-doped systems as a result of dense, fine-grained, and homogeneous microstructures. In particular, large tensile elongation exceeding 990% can be obtained for Alumina doped Y-TZ. Y-TZ with a grain size of 300 nm was successfully prepared by sintering chemically synthesized powder. To obtain a dense Y-TZ with a grain size less than 100 nm, however, a special procedure is necessary. We processed fine-grained (1) monoclinic zirconia polycrystal using a monoclinic zirconia sol prepared by wet processing, and (2) CuO-doped TZ using a Cu-adsorbed Y-TZ suspension, where both suspensions were directly consolidated by pressure filtration without a dry powdering process.

**4:00 PM F2.6**

PREPARATION AND CHARACTERIZATION OF LARGE AREA NANOCRYSTALLINE TiO<sub>2</sub> FILMS FOR SOLID STATE SOLAR CELLS. Krishna C. Mandal, Bryce K. Dille, David Rauh, EIC

Laboratories, Inc., Norwood, MA; O. Savadogo, Materials Engineering Department, Ecole Polytechnique, Montréal, CANADA.

This paper describes a novel large area nanocrystalline titanium dioxide (TiO<sub>2</sub>) film used in fabricating high efficiency photoelectrochemical (PEC) solar cells. The prepared films are highly reproducible and were thoroughly characterized by XRD, EDX, AFM, and XPS methods. These films have been dye-sensitized using a Ru-bipyridyl based dye, and passivated using either tert-butyl pyridine or ammonia. The sensitized and passivated films are then used in fabricating Li-based polymer electrolyte solar cells. The devices demonstrated open-circuit voltages (V<sub>oc</sub>) of ~0.68V, short-circuit current densities (J<sub>sc</sub>) of 13.2 mA/cm<sup>2</sup>, fill factors of 0.72, and conversion efficiencies of 8.62%. The fabrication steps, directed toward large production volumes, included a quality controlled lamination procedure developed at EIC Laboratories, Inc. The results presented in this paper show the highest achieved efficiency obtained so far for a polymer-based nanocrystalline TiO<sub>2</sub> solar cell.

**4:15 PM F2.7**

THE PROCESSING OF NANOSTRUCTURED ZIRCONIUM OXIDE-BASED MATERIALS FOR SOLID ACID CATALYSIS. Michael S. Wong and Jackie Y. Ying, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

Zirconium oxide-based materials have garnered much interest as solid acid catalysts, due to the unusual surface acidic properties of zirconium oxide. The acidic strength and type of acid site of zirconia can be manipulated by adding anionic species to the surface or by combining with a second metal oxide in the bulk. Accordingly, a variety of zirconium oxide-based acid materials have been synthesized in such manner. As the conventional preparation methods involve only the control of (bulk and surface) compositions of these materials, relatively little importance has been placed on the effect of microstructure on surface acidity and acid catalytic activity. Through novel wet chemical techniques, nanostructured zirconia-based composites can be prepared, and the catalytic properties of these acidic materials can be observed. Nanostructured zirconia-based acid catalysts were synthesized through several different methods. Surfactant-mediated processing led to highly porous zirconia acidic composites, such as zirconia-phosphates and zirconia-silicates, that contain tremendous internal surface areas. The pore sizes could be tailored in the range of 2-10 nm diameter by adjusting the length of the surfactant templating molecule and by using auxiliary organics. Hydrothermal processing of sulfated zirconia composites led to nanocrystalline materials that demonstrated enhanced resistance to deactivation from coking, the major problem limiting industrial use of solid acid catalysts. Grain size and crystal phase could be controlled with hydrothermal treatment temperature and with the use of yttria as a second oxide. The preparation of other zirconia composites involved the mutual dispersion of zirconia and the second oxide. Targeted for acidic catalytic applications, these different types of zirconia materials represent the successful engineering of nanostructural features through many processing techniques.

**4:30 PM F2.8**

CONTINUOUS WAVE LASER ACTION FROM LANTHANIDE DOPED NANOALUMINA POWDERS, SYNTHESIS AND PROPERTIES. R.M. Laine, T. Hinklin, S. Rand, and G. Williams, Depts. of Materials Science and Engineering, Chemistry and the Applied Physics Division, University of Michigan, Ann Arbor, MI.

Nanosized d-alumina powders doped with lanthanides can be produced by flame spray pyrolysis (FSP) of very simple, low cost aluminum precursors doped with ceria. This scalable synthesis route produces single crystal nanopowders at > 100 g/h with surface areas of 50-120 m<sup>2</sup>/g. Typical powders consist of homogeneously doped unaggregated single crystals, with particle sizes ranging from 10-30 nm average diameter. Similar micron sized powders are exploited for their cathodoluminescence behavior. By reducing the size of the particles and thus the interparticle cavity, the scattering regime is changed from diffusive to strong scattering causing photon localization. Lasing occurs due the localization within the gain medium. Details concerning the alkoxide chemistry, flame spray pyrolysis, and the lasing behavior of nanosized doped powders will be discussed.

**4:45 PM F2.9**

HIGH SURFACE AREA CERAMIC POWDERS WITH MINIMAL AGGREGATION. Ganesh Skandan, Amit Singhal, Nanopowder Enterprises Inc., Piscataway, NJ; Nick Glumac, Bernard H. Kear, Rutgers-The State University of New Jersey, Piscataway, NJ.

For many applications, it is essential to have high surface area powders that have a narrow primary particle size distribution and a minimum amount of aggregation. We have addressed the challenge to produce such nanopowders at high production rates and an

economical cost, by making use of chemical precursors as starting material, and a low pressure flat flame combustion process to provide the thermochemical energy required to pyrolyze the precursors. The process, called Combustion Flame - Chemical Vapor Condensation (CF-CVC), was used to produce nanopowders of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CoO<sub>x</sub> and others, with a primary particle size of 12 - 25 nm and an average secondary particle size < 100 nm. Process parameters were modified to alter particle characteristics, such as, primary and secondary particle sizes. Results obtained from different characterization techniques, such as TEM, BET, XRD and Small Angle X-ray Scattering (SAXS), will be discussed and correlated with the production process.

### SESSION F3: SOL-GEL AND ORGANIC/INORGANIC NANOCOMPOSITES

Chair: Richard M. Laine  
Tuesday Morning, November 30, 1999  
Salon F (M)

#### 8:30 AM \*F3.1

TRANSPARENT MONOLITHIC TRANSITION METAL ION CONTAINING NANOPHASE AEROGELS. William M. Risen, Jr., Shuang Ji and Xiangjun Hu, Brown University, Department of Chemistry, Providence, RI; David Pickles, Corning, Inc., Corning, NY; Kenneth C. Littrell, IPNS, Argonne National Laboratory, Argonne, NY.

The formation of monolithic and transparent transition metal containing aerogels has been achieved through cooperative interactions of high molecular weight functionalized carbohydrates and silica precursors, which strongly influence the kinetics of gelation. After initial gelation, subsequent modification of the ligating character of the system, coordination of the group VIII metal ions, and supercritical solvent extraction afford the aerogels. The structures at the nanophase level have been probed by photon and electron transmission and neutron scattering techniques to help elucidate the basis for structural integrity together with the small entity sizes that permit transparency in the visible range, and to help understand the chemical reactivities of the metal-containing sites in these very high surface area materials. These results will be discussed in connection with new chemical reaction studies to explore catalytic and gas sensor applications.

#### 9:00 AM F3.2

SOLUTION MINERALIZATION OF ALUMINUM OXIDE ONTO FUNCTIONALIZED ORGANIC MULTILAYER FILMS. Peter J. Stenhouse<sup>1</sup>, Changmo Sung<sup>2</sup>, Tigran Dolukhanyan<sup>2</sup>, Lynne M. Samuelson<sup>1</sup>, Il-Young Kim<sup>1</sup> and Lajos Balogh<sup>3</sup>; <sup>1</sup>US Army SBCCOM, Natick Soldier Center, Natick, MA; <sup>2</sup>Center for Advanced Materials, Department of Chemical Engineering, University of Massachusetts, Lowell, MA; <sup>3</sup>Center for Biologic Nanotechnology, Medical School, University of Michigan, Ann Arbor, MI.

Aluminum oxide crystals were grown onto sulfonate- and carboxylate-functionalized organic templates in solution at low temperatures. Templates were produced by casting multilayer films onto solid substrates. Conditions (template structure, concentration, temperature, mineralization time) were varied so as to optimize crystal size and perfection. Large platelets of alpha-aluminum oxide were produced and characterized by transmission electron microscopy with energy dispersive x-ray spectroscopy and microdiffraction analysis, scanning electron microscopy, and atomic force microscopy. The formation of precursors and various morphologies of alumina particles as a function of processing conditions will be discussed, and the mechanism of crystalline alumina formation onto functionalized organic templates will be suggested based on experimental results.

#### 9:15 AM F3.3

INORGANIC-ORGANIC HYBRID AND COMPOSITE RESIN MATERIALS USING CARBOXYLATE-ALUMOXANES AS FUNCTIONALIZED CROSS-LINKING AGENTS. Cullen T. Vogelson, Simon G. Bott and Andrew R. Barron; Rice University, Houston, TX and University of Houston, TX.

We report that p-hydroxybenzoate or lysine substituted alumoxanes are readily prepared from the reaction of boehmite with the parent acid. The surface hydroxides and amines of these alumoxanes react with epoxides such as the diglycidylether of bisphenol-A (DGEBA) to give a new class of inorganic-organic hybrid material. These same alumoxanes can further be incorporated into commercially available epoxy-resin systems to give a new inorganic-organic composite material with numerous industrial applications. Details of the process will be reported as well as NMR and X-Ray structural studies of model systems. Physical properties of a variety of functionalized alumoxane based composites will be discussed, and their applications in structural materials will be presented.

#### 9:30 AM F3.4

PROTON CONDUCTING ORGANIC/INORGANIC NANOCOMPOSITES POLYMER ELECTROLYTE MEMBRANE THROUGH SOL-GEL PROCESSES. Itaru Honma, H. Nakajima.

High temperature protonic conducting polymer membrane provides new technological applications in the electrochemical devices including electrochromic displays, chemical sensors, fuel cells and others. Organic/inorganic nanocomposites membrane consists of SiO<sub>2</sub>/PEO (Polyethylene Oxides) or SiO<sub>2</sub>/PTMO (polytetramethylene oxides) hybrid are remarkable family of isotropic, flexible, amorphous polymer materials, which has been synthesized through sol-gel processes. The hybrid membrane doped with acidic moieties such as monododecylphosphate or phosphotungstic acid shows good protonic conductivities at high temperatures above 100°C. The protonic conducting membrane was found to be thermally stable at high temperatures because of the inorganic SiO<sub>2</sub> framework in the nanocomposites matrix. In this paper, economic organic/inorganic nanocomposites membrane consists of SiO<sub>2</sub>/PEO as well as SiO<sub>2</sub>/PTMO hybrids has been synthesized through sol-gel processes. The composite membrane can be derived by hydrolysis and condensation reaction of polymer precursors consists of polyethylene oxides endcapped with triethoxysilane and monophenyl-triethoxysilane (Mph). The process is same for PTMO derivatives. The membrane was found to be composed of nanophase composites between inorganics and organics at nm scale. The membrane doped with acidic molecules such as monododecylphosphate (MDP) or phosphotungstic (PWA) shows good protonic conductivities around 0.1 - 1.0 mS/cm at high temperatures up to 160°C and was found to be a flexible as well as thermally stable ionic conducting polymer electrolyte for high temperature electrochemical devices.

#### 9:45 AM F3.5

PREPARATION OF AEROGEL AND XEROGEL NANOCOMPOSITE MATERIALS. Maria Francesca Casula, Anna Corrias, Giorgio Paschina, Cagliari Univ, Dept of Chemical Science, Cagliari, ITALY.

Nanocomposite materials composed of nanometric metal or metal oxide particles embedded in amorphous matrices, present a variety of interesting magnetic, electric and catalytic properties, that are strongly size-dependent. Nanocomposites can be prepared by several techniques such as impregnation, deposition methods and ball milling techniques. The sol-gel process has been also used for the preparation of nanocomposite materials. The process is affected by several parameters which allow a versatile control of the structural, morphological and chemical properties of these materials. In this paper we present the results of the sol-gel preparation of nickel oxide-silica and iron oxide-silica nanocomposite materials using TEOS and either nickel nitrate or iron nitrate as precursors. In order to obtain aerogels with a high surface areas and pore volumes the drying step of the alcogels is performed under supercritical conditions while xerogels, in which the original pore structure of the alcogels is lost, are obtained by slowly removing the solvent. The effects of different drying procedures on the structural and morphological properties of aerogels and xerogels nanocomposites of similar composition heat treated at increasing temperatures are studied using TGA/DTA, BET, XRD and TEM techniques. In nickel containing samples the final aerogel and xerogel nanocomposites are both constituted of nickel oxide nanoparticles dispersed in the silica matrix, the main difference being the different superficial areas as a consequence of the drying procedure. In iron containing samples some stronger differences are observed since xerogels show the presence of a larger percentage of iron oxide in the form of maghemite compared to aerogels.

#### 10:30 AM F3.6

CERAMIC NANOCOMPOSITES AS NEW BUILDING BLOCKS FOR MEMS. Alfredo M. Morales, Marcela Gonzales and Jill M. Hruby, Sandia National Laboratories, Livermore, CA.

Many revolutionary devices and processes in the macroscopic world involve ceramics and composites. In contrast, very few ceramic materials are available for the fabrication of microelectromechanical systems (MEMS). The incorporation of ceramics into microscopic devices would allow the exploitation of novel properties such as increased toughness, high temperature inertness, chemical and biological compatibility, magnetism, piezoelectricity, and photochromism. In this talk, we will present recent results on the use of ceramic nanocomposites in the fabrication of MEMS microcomponents. Our fabrication technique consists of: 1) formulation of a nanocomposite mixture; 2) micromold filling; 3) curing and planarization; 4) chemical removal of the mold. Micromolded components can be produced free standing or assembled on substrates. By using particles with nanometer diameters, we are able to mold components with lateral dimensions in the order of a few

microns. Microscopy studies indicate that molding of submicron size features should be possible with nanocomposites. Government Notice: The submitted manuscript has been authored by a contractor of the United States Government under contract. Accordingly the United States Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for United States Government purposes.

#### 10:45 AM F3.7

MOLECULAR WEIGHT CONTROL IN A POLYMER MONOLAYER FORMED BY A SURFACE INITIATED POLYMERIZATION. Dale L. Huber, and Thomas A. P. Seery, University of Connecticut, Polymer Program, Storrs, CT.

A model nanocomposite consisting of gold nanoparticles coated with a monolayer of poly (hexyl isocyanate) has been prepared through a polymerization reaction initiated at the surfaces of the particles. This polymerization has been studied in real time by infrared spectroscopy to determine the kinetics of the reaction, and this knowledge utilized to prepare nanocomposites with carefully tailored molecular dimension. Dynamic light scattering in conjunction with transmission electron microscopy have been used to characterize the sizes of the resultant nanocomposites, and the measured sizes have been related to scaling predictions for tethered polymers. The polymeric constituent of the prepared nanocomposites has been thoroughly characterized to determine the molecular weight and polydispersity of the surface bound polymer. The properties of the polymer formed at surfaces were then compared to polymers formed through analogous solution polymerizations.

#### 11:00 AM F3.8

SURFACE METALLIZED COMPOSITE POLYIMIDE FILMS VIA IN SITU REDUCTION OF SILVER(I) BETA-DIKETONATE COMPLEXES IN THERMALLY CURING POLY(AMIC ACID)S. Robin E. Southward, National Research Council, Langley Research Center, NASA, Hampton, VA; David W. Thompson, Department of Chemistry, The College of William and Mary, Williamsburg, VA.

The fabrication of optical mirrors with polymeric rather than glass supports can reduce weight and fragility. Silver is a metal of choice for a reflecting surface. Here we report that thermal curing of a silver(I)-beta-diketonate-containing poly(amic acid) formed from 3,3',4,4'-biphenyltetracarboxylic dianhydride, BTDA, and 4,4'-oxydianiline, ODA, in dimethylacetamide leads both to polyimide films via cyclodehydration and to reduction of silver(I) to give nanometer-sized metal particles dispersed throughout the bulk of the film. During the cure a portion of the silver aggregates at the surface to give films which have outstanding reflectivity. Adhesion of the surface silver to polyimide is superb via a mechanical interlocking mechanism. The resulting metallized composite films retain mechanical and thermal properties similar to the parent polyimide. X-ray diffraction shows crystalline fcc silver in the films after thermal curing. Silver remains in the bulk of the polyimide film with varying particle sizes of ca. 10-20 nm. The interior of the metallized films is not electrically conducting. Films were characterized by X-ray, DSC, TGA, XPS, TEM, and SEM.

#### 11:15 AM F3.9

QUANTUM CONFINED GALLIUM NITRIDE IN A MESOPOROUS MATRIX OF MCM-41. Holger Winkler, Roland A. Fischer, Ruhr-Universitaet Bochum, Inst of Inorganic Chemistry, Bochum, GERMANY; Roland Schmechel, Heinz von Seggern, Technische Universitaet Darmstadt, Dept of Material Science, Darmstadt, GERMANY.

The semiconducting group-III nitrides show great promise for electronic and optoelectronic devices. In the case of Gallium Nitride there are some unique properties like a wide and direct bandgap of 3.45 eV, low compressibility, high thermal conductivity, chemical inertness and radiation resistance. While the formation of thin films of GaN realized by MOCVD or MBE has been well established leading to quantum wells currently used in devices (bright blue LEDs and laser diodes), there is no satisfying chemical process available to produce quantum-confined GaN structures in less than two dimensions. Conventional lithographic or etching techniques are rather costly and connected with limited resolution. Besides there is excitonic quenching at etchdamaged boundaries. The mesoporous molecular sieve MCM-41 that consists of tunable hexagonally arranged uniform pores (2-10 nm in diameter) of hollow cylinders offers a possibility for synthesizing mesoscopic composites by inclusion chemistry. If homogeneously filled with GaN, a GaN@MCM-41-composit would result in an ordered array of uniform quantum wires/ dots in the molecular sieve matrix. We describe the organization of nanodispersed GaN in MCM-41 of 2.7 nm pore diameter via impregnation with a solution of the single-source precursor triazido(trimethylamin)-gallium in toluene. TEM investigations showing the well ordered porous system of MCM-41 still being intact after the loading with Gallium

Nitride (Ga-content about 10 wt.-%, molar ratio Ga : N = 0.7 to 1.1). The decrease of the BET surface area of the composites GaN@MCM-41 of about 75 % in comparison of that of pure MCM-41 material give a strong hint for porefilling, which is emphasized by the overall lowered intensity of the low-angle XRD pattern of the composites. In addition optical investigations (photoluminescence and excitation spectroscopy) showing a green luminescence and a blue-shifted bandgap of about 3.7 eV indicate nanodispersed Gallium Nitride to be present inside the pores of MCM-41.

#### 11:30 AM F3.10

PREPARATION OF A HOMOGENEOUSLY DISPERSED BARIUM TITANATE/POLYMER NANOCOMPOSITE THIN FILM. David E. Collins, Elliott B. Slamovich, School of Materials Engineering, Purdue University, West Lafayette, IN.

Crystalline nanoparticles of barium titanate (BTO) dispersed in a polymer matrix were processed by reacting block copolymer films loaded with titanium diisopropoxide bis(ethylacetoacetate) (TIBE) in aqueous solutions of barium hydroxide at 80°C. Using a polystyrene-polybutadiene triblock copolymer (SBS) as the polymer matrix resulted in segregated polymer-rich or BTO-rich regions in the film. In contrast, a homogeneous dispersion of BTO particles was achieved by using poly(styrene-co-maleic anhydride) as the polymer matrix. For TIBE concentrations in large molar excess of the maleic anhydride, BTO nanoparticles were observed throughout the polymeric matrix. However, BTO was absent from the film at lower TIBE concentrations. Fourier transform infrared spectroscopy suggests that the TIBE altered the maleic anhydride functionality. This resulted in an increased miscibility between the TIBE and the polymer, thereby facilitating BTO dispersion.

#### 11:45 AM F3.11

NANOPHASE FIBER COATINGS BY ELECTROPHORETIC DEPOSITION FOR CERAMIC MATRIX COMPOSITES. Theodore M. Besmann, John J. Henry, Jr., Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Control of the mechanical properties of the fiber-matrix interface in ceramic fiber-ceramic matrix composites is critical for obtaining desired composite properties. Typically, adhesion between the fiber and matrix must be sufficiently weak to allow crack deflection around the fibers. This is generally accomplished with a fiber coating that either adjusts the adhesion between fiber and matrix or is itself sufficiently weak to provide a crack pathway. This paper reports the initial development of such an interface coating prepared from electrophoretically deposited, nanoscale, silicon-carbide powder for silicon-carbide matrix, silicon carbide-based fiber systems. Research sponsored by the U. S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

#### SESSION F4: NANOPHASE SEMICONDUCTORS

Chair: John C. Parker

Tuesday Afternoon, November 30, 1999

Salon F (M)

#### 1:30 PM F4.1

NANO-CRYSTAL ENGINEERING: 3-D SELF-ASSEMBLY OF SEMICONDUCTORS. Geoffrey F. Strouse, University of California at Santa Barbara, Santa Barbara, CA.

The assembly of semiconductor components into flexible, 3-dimensional arrays opens new routes into the design and preparation of nano-scale electronic materials. Efforts in metal chalcogenides at the 1-3 nm scale have opened new routes into materials that exhibit quantized physical properties, with the capacity for selective surface capping. These materials can be synthesized as nearly mono-disperse with controlled surface capping via lyothermal methods. Selective capping of the compounds with energy and electron transfer appendages allow analysis of carrier transport in 3-d architectures. We have developed novel approaches for the selective substitution and assembly of a series of nano-scale metallo-sulfur, -seleno semiconductors that are readily modified at both the metal-chalcogenide core and surface capping, making these materials ideal for crystal engineering approaches to nano-electronics. We will discuss the unique advantage of using metal-cluster precursors for nano-assembly and the application of bio-inspired self-assembly for the preparation of a 3-dimensional architectures. Applications of 3-d engineering for electron transport will be probed. Correlation of the optical properties and mass spectrometry will be discussed.

#### 1:45 PM F4.2

ALL-INORGANIC FIELD EFFECT TRANSISTORS FABRICATED BY PRINTING. Brent A. Ridley, Babak Nivi, Joseph M. Jacobson,

Massachusetts Institute of Technology, Media Lab, Cambridge, MA.

We have developed a novel nanocrystal preparation that yields a monodisperse 1.7 nm CdSe nanocrystal solution without intimately bound organic capping groups. This solution is used to print the semiconductor in an inorganic thin-film transistor (TFT) with field effect mobilities surpassing the best printed organic semiconductors. The printed films assemble into single crystalline domains consisting of tens of nanocrystals. To the best of our knowledge, these devices represent the first all-inorganic transistors with a printed inorganic semiconductor and represent the highest mobility printed TFTs to date. This process suggests a new, all-printed, method of fabricating high performance inorganic logic.

#### 2:00 PM F4.3

##### SYNTHESIS OF UNAGGLOMERATED, NON-OXIDE NANOPHASE POWDERS IN A TURBULENT JET FLAME.

Lee J. Rosen, Richard L. Axelbaum, Washington Univ., Dept. of Mechanical Engineering, St. Louis, MO.

Of the many different methods used to produce nanophase powders, few are able to achieve high production rates while minimizing the agglomeration of particles. Furthermore, the powders produced, if non-oxide, must be handled using costly techniques due to their highly reactive nature. Recently, a flame synthesis process conceptually similar to commercial flame processes used to produce millions of tons of ceramic and carbon black powder annually, was extended to allow the production of unagglomerated, non-oxide nanophase powders. This technique employs an encapsulation step during the aerosol growth stage to control particle size, prevent agglomeration and protect the powders from oxidation/hydrolysis during post-synthesis handling. The encapsulation material (typically a salt) can be removed during post-flame processing. A Monte Carlo numerical simulation suggests that the encapsulation process occurs in two steps. Initially the flame-synthesized particles grow normally, but upon condensation of the encapsulate material (salt) the size distribution transitions into a bimodal size distribution, with the coarse mode consisting primarily of salt. The coarse mode then acts to scavenge the fine mode. The final morphology of the core particles will depend on the scavenging process and the behavior of the core particles within the scavenging particles. Numerical results suggest that the size distribution of the core particles within the scavenging particles can be much narrower than that of a single-component self-preserving aerosol. The sodium/halide flame and encapsulation process has been used to produce a variety of metals and ceramics (e.g. Ti, W, Al, TiB<sub>2</sub>, AlN, TiN) of various sizes (ca. 2-60 nm) using a laminar jet flame. Recently, the laminar facility has been converted to a turbulent jet facility to demonstrate the scalability of the process. Experimental results will be presented for the synthesis of metal powder in the turbulent jet facility showing the influence of various process parameters on encapsulation efficiency as well as particle morphology.

#### 2:15 PM F4.4

##### SYNTHESIS AND CHARACTERIZATION OF STRONGLY FLUORESCENT CdTe NANOCRYSTAL COLLOIDS.

Frederic V. Mikulec, Mounqi G. Bawendi, Massachusetts Institute of Technology, Dept. of Chemistry, Cambridge, MA.

We present a synthesis of colloidal CdTe nanocrystals whose absolute room temperature quantum yields are routinely above 60%. The preparation is based on the trioctylphosphine oxide (TOPO) method reported by Murray, with a more stable tellurium precursor now used as the chalcogenide source. The photoluminescence is continuously tunable over the range 590-760 nm and is as narrow as 135 meV (45 nm) FWHM. No deep trap luminescence is detected for the diameter range 4-11 nm. CdTe nanocrystals are characterized by transmission electron microscopy and powder X-ray diffraction. Explanations are proposed as to why these CdTe nanocrystals are so much brighter than CdTe synthesized by an older method using trioctylphosphine telluride.

#### 2:30 PM F4.5

##### LOCAL ORDERING OF SEMICONDUCTOR SINGLE CRYSTALS FOLLOWING NONLINEAR EXCITATION OF LATTICE ATOMS.

P. Sen, School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India; J. Akhtar, Semiconductor Devices Area, CEERI, Pilani, INDIA.

Organization of atoms in the nanometer scale require both energy and novel processing techniques. Low energy ion implantation and irradiation effects take place on a local length scale compared to the size of the system under implantation, and has been extensively employed for modifying bulk electrical as well as mechanical properties. But attempts to construct isolated small regions with unique properties has failed to yield results, due the formation of complex defects and defect clusters which interfere with any desirable

atomic arrangement. With the advent of MeV ions, a new scenario has emerged with the possibility of nonlinear energy transfer from the ions to the lattice taking place, first to the electrons, and later to the lattice through electron-phonon coupling[1]. Further, these ions travel considerable distance (several microns) inside a solid, slowing down while transferring its energy, making it possible to process bulk materials. In this presentation we show that this novel energy transfer mechanism is capable of modifying an already ordered lattice into small locally reordered phases producing atomically sharp interfaces. Employing scanning tunneling microscopy (STM) we study these interfaces and determine their ordering. The modified atomic arrangements alter the local electron density of state (DOS) which is reflected in the adsorption/wetting property of these surfaces, shown here in a time-elapsing water adsorption experiment.

1. P. Sen, G. Aggarwal and U. Tiwari, Phys. Rev. Lett. 80, 97 (1998)

#### 2:45 PM F4.6

##### SYNTHESIS OF SILICON NANOPARTICLES BY CO<sub>2</sub> LASER PYROLYSIS METHOD AND GROWTH OF HIGHLY TEXTURED DIAMOND FILMS ON Si (100) SUBSTRATES BY NANOPARTICLE SEEDING TECHNIQUE.

Ashok Kumar, Sabina Botti<sup>1</sup>, M. Gallev, M.A. George<sup>2</sup> Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL; <sup>1</sup>ENEA, Dipartimento Innovazione, Divisione Fisica Applicata, Centro Ricerche Frascati, Rome, ITALY; <sup>2</sup>Center for Materials and Surface Science, The University of Alabama in Huntsville, AL.

Nanostructures powders, with particle size in the 1-10 nm range, have shown great promise in the forming of advanced structural and functional materials for applications as tribological coatings, high surface area catalyst support for cutting tools, thermal barrier coatings, capacitor and battery materials, dielectric and optoelectronic materials. CO<sub>2</sub> laser synthesis of ceramic powders from gas-phase precursors is an ideal method for growing nanosized, pure and nearly mono-dispersed particles. The silicon nano-particles have been grown by CO<sub>2</sub> laser induced pyrolysis of silane in gas flow reactor. The Si nano-particles have been characterized using SEM, TEM, XRD and XPS techniques. We report a novel approach of seeding Si nano-particles on Si(100) substrates, which has resulted high quality smooth diamond films deposited by HFCVD method. The seeding technique has increased the adhesion of diamond films and helps to grow high quality textured diamond films. The detailed investigations to grow high quality diamond films will be discussed in this paper.

#### 3:30 PM F4.7

##### OPTICAL EFFECTS OF SURFACE MODIFICATION OF SEMICONDUCTOR NANOPARTICLES USING CHALCOGEN SITES.

Tong Ni, Dattatri Nagesha, Nicholas Kotov, Oklahoma State University, Chemistry Department, Stillwater, OK.

Chemical binding to metal atoms located on the surface of II-VI semiconductor nanoparticles, NP, is widely used for their surface modification including the derivatization with various organic moieties. Conversely, interfacial chalcogen atoms have not been utilized for binding of organic ligands to NP. Among the properties that differ them from the metal sites, the most important one is the fact that the surface chalcogen atoms are electronically conjugated to the ground state of NP. This feature warrants the consideration of chalcogen modification as tool for controlling optical and electronic properties of nanoclusters. The attachment of organic groups with delocalized pi-systems to chalcogen atoms was achieved by reaction with mixed bipyridine complexes of copper, ruthenium, platinum and palladium. The structure of the complexes was confirmed by NMR, ESR, TEM, XRD and ES-MS data. UV-VIS absorption, emission, and excitation spectra suggest relaxation of the electron confinement effect and partial mixing of electronic states of the semiconductor core and pi-systems of the aromatic ligands. Quantum mechanical calculations demonstrate the formation of electronic states connecting the nanoparticle core and the delocalized pi-system of bipyridine ligand, which is supported by the observation of efficient excitation transfer between the semiconductor core and the modifier. The transfer of excitation energy was observed for the excitonic emission of the semiconductor core as well as for the surface trap emission. Chalcogen modification was demonstrated to be applicable to various size-quantized semiconductor colloids - CdS, CdSe and newly synthesized strongly luminescing Bi<sub>2</sub>S<sub>3</sub>.

#### 3:45 PM F4.8

##### FORMATION OF NANOCRYSTALLINE SiC POWDER FROM CHLORINE-CONTAINING POLYCARBOSILANE PRECURSORS.

Brian S. Mitchell, Haoyue Zhang, Nikica Maljkovic, Tulane University, Dept. of Chemical Engineering, New Orleans, LA; Martin Ade, Dirk Kurtenbach, Eberhard Müller, TU Bergakademie Freiberg, Institute für Keramische Werkstoffe, Freiberg, GERMANY.

Nanocrystalline  $\beta$ -SiC particulates with a grain size range of 5-20 nm were prepared by heating a pre-pyrolyzed, chlorine-containing

polysilane/polycarbosilane (PS/PCS) to 1600°C. The transformation from the pre-pyrolyzed PS/PCS to nanocrystalline SiC was investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), mass-spectrometry and infrared spectroscopy. The results indicated that the nanocrystalline  $\beta$ -SiC was formed by the crystallization of the PS/PCS random network, and crosslinking of Si-Si, Si-Cl, and Si-CH<sub>2</sub>-Si bonds. The TEM observation showed that SiC particulates consist of equiaxed, randomly oriented, ultrafine grains.

#### 4:00 PM F4.9

STRUCTURE OF POLYCRYSTALLINE SILICON FILMS BY GLOW-DISCHARGE DECOMPOSITION USING SiH<sub>4</sub>/SiF<sub>4</sub> AT LOW-TEMPERATURE. Moniruzzaman Syed, Ryo Tsuchida, Takao Inokuma, Yoshihiro Kurata, Seiichi Hasegawa, Department of Electronics, Faculty of Technology, Kanazawa University, Kanazawa, JAPAN.

Polycrystalline silicon (poly-Si) films were prepared on a Corning 7059 at 300°C by a plasma-enhanced chemical vapor deposition method using a mixture of gases SiH<sub>4</sub>/SiF<sub>4</sub> with two different H<sub>2</sub> flow rates ([H<sub>2</sub>] = 0 or 10 sccm) as a function of RF power. Effects caused by the addition and without addition of H<sub>2</sub> on the structural properties of the films were investigated by means of Raman scattering, X-ray diffraction (XRD), Electron spin resonance (ESR), Fourier-Transform Infrared spectroscopy (FT-IR), and AFM measurements. The poly-Si films deposited under the both deposition conditions had shown <110> preferential orientation and the deposition rate were in the range of 9-20 nm/min. For [H<sub>2</sub>] = 0 sccm, both the grain size ( $\delta$ ) and the crystalline volume fraction ( $\rho$ ) were increased first and then decreased, having the maximum value around 120nm, 80% respectively, as the rf power increased. On the other hand, for [H<sub>2</sub>] = 10 sccm, both  $\delta$  and ( $\rho$ ) values were deteriorated as the rf power increased having the maximum value around 30 nm and 70% respectively. It was suggested that the deterioration of the crystalline quality with the addition of hydrogen, is likely to be caused by the suppression of the role of F-related radicals along with the effect of a change in the surface morphology of the substrate as well as the effect of in situ chemical etching on the growing surface. Probable mechanisms causing the change in the crystalline quality are also discussed.

#### 4:15 PM F4.10

SYNTHESIS OF CdSe/CdS CORE/SHELL NANOCRYSTALS FROM STABLE SINGLE MOLECULE PRECURSORS. M. Azad Malik, Paul O'Brien and Neerish Revaprasadu, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK.

TOPO (tri-n-octylphosphine oxide) capped CdSe/CdS, CdSe/ZnS, and CdSe/ZnSe core/shell nanocrystals have been synthesized from the thermolysis of *bis*(methyl(n-hexyl)diselenocarbamate)-cadmium(II) and *bis*(methyl(n-hexyl)dithio-/diseleno-carbamato)-Cadmium-/Zinc(II), as precursors. The nanoparticles obtained show a red shift in their absorption spectrum with an enhanced photoluminescence. The Selected Area Electron Diffraction (SAED), X-ray diffraction (XRD) pattern, and Transmission Electron Microscopy (TEM) show the material to be predominantly of the hexagonal phase. Energy dispersive analysis by X-ray (EDAX) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) show the presence of Cd, Se and S. The properties of these structures will be compared against the ternary and quaternary phases (CdZnS, CdZnSe and CdZnSse) which are being synthesised.

#### 4:30 PM F4.11

ELECTROCHEMICAL ATOMIC LAYER EPITAXY: ELECTRODEPOSITION OF III-V AND II-VI SEMICONDUCTORS COMPOUNDS. Travis L. Wade, Billy H. Flowers Jr., John L. Stickney, Univ. of Georgia, Dept. of Chemistry, Athens, Georgia, GA; Uwe Heppke, University of Georgia, Dept. of Physics, Athens, GA.

Thin films of InAs and CdTe have been electrodeposited by electrochemical atomic layer epitaxy (electrochemical ALE). The deposition process involves formation of the compounds an atomic layer at a time. This atomic layer deposition takes advantage of surface limited reactions referred to as under potential deposition (UPD). UPD occurs when it is energetically more favorable for one element to deposit on another element than for it to deposit on itself, due to the energy of compound formation. Once the substrate is coated with an atomic layer of an element, the deposition will stop. Next a second element is introduced, resulting in a layer of the compound. This sequence is repeated to form a thin film of desired thickness using a flow cell with automated solution delivery. The sequence is termed electrochemical ALE.

#### 4:45 PM F4.12

TAYLORED SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF CHALCOGENIDE NANOCRYSTALS FROM LANGMUIR-BLODGETT TEMPLATES. L. Cristofolini, M.P. Fontana, Dipartimento di Fisica, Universita' di Parma, ITALY; P. Facci, Dipartimento di Scienze Ambientali, Universita' della Tuscia, Viterbo, ITALY.

We synthesized II-VI chalcogenide nanocrystals (size 1 to 4 nm) of mixed composition grown in fatty acid Langmuir-Blodgett multilayer templates. The controlled production of *i* homogeneous nanocrystalline Cd<sub>1-x</sub>Zn<sub>x</sub>Se alloys and *ii* heterogeneous mixtures of different pure composition II-VI semiconductors such as CdSe and ZnSe provides, in addition to the size control, the parameter of the chemical composition for the fine tuning of the electronic properties of semiconductor nanocrystals and in particular the band gap. The samples thus produced are characterized by quasi-resonance micro-Raman and optical spectroscopy.

SESSION F5: POSTER SESSION:  
NANOCOMPOSITES-SYNTHESIS,  
CHARACTERIZATION, AND PROPERTIES  
Chairs: Horst Hahn, Sridhar Komarneni and  
John C. Parker  
Tuesday Evening, November 30, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### F5.1

MICROSTRUCTURAL AND ELECTRICAL CHARACTERIZATION OF SOL-GEL DERIVED Pb(Zr,Ti)O<sub>3</sub> NANOCOMPOSITE CERAMICS AND THIN FILMS. Ming Dong, Zuo G. Ye, Department of Chemistry, Simon Fraser University, Burnaby, BC, CANADA.

Ferroelectric Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> nano-powders were synthesized by an air-stable sol-gel route. These fine powders allow us to sinter high purity and high density PZT ceramics at temperatures lower than 1000°C. The specimens attained about 97% of the theoretical density. PZT nanocomposite ceramics and thin films were prepared from high purity sol-gel derived PZT powder and small amount (0.1-1.0 vol%) of sol-gel derived MgO. The microstructure of the nanocomposites were investigated by XRD and SEM. The piezo- and ferroelectric properties were measured using an RT66A Standard Ferroelectric Test System and an MTL-200 Fotonic Sensor. The frequency and temperature dependence of the dielectric properties of these ceramics were determined by impedance spectroscopy from room temperature to 500°C at frequencies ranging from 1 to 10<sup>7</sup> Hz, using a Solartron 1260 Impedance analyzer combined with a Solartron 1296 Dielectric Interface. The pure PZT ceramics show a Curie temperature of 400°C with a significant frequency dispersion of the dielectric constant observed at TC, which was attributed to the highly conductive grain boundary effects. At room temperature, the dielectric constant  $k$  and the dissipation factor  $\tan \delta$  at 1kHz are 820 and 0.025, respectively. The temperature dependences of both ac and dc resistivity indicate an activation energy of 1.10eV. The bulk conductivity of the pure PZT ceramics is about 10<sup>-12</sup> Sm<sup>-1</sup> at 40°C. Effects of the oxide additives on the electric microstructure, the grain size and grain boundary, the ac and dc conductivity, and the dielectric and piezoelectric properties of the PZT-related nanocomposites were discussed based on the experimental results.

#### F5.2

OPTICAL CHARACTERIZATION OF PMMA-CARBON NANOTUBE NANOCOMPOSITES. E. Gregory, D.J. Tarbox, R. Czerw, Dept. of Physics and Astronomy Clemson University, Clemson SC; J. Ballato, Dept. of Ceramic and Materials Engineering, Clemson University, Clemson SC; P.M. Ajayan, Dept. Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY; D.L. Carroll, Dept. Physics and Astronomy Clemson University, Clemson SC.

Optical phenomena in composites of poly(methylmethacrylate) (PMMA) and purified carbon nanotubes have been quantified as a function of nanotube conformation (multiwalled vs. single walled), doping, and dispersion. The optical response of multiwalled nanotubes (MWNT's) well dispersed in a PMMA matrix shows scattering to be dominate from the Near-UV to the Near-IR. However, single walled nanotube dispersions show several absorption features in the UV-Vis and FTIR spectra. This work coupled with TEM observations suggests that SWNT-PMMA and MWNT-PMMA interactions differ dramatically. The effect of these differences will be discussed in terms of the resulting optical, electronic, and thermal properties of the composite.

#### F5.3

NANOTUBE-POLYMER COMPOSITES: MECHANICAL AND

ELECTRICAL PROPERTIES. Bouchra Safadi, Rodney Andrews, Frank Derbyshire, Center for Applied Energy Research, University of Kentucky, Lexington, KY.

The inclusion of multiwalled carbon nanotubes (MWNTs) in polymer matrices greatly enhances the physical properties and electrical conductivity of the formed composites. In this work, MWNTs were dispersed in matrices of polystyrene (PS) or polyfurfural (PFF) resin at concentrations of up to 7.5 wt%. The tensile strength, elastic modulus, strain to failure and electrical conductivity of the resulting composites were measured for various MWNT loadings. Uniform dispersion of the MWNTs into the matrix proved to be a critical factor, with optimal property enhancement achieved by dispersion in which the nanotube bundles were separated and dispersed. The PS films were transformed from an insulating to a conductive material, with conductivities approaching  $1 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The properties of the PFF-MWNT composites were similarly changed. This increase in composite conductivity increased with increasing MWNT loading and nanotube dispersion for both matrices. The addition of MWNTs to the PS films approximately doubles both the tensile strength and the stiffness at about 5% MWNT loading. While blank PS samples fail plastically, the MWNTs-PS composites show little plastic deformation on failure, indicating a stiffening of the composite with nanotube inclusion. In contrast, for the brittle PFF matrix, improvements to the polymer flexibility (65% reduction in flexural modulus) were observed. It is tentatively concluded that the properties of the MWNTs dominate those of the matrix in determining the composite material behavior.

**F5.4**  
PHASE TRANSITION AND CONTROL OF SELF-ASSEMBLED MESOSTRUCTURED VANADIA/SURFACTANT COMPOSITES. Itaru Honma, Y. Yagi, H.S. Zhou, A. Endo, M. Miyayama, T. Kudo.

Mesoporous materials invented by scientists of the Mobil Corporation have attracted considerable interest for application in electronics, energy and environmental device materials. In this work, we have synthesized mesoporous vanadia/surfactant composite in powder as well as thin film form and characterize its mesostructure and electrochemical properties. The mesoporous Vanadate materials were formed by surfactant templated mechanism as similar to MCM silica synthesis and phase transformation among lamellar, hexagonal, cubic were investigated. The vanadia mesostructure was synthesized as follows; the ammoniumvanadate ( $\text{NH}_4\text{VO}_3$ ); 1.0 g, was first dissolved in a aqueous water (18g) with an addition of amount of NaOH (1.2g) to be solvated completely at high pH. And the C16TMA (0.54g) are dissolved in the above solution with no precipitation at this high pH condition. HCl (5N) are added drop wise to gradually decrease a solution's pH to around 1.0. As HCl adding, passing neutral point, vanadia start precipitating at the surface of the micelle and mesostructured vanadia were formed. Also, similarly, the mesostructure of vanadia/surfactant thin films were synthesized on the substrate by spin casting technique. Casting solution was prepared by hydrolyzed sol of Vanadium alkoxides precursors. Homogeneous, colored flat thin films were synthesized on silica substrate and phase structure was characterized by low angle XRD. The film as casted has lamellar structure and changed to cubic phase by 5 hour annealing at 160C. Then further annealing for 12.5 hours at 160C induces phase change to hexagonal one. The surfactants were removed by calcination, solvent and super critical fluid and mesoporous structure was characterized by XRD, BET and CV.

**F5.5**  
NANOCOMPOSITE MATERIAL LIQUID CRYSTAL-AEROSIL PARTICLES: DIELECTRIC AND PHOTON CORRELATION SPECTROSCOPY INVESTIGATIONS. F.M. Aliev and G.P. Sinha, Department of Physics, University of Puerto Rico, San Juan, PR.

Nematic liquid crystal (LC) filled with aerosil particles – prospective inorganic-organic nanocomposite material for optoelectronic application – have been investigated by broadband dielectric spectroscopy (BDS), static light scattering and photon correlation spectroscopy (PCS). The aerosil particles of  $\approx 10 \text{ nm}$  in diameter in filled nematic liquid crystals form a network structure with linear size of LC domains about 250 nm with random distribution of the director orientation of each domain. This material has very developed liquid crystal-solid particle interface that makes the role of the surface layers of LC extremely important in the determination of the properties of the material. We used particles, both with hydrophilic and hydrophobic surfaces, filling nematic liquid crystal-5CB. PCS probes dynamics of collective modes associated with director fluctuations while BDS provides information on reorientational motion of polar molecules of liquid crystal. We found that the properties of 5CB are considerably affected by the network. Two bulk-like modes due to the rotation of molecules around short axes and the tumbling motion were found to be modified in filled 5CB. Additionally, a low frequency relaxation process and dispersion of dielectric permittivity due to

conductivity were also observed. The treatment of the surface of filling particles has strongest influence on the properties of the slow process and it is less important for molecular modes. The characteristic frequencies of the slow process are lower for hydrophilic particles and in this sample the contribution of this process to the total polarization was greater than in the case of hydrophobic particles. PCS experiment shows that two new relaxation processes appear in filled 5CB in addition to the director fluctuation process in bulk. This work is supported by DoD grant N00014-99-1-0558.

**F5.6**  
MECHANICAL PROPERTIES OF NANOPARTICLE FILLED POLYMERS. L.S.Schadler, R.W. Siegel, C.B. Ng, B.J. Ash, Rensselaer Polytechnic Institute, Materials Science and Engineering Department, Troy, NY.

The tensile, scratch, and impact properties of nanocomposites made from either epoxy or polymethylmethacrylate (PMMA) filled with titania nanoparticles were evaluated as a function of particle size, loading, dispersion, and filler/matrix interaction. The filler was dispersed using sonication, and we found that there is a narrow viscosity window in which fillers with relatively poor filler/matrix interaction can be dispersed. In addition, we characterized the change in epoxy resin chemical structure as a result of the sonication using infrared and solid state nuclear magnetic resonance spectroscopies. In the epoxy based nanocomposites, we observed a simultaneous increase in modulus and strain-to-failure, and a dramatic improvement in the scratch resistance compared to epoxy composites containing micron sized titania particles. The dispersion of the nanoparticles was crucial in obtaining the increase in strain-to-failure. The addition of the nanofiller decreased the glass transition temperature by  $7^\circ\text{C}$  at 20 wt% loading. Similar behavior was observed in filled PMMA samples. The latest results from this ongoing project will be reported. This work was supported by the National Science Foundation.

**F5.7**  
NANOCOMPOSITES BASED UPON ALUMINA -AND ZIRCONIA PILLARED CLAYS LOADED WITH TRANSITION METAL CATIONS AND CLUSTERS OF PRECIOUS METALS: SYNTHESIS, PROPERTIES AND CATALYSIS OF  $\text{NO}_x$  SELECTIVE REDUCTION BY HYDROCARBONS. Vladislav A. Sadykov, V.P. Doronin, D.I. Kochubei, E.A. Paushtis, V.B. Fenelonov, A.S. Ivanova, V.I. Zaikovskii, T.G. Kuznetsova, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA; A. Ya. Rozovskii, V.F. Tretyakov, Topchiev Institute of Petrochemical Synthesis RAS, Moscow, RUSSIA; V.A. Matyshak, Semenov Institute of Chemical Physics RAS, Moscow, RUSSIA; J. Ross, University of Limerick, Limerick, IRELAND.

Pillared clays now attract a great deal of attention as catalysts of various industrially important processes including those of environmental catalysis such as  $\text{NO}_x$  selective reduction by ammonia and/or hydrocarbons. This work will present results of design and studies of systems based upon alumina- and zirconia -pillared montmorillonite. To modify pillars adsorption properties and thermal stability, lanthanum and alkaline-earth cations were introduced into polyoxocations. Clusters of copper and cobalt cations were fixed at pillars using cation exchange with their acidic protons, and nano-particles of Pd, Pt and Ag were then inserted into galleries using impregnation or photo-assisted deposition. For comparison, model nanocomposites comprised of copper and cobalt cations clusters with juxtaposed precious metals clusters supported onto highly dispersed alumina and zirconia partially stabilized by Ca, Sr, Ba and La were also synthesized. Pore structure of samples was characterized using detailed analysis of nitrogen adsorption isotherms and XRD. Bulk structure, microtexture and spatial distribution of separate components studied by TEM, XRD, SAXS and EXAFS were compared with the surface properties of nanocomposites characterized by IR spectroscopy of hydroxyls and adsorbed test molecules ( $\text{CO}$ ,  $\text{NO}$ ), TPD, TPR. Specificity of pillars structure as compared with that of bulk dispersed alumina and zirconia phases was revealed, and its effects on interaction between oxidic and metallic particles was elucidated. Nanocomposites performance in the reaction of  $\text{NO}$  selective reduction by C3-C10 hydrocarbons in the excess of oxygen was shown to be enhanced due to co-action of oxidic and metallic components. FTIRS in situ was applied to detect surface reaction intermediates (nitrite-nitrates, isocyanates etc) and estimate their reactivity. All these data were used to discuss catalytic properties of nanocomposites based upon pillared clays. This work is supported by INTAS under INTAS 97-11720 project.

**F5.8**  
NEW PREPARATIVE METHODS FOR ORGANIC-INORGANIC POLYMER HYBRIDS. Ryo Tamaki, Yoshiki Chujo, Kyoto Univ, Dept of Polymer Chemistry, Kyoto, JAPAN.

This paper describes new methods for the preparation of

organic-inorganic polymer hybrids. (1) Aromatic interaction between organic and inorganic matrix: The combination of polystyrene and tetramethoxysilane produced only turbid materials. On the other hand, in the presence of polystyrene, the sol-gel reaction of phenyltrimethoxysilane gave homogeneous polymer hybrids. In this reaction, the interaction of phenyl groups of polystyrene and phenyl groups of silica gel matrix was found to play an important role for the preparation of homogeneous polymer hybrids. By using this idea, the polymer hybrids based on polycarbonate or poly(diallyl phthalate) were also prepared starting from phenyltrimethoxysilane. (2) Ionic interaction between organic and inorganic matrix: Sulfonated polystyrene was used as a starting organic polymer for the preparation of polymer hybrids. As an inorganic component, 3-aminopropyltrimethoxysilane was used together with tetramethoxysilane. After sol-gel reaction, ammonium groups in silica gel and sulfonate groups in polystyrene have a strong affinity via ionic interaction. As a result, homogeneous and transparent polymer hybrids were successfully obtained. (3) In-situ polymerization method: The radical polymerization of N,N-dimethylacrylamide or styrene was carried out simultaneously together with the sol-gel reaction (hydrolysis and condensation of alkoxy silanes) to produce homogeneous and transparent polymer hybrids. IPN (Interpenetrating polymer network) hybrids were prepared by this method using bifunctional vinyl monomers (methylenebisacrylamide or divinylbenzene). The IPN polymer hybrids obtained showed excellent solvent-resistant properties.

#### **F5.9**

**THEORETICAL PHASE DIAGRAMS OF POLYMER/CLAY NANOCOMPOSITES.** Valeriy V. Ginzburg, Chandrelekha Singh, Anna C. Balazs, Dept of Chemical and Petroleum Engineering, Univ of Pittsburgh, Pittsburgh, PA.

We develop a theoretical model to describe the equilibrium phase behavior of polymer/silicate nanocomposites. By combining the mesoscopic density functional theory (DFT) and the lattice self-consistent field (SCF) model, we write down a free energy expression for the binary mixture of rigid discs (representing organically modified clay particles) and flexible polymer chains. Depending on the polymer chain length  $N$ , clay volume fraction  $\phi$ , and the Flory-Huggins interaction parameter  $\chi$  between the polymer and the organically modified clay, the system may be in an exfoliated (isotropic or nematic), intercalated (smectic), or immiscible (two-phase coexistence) state. We calculate the phase diagrams for several model systems and show how the features of these phase diagrams depend on the size of the clay particles, the polymer chain length, the density and length of the grafted organic modifiers (surfactants), and the strength of the polymer-surfactant attraction. The findings can be used as guidelines for the development of new polymer/silicate nanocomposite materials.

#### **F5.10**

**HIERARCHICAL STRUCTURE-PROPERTY RELATIONSHIPS OF NANOPATTERNED BARIUM TITANATE ON BLOCK COPOLYMER.** Tu Lee, Ilhan A. Aksay, Princeton University, Department of Chemical Engineering and Princeton Materials Institute, Princeton, NJ; Douglas H. Adamson, Corine Gerardin, Nan Yao, Princeton University, Princeton Materials Institute, Princeton, NJ; Boris E. Vugmeister, Princeton University, Department of Chemistry, Princeton, NJ.

A triblock copolymer of polystyrene-polybutadiene-polystyrene (Kraton D1102<sup>TM</sup>) was used to pattern barium titanate (BaTiO<sub>3</sub>) with nanoscale modulations. This BaTiO<sub>3</sub>/Kraton D1102<sup>TM</sup> nanocomposite had two phases. Generally, the BaTiO<sub>3</sub> phase contained numerous levels of structure: ionic distances, polymorphs, twins and particle sizes; and the block copolymer phase also contained several levels of structure: molecular configurations, conformations, nanodomains and film thickness. Engineering efforts were made to achieve a uniform monolayer (31 nm in thickness) of Kraton D1102<sup>TM</sup> with self-assembled nanodomains over the substrate area. The particle size of the BaTiO<sub>3</sub> phase was then confined by the nano-regions. The dielectric property of the nanocomposite was firstly related to the higher structural level of the BaTiO<sub>3</sub> phase by the dielectric mixing rules in terms of volume fraction,  $\phi$ , and relative positions,  $\zeta$ . It was then related to the lower structural level by the random field theory in terms of BaTiO<sub>3</sub> lattice defects. This level by level dissection serves as an analytical framework for identifying the most influential structure-property relationship in hierarchical structures.

#### **F5.11**

**THIN POLYTETRAFLUOROETHYLENE ORGANOSILANE NANOCOMPOSITE FILMS USED AS ULTRA LOW DIELECTRIC CONSTANT MATERIALS IN MICROELECTRONICS.** Shichun Qu, Tom Rosenmayer, W.L. Gore and Associates, Inc., Eau Claire, WI; Ping Xu, Perry Spevack, W.L. Gore & Associates, Inc., Elkton, MD.

Replacing the current on-chip insulator (silicon dioxide, dielectric constant of approximately 4.0) with low dielectric constant materials can greatly improve the performance of high density VLSI device by reducing crosstalk and capacitive coupling between metal interconnects. Polytetrafluoroethylene (PTFE) has the lowest dielectric constant ( $k < 2.0$ ) of any full density material, which makes it a promising candidate for this IC application. Pure PTFE thin films cast from PTFE nanoemulsion containing sub-20nm PTFE particles, though thermally stable, has some inherent sub-optimal properties including adhesion strength to other inorganic materials and mechanical strength at high processing temperatures. In order to improve these properties, we have developed a PTFE / silicon compound nanocomposite material. Initial tests have shown that this nanocomposite material has significantly improved high temperature mechanical properties and interfacial properties between the composite and inorganic materials such as silicon, silicon oxide, silicon nitride and some metals. The surface roughness of the thin film coatings is also reduced compared to the pure PTFE thin film coatings. Characterization work has been carried out with different techniques such as DMA, FTIR, XPS depth profiling, SIMS, NR, SANS and AFM with selective etching, in order to understand this novel nanocomposite and its surface and interfacial properties.

#### **F5.12**

**A NOVEL LIQUID PHASE PROCESSING ROUTE TO CONTROL GRAIN GROWTH IN NANOPHASE AND NANOCOMPOSITE ALUMINA COMPOSITES.** Deborah M. Vernon, James C. Truman, Elizabeth K. Reilly and Janet Rankin, Brown University, Division of Engineering, Providence, RI.

A novel processing route to produce nanophase and nanocomposite materials is being investigated. Pellets of submicron and nanoscale starting powder are pressed to ~50% theoretical density. Processing involves the introduction of an intermediary step between initial powder pressing and sintering. During the intermediate step, a second phase precursor is introduced into the pore structure via liquid phase infiltration. The infiltrated porous pellet is subsequently heated to elevated temperatures between 1200 and 1650 C for a range of times, to produce a fully dense final microstructure. The effects of varying: initial pellet densities, infiltrant concentrations, infiltrant species and final sintering schedules have been studied. Final-state microstructures were characterized using a variety of techniques. Grain growth and depth of infiltration were measured using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). High resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS) were used to study the grain boundaries in the infiltrated pellets. Microhardness measurements were also performed. For most cases studied here, the introduction of a second phase via liquid infiltration produced a microstructure with significantly reduced grain growth, and improved hardness measurements when compared to control samples.

#### **F5.13**

**MICROSTRUCTURAL INVESTIGATION OF MONOLITHIC ZrB<sub>2</sub> AND ZrB<sub>2</sub>-ZrC COMPOSITE.** Kyoung Hun Kim, Seon Woo Lee, Kwang Bo Shim, Hanyang Univ, Ceramic Processing Research Center, Dept of Ceramic Engineering, Seoul, KOREA.

The addition of rare-earth elements (La and Nd) to pure boride (ZrB<sub>2</sub>) and ZrB<sub>2</sub>-ZrC composite was considered to improve their sinterabilities during pressureless sintering. And other solidification methods such as GPS and SPS also were employed to compare with the convention pressureless sintering method. In case of composite three different batch compositions were selected near the eutectic point of ZrB<sub>2</sub>-ZrC. It was found that the additives improve remarkably the sinterability but their effective parameters were different from two additives in both two bodies. Transmission electron microscopy was performed to analyze their aspects in micro-scale.

#### **F5.14**

**PERIODIC METAL AND CARBON NANOFOAMS FOR THERMOELECTRICITY AND THERMO-ELECTROCHEMICAL POWER GENERATION.** Ilyas I. Khayrullin, Mikhail E. Kozlov, New Jersey Institute of Technology, Newark, NJ; Igor Udod, L-M. Liu, Anvar A. Zakhidov, Ray H. Baughman, AlliedSignal, Inc., Morristown, NJ; Geoff M. Spinks, University of Wollongong, Wollongong, AUSTRALIA.

Three-dimensionally periodic metal and carbon nanofoams have been fabricated that are the inverse of the precursor silica opals used as molds. In the two-step preparation, either molten bismuth, antimony and their alloys were infiltrated into the opal under high pressure or carbon was infiltrated into the opal by both the CVD technique and the precursor pyrolysis route. At the second step, silica was chemically removed by hydrofluoric acid to leave a periodic mesh of the metal or carbon tetrahedrons and octahedrons connecting through narrow interconnects. For thermoelectrics, we anticipated that

scattering processes at the interconnects and the highly extended internal surface might improve performance by having a greater effect on phonon-mediated (lattice) thermal conductivity than on electrical conductivity. As expected, the thermal conductivity reduction is much larger for vacuum-filled nanofoams than for the unetched thermoelectric-silica nanocomposite. Also, the electrical conductivity of the thermoelectric nanofoam shows semiconductor-type behavior (in contrast to the metallic type behavior of the bulk thermoelectric), which can be described by weak 3-D localization in a mesoscopic system. For power generation, the carbon nanofoams (having great internal surface) have been tested as electrodes in electrochemical thermoelectric converters (TICs) that can convert waste heat to electrical energy. Maintaining the temperature gradient of only about 60°C between two carbon nanofoam electrodes in a 30% HNO<sub>3</sub> aqueous electrolyte, we obtain an open circuit voltage of 70 mV and a short circuit electric current of 3.6 mA per gram of electrode material. The values obtained are comparable to those provided by more expensive carbon nanotubes and nanofibers electrodes. Various electrode configurations are discussed to improve the characteristics of the carbon nanofoam TIC. \*Supported by DARPA grants DAABO-97-C-J-036 and N00173-99-2000

#### **F5.15**

##### **SYNTHESIS AND MECHANICAL PROPERTIES OF TiC/a-C:H NANOCOMPOSITE THIN SURFACE COATING.** W.J. Meng,

Department of Mechanical Engineering, Louisiana State University, Baton Rouge, LA; P.M. Baldo, L.E. Rehn, Materials Science Division, Argonne National Laboratory, Argonne, IL.

We report the use of a conventional reactive sputtering system and a low-pressure high-density plasma based hybrid physical vapor deposition (PVD)/chemical vapor deposition (CVD) system for the synthesis of titanium-containing hydrocarbon (Ti-C:H) thin surface coatings with widely varying Ti concentrations. We show that all Ti-C:H coatings are titanium carbide/amorphous hydrocarbon (TiC/a-C:H) thin film nanocomposite materials. We show further that elastic modulus (E) and hardness (H) of reactively sputtered TiC/a-C:H nanocomposites appear to conform to macromechanical bounds on E and H for two-phase composites. We observe in addition that E and H of TiC/a-C:H made by hybrid PVD/CVD exhibit large apparent deviations from the macromechanical bounds. We probe the hydrogen concentration in Ti-C:H nanocomposites experimentally, and discuss the role of hydrogen in determining the mechanical properties of TiC/a-C:H nanocomposites.

#### **F5.16**

##### **MICROSTRUCTURE AND OPTICAL PROPERTIES OF NANOCRYSTAL PRECIPITATES OF NiS IN SiO<sub>2</sub> AND Al<sub>2</sub>O<sub>3</sub>.**

Alkiviathes Meldrum, E. Sonder, C.W. White, L.A. Boatner, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; R. Mu, Physics Dept., Fisk University, Nashville, TN.

Ion implantation and thermal processing were used to create NiS nanocrystals in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> hosts. Compounds containing Ni plus S are particularly interesting because they span a wide range of compositions and crystal structures with different electronic properties. Pure stoichiometric NiS is hexagonal (NiAs structure) at temperatures above 380°C. Bulk hexagonal NiS, when stabilized at room temperature by rapid cooling, undergoes a metal-semiconductor transition at ~10°C. If cooled slowly below 380°C, it spontaneously transforms to the metallic millerite form. Nonstoichiometry may also occur to produce compounds such as polydymite (Ni<sub>3</sub>S<sub>4</sub>) and godlevskite (Ni<sub>9</sub>S<sub>8</sub>). In the present work, we study the formation of nanocrystal precipitates containing Ni and S formed by ion implantation into SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> hosts. The optical data are compared to those obtained for a reference sample implanted with Ni only. When formed in SiO<sub>2</sub>, the resulting particles have a composition close to NiS, as measured by energy dispersive X-ray spectroscopy. The microstructure, size, and crystallinity of the nanocrystals was controlled by varying the thermal processing parameters. The optical transmission data showed a sharp absorption peak at 450 nm that did not occur for the sample implanted with nickel only. Initial data suggest that this may be the surface plasmon for metallic NiS. The peak becomes more pronounced at higher annealing temperatures. In Al<sub>2</sub>O<sub>3</sub>, both the optical and the X-ray diffraction data imply the presence of more than a one NiS phase and the strong absorption at 450 nm was considerably weaker than for an SiO<sub>2</sub> host. An additional absorption peak occurred at 242 nm in Al<sub>2</sub>O<sub>3</sub> specimens annealed above 800°C. The presence of a potential metal semiconductor transition was investigated by performing the absorption measurements at cryogenic temperatures. The results suggest that there is no sharp transition between the metallic and semiconductor phases.

#### **F5.17**

##### **ULTRAHARD NANOCOMPOSITES TITANIUM NITRIDE/TITANIUM SILICIDE WITH HARDNESS EXCEEDING**

100 GPa AND HIGH FRACTURE TOUGHNESS. Stan Veprek, Andreas Niederhofer, Keba Moto, Pavel Nesladek, T. Bolom and Hans Maennling, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, Munich, GERMANY.

In course of a further development of our concept for the design of superhard nanocomposites we succeeded to prepare coatings consisting of nanocrystalline titanium nitride and titanium disilicide which reach vickers microhardness of more than 100 GPa independent of the applied load between 30 and 100 mN. The absence of any radial cracks even at a load of 1000 mN indicates a high fracture toughness of these coatings which also show a high elastic recovery approaching 90%. The elastic modulus and the universal hardness ('hardness under load') compare with those of diamond which was measured for comparison. The coatings of a thickness of up to 11 microns were prepared by means of plasma CVD at 560°C. We shall present the results of the hardness measurements to underline their reliability. In the second part of the presentation we shall report experimental data and discuss the thermodynamics of the evolution of two- and three-phase nanocomposites with increasing content of silicon in the coatings. The data strongly support the view that these nanophases are thermodynamically stabilized.

#### **F5.18**

##### **CRACK HEALING IN ALUMINA/SILICON CARBIDE NANOCOMPOSITES AFTER GRINDING AND ANNEALING.**

H.Z. Wu, J.M. Titchmarsh, S.G. Roberts, Department of Materials, University of Oxford, Oxford, UK; B. Derby, Manchester Materials Science Centre, UMIST, Manchester, UK.

Alumina/silicon carbide nanocomposites are known to show their highest strength levels after surface grinding followed by annealing. The strength of bend specimens with coarsely ground nanocomposite surfaces exceeds that of specimens with a well polished surface after annealing in flowing Ar. The bend strength of specimens with lapped surface also shows some small improvement on annealing. TEM investigations of annealed cross-sections show that the annealing process leads to surface crack healing. The chemical composition of the healed cracks has been studied by high resolution FEGSTEM and the likely chemical reactions will be discussed.

#### **F5.19**

##### **PHASE EVOLUTION IN SPUTTER DEPOSITED ZIRCONIA-TITANIA NANOLAMINATE FILMS.** J.D. DeLoach and

C.R. Aita, University of Wisconsin-Milwaukee, Department of Electrical Engineering and Computer Science, Department of Materials, and the Laboratory for Surface Studies, Milwaukee, WI.

The films in this study consist of multiple bilayer stacks containing zirconia and titania laminated together on the nanometer scale by the reactive sputter deposition process. We previously used a ceramic nanolaminate structure for phase control in zirconia-alumina and zirconia-yttria nanolaminates grown at room temperature. In zirconia-alumina nanolaminates, the components retained their chemical identity, and there was no interfacial reaction. In contrast, an interfacial reaction in zirconia-yttria nanolaminates completely obliterated yttria as a separate entity. Work on zirconia-yttria nanolaminates demonstrated that interfacial oxide solid solutions form at low temperature in a system in which the bulk equilibrium phase diagram predicts reaction between components. The zirconia-titania system provides a middle ground in constituent reactivity with the extremes provided by noninteractive zirconia-alumina and very interactive zirconia-yttria. The goal of the present paper is to correlate bilayer architecture with phase evolution and interface structure in zirconia-titania nanolaminate films grown on room temperature silica substrates by sequential reactive sputter deposition from zirconium and titanium elemental targets. Nanolaminates with seventeen different bilayer architectures were studied. Diffraction and ultraviolet-visible spectrophotometry techniques were used for film characterization. The results show that an interfacial reaction occurred between zirconia and titania layers. Phase evolution in the zirconia layers in nanolaminates with ultrathin (1.5 nm) titania layers was dependent upon this interfacial reaction. Specifically, < 100 > orientation, high refractive index cubic zirconia was stabilized in zirconia layers between 16 and 22 nm. This crystal orientation indicates that cubic zirconia growth is ordered by the lowest energy planes of the simple cubic anion sublattice of the fluorite structure. Increasing the zirconia layer thickness beyond 22 nm in nanolaminates with ultrathin titania layers resulted in zirconia renucleation and the formation of other zirconia phases. Increasing the titania layer thickness quenched the formation of < 100 > cubic zirconia resulting in a vitreous structure.

#### **F5.20**

##### **COATING OF SILICON CARBIDE ON SILICON NANOWIRES BY DIRECT LOW-ENERGY ION BEAM DEPOSITION.**

Hongying Peng, X.T. Zhou, N. Wang, S.T. Lee, City University of

Hong Kong, Dept of Physics and Materials Science, Hong Kong, CHINA.

The successful bulk-scale synthesis of Si nanowires by laser ablation or thermal evaporation has aroused great interest in this one-dimensional material. The field emission current of silicon emitters widely used for flat panel display devices was found to increase significantly by a thin SiC coating through a chemical conversion process. In present study, silicon nanowires with diameters around 20 nm were subjected to methane, argon and hydrogen ions bombardment at 997K for 10 hours with an ion energy of 200 eV. TEM observations showed that the product remained to be nanowires with diameter ranging from 20 nm to 40 nm. The corresponding electron diffraction pattern revealed that both Si and beta-SiC phases were present. Dark field TEM images showed that the silicon diffraction ring comes from the core of the nanowires, while the silicon carbide ring comes from the outside layers of the nanowires. Detailed observations at high magnification identified that a thin silicon carbide polycrystal was grown uniformly on the silicon nanowire surface. The thickness of this SiC outer layer was found to be as thin as 2-4 nm. Most of the SiC nanoparticles were randomly oriented and separated with its Si core by a thin layer of Silica. The Raman peak of the composite nanowires was about 20 1/cm lower than that of the silicon nanowires. The photoluminescence intensity of the nanowires after coating with SiC became stronger and sharper, and the peak blueshift appeared much larger.

#### F5.21

OPTICAL RESPONSE OF COMPOSITE  $Al_2O_3$  FILMS WITH Cu EMBEDDED NANOCRYSTALS PRODUCED BY PULSED LASER DEPOSITION. R. Serna, J. Gonzalo, J. M. Requejo, J. Solis, C.N. Afonso, Instituto de Optica, CSIC, Madrid, SPAIN; F. Stietz, F. Traeger, Universitaet Gesamthochschule Kassel, Kassel, GERMANY.

Thin films formed by metal nanocrystals embedded in insulating matrices, usually oxides, are being intensively investigated for the development of compact integrated ultrafast optical switches. Thus synthesis methods compatible with the growth of good quality oxides and the development of metal nanostructures are required. Pulsed laser deposition has demonstrated to have high potential both for oxide deposition and for the development of artificial structures. In this paper we aim to show a systematic study of the optical linear and nonlinear properties of nanophase systems formed by Cu nanocrystals embedded in an amorphous  $Al_2O_3$  matrix, in which a good control of the average size of the metal nanocrystals and its in-depth distribution are achieved. The Cu: $Al_2O_3$  thin films are produced by alternate ablation of independent targets, in a controlled gas environment. Nanostructured films have been obtained with characteristic nanocrystal Cu sizes varying from 2 nm to 8 nm, and with Cu-Cu nanocrystal in-depth separations changing from 5 nm to 20 nm. The optical absorption spectra of the films show the characteristic enhancement close to the expected surface plasmon resonance wavelength for Cu nanocrystals. The changes in the linear and non linear optical properties will be discussed as function of the Cu nanocrystal size, morphology, in-depth separation, in addition to the possible reactions at the metal nanocrystal- oxide interface.

#### F5.22

THE FORMATION OF HIGH-COERCIVITY, ORIENTED NANOPHASE MAGNETIC PRECIPITATES IN OXIDE SINGLE CRYSTALS BY ION IMPLANTATION. Shin-ichi Honda, Frank A. Modine, Tony E. Haynes, Alkiviathes Meldrum, John D. Budai, Kyujeong Song, James R. Thompson, and Lynn A. Boatner, Solid State Division, Oak Ridge National Laboratory Oak Ridge, TN.

Ion-implantation and thermal-processing methods have been used to form nanophase ferromagnetic or superparamagnetic precipitates that are embedded in the near-surface region of single crystals of  $Al_2O_3$  and yttrium-stabilized (cubic) zirconia (YSZ). Specifically, ferromagnetic precipitates have been produced by the ion implantation of Co, Ni, and Fe; and either metal or oxide precipitates may be formed depending on the properties of the annealing atmosphere. In general, the precipitates are faceted, isolated single-crystal particles that are crystallographically oriented with respect to the host  $Al_2O_3$  or YSZ lattice. In the Co case, embedded nanophase precipitates were formed by the implantation of  $Co^+$  at an energy of 140 keV and a dose of  $8 \times 10^{16}$  ions/cm<sup>2</sup> followed by annealing in a reducing atmosphere. The implanted/annealed Co depth profile, the particle size distributions and shapes, and the orientational relationship between the ferromagnetic nanophase precipitates and the host crystal lattice were determined using RBS/channeling, transmission electron microscopy, and x-ray diffraction. Magneto-optical effects arising from the ferromagnetic precipitates formed in both the  $Al_2O_3$  and YSZ host were observed and characterized using magnetic circular dichroism. The details of the magnetic properties of the implantation-produced ferromagnetic-particle/host surface nanocomposites (including large magnetic anisotropy effects) were investigated in the temperature

range of 5 to 295 K in applied fields of up to 60 kG using a superconducting quantum interference device (SQUID)-based magnetometer. In the case of ferromagnetic precipitates formed in  $Al_2O_3$  by the implantation of Co followed by annealing, the subsequent ion implantation of Pt was found to produce a large anisotropic increase in the coercivity. Accordingly, magnetic nanoparticle systems of this type may be of interest for applications in the field of magnetic data storage. Details of the magnetic properties of these near-surface nanocomposites including the retentivity, coercivity, saturation field, and magnetic anisotropy will be presented.

#### F5.23

NANOCASTS FROM LYOTROPIC ABC PHASES. Christine G. Goltner, School of Chemistry, Cantock's Close, Bristol, UNITED KINGDOM; Beate Berton, Hans-Peter Hentze, Eckart Kramer, Markus Antonietti, Max-Planck Institute for Colloids and Interfaces, Am Muehlenberg, Potsdam, GERMANY.

As a result of selective-solvent interaction, amphiphilic block copolymers (ABCs) form lyotropic aggregates of sometimes surprisingly high structural regularity. As these aggregates are kinetically and thermodynamically very stable, they represent versatile structure-directing media for the synthesis of inorganic-organic hybrid materials. These hybrids can be converted into porous inorganic nanostructures of tunable pore size, pore structure and large specific surface area. The structure control via different experimental parameters as well as the synthesis of hierarchical pore systems are discussed.

#### F5.24

A NANO-COMPOSITE POLY(METHYL METHACRYLATE) BONE CEMENT. Andreas Gomoll, Anuj Bellare, Wolfgang Fitz, Thomas S. Thornhill, Richard D. Scott, Orthopaedic Research Laboratory, Brigham and Women's Hospital, Boston, Harvard Medical School, Boston, MA; Peter R. Jemian, University of Illinois, Urbana-Champaign, IL; Gabrielle G. Long, National Institute of Standards & Technology, Gaithersburg, MD.

Poly(methyl methacrylate) (PMMA) based bone cement is widely used for fixation of orthopedic implants. These cements contain micrometer size filler particles of either barium sulfate or ceramic particles such as zirconium oxide. The purpose of adding fillers is to radiopacify the cement, thereby enabling the orthopedic surgeon to monitor the cement using x-ray radiographs. A problem associated with the use of 1-10 micrometer diameter radiopacifier particles is that incomplete dispersion of the particles during mixing of the monomer and prepolymerized powder results in the formation of particle agglomerates of 50-200 micrometer diameter. These large defects are sites of high stress concentration that reduce the fracture toughness of PMMA cements, leading to early fracture of the cement and loosening of the implant, ultimately necessitating early revision surgery to replace the implant. In this study, the micrometer size radiopacifier particles were replaced by commercially available nano-sized (approximately 60 nanometer diameter) aluminum oxide radiopacifying particles (Nanophase Technologies Corp) in commercial PMMA bone cements. These nanocomposite PMMA bone cements were thereafter characterized using ultra-small angle x-ray scattering (USAXS) at the UNICAT beamline of the Advanced Photon Source, Argonne National Laboratory. The advantage of using USAXS over conventional SAXS is that the angular range of scattered synchrotron x-rays enables the morphology to be quantitatively characterized over a large range of length scales, from approximately 4 micrometer down to 2 nanometer. The nanocomposite and microcomposite PMMA bone cements were also subjected to ASTM standard mechanical tests to determine their fracture toughness. These results and the effect of varying the volume fraction of the nano-sized particulate fillers on the morphology and toughness of nanocomposite PMMA bone cement will be discussed.

#### F5.25

MANIPULATION OF THE CORE-SHELL PROPERTIES IN GOLD-THIOLATE NANOCOMPOSITE MATERIALS. Chuan-Jian Zhong, Chuan-Jian Zhong, Wenxia Zheng, Frank L. Leibowitz, Mathew M. Maye, Steven R. DeLaCruz, Nam. K. Ly, Yoon. A. Kim, Edward. T. Phillip, State Univ. of New York, Binghamton, NY.

In this report, we present recent findings of an investigation of the manipulation of core and shell properties in nanomaterials derived from organosulfurs and gold nanocrystals. The creation of nanocomposite interfacial architectures for chemical sensing and energy storage via combinations of functionalized thiolate shells and shaped metallic cores constitutes the motivation of the work. One pathway that has been developed for core size and shape control is the desorption/re-deposition of the shell components and the coalescence/growth of the core under temperature manipulation in solutions [1]. Remarkable size and shape evolution has been demonstrated for preformed nanoparticles. Another pathway that is

found effective for assembling thin films is the one-step exchange-precipitation route [2]. Interesting electrochemical, spectroscopic and microscopic properties have been observed for the resulting nanocomposite thin films. Mechanistic aspects involved in these processes will be discussed. References: [1] Zhong, C.J.; Zheng, W.X.; Leibowitz, F.L.; Eichelberger, H.H., Chem. Commun., in press. [2] Zhong, C.J.; Zheng, W.X.; Leibowitz, F.L., Electrochem. Commun., 1, 72 (1999).

#### **F5.26**

**XPS STUDY OF Pt/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>/Si COMPOSITE SYSTEMS.** R. Sporken, A. Galtayries, Univ. of Namur, Laboratoire LISE, Namur, BELGIUM; K. Keveney, M.Pijolat, Ecole des Mines, Saint-Etienne, FRANCE, R. Baker and S. Bernal, Universidad de Cadiz, Cadiz, SPAIN.

Cerium oxide is widely used as a promoter in three-way catalysts for exhaust systems in gasoline burning car engines. Adding ZrO<sub>2</sub> to CeO<sub>2</sub> significantly improves its thermal stability and its ability to store and release oxygen under reaction conditions. To study the interaction between noble metals and the mixed oxide on a model system, we have prepared Pt/Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>/Si(111) composite systems and studied them with x-ray photoelectron spectroscopy and x-ray diffraction. Thin films of Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> mixed oxides (about 10-30 nm thick) were grown on Si(111) substrates by electron beam evaporation. The composition of the films was determined by XPS and EDX and was found to be slightly enriched in Ce compared to the source material. XPS depth profiles showed the following structure, starting from the substrate: a region of interdiffused Zr and Si, a CeSiO<sub>x</sub> layer mixed with ZrO<sub>2</sub> and finally a homogeneous Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> film. x-ray diffraction confirmed the presence of CeZrO<sub>2</sub> mixed oxide and suggests the presence of ZrO<sub>2</sub> and CeO<sub>2</sub> in some of the samples. Pt was evaporated onto these mixed oxide films. The deposition of Pt was interrupted several times to record XPS spectra. Eventually, the Pt/(Ce,Zr)O<sub>2</sub> system was submitted to reducing and oxidizing conditions to study the effect on the noble metal - support interaction. It was found that, in contrast to noble metal - oxide powder composite systems, the noble metal always stays in the fully reduced state in the case of Pt on mixed oxide thin films. Zr remains in the 4+ oxidation state, whereas Ce oscillates between 3+ and 4+. For mild reducing conditions (10<sup>-3</sup> Torr H<sub>2</sub>, 350°C), we observe an increase of Ce<sup>3+</sup> concentration of up to 30%, which we do not observe in the absence of Pt. A small shift of the Pt 4f binding energy to higher binding energies (about 0.5 eV) for very low Pt coverage can be explained by a cluster size effect, where screening of the core hole created by the photoemission is less efficient for very small clusters.

#### **F5.27**

**PHOTOVOLTAIC DEVICES FROM POLYMER-NANOPARTICLE COMPOSITES.** Shau Y. Tsai, John H. Riley, Ramesh Sivarajan, Emmanuel P. Giannelis, George G. Malliaras, Cornell University, Dept. of Materials Science and Engineering, Ithaca, NY.

Photovoltaic devices based on composites of polythiophene with silica and titania nanoparticles have been fabricated. The device efficiency was measured as a function of the nanoparticle concentration, the thickness of the composite layer and for various electrode materials. The optical and electrical properties of the composites were studied in order to elucidate the mechanism of device operation. The results were correlated with the morphology of the composites. The influence of organic modification of the nanoparticles on the device performance was also investigated.

#### **F5.28**

**MICROSTRUCTURAL EVALUATION OF PRECURSOR DERIVED Si-C-O BULK CERAMICS.** Ken-ichi Kakimoto, Fumihiko Wakai, Japan Science and Technology Corporation, Nagoya, JAPAN; Joachim Bill, Fritz Aldinger, Max-Planck-Institute for Metals Research, Stuttgart, GERMANY.

We have recently fabricated Si-C-O bulk ceramics with a variety of non-equilibrium compositions by pyrolysis of shaped polycarbosilane (PCS) body with given amounts of oxygen. The oxygen introduction within PCS molecular structure made the body infusible during the pyrolysis step, and supported its sintering as well as an increase of the ceramic yield. The C/O atomic ratio of the ceramics was easily controllable and much higher than that of conventional Si-C-O glass ceramics which are derived from silicon alkoxide precursors including some tetraordinated carbon units. Therefore, this procedure is also expected to be suitable for preparation of SiC/Si-C-O nanocomposite by in-situ carbothermic reduction reaction at high temperature. The present paper specifically reports the microstructure of the various PCS-derived Si-C-O ceramics and describes the effect of different processing conditions on the microstructure. The ceramic body after pyrolysis to 1573K showed fine microstructure of SiC nano grains with amorphous phases. The grain diameter and the porosity of the body decreased with increasing oxygen content. The specimen with a higher

packing density also demonstrated both of a smaller SiC grain size and a finer pore size. This microstructure particularly contained a large number of free-carbon phases which is believed to have been caused by the self internal gaseous reaction of pyrolytic methane and hydrogen gases. Such a carbon phase was useful to inhibit rapid SiC grain growth. A SiC/Si-C-O nanocomposite which was prepared at 1873K kept fine microstructure with SiC grains of 40nm at maximum. The relationship between processing atmosphere and surface bulk composition is also discussed in this paper.

#### **F5.29**

**MICRO-RAMAN STUDY OF SELF-ASSEMBLED NANO-STRUCTURES: (1-x)PZN-xPT SOLID SOLUTION.** S. Gupta, R.S. Katiyar, Department of Physics, Univ. of Puerto Rico, San Juan, PR; A.S. Bhalla, Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Relaxor ferroelectrics are one of the important class of self-assembled nano structure composite materials. Interesting features associated with the nanoregions give rise to the most interesting device related characteristics and unusual properties in these materials. Besides, they possess the largest property coefficients alone and when modified with lead titanate (PT) as well. In this report, a detailed study has been carried out on (1-x)PZN-xPT relaxors with compositions x = 0.05 and 0.085 by polarized Raman scattering under various optical and E-field variables and inferred the structure-property relations in order to obtain enough information to curtail the material for matching the application criteria. In addition, phase transitions associated with the relaxors have also been investigated to understand the polarization mechanism(s) for unpoled and poled specimen. Authors wish to acknowledge the following NSF-DMR-9801759 and DAAG55-98-1-0012 US grants for financial support.

#### **F5.30**

**ROOM TEMPERATURE LUMINESCENCE FROM ULTRATHIN Si/SiO<sub>2</sub> MULTILAYERS PREPARED BY RF CO-SPUTTERING.** M. Buzaianu, O. Resto, L.F. Fonseca, and S.Z. Weisz, Department of Physics, University of Puerto Rico, San Juan, PR.

Multilayered structures of Si and SiO<sub>2</sub> films with thicknesses ranging between 40nm to 2nm were deposited by using sequential RF sputtering. The depth profile of the layered structures were characterized by Auger spectroscopy and TEM microscopy. The crystallinity was studied by electron diffraction technique. We discuss about the dependence of the room temperature photoluminescence on the thickness of the films and the number of layers. Other optical properties as optical absorption were also obtained to get information about the energy gap size of the silicon films. We discuss the dependence of the optical properties of the multilayers on the structural parameters and we compare our results with photoluminescent nanocrystalline-Si/ SiO<sub>2</sub> samples grown with the same technique.

#### **F5.31**

**STUDY OF THE LUMINESCENCE OF Eu-DOPED NANOCRYSTALLINE Si/SiO<sub>2</sub> SYSTEMS PREPARED BY RF CO-SPUTTERING.** G. Nery, L.F. Fonseca, O. Resto, and S.Z. Weisz, Department of Physics, University of Puerto Rico, San Juan, PR; A. Mahfoud and H. Liu, Department of Physics, University of Puerto Rico, Mayaguez, PR.

Eu-doped nanocrystalline silicon structures were prepared by RF co-sputtering. The host material was silicon particles with sizes ranging from ~1.2nm to ~3nm embedded in SiO<sub>2</sub>. The optical properties of the undoped and doped materials were characterized using picosecond and CW laser sources. We found that the luminescence due to Eu-doping is strongly dependent on the synthesis conditions. We correlated the optical properties with the nanoparticle size distributions and the valence state of the dopant. We offer conclusions about the dependence of the Eu-photoluminescence intensity on the energy gap sizes of the semiconductor nanocrystals.

#### **F5.32**

**TITANIUM DIOXIDE AND APATITE COATED POUROUS CERAMICS PHOTOCATALYST.** Toru Nonami, Shinji Kato\*, Hiroshi Taoda, National Industrial Research Institute of Nagoya, Dept of Multi Functional Materials, Nagoya, JAPAN. \*Noritake Co., Ltd, Nagoya, JAPAN.

Titanium dioxide can photo-oxidize organic chemical materials in water and air, when it is illuminated. Apatite is useful in absorption of bacteria, viruses etc. If apatite and titanium dioxide can be combined into a composite with the attributes of both, this composite may be a good antibacterial and environmental purification material, having the ability to absorb and to decompose bacteria and other organic materials. Titanium dioxide was coated on the surface of the porous ceramics by sol-gel method, then the ceramics was soaked in a

pseudo body solution containing excess phosphate ions. After soaking in the pseudo body solution for 1 day, a bone like apatite layer was formed on the surface of the titanium dioxide. This ceramic has resolved various organisms such as methylene blue. The apatite coated titanium dioxide thin film could be used for antibacterial and environmental purification.

#### **F5.33**

**SYNTHESIS OF LOW-DIMENSIONAL NANOSTRUCTURES USING LAYERED DOUBLE HYDROXIDES AS NANOREACTORS.** Alexey V. Lukashin, Alexei A. Vertegel, Sergei V. Kalinin, Maxim P. Nikiforov, Yuri D. Tretyakov, Higher School of Materials Science, Moscow State University, Moscow, RUSSIA.

A novel method for the preparation of nanostructured materials is discussed. The method is based on the chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and a possibility of preparation of two-, one- or zero-dimensional nanoparticles in oxide-hydroxide matrices. LDHs have a general formula  $M_{1-x}M''_x(OH)_2[(anion)_{x/n} \bullet mH_2O]$ , where  $M'$  and  $M''$  are metals in the oxidation state +2 and +3, respectively, and anion  $n^-$  is virtually any anion, which does not form a stable complex with  $M'$  or  $M''$ . A structure of an LDH consists of positively charged hydroxide layers  $[M'_{1-x}M''_x(OH)_2]^{x+}$  bonded with negatively charged anions, which occupy the interlayer space. Due to the relatively large interlayer distance, the anions in LDHs are readily exchangeable and it is possible to obtain species with practically stoichiometric content of an appropriate anion  $n^-$ . In the present paper, we use the reduction of LDHs containing EDTA complexes of Fe(III), Ni(II) and Co(II) in the interlayer space for the preparation of magnetic nanoparticles of the corresponding metals. Also, thermal decomposition of an LDH substituted with  $[Pb(S_2O_3)]^{2+}$  anions has been used for the preparation of PbS nanoparticles. When reduction or decomposition of an anion  $n^-$  occurs, hydroxide layers of LDH restrict the reaction area. Thus, the interlayer space of LDH serves as a two-dimensional nanoreactor resulting in the formation of low-dimensional nanostructures.

#### **F5.34**

**STOICHIOMETRY CONTROL IN MOLECULAR BEAM DEPOSITED NANOCRYSTALLINE  $SnO_2$  and  $TiO_2$  THIN FILMS.** Holger Hoche, Horst Hahn, Felix Edelman, Ralf Nagel, Stefan Flege, Adam Balogh, Technical University of Darmstadt, Dept of Materials Sciences, GERMANY.

Molecular beam deposition (MB) of thin film metal oxide is prospective for application in gas sensor technology due to the well-controlled oxide molecular fluxes during creation of multi-oxide structures with improved characteristics. However, the MB process leads to some oxygen deficiency in the oxide. Further application of the MB technology (and, in general, the e-beam oxide deposition in vacuum) for processing of sensor structures needs the control and correction of the oxygen stoichiometry by adding in-situ atomic oxygen to the growing material or via the thin film oxidation after deposition. Thin films (about 50nm) of  $SnO_x$  and  $TiO_x$  were deposited on  $SiO_2/(001)Si$  substrates at 100°C by MB from  $SnO_2$  and  $TiO_2$  sources. The film stoichiometry in the as-deposited state is characterized by XRD, RBS and SIMS. The films were annealed in oxygen at various temperatures and time to characterize changes in the film stoichiometry and kinetics of  $O_2$  reaction with  $SnO_x$  and  $TiO_x$ . The grain size evolution in films during  $O_2$ -annealing was controlled by TEM. The results of in-situ oxygen control in evaporating oxides using a special system for atomic oxygen formation in the MB setup will be presented. In conclusion, we discuss a problem, whether this system makes possible to eliminate the high-temperature postdeposition stage of the oxygen stoichiometry correction in the oxide.

#### **F5.35**

**BLOCK AND STAR COPOLYMER NANOCOMPOSITES.** H. Chen, E.P. Giannelis, Cornell Univ., Dept. of Materials Science and Engineering, Ithaca, NY; M.W. Weimer, O.A. Scherman, D. Sogah, Cornell Univ., Dept. of Chemistry and Chemical Biology; M. Pitsikalis, N. Hadjichristidis, Univ. of Athens, Dept. of Chemistry, Athens, GREECE.

Polymer-silicate nanocomposites has generated great interest among researchers, mainly because of their much more improved properties comparing with their bulk counterparts or conventional composites. They also provide an ideal model to investigate the structures and dynamics of polymer in nanoconfinement. However, most of the work to date has focused on homopolymers. Here we present work on nanocomposites made of block and star copolymer and organically modified silicates. The mobility of confined copolymers both under and above their respective order-disorder-transition temperatures, as well as the effect of the existence of silicate nanolayer on the microphase transition of the copolymer will be discussed.

#### **F5.36**

**SOFT  $ZnWO_4$  ON HARD WN SELF-LUBRICATING NANOCOMPOSITE COATINGS.** M. Vedawyas, D. Patel, G. Wattuhewa and Ashok Kumar Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL.

The significance of using nano-phase ceramic materials is the benefit of increased performance for metal properties with respect to strength, hardness, toughness and ductility at elevated temperatures. In this work we propose to develop a self-lubricating nano-composite material comprising of nanolayers of soft high temperature lubricant material  $ZnWO_4$  in a hard wear resistant matrix of WN. WN is a known to be a wear resistant at elevated temperatures and  $ZnWO_4$  is a high temperature adaptive lubricant. WN films are deposited on Si(100) substrates by pulsed laser deposition (PLD) technique in nitrogen atmosphere. Then the  $ZnWO_4$  lubricant layers are coated by laser ablation of  $ZnWO_4$  target in oxygen atmosphere. The composite coatings are prepared at various temperatures and oxygen partial pressures, so as to optimize the parameters to get good crystalline phase of  $ZnWO_4$  coatings. The composite coatings are characterized by Raman spectroscopy, x-ray diffraction, scanning electron microscopy and atomic force microscopy to study their morphology and crystallinity. The mechanical properties like the modulus of elasticity and hardness are evaluated by the nano indentation technique. This research is supported by NSF-DMII - 9900459 MRS 1999 Fall Meeting Symposium L : Fundamental Mechanism of low-energy beam-modified surface growth and processing. Enhancement in the growth of textured HFCVD diamond coatings on modified Ti-6Al-4V substrate by excimer laser processing Mikhail T. Galeev, M. Vedawyas, G. Sivanathan and Ashok Kumar Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL-36688, USA Currently, a major focus in diamond film technology is on the chemical vapor deposition of diamonds on metal substrates, for enhancing the durability of widely used metals. For a number of reasons, high quality diamond coatings are difficult to achieve on metal surfaces. In this work we address, the studies of enhancement in diamond growth on Ti-6Al-4V metal alloy by modifying the surface using the excimer laser ablation technique, prior to deposition of diamond. Ti-6Al-4V is chosen for its technological importance in aerospace industry, dental and bio-implant applications. Analysis of the structures of the film is done using X-ray diffraction, scanning electron microscopy and Raman spectroscopy. Ablation of the alloy by excimer laser pulses produces periodically hill/valley structures on the surface, thus increasing the density of diamond nucleation and film adhesion. The roughness of the alloy surface was measured to be in the 0.5mm - 1mm range with an average distance between peaks of the hill/valley structure measuring 1.5mm. This research was supported by Alabama NASA EPSCoR program.

#### **F5.37**

**COMPLEXES OF Cu(II) WITH POLYVINYL ALCOHOL AS PRECURSORS FOR THE PREPARATION OF  $CuO/SiO_2$  NANOCOMPOSITES.** Andrey A. Eliseev, Lidia I. Soboleva, Alexander I. Zhironov, Alexey V. Lukashin, Konstantin V. Tomashevitch, Alexei A. Vertegel, Higher School of Materials Science, Moscow State University, Moscow, RUSSIA.

Cupric oxide ( $CuO$ ) nanoparticles have been prepared in amorphous  $SiO_2$  matrix using a novel variant of sol-gel technique. The method is based on the polycondensation of a silica source (sodium silicate or tetraethoxysilane) in the presence of an aqueous solution containing complex of Cu(II) with polyvinyl alcohol (CuPVA). Studies of the gelation kinetics show that the process is the first order reaction with respect to CuPVA. After gelation, polymeric complexes containing several thousand Cu atoms each are incorporated into the silica network forming a precursor, which is then freeze-dried and annealed in oxygen to get rid of organic components. The freeze-dried gels and the annealed products were characterized by SDR, IR-spectroscopy, ESR, and TEM. The formation of  $CuO$  nanoparticles was confirmed by electron diffraction studies. The size of nanoparticles can be controlled by varying the concentration of CuPVA in initial solution and using polyvinyl alcohol species with different molecular weight.  $CuO$  nanocomposites are characterized by high specific surface areas as measured by capillary absorption of nitrogen at 77 K, suggestin their possible use in catalysis.

#### **F5.38**

**LIGAND, VISCOSITY, AND POLYMER STRUCTURAL EFFECTS IN THE SYNTHESIS OF SURFACE METALLIZED POLYIMIDE FILMS VIA IN SITU REDUCTION OF SILVER (I) COMPLEXES.** Robin E. Southward, National Research Council, Langley Research Center, National Aeronautics and Space Administration, Hampton, VA; Elizabeth Cornell, Christopher J. Dean, David W. Thompson, Department of Chemistry, The College of William and Mary, Williamsburg, VA.

Metallized polymeric films are commonly prepared by physical vapor deposition (PVD); however, poor adhesion results with passive metals. We report an in situ single-stage preparation of silver(I) complexes in solutions of poly(amic acids) for the fabrication of silvered polyimide films which are highly reflective and conductive and which exhibit superb adhesion. Silver(I) complexes of trifluoroacetate anion and the beta-diketonate anions, trifluoroacetylacetonate, thenoyltrifluoroacetate, and hexafluoroacetylacetonate, with poly(amic acid)s in dimethylacetamide are cast as films. Thermal curing to 300°C effects silver(I) reduction with subsequent migration to form a surface metallized film. Similar phenomena are observed when silver nitrate and silver tetrafluoroborate are used as the silver(I) precursor. Comparisons among these six silver(I) precursors for the surface metallization of three polyimides at differing viscosities will be discussed with regard to reflectivity, conductivity, and surface and bulk particle distribution and morphology.

#### **F5.39**

**SELF-ASSEMBLED CdS-DENDRIMER NANOCOMPOSITES.** Lisa Pasierb, David W. Wright, Duquesne University, Dept. of Chemistry and Biochemistry, Pittsburgh, PA.

The development of new types of functionalized nanocomposites that are based on quantum-confined CdS nanoparticles within a dendrimer aggregate matrix is of current interest. Such materials have potential applications in optical-electrical devices and catalysis. Using a series of PAMAM dendrimers (G2-OH through G4-OH), we have successfully stabilized several populations of CdS nanoclusters within the resulting dendrimeric aggregate. A number of factors can be used to control the distribution of CdS particle sizes including reactant stoichiometries, solvent, and reaction time. Gel permeation chromatography (GPC) has shown that the CdS-dendrimer aggregate yields nanocomposites of roughly the same size, regardless of the dendrimer generation. Such a result is consistent with a self-assembly process in the formation of the aggregates. The photophysical and photocatalytic properties of the CdS-dendrimeric nanocomposite will be reported.

#### **F5.40**

**FLEXIBLE INORGANIC/ORGANIC HYBRID SHEETS FABRICATED FROM METAL ALKOXIDES AND PLOYDIMETHYLSILOXANE.** Noriko Yamada, Ikuko Yoshinaga and Shingo Katayama, Nippon Steel Corporation, Advanced Technology Research Laboratories, JAPAN.

Flexible inorganic/organic hybrid sheets were synthesized from polydimethylsiloxane and chemically modified metal alkoxides. The chemical modification of metal alkoxides formed no precipitate in the synthesis process, resulting in homogeneous and transparent hybrids that contain various inorganic components derived from Al, Ti, Zr and Ta alkoxides. The inorganic species derived metal alkoxides were less than several nm sizes, because any inorganic particles were not observed by TEM even with 1M magnifications. The hybrids also exhibited excellent flexibility with the storage modulus of 106-7 Pa. The flexibility was constant up to about 300°C. Especially, we succeeded in fabricating large sheets of A4 size for the hybrids containing the inorganic component derived from Zr alkoxide. The incorporation of nano-particles of titania prepared by hydrolysis of Ti alkoxide into the hybrid was also carried out to improve the mechanical properties. The tensile strength showed an abrupt increase and leveled off at a low particle content of 2.7 vol %. The DSC experiments revealed that the DSC peaks for crystallization and melting of PDMS in the hybrid were reduced and shifted by addition of the particles. The reduction and shift of the DSC peaks are due to the lesser mobility of PDMS. The decrease in mobility is attributed to the strong interaction between the particles and PDMS, possibly leading to a change of the hybrid structure for the increase in tensile strength. Research supported by NEDO, under the Synergy Ceramics Project of the ISTF program promoted by AIST, MITI, Japan.

#### **F5.41**

**SOFT CHEMICAL DESIGN OF TRANSITION-METAL-OXIDE / CLAY LAYERED NANOCOMPOSITES.** Kiyoshi Fuda, Shuji Narita, Shuji Kudo, Kenji Murakami, Toshiaki Matsunaga, Dept of Material-Process Engineering and Applied Chemistry, Akita Univ, JAPAN.

Metal / insulator layered nanocomposite has attracted great interest from not only scientific but also industrial aspects. For constructing such composites, layered transition metal dioxide and clay minerals are expected to be the conductor and insulator parts of the structure. Here we would like to show a new synthetic approach based on soft chemical techniques to form a layered nanocomposites wherein transition metal oxide and silicate layers are alternately stacked with nanometer order of period. The processing involves the two-dimensional polymerization of metal hydroxide monolayers through hydrolysis of cations (intercalation) and oxidation of the

hydroxide layers with aqueous NaClO solution (chimie douce reaction). This successive processing affords a new expanded structure of periodic length of 1.96 nm. The distribution of the atoms along c-direction was determined with the aid of one-dimensional Fourier analysis, indicating that MO<sub>2</sub> slabs (M = Ni, Co and Mn) are sandwiched by two monolayers of hydrated alkali cations in the interlayer space of the clay. The relation between structure and properties will be discussed.

#### **F5.42**

**STRUCTURAL STUDIES OF NANOPHASE SILICA-CHITOSAN-METAL AEROGELS.** Xiangjun Hu, Shuang Ji, William M. Risen, Jr., Brown University, Dept of Chemistry, Providence, RI; David Pickles, Corning Inc, Corning, NY; Kenneth Littrell, Argonne National Lab, IPNS, Argonne, IL.

Aerogels containing silica, the bio-derived polymer chitosan, and transition metal ions have been studied by spectroscopic, microscopic, optical, and neutron scattering methods to determine the essential nanoscale and molecular scale features of their structures. The optical and spectroscopic investigations show that the chitosan is incorporated as an integral component of the nanophase, and that the metal ions, including Rh, Ru, Co, Ni, or Cu, are coordinated to it. The transmission electron microscopic (TEM) and small angle neutron scattering (SANS) studies have served to elucidate the nanophase structure itself. The TEM work will be presented in both direct and replica modes. The SANS data were obtained in the range of q values of 0.004 to 0.5 (reciprocal Angstrom), and analyzed in the context of the TEM data by several approaches. In the log q range -1.8 to about -0.8, the data show a power law correlation. The data from these studies will be interpreted in terms of the relation between particle size and a correlation length associated with collections of particles.

#### **F5.43**

**CATALYTIC STUDIES OF NANOPHASE SILICA-CHITOSAN AEROGELS CONTAINING RHODIUM OR RUTHENIUM IONS.** Shuang Ji, Xiangjun Hu, William M. Risen, Jr., Brown University, Dept of Chemistry, Providence, RI; Richard Gonzalez, Tulane University, Dept of Chemical Engineering, New Orleans, LA.

Aerogels containing metal ions coordinated to chitosan have been reacted with carbon monoxide, nitric oxide, hydrogen, and oxygen in both the hydrated and dehydrated states in order to investigate their potential application as catalysts. The monolithic form of the aerogel samples permits the reactions to be monitored directly by infrared and visible spectroscopy. The studies of the Rh or Ru forms of the aerogels reveal a rich reaction chemistry as well as a range of gas absorption phenomena. The reactions with CO, for example, lead to the formation of metal carbonyls of Rh in oxidation states from +3 to 0, either as a consequence of the catalysis of the water-gas shift reaction (leading to reduced Rh species) or the direct reaction with hydrogen and subsequent reaction with CO. Reactions with NO lead directly to the formation of Rh nitrosyls. Analogous reactions with Ru forms of the aerogels also show the formation of a range of carbonyls and nitrosyls. The results of catalytic studies for the use of these aerogels as catalysts for carbonylation, oxidation and other relatively low temperature reactions will be presented.

#### **F5.44**

**CHARACTERIZATION OF Pt/TiO<sub>2</sub> NANOCOMPOSITE-SITE FILMS PREPARED BY CO-SPUTTERING.** Takeshi Sasaki, Naoto Koshizaki, Nat Inst of Matls & Chem Res, Dept of Composite Matls, Tsukuba, Ibaraki, JAPAN; Michio Koinuma, Masayuki Noguchi, Yasumichi Matsumoto, Kumamoto Univ, Dept of Applied Chemistry & Biochem, Kumamoto, JAPAN.

It is well known that Pt/TiO<sub>2</sub> composite has been used as the photocatalyst for decomposition of water. Pt/TiO<sub>2</sub> composites have been prepared by a variety of methods such as sol-gel methods and thermal decomposition. In this paper the preparation of Pt/TiO<sub>2</sub> nanocomposite films (platinum nanoparticles dispersed in TiO<sub>2</sub> films) by co-sputtering method and optical properties of these films were demonstrated. TEM, TED, XPS and XRD measurements of the films revealed that annealed Pt/TiO<sub>2</sub> nanocomposite films consist of Pt metal nanoparticles in the matrix of rutile-type TiO<sub>2</sub>. The size of Pt nanoparticles in the composite films increased with the heat-treatment temperature. The Pt nanoparticle size in the film with a Pt/Ti atomic ratio of 0.18 annealed at 600°C ranged from 5 to 10 nm. The photoelectrochemical behaviors of the Pt/TiO<sub>2</sub> nanocomposite films in aqueous solutions were investigated. Anodic photocurrents of Pt/TiO<sub>2</sub> nanocomposite film at 1.0 V vs. Ag/AgCl were observed at the wavelength region of visible light. Wavelength of optical absorption edges of the Pt/TiO<sub>2</sub> nanocomposite films was around 450 nm, which was much longer than that of TiO<sub>2</sub>. Luminescence emission at 700 nm was also observed by UV excitation from the Pt/TiO<sub>2</sub> nanocomposite films at liquid nitrogen temperature. Thus, the optical properties of Pt/TiO<sub>2</sub> nanocomposite films were much different from

those of TiO<sub>2</sub>. It appears that interfacial or surface states between homogeneously dispersed Pt nanoparticles and TiO<sub>2</sub> matrix produce new energy levels within the bandgap of TiO<sub>2</sub>.

#### **F5.45**

**RADIATION-INDUCED CRYSTALLIZATION AND AMORPHIZATION OF Si NANOPRECIPITATES, EMBEDDED IN SiO<sub>2</sub>.** G.A. Kachurin, S.G. Yanovskaya, A.K. Gutakovskiy, K.S. Zhuravlev, Inst of Semiconductor Physics SO RAN, Novosibirsk, RUSSIA; M.-O. Ruault, O. Kaitasov, H. Bernas, Orsay, FRANCE.

Due to the quantum-size effect Si nanocrystals (Si-ncs) can emit strong visible light, therefore they are widely considered as the most promising candidates for the future Si-based integrated opto-microelectronics. In spite of the extensive studies of Si-ncs, the physical aspects of their synthesis, processing and stability are still not clarified. This report describes the unusual behavior of Si nanoprecipitates under irradiation. The Si-ncs have been synthesized by Si ion implantation in the 75 nm thick SiO<sub>2</sub> layers and subsequent annealing at 1150 C for 30 mins. Then the layers were irradiated with the 30-130 keV He ions to the doses of 1x10E13-3x10E16/cm<sup>2</sup> or with the 400 keV, 60 A/cm<sup>2</sup> electron beam in the HREM column for 2-90 mins. In-situ TEM, photoluminescence (PL) and HREM were used for the characterization. Low dose room temperature irradiation caused the decrease in the PL intensity, but the number of Si-ncs after irradiation was found to be increased. Both effects were observed, when the ion and electron doses provided about 1 displacement/Si-nc. Further irradiation up to ~0.1 displ./atom (~500 displ./Si-nc) amorphized Si-ncs. This contrasts with the known results on the bulk Si, in which light particle irradiation never led to amorphization. After the low dose irradiations the ~600 C anneal was sufficient to restore the initial PL, while the recrystallization of the amorphized Si-ncs needed >900 C. When annealed at 1000 C, the layers with the restored Si-ncs and with radiation-induced new ones emitted much stronger light, than the as-prepared at 1150 C layers. It was shown, that Si-ncs may be obtained without any additional annealing if Si ions are implanted in SiO<sub>2</sub> at the target temperature as low as 600 C. In the effects observed, the elastic losses of particles are suggested to play more important role than ionization and thermal processes.

#### **F5.46**

**PREPARATION OF HIGHLY ORDERED MESOPOROUS THIN FILM WITH ALKYLTRIMETHYLAMMONIUM (C<sub>n</sub>TMA<sup>+</sup>).** Yasutomo Goto, Japan Chemical Innovation Institute, Gifu, JAPAN; Noriaki Sugimoto, Yoshiaki Fukushima, Toyota Central R&D Labs. Inc., Aichi, JAPAN; Yoshihiro Kubota, Yoshihiro Sugi, Gifu Univ, Dept of Applied Chemistry, Gifu, JAPAN.

Much attention has been paid for mesoporous molecular sieves because of its application for separator, adsorbent, and catalyst. The morphology of mesoporous molecular sieves is also an important factor for the applications. We synthesized the highly ordered mesoporous thin films with alkyltrimethylammonium (C<sub>n</sub>TMA<sup>+</sup>). We prepared the surfactant/tetramethoxyorthosilicate/water mixtures with the different acid condition, in which glass plates were dipped and dried at 373K for 1 hour. The glass plates with mesoporous silica film were obtained by calcination at 773K for 6 hours. The thickness of the thin films was about 100-500nm. The samples were studied by XRD, TEM, and nitrogen adsorption isotherms. The arrangement of mesopores was depend on the Surfactant/Si ratio. The hexagonal (P6m) arrangement was observed, when Surfactant/Si ratio was 1/10. Increasing the Surfactant/Si ratio to 1.6/10, the cubic (Pm3n) arrangements were observed. A stainless vessel for the measurement of the nitrogen adsorption isotherms of thin film on the substrate was designed. It was found that mesopore arrangements in the film was more regular than that in the powder samples prepared by the same acidic synthesis conditions. The films with 1.5-3.5nm of pore diameter were also made by using surfactants with various chain length. The pore size distribution was also narrow. We will also report the catalytic properties.

#### **F5.47**

**ELECTROLUMINESCENCE DEVICES WITH CdS AND CdS:Mn NANOPARTICLES AND POLYMER BLENDS.** Ch. Brugger, S. Tasch, G. Leising, Institut fuer Festkoerperphysik, Technische Universitaet Graz, AUSTRIA; M. Lal, P.N. Prasad, Photonics Research Laboratory, State University of New York at Buffalo, Buffalo, NY.

We have investigated the photophysical properties of surface capped CdS and CdS:Mn nanoparticles in the form of spin casted thin films of the pure nanoparticles and nanoparticle - polymer blends. The organic capping reagent was p-thiocresol. Electroluminescence (EL) devices were fabricated and characterized by their current / voltage characteristics and EL emission performance. This is to our knowledge the first report on Mn doped CdS nanoparticles applied in EL devices with a single layer device structure (ITO/CdS:Mn/Al).

Photoluminescence (PL) and PL excitation measurements were performed on CdS:Mn nanoparticles in pyridine dispersion and on thin films. The PL excitation spectrum shows a narrow peak at 390nm. Excitation at this wavelength yields a broad PL spectrum spanning from about 450 to 700nm, which is dominated by a strong emission band at 585nm. This emission is attributed to transitions involving Mn levels in previous works. The EL emission is shifted to the red compared to the PL emission spectra. The characteristics and performance of these new types of EL devices will be presented and discussed. One of us (Ch. Brugger) would like to gratefully acknowledge the financial support provided by a Stipendium fuer kurzfristige wissenschaftliche Arbeiten im Ausland and the Research Foundation of SUNY.

#### **F5.48**

**MOSSBAUER AND MAGNETIC INVESTIGATION OF AEROGEL AND XEROGEL NANOCOMPOSITE MATERIALS CONTAINING IRON OXIDES.** Giorgio Concas, Andrea Falqui, Giorgio Spano, Cagliari Univ, Dept of Physics and INFN Cagliari, ITALY; Dante Gatteschi, Claudio Sangregorio, Florence Univ, Dept of Chemistry, Florence, ITALY; Carla Cannas, Maria Francesca Casula, Anna Corriari, Anna Musinu, Cagliari Univ, Dept of Chemical Science, Cagliari, ITALY.

Nanocomposite materials constituted of iron oxide nanoparticles dispersed into an amorphous silica matrix have attracted technological and scientific attention since it is possible to stabilize maghemite which presents interesting magnetic and catalytic properties. These nanocomposite materials can be prepared using a simple sol-gel method starting from TEOS and iron nitrate as precursors. Depending on the adopted drying conditions samples with very different surface areas can be obtained. In particular, aerogels with a high surface areas and pore volumes can be obtained by performing the drying step under supercritical conditions while xerogels, in which the original pore structure of the alcogels is lost, can be obtained by slowly removing the solvent. In this paper aerogel and xerogel samples containing the same amount of iron oxide and treated at the same temperatures are studied. The superparamagnetic behaviour of the samples is investigated using magnetic susceptibility measurements, magnetization curves and Mössbauer spectra collected at different temperatures. All these measurements show the variation of the effective maghemite content and size distribution of nanoparticles as a function of thermal treatment. Moreover, the comparison between aerogel and xerogel samples allows to understand the effect of the surface area on the abundance of maghemite formation.

#### **F5.49**

**Z-CONTRAST SCANNING TRANSMISSION ELECTRON MICROSCOPY AS A TOOL FOR INTERFACE ANALYSIS IN NANOCRYSTAL-POLYMER NANOCOMPOSITES.**

Andreas V. Kadavanich, Tadd Kippeny, Meg M. Erwin, Sandra J. Rosenthal, Vanderbilt University, Dept. of Chemistry, Nashville, TN; Stephen J. Pennycook, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

We have applied Atomic Number Contrast Scanning Transmission Electron Microscopy (Z-Contrast STEM) [1] towards the study of colloidal CdSe semiconductor nanocrystals embedded in MEH-PPV polymer films as used for a prototype photovoltaic device. [2] Atomic resolution imaging reveals both the lateral shape and thickness profile of nanocrystals embedded in the film. Electron Energy Loss Spectroscopy (EELS) at sub-nanometer resolution was used to investigate the chemical composition at the nanocrystal polymer interface. We find evidence for oxygen aggregation at the interface, consistent with at maximum one monolayer of surface oxide on the nanocrystals. 1. Nellist, P.D. and Pennycook, S.J., Accurate structure determination from image reconstruction in ADF STEM. *Journal of Microscopy-Oxford*, 1998 : p. 159-170. 2. Greenham, N.C., Xiaogang, P., and Alivisatos, A.P., Charge separation and transport in conjugated-polymer/semiconductor-nanocrystal composites studied by photoluminescence quenching and photoconductivity. *Physical Review B (Condensed Matter)*, 1996. 54 (24): p. 17628-37.

#### **F5.50**

**ATOMIC FORCE MICROSCOPY INVESTIGATION OF THE MORPHOLOGY OF HYBRID ORGANIC-INORGANIC COMPOSITES.** Lee C. Zhao, Anthony B. Brennan, Univ. of Florida, Dept. of MS&E, Gainesville, FL.

We present the use of phase detection imaging by the atomic force microscope (AFM) to analyze the morphology of novel organic-inorganic hybrids. Using the sol-gel process, we synthesized hybrid organic-inorganic composites from tetraethoxy silane (TEOS), and poly(tetramethylene oxide) (PTMO). These composites contain a mixture of domains ranging from silica to polymeric. Composites were synthesized under acid catalyzed and base catalyzed conditions to generate different morphologies. Previous research has shown that

samples made under base catalyzed conditions demonstrate more phase separation than acid catalyzed samples. These samples were fractured, and analyzed using tapping mode AFM. We used phase detection imaging to distinguish between the inorganic silicate phase and the organic polymeric phase. The AFM data showed significant differences in sample morphology due to the different synthesis conditions. Dynamic mechanical spectroscopy was also performed to correlate with the AFM data. We also studied the effect of using different molecular weight PTMO on the morphology.

#### **F5.51**

**MODIFIED SOL-GEL SYNTHESIS OF VANADIUM OXIDE NANOCOMPOSITES CONTAINING SURFACTANT IONS.** Arthur Doble, SUNY-Binghamton, Dept of Chemistry, Binghamton, NY; M. Stanley Whittingham, SUNY-Binghamton, Dept of Chemistry, Binghamton, NY.

Recently, there has been much interest in creating new layered metal oxides. Vanadium oxides may be used as sorbents, catalysts, and cathodes. The modified sol-gel technique allows for some control towards the final structure of the compound. Using this technique, new layered vanadium oxide compounds, containing the surfactant dodecylphosphate, have been synthesized. The compounds were analyzed using FTIR, XRD, TGA, and NMR.  $\text{VO}_2\text{PO}_4\text{C}_{12}\text{H}_{25}$  is the general formula of the layered products with a layer spacing of about 37 Å. The synthesis, composition, and structure of these compounds will be discussed. This work was supported by The National Science Foundation.

#### **F5.52**

**OPTICAL PROPERTIES OF SILICON NANOCRYSTALS PREPARED BY Si ION IMPLANTED  $\text{SiO}_2$  LAYERS.** Z.P. Wang, K. Ding, H.X. Han and G.H. Li, National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, CHINA.

The samples were prepared by Si ion implanted  $\text{SiO}_2$  layers grown on n -  $\text{Si}(100)$  substrate and annealed at 400 - 1200°C in  $\text{N}_2$  atmosphere for 30 min. PL and Raman scattering spectra and their dependence on annealing temperature have been measured at the room temperature. The PL peaks observed in as-implanted sample originate from the defects in  $\text{SiO}_2$  layers caused by ion implantation, which disappear actually after the thermal annealing of 800°C. The PL peak from silicon nanocrystals was observed when the thermal annealing temperatures are higher than 900°C. PL peak is redshifted to 1.7 eV and its intensity reaches maximum at the thermal annealing of 1100°C. Raman scattering spectra were measured at the right angle scattering configuration. The results show that only optical phonon mode from Si substrate was observed below the annealing temperature of 800°C, and the characterized scattering peak of silicon nanocrystals was observed when the annealing temperature is higher than 900°C. The size of silicon nanocrystals after thermal annealing of 1100°C is about 3 - 4 nm as estimated from the position of the characterized Raman peak of silicon nanocrystals. After the thermal annealing of 1200°C the intensity of PL peak decreases, and the characterized scattering peak of silicon nanocrystals is disappeared and a Raman peak centered at about 490  $\text{cm}^{-1}$  appears which is similar to the optical phonon peak of noncrystalline Si. Thus we suppose that silicon nanocrystals can not bear the thermal annealing at 1200°C.

#### **F5.53**

**NANOCOMPOSITES OF TITANIUM DIOXIDE AND CONJUGATED POLYMERS.** Shujian Yi and Samson A. Jenekhe, Department of Chemical Engineering, University of Rochester, Rochester, NY.

Dispersions of nanoparticles of inorganic semiconductors in polymers are of wide interest for applications ranging from light-emitting devices to photovoltaic cells. Because titanium dioxide is an n-type semiconductor, its nanocomposites with conjugated polymers can exhibit enhanced charge photogeneration in photodiodes due to photoinduced electron transfer between the components. We have used a new synthetic method to prepare new titanium dioxide/polythiophene nanocomposites of diverse compositions. Characterization of their morphology by scanning electron and transmission electron microscopies show that the titanium dioxide phase forms mesoporous coral-like network structure in composites of low concentration (less than 15 wt%  $\text{TiO}_2$ ) and 50-120 nm diameter spherical particles at higher concentrations. The optical absorption and photoluminescence spectra depended on the nanocomposite composition. Among the unusual photoelectronic properties of the  $\text{TiO}_2$ /polythiophene nanocomposites is a six-fold enhancement in luminescence, which can be understood as a result of reduced interchain exciton quenching in the nanocomposites.

#### **F5.54**

**IN-SITU TEM STUDIES OF POLYMER- CARBON NANOTUBE**

**COMPOSITE DEFORMATION.** Dali Qian, Elizabeth Dickey, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY; Terry Rantell, Rodney Andrews, Frank Derbyshire, Center For Applied Energy Research, Lexington, KY.

Carbon nanotubes are known to have both high moduli and tensile strengths along the tube axes. Potentially, they could be used as a reinforcing phase in polymer matrices to tailor the mechanical behavior of polymer materials. The utility of the nanotubes as a reinforcing phase depends strongly on the ability to disperse the nanotubes homogeneously throughout the matrix without destroying the integrity of the nanotubes. Furthermore, interfacial bonding between the nanotube and matrix is necessary to achieve load transfer across the interface. Here we investigate polymer matrices (polystyrene and polyethylene) reinforced with multiwall or single wall carbon nanotubes. Several loadings of nanotubes were studied, including 1% and 5%. In the polystyrene matrix, 1% multiwall nanotube additions resulted in a 25% increase in ultimate tensile strength. The structure and real-time deformation of the composites were studied by transmission electron microscopy (TEM). Conventional TEM was used to quantify the dispersion of nanotubes throughout the matrix and to define preparation conditions that lead to a homogeneous dispersion. In-situ TEM deformation studies provided information regarding deformation mechanisms and interfacial bonding between the carbon nanotubes and polymer matrices. Correlations between the TEM and mechanical properties data will be discussed. This work was supported by a National Science Foundation MRSEC (DMR-9809686).

#### **F5.55**

**SYNTHESIS AND CHARACTERIZATION OF  $\text{Fe} - \text{Al}_2\text{O}_3$  NANOCOMPOSITE.** Armindo Santos, Waldemar A.A. Macedo, José D. Ardisson, Laboratório de Física Aplicada, CDTN / CNEN, Belo Horizonte, BRAZIL; Alexandre D.C. Viegas, João E. Schmidt, Instituto de Física, UFRGS, Porto Alegre, BRAZIL.

We have investigated the synthesis and the structural and magnetic properties of Fe nanoparticles embedded in  $\text{Al}_2\text{O}_3$  matrix, a granular nanocomposite prepared by sol-gel processing. Samples with volumetric Fe content ranging from 16 to 50% were obtained starting from Al nitrate and Fe sulfate as precursors. The preparation method results initially in a mixture of Fe- and Al oxides; the conversion of Fe oxides into metallic Fe was done by calcination at 800°C followed of reduction at 600°C, for 2 hours, in  $\text{H}_2$  atmosphere. The obtained powder samples were characterized by X-ray diffraction, Mössbauer spectroscopy and vibrating sample magnetometry. Our Mössbauer and X-ray diffraction results indicated the following phases after reduction:  $\alpha$ -Fe, the main phase,  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and some  $\text{FeAl}_2\text{O}_4$ . For the investigated system, Fe reduction rate was very sensitive to the sample porosity and with the applied method we have obtained reductions of the Fe atoms into metallic Fe ranging from 60 to 81%, preserving the mean diameter of the  $\text{Fe}^0$  nanoparticles between 60 and 70 nm. VSM measurements at room temperature resulted in coercivities around 450 Oe and saturation magnetization between 60 and 110 emu/g. Magneto-transport measurements are in development. Preliminary measurements for a sample with 31% metallic Fe (and about 50% total Fe) reveal  $\Delta R/R$  equal to 2.2% at room temperature. Financial support: CNEN, CNPq, FAPEMIG and FAPERGS.

#### **F5.56**

**FABRICATION OF LAYERED NANOCOMPOSITE CERAMICS FOR SENSING AND ACTUATING.** Masanobu Awano, Yoshinobu Fujishiro, Hiroyoshi Takagi, Jooho Moon, National Industrial Research Inst. of Nagoya, JAPAN; Sergei Bredikhin, Inst. of Solid State Ionics, Russian Academy of Science, Chernogolovka, RUSSIA; Koichi Niihara, ISIR, Osaka Univ., Osaka, JAPAN.

A layered nanocomposite ceramics was fabricated to realize materials devices, which reveals novel functions such as remote sensing, remote actuating and self power sourcing. Nanosize effect has been expected for its application based on physical phenomenon such as single domain structure, nano-crystal effect, spin electronics and so on. On the other side, development of the nanocomposite processing enables us to obtain synergistic enhancement of functional and structural properties leading to widen application. Layered nanocomposite of an ionic conducting material involving magnetic nano-dispersoids with a structural ceramics revealed integrated functions of remote sensing of applied stress and fracture, remote actuating by magnetic and electronic response with improved mechanical properties. The nanocomposite is applicable as a sensor and an actuator in severe circumstances.

#### **F5.57**

Transferred to F1.9.

#### **F5.58**

**SPECTROSCOPIC ELLIPSOMETRY OF NANOCOMPOSITE Si:H**

LAYERS FORMED BY HIGH-DOSE IMPLANTATION OF SILICON. V.P. Popov, E.V. Spesivtsev, I.V. Antonova, L.N. Safronov, A.K. Gutakovskii, V.I. Obodnikov, Institute of Semiconductor Physics, Novosibirsk, RUSSIA; I.I. Morosov, Institute of Nuclear Physics, Novosibirsk, RUSSIA.

Spectroscopic ellipsometry study of Si:H layers formed by high fluence hydrogen implantation (up to  $5 \times 10^{17} \text{ cm}^{-2}$ ) using pulsed 30 keV proton beams with current up to  $40 \text{ mA/cm}^2$  was carried out in the present work. The Si:H silicon films were characterized also using transmission electron microscopy, secondary ion mass spectroscopy, and infrared spectrometry. Hydrogen solubility in crystalline silicon is low but ion implantation allows introducing of  $2 \times 10^{22} \text{ cm}^{-3}$  of the hydrogen atoms or even more in thin silicon layer. High defect concentration in combination with the very active hydrogen impurity causes the formation of film with structural properties similar to porous silicon produced by electrochemical anodization. The transformation of optical properties of Si:H films during annealing in temperature range of 200-1050°C was investigated in the work. Structural characteristics have allowed us to distinguish the relative contributions of hydrogen filled voids, amorphous and crystalline zones to optical properties of obtained layers.

**F5.59**  
UNDERSTANDING THE SECOND HARMONIC GENERATION OF LIGHT FROM NANOMETAL COMPOSITES VIA LOCAL FIELD ENHANCEMENT FACTORS. Marie Sandrock, Colby A. Foss Jr., Georgetown University, Department of Chemistry, Washington, DC.

We have synthesized two sets of nanometal composites of differing metal volume fractions via electrodeposition of gold into porous aluminum oxide membranes.<sup>1,2</sup> Within each set, both centrosymmetric and non-centrosymmetric particles were produced whose linear and second-order nonlinear optical effects were investigated. We discuss comparisons of the experimental linear optical spectra of gold non-centrosymmetric pair-particle structures to that of symmetric gold particle and pair-particle structures. We intend to correlate the intensity of the nonlinear response to that of the respective linear spectra. In general, increasing the rod size leads to an increase in the SHG intensity produced from the composite materials, regardless of symmetry. Additionally, we find that SHG intensities do not vary so greatly between different geometries of centrosymmetric particles (at constant metal volume fraction), while the linear spectra are quite different. Because our method of template synthesis allows for the close examination of our composite materials in terms of shape, size, and symmetry, we can evaluate the SHG response in terms of differences in local field enhancements of magnetic dipole and quadrupole modes.<sup>3</sup> **References** 1. Sandrock, M.L.; Pibel, C.D.; Geiger, F.M.; Foss, C.A., Jr., *J. Phys. Chem. B.*, 103, 2668 (1999). 2. Sandrock, M.L.; Foss, C.A., Jr., *J. Phys. Chem. B.*, submitted. 3. Leitner, Alfred, *Molecular Physics*, 2, 197 (1990).

**F5.60**  
THE THERMAL RESISTANCE OF ALUMINUM/TITANIUM MULTILAYER THIN FILMS AND THEIR INTERFACES. Daniel Josell, Eduardo J. Gonzalez, John E. Bonevich and Grady S. White, National Institute of Standards and Technology, Gaithersburg, MD.

As the individual layers within electronic materials become thinner, heat flow predictions based on bulk properties become increasingly inaccurate. This inaccuracy arises in part because the thermal transport properties of thin film materials can differ from those of bulk materials. In addition, the thermal resistance associated with interfaces between layers becomes more significant as the layers become thinner. Accurate modeling of heat flow in future devices will require at least empirical understanding of these individual effects. We have, therefore, measured the thermal diffusivity (thermal conductivity divided by specific heat per unit volume) of electron beam evaporated Al/Ti multilayer thin films. The multilayer films were all  $3 \mu\text{m}$  thick, each with a different Al/Ti bilayer thickness (between 5 nm and 80 nm). The properties of homogeneous Al and Ti films, also  $3 \mu\text{m}$  thick, were also obtained. Thermal diffusivities were measured both perpendicular and parallel to the plane of the layers using the Mirage (Photothermal Deflection) Technique. The interface thermal resistance was determined from the dependence of the thermal diffusivity on the Al/Ti bilayer thickness. Copper thin films ranging between  $0.1 \mu\text{m}$  and  $5 \mu\text{m}$  thick were also studied.

**F5.61**  
SELF-PROPAGATING REACTIONS IN NANOSCALE MULTILAYER FOILS. Tim Weihs, Dept. of Materials Science & Eng., Johns Hopkins Univ., Baltimore, MD; Omar Knio, Dept. of Mechanical Eng., Johns Hopkins Univ., Baltimore, MD.

This presentation describes the development of novel, self-propagating exothermic reactions in nanoscale multilayer foils. The reactive foils

are fabricated by vapor depositing many alternating layers of materials that have high heats of mixing, such as Al and Ni or Nb and Si. The individual layers are only nanometers thick, but each foil contains hundreds of these layers and has a total thickness between 10 and 100 microns. The thick foils are easily removed from their substrates after deposition, and their exothermic mixing can be started at room temperature with a spark or match. The reactions propagate at speeds greater than 5m/s, and they reach final temperatures as high as 1600 C. During the talk we will describe how these foils can be used as rapid heat sources for joining and ignition, and we will review experimental characterizations of the heats, the velocities, the temperatures, and the transformations of the reactions. For example, we will show that reaction velocity depends strongly on the measured heats that drive the reactions and the individual layer thicknesses that determine diffusion distances. These experimental results will be compared with extensive predictions from analytical and numerical models.

**F5.62**  
HIGH-PRESSURE SYNTHESIS OF BISMUTH NANO-COMPOSITES FOR THERMOELECTRIC APPLICATIONS. Tito E. Huber and Pierre Constant, Howard University, Washington, DC; Michael Graf, Department of Physics, Boston College, Chestnut Hill, MA; Colby A. Foss, Department of Chemistry, Georgetown University, Washington, DC.

We have fabricated Bi nanowire array composites with wire diameters from 30 to 200 nm by high-pressure-injection of Bi melt into porous anodic alumina templates. The composites are dense, with Bi volume fraction in excess of 50%. The parallel Bi nanowires terminate at both sides of the composite in the Bi bulk. We have employed scanning electron microscopy, energy dispersive X-ray-Spectroscopy, and X-ray diffraction to characterize the composites. We are interested in the potential application of these arrays as a thermoelectric device. Bi and its alloys are the best thermoelectric materials at moderately low temperatures ( $\sim 100 \text{ K}$ ). It has been suggested that microengineering traditional thermoelectric materials into composites may lead to improvement of their thermoelectric performance because of the reduction of phonon thermal conductivity. Also, the thermoelectric figure of merit may be dramatically increased over that of the bulk because of the increase of the electronic density of states that occur in low dimensionality systems.

**F5.63**  
ROOM TEMPERATURE COERCIVITY ENHANCEMENT IN MECHANICALLY MILLED FERROMAGNETIC-ANTIFERROMAGNETIC COMPOSITES. J. Sort, J. Nogués, X. Amils, S. Suriñach, J.S. Muñoz, M.D. Baró, Dept. de Física, Univ. Autònoma de Barcelona, Bellaterra, SPAIN.

Mechanical alloying has been used to induce exchange interactions in for example remanence enhanced hard magnetic materials [1] or in giant magnetoresistance alloys [2]. We have used mechanical milling to induce an exchange interaction between ferromagnetic (FM) and antiferromagnetic (AFM) materials. By mechanically milling FM and AFM materials with Néel temperature,  $T_N$ , above room temperature the room temperature coercivity,  $H_C$  of the FM material can be markedly increased. In particular, Co has been mechanically milled with NiO ( $T_N = 590 \text{ K}$ ) and FeS ( $T_N = 610 \text{ K}$ ) in different conditions. A substantial increase in  $H_C$  was found if the AFM/FM composite was field annealed above  $T_N$  and field cooled to room temperature. The increase of  $H_C$  disappears above  $T_N$ . The dependence of  $H_C$  on the annealing and measuring temperature indicate that the exchange bias [3] is the origin of the observed effect. This work was supported in part by CYCIT (MAT98-0730). J.S. thanks the DGU for his fellowship. [1] P.G. McCormick et al., *J. Magn. Magn. Mater.* 157/158 (1996) 7; [2] S.M. Thompson et al., *Phil. Mag. B* 68 (1993) 923; [3] J. Nogués and Ivan K. Schuller, *J. Magn. Magn. Mater.* 192 (1999) 203.

**F5.64**  
3-D PERIODIC NANOCOMPOSITES FOR METALLIC PHOTONIC CRYSTALS AND HETEROJUNCTION ARRAYS. Anvar A. Zakhidov, Ray H. Baughman, Igor A. Udod, Lo-Min Liu, Changxing Cui, Research and Technology, AlliedSignal, Inc., Morristown, NJ; Ilyas I. Khayrullin, Mikhail E. Kozlov, New Jersey Institute of Technology, Newark, NJ; Nair Eradat, Valy Z. Vardeny, Dept. Physics, University Of Utah, Salt Lake City, UH.

We have created highly porous nanofoams and nanocomposites that are highly periodic at optical wavelengths and can be made as two-component systems. In the first part of this talk we show that metallo-dielectric systems of this type demonstrate interesting optical properties in infrared bands, confirming the metallic photonic crystal structure of nanocomposites and the existence of a metallic photonic band gap below the plasmon derived cut-off frequency. In a second part, we discuss transport and thermoelectric properties, including

suppression of thermal conductivity, and change of the temperature dependence of conductivity. With the aim to increase thermopower  $S$ , we suggest the formation of heterojunction arrays between two components of semiconductor (SC1/SC2) or metallic (M1/M2) nanocomposite networks. This arrays can be created so that substantial charge transfer occurs between components, creating modulation doping in the interfacial layer. Another way is to create 3-D arrays of p/n junctions by non-homogeneous doping during a micro-molding process. The optimal design of such heterojunction arrays geometry and electronic bands matching are discussed following our theory of S-enhancement in asymmetric p/n junctions. For fabrication of 3-D superlattice nanocomposites, a simple method is developed using porous nanofoams of SC1 as a template for infiltration with second SC2 material. The fabrication steps include creation of porous nanofoam from SC1 material, with high melting point: either Sb or Te, both being chemically stable in HF (which is used to dissolve the initial silica opal). As a second step, low melting point Bi as SC2 is infiltrated into SC1 inverted opal matrix either by high pressure infiltration from a melt or by a CVD process. The obtained nanostructures are characterized by SEM, TEM optical reflectivity and low angle X-rays, and show drastic changes of optical, thermoelectric and transport properties upon formation of a 3-D nanocomposite. \*Research supported by DARPA grant DAAB07-97-C-J036

#### F5.65

CORRELATION OF MICROSTRUCTURAL PROPERTIES WITH THE MAGNETORESISTANCE OF THE MAGNETIC NANOSTRUCTURED MULTILAYERS. Jenica Neamtu, National Institute for Research and Development in Microtechnologies, Bucharest, ROMANIA; M. Volmer, Transilvania University, Brasov, ROMANIA.

In this work, the influence of the roughness and microstructure of the layers at the interface of multilayers on the magnetoresistive properties has been investigated. We present some results on the anisotropic magnetoresistance of permalloy thin films and the giant magnetoresistance (GMR) of NiFe/Cu/NiFe and Co/Cu/Co multilayer thin films, deposited by high vacuum evaporation and RF sputtering. The magnetic thin films have the thickness in the range 4-20 nm and the copper layer thickness was changed from 3 nm to 8 nm. The magnetic thin films were characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM) for surface texture, grain size and roughness. Although the thickness of layers has leading part for magnitude of GMR effect, described in terms of spin dependent electron scattering, quality of interfaces, amount of bulk scattering centers and the roughness not by neglected. Our results showed that for the average grain size of NiFe thin films smaller than the intrinsic mean free path of the electrons, grain boundaries are an important source of electron scattering, even up to large film thickness and influence the giant magnetoresistance of multilayers.

#### F5.66

CHEMICAL VAPOR DEPOSITION OF TiC, WC, AND TiC/WC COMPOSITE THIN FILMS. Kathryn Versprille, Carmela C. Amato-Wierda, University of New Hampshire, Materials Science Program, Durham, NH; Derk A. Wierda, Saint Anselm College, Dept of Chemistry, Manchester, NH.

Recent progress in hard coating research suggests that nanocrystalline composite materials show improved hardness and toughness. This present study investigates the chemical vapor deposition of TiC/WC multiphased nanostructured thin films. TiC is deposited using  $TiCl_4$ ,  $H_2$  (diluent and carrier gas), and  $CH_4$ , and WC is deposited using  $W(CO)_6$ ,  $H_2$ ,  $CH_4$ , and Ar as the carrier gas. The composition, morphology, and hardness of the individual TiC and WC films, as well as the co-deposited multiphased TiC/WC films, are characterized as a function of processing conditions, including reaction temperature, reaction pressure, residence time, and flow ratios.

#### F5.67

CRYSTALLIZATION BEHAVIOR OF AMORPHOUS SiGe FILMS OBSERVED BY POSITRON ANNIHILATION. F. Edelman, Technical University of Darmstadt, Dept of Materials Sciences, GERMANY; F. Borner, R. Krause-Rehberg, Halle Univ, Fac of Physics, Halle, Saale, GERMANY; P. Werner, Max Planck Inst of Microstructure Phys, Halle, Saale, GERMANY; R. Weil, Technion, Solid State Inst, Haifa, ISRAEL; W. Beyer, R. Butz, Inst of Thin Films and Ion Technology, Res Centre, Jülich, GERMANY.

The crystallization of undoped and boron doped  $Si_{0.5}Ge_{0.5}$  films, deposited on  $SiO_2/Si(001)$  substrate by molecular beam in high vacuum at room temperature was studied by Doppler broadening spectroscopy using monoenergetic positrons. From X-ray diffraction (XRD) measurements it is shown that crystallization of amorphous films starts at 600°C. This process was completed at temperatures higher than 850°C. It can be distinguished between three phases of

crystallization. In phase 1 up to temperatures 550°C there is no crystalline lattice structure detectable. Phase 2 (600-800°C) shows broad XRD spectra of crystalline SiGe. The broader peaks can be explained by the appearance of defects in the crystal structure and small crystal grain size. The films are fully crystallized in phase 3 after annealing higher than 850°C. With positrons as a probe an evolution process of the amorphous layer in phase 1 of the crystallization can be observed. In the as-grown amorphous SiGe layer, the positrons annihilate in the open volume of atom arrangement. The positrons are located in traps of very high density. This fact can be seen by the short positron diffusion length of about 10 nm. The first evolution step can be observed at an annealing temperature of 150°C. A change in the annihilation line-shape parameter  $W$  shows that the positrons were located in open volume which is mainly surrounded by Ge atoms. A second change of the of the  $W$  parameter at a temperature of 250°C indicates an evolution of the amorphous layer to a more homogenous distribution of the Si and Ge atoms being next to the positron traps. This fact could mean that a first close order structure of the SiGe lattice is come into being. In conclusion, positron annihilation spectroscopy reveals that structural changes occur in amorphous SiGe layers far below the crystallization temperature.

#### F5.68

A NEW METHOD FOR CALCULATION OF STRAINS IN NANOCOMPOSITE SEMICONDUCTORS. Vadim Yu. Mirovitskii, Inst of Chemistry, Dept of Quantum Chemistry, Kishinev, MOLDOVA.

A general approach is developed for calculation of both uniform and nonuniform strain fields created by *periodically arranged* quantum dots (wires, layers) in semiconductors. These thermodynamically nonequilibrium composites with coherent interfaces between different materials are formally considered as complex superstructures derived from simple, more symmetrical and stable initial crystal phase, namely a completely disordered solid solution with zinc-blende structure. From this viewpoint the superstructural heterogeneities can be imagined as the modulation of composition and described in terms of concentration waves superposition. Then every concentration wave induces the wave of displacements. Mechanical equilibrium conditions imposed on such a superstructure by procedure of thermodynamic-potential variation with respect to Fourier-components (FC) of strain fields allow one to derive analytic expressions for each type of strain as a function of spatial distribution of alternative atoms. Specifically, it is shown that in the simplest approximation the FC of nonuniform strain depend linearly on the FC of concentration waves. The diagonal components of uniform-strain tensor are proportional to the second power of the FC of composition. As to the off-diagonal components, their values depend on the  $n$ -th power of the same FC, where  $n$  is the ratio of minimal superperiod and initial period lengths. All coefficients in these dependences are determined only by the properties of disordered solution. So, it is demonstrated that the method proposed reduces the initial bulky problem to a simpler one because all we need to know for a numerical estimation of strains are only *the geometry of superstructure and some physical characteristics of disordered solid solution*.

#### F5.69

THERMALLY DRIVEN SHAPE INSTABILITY OF MULTILAYER STRUCTURES. Peter Troche, Jörg Hoffmann, Carsten Herweg, Jörg Schleiwies, Herbert C. Freyhardt, Universität Göttingen, Institut für Materialphysik, Göttingen, GERMANY; Dietbert Rudolph, Universität Göttingen, Institut für Röntgenphysik, Göttingen, GERMANY.

The thermal disintegration of multilayers consisting of non miscible metals (e.g. Nb/Cu, Fe/Au, Fe/Ag, Cu/Co) was investigated by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray microscopy (XRM). The single-layer thickness of one of the components was typically fixed to 10 nm, whereas the thickness of the second one was varied between 0.4 nm and 4 nm. The temperature of disintegration depends on the combination of the chosen metals, the microstructure of the interfaces, and the thickness of the thinner layer. Up to a critical thickness, the disintegration temperature rises proportional to the reciprocal thickness of the thinner layer. The minimum disintegration temperature ranges from 580 K to 1000 K for Fe/Au and Cu/Co multilayers, respectively. TEM pictures reveal a columnar growth of the film. These highly orientated columns with a width of some tens nanometers grow up to 800 nm in height, depending on the observed system. After disintegration the thinner layer has developed spherically shaped nano-particles, located at the grain boundaries between the columns. Therefore, after disintegration the nano-particles are more or less well-ordered like a string of pearls perpendicular to the substrate. The driving force of this process is assumed to be caused by gradients in interfacial stress and by local variations of the curvature of the interfaces.

### F5.70

**BANDGAP ENGINEERING STUDIES WITH MESOSCOPIC GALLIUM NITRIDE COMPOSITES.** Holger Winkler, Oliver Stark, Roland A. Fischer, Ruhr-Universitaet Bochum, Bochum, GERMANY; Roland Schmechel, Heinz von Seggern, Technische Universitaet Darmstadt, Darmstadt, GERMANY.

By varying the composition of specific ternary systems like  $\text{In}_{1-x}\text{Ga}_x\text{N}$  and  $\text{Al}_{1-x}\text{Ga}_x\text{N}$  or changing the thickness of quantum well-two dimensional semiconducting thin films it is possible to tune the bandgap of the materials within certain ranges. Transferring the idea of bandgap engineering to materials with quantum confinement in less than two dimensions by decreasing the materials size leading to increasing bandgap energy there are no as well established methods as mentioned above. Physical methods are rather costly and common colloid-chemical approaches are usually combined with disadvantages like broad size distributions. Here we present our studies concerning bandgap engineering of Gallium Nitride allowing access to bandgap energies higher than 3.45 eV by inclusion chemistry by filling the tunable (2-10 nm in diameter) pores of a well defined porous template (MCM-41) with Gallium Nitride. If impregnated with a solution of the precursor triazido(trimethylamin)-gallium followed by thermal treatment in ammonia the porous system of the molecular sieve MCM-41 can be homogeneously filled with Gallium Nitride aggregates which size is limited by the pore diameter of the template leading to composites with a extremely narrow size distribution of Gallium Nitride. We show different composites which differ from each other in the porediameter of the template and therefore in the size of the Gallium Nitride material in the pores. Besides analytical techniques like TEM and XRD, the bandgap of the composites is characterised by optical investigations (photoluminescence and excitation spectroscopy).

### F5.71

**NOVEL METHOD FOR FABRICATION OF NANOCRYSTALLINE COPPER COMPOSITES.** A.Pharkya, A.K. Sharma, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

The formation of nanocrystalline metal (such as Cu, Zn) composites represents a major challenge because of grain growth, which can occur at very low temperatures. We have adopted a novel pulsed laser deposition procedure where Cu deposition is followed by a couple of monolayers of insoluble constituent such as W and TiN, which is followed by Cu deposition and so on. The role of W or TiN is to modify the interfacial energy and provide the fresh nucleation sites in addition to grain boundary pinning. The grain size of copper is controlled by the thickness of the deposited layer and the substrate annealing temperature. The grain growth is impeded by pinning of grain boundaries via alloying with W or TiN. Using this ingenious approach we have been able to obtain grain sizes ranging from 7 to 13 nm. We envisage mechanical properties of these novel composites to be significantly better because of grain boundary pinning characteristics. These studies are currently underway.

### F5.72

**COLOSSAL HOPPING MAGNETORESISTANCE OF GaAs/ErAs NANOCOMPOSITES.** A. G. Petukhov, M. Foygel, and A. Chantis, Dept of Physics, South Dakota School of Mines and Technology, Rapid City, SD.

We report our results on theoretical analysis of hopping magneto-transport in quasi-2D nanocomposites comprised of ErAs paramagnetic nano-islands immersed into GaAs matrix (D. Schmidt, A. G. Petukhov, M. Foygel, J. Ibbetson, and S. J. Allen, Phys. Rev. Lett. **82**, 823 (1999)). The almost universal feature of all experiments on magneto-transport in insulating region is a significant positive component of magnetoresistance preceding the negative one. The model is based on fluctuation mechanism of bound magnetic polaron (BMP) hopping. The negative component of the magnetoresistance is attributed to quenching of BMPs in high magnetic fields as it is anticipated in any model involving BMP hopping. The scale of the negative magnetoresistance critically depends on the BMP radius (i.e. on the ErAs island size in the case of nanocomposites) and on disorder in the system. The positive component is a striking feature of the fluctuation-driven BMP hopping. It depends on the orientation of the magnetic field with respect to the plane of quasi-2D quantum dots. We explain the anisotropy of the positive magnetoresistance in terms of an anisotropic exchange coupling and shape anisotropy of the islands.

### F5.73

**NANOCOMPOSITES IN THE SYSTEMS  $\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$  AND  $\text{MgO}-\text{MgFe}_2\text{O}_4$  PRODUCED BY MECHANICAL ALLOYING.** A. Huerta, R. Ordoez, H.A. Calderon, H. Balmori, E. Reguera, H. Yee-Madeira, Instituto Politecnico Nacional, Apdo., Mexico DF; M. Umemoto, K. Tsuchiya, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, JAPAN.

This investigation has been undertaken to produce, characterize and measure the properties of oxide ceramics that contain second phase particles. Mechanical alloying techniques are used to produce nanocomposites in the systems  $\text{Fe}_{1-x}\text{O}-\text{Fe}_3\text{O}_4$  and  $\text{MgO}-\text{MgFe}_2\text{O}_4$ . In equilibrium, precipitate particles of  $\text{Fe}_3\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$  can be produced, respectively. The combination of magnetic particles in a non-conductive matrix can have various applications such as electromagnetic energy absorption. The milled powders are sintered by means of spark plasma assisted techniques at temperatures varying from 673 to 1273 K and a pressure ranging from 100 to 50 MPa. This technique allows consolidation in sufficiently short times to preserve the nanocrystalline microstructure developed during milling. Characterization is performed by means of X-Ray diffraction, Mossbauer Spectroscopy and transmission electron microscopy. Results show the development of a nanocomposite during milling. Different volume fractions of the original components can still be detected but also formation of the equilibrium phases. After sintering, the microstructure is formed by a dispersion of two or more phases in nanocrystalline grains. Heat treatment in controlled atmospheres produces dispersions of precipitates which give rise to different properties. Preliminary measurement of the electromagnetic energy absorption properties shows dependence on the particle size and spatial distribution.

Work supported by CONACYT (Proy. 28952U) and COFAA-IPN.

### F5.74

**RELATIONSHIP BETWEEN THERMALLY ACTIVATED ATOMIC DIFFUSION PROCESSES IN Co-Cu NANOSCALE GRANULAR FILMS AND ELECTRIC/MAGNETIC PROPERTIES.** F. Spizzo, F. Ronconi, P. Vavassori, G. Bordin, I.N.F.M. and Dept. of Physics, University of Ferrara, ITALY; D. Bisero, I.N.F.M. Udr Ferrara; L. Pareti and G. Turilli, MASPEC-CNR, Parma, ITALY.

The effect of thermally activated diffusion processes on Co-Cu multilayer granular films grown by RF-sputtering on Si substrates has been studied. The films show giant magnetoresistance and both their magnetisation curves and the variation of resistivity as a function of reduced magnetisation display features characteristic of a granular solid constituted by non-interacting superparamagnetic particles. Thermal treatments with different heating rates, have been performed by a differential scanning calorimeter under Ar flow. A strong dependence of the type of diffusing element on heating rate has been observed. The changes in composition have been detected by X-ray Photoemission measurements performed at various depths inside the films. Results concerning electric and magnetic properties of the films are reported.

### F5.75

**MORPHOLOGICAL STABILITY OF Ni/Ni<sub>3</sub>Al NANOLAMINATE COMPOSITES.** Jason P. Fain, Rajarshi Banerjee, Daniel Josell<sup>1</sup>, Natalia Tymiak<sup>2</sup>, Peter M. Anderson, Hamish Fraser, and William Gerberich<sup>2</sup>, Dept. Materials Science and Engineering, The Ohio State University, Columbus, OH; <sup>1</sup>National Institute of Standards and Technology, Gaithersburg, MD, <sup>2</sup>Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Nanolaminate composites consisting of alternating phases with nanometer-scale individual layer thicknesses may be useful as elevated temperature coatings. At ambient temperature, nanolaminates with metallic and/or intermetallic layers display extraordinary strength. The strength typically increases with decreasing layer thickness, due to the confinement of plastic slip to small volumes by nearby interfaces. Further, fracture strength is expected to increase with decreasing layer thickness, due to a smaller characteristic flaw size. However, at elevated temperature, modeling suggests that decreasing layer thickness may be detrimental to the morphological stability of nanolaminates. For example, multilayers of pure Ni and Ni<sub>3</sub>Al, produced by UHV magnetron sputtering, changed to equiaxed Ni particles surrounded by a continuous matrix of Ni<sub>3</sub>Al, when heated to 500C for several hours. The process of pinching off layers by grain boundary grooving would appear to be easier as layer thickness is decreased. Thus, there would appear to be a compromise between room temperature strength and elevated morphological stability, as layer thickness is reduced. In this work, UHV sputtering is used to produce nanolaminates with layer thickness ranging from 20nm to 120nm and interfacial orientations of either (111)Ni(Al)/(111)Ni<sub>3</sub>Al or (002)Ni(Al)/(002)Ni<sub>3</sub>Al. Thus, the phases are analogous to those used in Ni-base superalloys, but the morphology as produced is in layered rather than particulate form. The system chosen permits the interfacial energy and hence stability of the layers to be changed via the choice of interfacial orientation and layer thickness. The morphology of samples with different layer thickness and interfacial orientation is monitored as a function of heat treatment temperature and time, and subsequent room temperature values of hardness are made to understand the effect of the morphological changes on deformation resistance.

SESSION F6: APPLICATIONS AND PROPERTIES  
OF NANOPHASE AND NANOCOMPOSITE  
MATERIALS - I

Chair: Kwant Leong Choy  
Wednesday Morning, December 1, 1999  
Salon F (M)

**8:30 AM \*F6.1**

**NANOSIZED SEMICONDUCTING OXIDE POWDERS FOR THICK FILM GAS SENSORS: FROM POWDER PROCESSING TO ENVIRONMENTAL MONITORING DEVICES.** Enrico Traversa, Univ of Rome Tor Vergata, Dept of Chemical Science and Technology, Rome, ITALY; Maria Cristina Carotta, Giuliano Martinelli, INFN, Univ of Ferrara, Dept of Physics, Ferrara, ITALY.

The surface properties become paramount for nanosized materials, making them particularly appealing in applications where such properties are exploited, as in gas sensors. Grain size reduction is one of the main factors enhancing the detection properties of semiconducting oxides used for gas sensing. Sharp increases in sensitivity are to be expected when the grain size becomes smaller than the space-charge depth. The development of reliable and selective gas sensors is strongly needed for the control and monitoring of pollutants for ambient air quality, because the methods currently approved by the existing standards need the use of costly analytical equipment that limits the number of monitoring locations. The improvement of gas sensors' performance can be achieved using nanostructured materials. Chemical routes such as sol-gel techniques and thermal decomposition of heteronuclear complexes have been used to prepare nanosized powders of n-type ( $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$ ) and p-type ( $\text{LaFeO}_3$  and  $\text{SmFeO}_3$ ) semiconducting oxide materials. Thick film gas sensors have been fabricated using these powders, printed on laser precut 96% alumina substrates, each 2x2 mm element being provided with a heater, Au interdigitated contacts and a Pt-100 resistor for controlling the operating temperature. The structural analysis of the nanosized powders is considered in addition to that of the resulting films. The firing of the films has been performed in conditions able to keep grain size at nanometer level. Electrical responses to some major polluting gases ( $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ ) have been tested in the laboratory and in the field, compared with the internationally-standard analytical techniques. The array of prototype devices have been located at the same place of a conventional station of environmental monitoring. The results obtained allow us to consider as feasible the use of thick-film oxide sensors for cheap, innovative stations for environmental monitoring.

**9:00 AM \*F6.2**

**STRUCTURE AND PROPERTIES OF  $\text{SnO}_2$ - $\text{TiO}_2$  NANOCRYSTALLINE FILMS FOR GAS SENSORS.** Felix Edelman, Horst Hahn, Holger Hoche, Technical University of Darmstadt, Dept. of Material Sci., GERMANY; Peter Werner, Max Planck Institute of Microstructural Physics, Halle, GERMANY; Albert Chack, Vissarion Mikhelashvili, Ghadi Eisenstein, Technion, ISRAEL; N. Barsan, Institute of Phys. and Theor. Chemistry, Uni. of Tübingen, GERMANY.

Thin films (50 and 500nm) of  $\text{SnO}_2$ - $\text{TiO}_2$  were prepared at 100°C on Si and quartz glass substrates by molecular beam deposition (MB) before annealing in oxygen at 300 to 800°C. Particular attention has been given to the compensation of the oxygen non-stoichiometry in the oxide films (especially manifested in the  $\text{SnO}_2$ -rich films). Apart from the high-temperature oxidation, the use of in-situ atomic oxygen (which is the low-temperature layer-by-layer process) during the film deposition is used. TEM, XRD, RBS, SIMS, XPS, Raman and IR-spectroscopy were employed to analyse the structure evolution in the  $\text{SnO}_2$ - $\text{TiO}_2$  films. In the as-deposited state, the films are amorphous. Crystallization occurs at higher temperatures (above 500°C) forming nanosized grains. The problem of the spinodal decomposition of the  $\text{SnO}_2$ - $\text{TiO}_2$  under oxidation annealing is discussed first for the low-temperature annealing (earlier, the spinodal decomposition was demonstrated in  $\text{SnO}_2$ - $\text{TiO}_2$  system for monocrystals and ceramics above 800-900°C). The effect of the film densification upon annealing is investigated and problem of oxygen gas permeability through oxide film is analysed. In conclusion, electrical conductivity and sensing properties of the  $\text{SnO}_2$ - $\text{TiO}_2$  films in oxidation or reduction environment are presented.

**9:30 AM F6.3**

**SCREEN-PRINTED DYE-SENSITIZED NANOCRYSTALLINE SOLAR CELL.** T.K. Gupta, L.J. Ciriganao, K.S. Shah, L.P. Moy, D.J. Kelly, M.R. Squillante, and G. Entine, Radiation Monitoring Devices, Watertown, MA.

A new type of screen printed dye-sensitized large solar cell (15cm x 15 cm) based on nanocrystalline  $\text{TiO}_2$  is described. It is the largest photo-electrochemical (PEC) cell that is based on the dye sensitization of thin ( 8-18  $\mu\text{m}$  ) films of  $\text{TiO}_2$  nanoparticles in

contact with a non-aqueous liquid electrolyte. The cell has the potential to be a low cost, commercial, environmentally friendly, photovoltaic option. Surface and interface characterizations of the nanostructured PEC cells as well as electrical characterization, e.g., quantum efficiency and fill factor, have also been performed. The efficiency of these large commercial cells are compared to the laboratory-made small PEC cells.

**9:45 AM F6.4**

**DIELECTRIC CHARACTERIZATION OF THIN FILMS CONSISTING OF TIN DOPED INDIUM OXIDE NANOPARTICLES.** Annette Hultåker, Gunnar A. Niklasson, Uppsala Univ, Dept of Materials Science, Uppsala, SWEDEN; A.W.M. de Laet, Chris van Haag, Philips CFT, Eindhoven, THE NETHERLANDS.

In recent years there has been a growing interest in cheap and easy production techniques for transparent conducting films. Thin layers of tin doped indium oxide (ITO) have been prepared by spin-coating of a solution of nano-particles. In order to study the sintering behavior of these ceramic particles the dielectric response function has been studied and grazing incidence XRD measurements have been performed. The grain growth starts at 1000°C and is much more prominent at 1250°C. However, the conductivity reaches a maximum below these temperatures. The results are compared with theory for grain growth of ceramic nanoparticles and of conduction mechanisms in nanocomposites.

**10:15 AM \*F6.5**

**CARBON NANOTUBE POLYMER COMPOSITES.** Pulickel M. Ajayan, Linda Schadler, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY.

Carbon nanotubes should be the ideal reinforcing fibers for composites. They have high aspect ratios, are extremely strong individually and are very light. The goal of creating high strength, lightweight polymer composites using nanotube fillers has been pursued in recent years by many workers. Although nanotubes are ideal fillers, the effectiveness of the composite will depend on the interface between the filler and the matrix as this will govern the load transfer properties of the composites. In addition, the behavior of nanotube aggregates such as singlewalled nanotube ropes and multiwalled nanotube assemblies is markedly different from the idealized individual nanotubes which have been used in theoretical predictions. Our experiments (processing, characterization, mechanical testing, and Raman spectroscopy to monitor load transfer) on nanotube-polymer systems reveal several important features which could lead to the development of optimized composites. A summary of these results will be presented in this talk.

**10:45 AM F6.6**

**PREPARATION OF OPTICAL COMPOSITES.** Leslie L. Isaacs, CCNY/CUNY Graduate Center, Dept of Chemical Engineering; Robert R. Alfano, Vladimir Petricevic, CCNY/CUNY Graduate Center, Dept of Physics and New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, BaoPing Wang, CCNY/CUNY Graduate Center, Dept of Chemical Engineering and New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications; Jinpin Ying, Institute for Ultrafast Spectroscopy and Lasers, New York, NY.

Sol - Gel technology is used to prepare micron size particles of Chromium(IV) doped materials, which show strong luminescence, as single crystals, in the 1-2  $\mu\text{m}$  range. Examples of such materials are  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  and  $\text{Cr}^{4+}:\text{Ca}_2\text{SiO}_4$ . The preparative process can be optimized to reduce the particle size to the sub-micron range and to obtain a narrow particle size distribution. Furthermore, optical composites can be prepared by dispersing the optically active particles into transparent glassy matrices.  $\text{SiO}_2$  and  $\text{SiO}_2$  -  $\text{TiO}_2$  are used as the glass forming matrix materials.

**11:00 AM F6.7**

**CATALYTIC ACTIVITY OF PALLADIUM SUPPORTED ON MESOPOROUS METAL OXIDES IN LOW TEMPERATURE METHANOL DECOMPOSITION.** M.P. Kapoor, Yasuyuki Matsumura, WenJie Shen, Osaka National Research Institute, AIST, Ikeda, Osaka, JAPAN.

Methanol decomposition [ $\text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO}$ ;  $\Delta H = 22 \text{ kcal.mol}^{-1}$ ] is applicable for waste heat recovery. Palladium supported on various metal oxides has received considerable attention and is preferable for the low temperature methanol decomposition. In the present work we have investigated mesoporous metal oxides ( $\text{ZrO}_2$ -MS41 and  $\text{TiO}_2$ -MS41) as an active support of palladium catalysts prepared by the deposition-precipitation method, which can provide nano-meter size metal particles and the strong contact with the mesoporous supports. All catalysts were well characterized using XRD, XPS and

BET surface area measurement, and hydrogen adsorption. The gas phase methanol decomposition was performed in a fixed-bed continuous flow reactor operating under atmospheric pressure. The catalyst was reduced with hydrogen for 1h at 300°C. The conversions of methanol decomposition at 160-200°C over 3-10 wt% Pd increased with increase in Pd loading. Compared to Pd/TiO<sub>2</sub>-MS41, the Pd/ZrO<sub>2</sub>-MS41 is found to be an effective catalyst for the methanol decomposition. The catalyst Pd/ZrO<sub>2</sub>-MS41 produced considerable higher activity than Pd/ZrO<sub>2</sub>. The effect of ultrasonic vibration during the deposition precipitation of Pd over the supports further enhances the catalytic activity. The results demonstrate that the methanol decomposition to hydrogen and carbon monoxide over palladium supported mesostructured metal oxides catalysts have considerably enlarge the range of decomposition catalyst family and opened up new opportunities in the field of methanol decomposition.

#### 11:15 AM F6.8

ATOMIC SCALE ANALYSIS OF ELECTRODEPOSITED NANOCRYSTALLINE Ni ALLOYS. Matthias Thuvander, Matthias Abraham, Helen Lane, Alfred Cerezo, George Smith, Department of Materials, University of Oxford, Parks Road, Oxford, UNITED KINGDOM.

Nanocrystalline Ni and Ni alloys have been prepared using electrodeposition in nickel sulphate based baths. This produces fully dense material with grain sizes in the range 3-30 nm. The deposits, having a thickness of typically 0.3 mm, were characterised by XRD, TEM, PIXE, micro-hardness and 3D atom probe analysis (3DAP). The 3DAP technique makes it possible to perform chemical analysis on a near-atomic scale, which is essential for the studies of nanocrystalline materials. Pure Ni and Fe-Ni were deposited using a pulsed voltage, whereas a constant voltage was used for Ni-P. The concentration of Fe and P, respectively, could be controlled in a wide range. Initial attempts to produce Ni-B were also undertaken. The impurity levels were found to be low, typically <0.3 at.%. In the as-deposited materials no significant enrichment of impurities or alloy elements at grain boundaries could be observed. The thermal stability and grain growth behaviour was also investigated. In Ni abnormal grain growth occurred for the temperatures 460K, 490K and 520K, but impurity segregation to grain boundaries seemed to be very limited. In Ni-P precipitation of Ni<sub>3</sub>P and P segregation was observed following heat treatment at 700K.

#### 11:30 AM \*F6.9

FEATURES OF FRACTURE SURFACE AND GRAIN BOUNDARY STRUCTURE OF BORIDE/NITRIDE NANOCOMPOSITE MATERIALS. Rostislav A. Andrievski, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, RUSSIA.

Fracture surfaces of TiB<sub>2</sub>, TiN, AlN, Ti(B,N), and (Ti,Al)N nanostructured bulks and films were investigated by FE-SEM, conventional SEM, and AFM. Two types of fracture connected with homogeneous and inhomogeneous deformation are described and discussed in detail. Localized inhomogeneous deformation with the formation of shear bands has been fixed in the case of TiB<sub>2</sub> and AlN films with partly columnar or stonelike structure. Homogeneous deformation at analogous test conditions is typical for films with clearly-defined columnar structure such as TiN, (Ti,Al)N, Ti(B,N) films. HREM images of these films are also demonstrated and nature of their grain boundaries discussed.

### SESSION F7: APPLICATIONS AND PROPERTIES OF NANOPHASE AND NANOCOMPOSITE MATERIALS - II

Chair: Enrico Traversa  
Wednesday Afternoon, December 1, 1999  
Salon F (M)

#### 1:30 PM \*F7.1

CATALYTIC BEHAVIOR AND SURFACE CHARACTERIZATION STUDY OF Pd SUPPORTED ON NANOCRYSTALLINE CeO<sub>2</sub>. Gar B. Hoflund, Department of Chemical Engineering, University of Florida, Gainesville, FL; Horst Hahn, Thin Films Division, Materials Science Department, Darmstadt University of Technology, Darmstadt, GERMANY.

Catalytic methane oxidation over polycrystalline and nanocrystalline CeO<sub>2</sub>-supported Pd/pCeO<sub>2</sub> and Pd/nCeO<sub>2</sub> has been studied using activity and surface characterization experiments. While the untreated nCeO<sub>2</sub> support gives 50% methane conversion at 420°C, the untreated pCeO<sub>2</sub> support exhibits little activity for the reaction conditions used. A Pd loading of 5 wt% increases the activity of pCeO<sub>2</sub> to 50% conversion at 260°C. The best catalyst examined was 40 wt% Pd/nCeO<sub>2</sub> yielding a 50% conversion at 240°C and a 100%

conversion below 300°C. The activity of 40 wt% Pd/nCeO<sub>2</sub> does not decrease during 100 hours of exposure to methane and O<sub>2</sub> at 240°C. X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) were used to characterize the surfaces of bare supports and catalysts before and after exposure to reactor conditions. The XPS results reveal that the Pd surface concentration is an order of magnitude higher for 5 wt% Pd/pCeO<sub>2</sub> than for 5 wt% Pd/nCeO<sub>2</sub> due to the increased surface area of the nanosupport. Higher PdO<sub>2</sub>/PdO ratios were observed for both supports than have been seen previously for Pd on ZrO<sub>2</sub> or CO<sub>3</sub>O<sub>4</sub>. Accumulation of H<sub>2</sub>O on the surface during reaction was significant for the Pd/pCeO<sub>2</sub> catalyst but not for the Pd/nCeO<sub>2</sub> catalyst. As the Pd loading on pCeO<sub>2</sub> is increased, the Ce(III)/Ce(IV) ratio also increases. The surface analysis data are consistent with a previously-proposed mechanism in which dissociative methane chemisorption results in a surface methoxy species, which undergoes dehydrogenation to yield hydroxyl groups and a reactive C species. Oxidation of this C species, yields adsorbed carbonate, which decomposes to CO<sub>2</sub> product, while the hydroxyl groups can combine with hydrogen atoms from methoxy dehydrogenation to desorb as H<sub>2</sub>O. For Pd/pCeO<sub>2</sub> the rate limiting step appears to be H<sub>2</sub>O desorption, while for Pd/nCeO<sub>2</sub> adsorption of methane appears to be the slow step. These data indicate that the electronic properties and hence the chemical behavior is different for Pd/nCeO<sub>2</sub> and Pd/pCeO<sub>2</sub>.

#### 2:00 PM F7.2

SOLAR CELL CONTACTS USING NANO-SIZED DISPERSIONS. Doug Schulz, Jason Underwood, Calvin Curtis, Dave Ginley, National Renewable Energy Lab, Golden, CO.

We have been investigating the use of nano-sized particle-based contacts for both CdTe and Si solar cell technologies. The primary motivation has been the development of synthetic approaches to writeable inks leading to ohmic and thermodynamically stable contacts. The ability to minimize metallization linewidth and processing temperature is highly desirable in a wide variety of energy conversion applications. In the area of contacts to CdTe, particles of Hg-Cu-Te and Sb-Te have been applied as contacts to CdTe/CdS/SnO<sub>2</sub> heterostructures prepared by the standard NREL protocol. First, Hg-Cu-Te and Sb-Te were prepared by a metathesis reaction. After CdCl<sub>2</sub> treatment and NP etch of the CdTe layer, particle contacts were applied. The Hg-Cu-Te contacted cells exhibited good electrical characteristics, with Voc >810 mV and efficiencies >11.5% for most cells. Although Voc >800 mV were observed for the Sb-Te contacted cells, efficiencies in these devices were limited to 9.1%, presumably by a large series resistance (>20 ohm) observed in all samples. In order to explore contacts to Si, we have employed powders of Al and Ag. These particles were first characterized by transmission electron microscopy (TEM), TEM elemental determination X-ray spectroscopy (TEM-EDS), and TEM electron diffraction (TEM-ED). Next, Al and Ag particles were slurried and tested as contacts to p- and n-type silicon wafers, respectively. Linear current-voltage (I-V) was observed for Ag on n-type Si, indicative of an ohmic contact, whereas the Al on p-type Si sample was non-ideal. A wet-chemical surface treatment performed on one Al sample and TEM-EDS indicated a substantial decrease in the O contaminant level. The treated Al on p-type Si films exhibited linear I-V after annealing. Finally, we will present preliminary results for ink-jet deposition of contacts to Si.

#### 2:15 PM F7.3

COLLOIDAL MICROWAVE PROCESSING (CMP) FOR POLYMER FUEL CELL AND PHOTOVOLTAIC APPLICATIONS.

Monika Willert-Porada, Christian Gerk and Tim Schubert, University Bayreuth, Faculty of Applied Natural Sciences, Dept of Materials Processing, Bayreuth, GERMANY.

Synthesis and processing of nanocomposite materials with a high degree of micro- and nanoscale organization is particularly versatile by application of non conventional processing conditions, e.g., of microwave radiation, to a ceramic- or a metal-precursor distributed within a matrix, such as to form a colloid, an emulsion or a co-polymer. In particular, microwave processing of precursor compounds within a self assembled matrix is of high technical importance for electrochemically and photochemically active materials, like e.g., nanoscaled oxides, noble metals as well as carbides and nitrides of the Group IV-VI-elements (Ti to W). Application of selective microwave heating enables the generation of the catalyst and the electric conductor within a MEA of a polymer fuel cell, preserving the microscale organization of the top layer of the membrane. Similar results are obtained on photochemically active materials. A model description of the nucleation step of the precursor pyrolysis reaction will be presented, based on experiments on artificial mixed dielectrics. The potential of colloidal microwave processing for nucleation control and for nano- as well as microscale organization in nanocomposite materials will be discussed, in comparison to thermal equilibrium conditions, with respect to the catalytic and photochemical properties

of nano-Pt and nano-TiO<sub>2</sub> dispersed within proton exchanging membranes or thermoplastic polymers. The microstructure of the products is characterised by low-kV-SEM and by Confocal Laser Microscopy.

### 2:30 PM F7.4

**CONTROLLING NANOSCALE MATTER AND NANOSCALE PORE ARCHITECTURES FOR MANGANESE DIOXIDE BATTERY MATERIALS.** Jeffrey W. Long, Karen E. Swider, Rhonda M. Stroud, and Debra R. Rolison, Surface Chemistry and Surface Modification Branches, Naval Research Laboratory, Washington, DC.

Aerogels, which are nanoscale mesoporous solids, have been shown to be excellent high surface area, sinter-resistant supports for catalysis. These attributes, when coupled to the excellent mass transport of molecular reactants and products to and from the nanoscale domains of the aerogel through the mesoporous structure, are also equally desirable for electrode materials and electrocatalysis. Our prior small-angle neutron scattering studies with aerogels have shown that aerogels with ~85% porosity can be re-wetted without discernible collapse of the aerogel structure. This allows liquid-phase catalysis and electrocatalysis to be pursued with aerogels, modified aerogels, or aerogel composites. We have explored manganese oxide (MnOx) as a cathode material for battery applications, including batteries based on lithium-ion insertion and the familiar Zn/MnO<sub>2</sub> alkaline chemistry. Lithium insertion to create mixed valent Mn(III/IV)Ox is often accompanied by irreversible structural changes that can limit the recharging capabilities of the resulting batteries. We have prepared MnOx aerogels, ambigels, and xerogels using sol-gel chemistry based on the reduction of permanganate by an organic reducing agent in aqueous solution. With appropriate reaction conditions, monolithic MnOx gels can be obtained in which the size of both the nanoscale MnOx domains and the porous network is varied, as characterized by multiple structural and chemical techniques. The electrochemical properties (voltammetry and galvanostatic discharge) and charging reversibility of these MnOx materials as xerogels, ambigels, and aerogel will be described with respect to their Li-ion capacities.

### 2:45 PM F7.5

**GRAIN-SIZE DEPENDENT THERMAL CONDUCTIVITY OF NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA AND DIAMOND COATINGS.** J.A. Eastman, G. Soysz, L.J. Thompson, O. Auciello, K.L. Merkle, Materials Science Division, Argonne National Laboratory; R.J. DiMelfi, Reactor Engineering Division, Argonne National Laboratory; J.P. Singh, Energy Technology Division, Argonne National Laboratory, Argonne, IL; A.R. Krauss, D. Gruen, Chemistry Division, Argonne National Laboratory, Argonne, IL.

Nanocrystalline coatings are theoretically predicted to exhibit reduced thermal conductivity compared with the conductivity of their coarse-grained or single-crystal counterparts when the grain size of the coating is reduced below the bulk phonon mean-free-path-length. Yttria-stabilized zirconia (YSZ) thin films with grain sizes as small as 10-15 nm or as large as epitaxial single crystals are being produced by metal-organic chemical vapor deposition (MOCVD). The thermal conductivity of these coatings is being measured using the 3-omega technique. Approximately a factor-of-two reduction in thermal conductivity is seen at ambient temperature for the smallest-grained coatings compared to the conductivity of coarse-grained or single crystal coatings. Biaxial disk-bend tests are being carried out on MOCVD-produced coated samples prepared under similar conditions to determine if expected improvements in ductility and fracture resistance accompany grain size reduction. A combination of lower thermal conductivity and improved mechanical behavior would make nanostructured zirconia coatings excellent candidates for future applications as thermal barriers. Measurements of the thermal and mechanical behavior of commercial YSZ thermal barrier coatings using the same techniques will also be described and discussed. In contrast to the low thermal conductivity of YSZ, diamond is well known to exhibit extremely high thermal conductivity. This, combined with excellent mechanical and tribological behavior, makes nanocrystalline diamond coatings potential candidates for a number of future applications, including applications in microelectro-mechanical systems (MEMS). Thermal conductivity measurements using the 3-omega technique are being carried out on diamond films prepared by chemical vapor deposition. Implications for potential future uses of diamond coatings will be discussed. This work is supported by the U. S. Department of Energy, BES-DMS, under Contract W-31-109-Eng-38 and by a grant from Argonnes Coordinating Council for Science and Technology.

### 3:30 PM F7.6

**CAN WE DETERMINE THE BARRIER RESISTANCE FOR ELECTRON TRANSPORT IN LIGAND STABILIZED NANOPARTICLES FROM INTEGRAL CONDUCTANCE MEASUREMENTS?** U. Simon, University of Essen, Institute for Inorganic Chemistry, Essen, GERMANY.

The small lateral size of chemically tailored ligand stabilized metal and semiconductor nanoparticles in the range of one or two nanometers leads to a ultra-small self capacitance in the order of  $10^{-19}$  F<sup>[1]</sup>. This enhances the charging energy essentially above  $k_B T$  even at room temperature, which make them interesting as building blocks for nanoscale microelectronic devices, like single electron transistors<sup>[2]</sup>.

By means of integral temperature dependent conductance measurements, the effective capacitance  $C_{eff}$  of the particles in two or three dimensional nanoparticle/ligand networks can be deduced from the activation energy  $E_A$  of the charge transport according to  $E_A - e^2/C_{eff}$ <sup>[3]</sup>. Determining the barrier resistance  $R_b$  of the insulating ligand molecules from the overall resistance falls, since the resistance is very sensitive towards disorder, which cannot be avoided in this size scale, by nature.

In this work the use of the Landauer formula<sup>[4]</sup> is proposed to deduce  $R_b$  from  $E_A$ , when it is taken as the barrier height. According to this, the barrier resistance in ligand stabilized nanoparticles, connected by spacer molecules to form networks,<sup>[5]</sup> depends exponentially on the inter particle spacing. Comparison with data of the single molecule resistance of different ligands determined by local probe techniques, like scanning tunnelling spectroscopy, shows remarkable correspondence. This shows that the method proposed is suitable to deduce single molecule properties on the nanoscale from integral measurements.

[1] G. Schön, and U. Simon, Colloid Polym. Sci. 1995, 273, 101; *idid.* 202

[2] D.L. Klein, et al. Nature 1997, 389, 699

[3] U. Simon, et al. J. Mater. Chem. 1998, 8 (5), 517

[4] S. Datta, Electronic Transport in Mesoscopic Systems, Cambridge University Press, 1995

[5] G. Schmid and L.F. Chi, Adv. Mater. 1998, 10, 515

### 3:45 PM F7.7

**PHYSICAL AND MECHANICAL PROPERTIES OF CO-CR COATINGS FOR APPLICATIONS AS ORTHOPEDIC IMPLANTS.** D. Cheng, M.L. Lau, E.J. Lavernia, Department of Chemical and Biochemical Engineering and Materials Science, University of California, Irvine, Irvine, CA; C.J. Lavernia, Department of Orthopedics and Biomedical Engineering, University of Miami, Miami, FL.

Conventional and nanocrystalline Co-Cr (ASTM F75) coatings were prepared by high velocity oxy-fuel (HVOF) thermal spraying. The adhesion of the coatings to the Ti substrate was tested by tensile test and microhardness and modulus of coatings were measured using a nano-indenter. The corrosion resistance was characterized by an in vitro potentiodynamic anodic polarization technique in a pseudo physiological solution. Both coatings show excellent adhesion strength while the nanocrystalline one has higher hardness and higher corrosion resistance, showing better application potential for orthopedic implants.

### 4:00 PM F7.8

**NANOPOROUS ALUMINA COATINGS FOR MEDICAL IMPLANTS AND STENTS - RADIOTHERAPY, DRUG DELIVERY, BIOLOGICAL COMPATIBILITY.** Wolfgang Brandau, Alfons Fischer, Guenter Schmid, Thomas Sawitowski.

A new method for engineering the surface - body - interaction occurring with implant material by applying a nanoporous coating is presented. This coating is made of nanoporous alumina, formed by anodizing aluminum plasma coated implants. By a simple electrochemically process pores perpendicular to the implant surface are formed, whose diameter is adjusted by the anodic potential and can be varied between 5 and 250 nm. By varying the thickness of the coating pores with aspect ratios between 1 and 200 are formed which can be used for radiotherapy, drug delivery and biological compatibility as well. After chemical modification of this coating applied on to an intravascular stent it is possible to bind various radioactive isotopes irreversibly to the inner pore wall which allows for effective radiotherapy. The effect of porosity and chemical modification on the stability of the binding of 99m-Tc to the implant surface is presented as well as first results on cell culture tests proving the biological activity of the radioactive nanoporous ceramic coating.

### 4:15 PM F7.9

**SITE-SPECIFIC SELF-ASSEMBLY OF Si/SiO<sub>x</sub> NANOPARTICLES ON PATTERNED PDMS/SiO<sub>x</sub> FILMS.** Thomas S. Phely-Bobin, Richard J. Muisener, Fotios Papadimitrakopoulos, and Jeffrey T. Koberstein, Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

The present paper discusses the site-specific self-assembly of Si/SiO<sub>x</sub>

nanoparticles, which provides the means for the formation of three-dimensional supramolecular structures. Ultrathin films of poly(dimethyl siloxane) (PDMS) were topologically patterned with exposure to ozone assisted ultra-violet (248 nm) conversion of PDMS to hydroxyl-free SiO<sub>x</sub> surfaces. Preferential deposition of SiO<sub>x</sub> coated Si nanoparticles, with average size of 20 nm and size distribution of about 25% onto unconverted PDMS surfaces rather than the oxidized hydroxyl-free SiO<sub>x</sub> surfaces enables a novel fabrication methodology of spatially patterned nanocomposites. These nanocomposites were characterized with an array of analytical techniques in order to provide insight on the nature of this self-assembly process. The coverage achieved by this method shows potential for use in numerous applications in the photonics area, particularly when it is incorporated with nano-stamping techniques.

**4:30 PM F7.10**

Abstract Withdrawn.

**4:45 PM F7.11**

**ELECTRICAL PROPERTIES OF NANOCRYSTALLINE TUNGSTEN TRIOXIDE.** A. Hoel, L.B. Kiss, R. Vajtai, G.

Niklasson, C.G. Granqvist, E. Olsson, Department of Materials Science, Uppsala University, SWEDEN.

Tungsten oxide is a material of significant interest for applications in several areas. It can, for example, be used as the absorbing material in solar cells or as the electrochromic film in smart windows. Tungsten trioxide nanoparticles were produced using an advanced gas evaporation unit where the tungsten was oxidized in low pressure ambient air. The tungsten trioxide particles were formed via vapor condensation and deposited by gas deposition technique to avoid coagulation effects. The average size of the primary particles was around 5 nm depending on the heating power and the pressure. The particles exhibited a body centred cubic structure. The impedance spectrum showed resonance and negative capacitance effects. The behavior is compared to the behavior of films produced by sputtering techniques. The correlation between, fabrication conditions, structure and impedance spectrum will be discussed.

**SESSION F8: POSTER SESSION:  
NANOPHASES-SYNTHESIS,  
CHARACTERIZATION, AND PROPERTIES**

Chairs: Horst Hahn, Sridhar Komarneni and  
John C. Parker

Wednesday Evening, December 1, 1999

8:00 P.M.

Exhibition Hall D (H)

**F8.1**

**MICROSTRUCTURE AND MECHANICAL PROPERTIES OF OXIDE EUTECTIC FIBERS.** Stephen D. Durbin, Akira Yoshikawa, Kenji Hasegawa, Jong-Ho Lee, Boris M. Epelbaum, Tsuguo Fukuda, Tohoku University, Institute for Materials Science, Sendai, JAPAN; Yoshihara Waku, Japan Ultra-High Temperature Materials Research Center, Ube, JAPAN.

Directionally solidified oxide eutectics have attracted much attention as structural materials because of their exceptional mechanical properties at high temperature [1]. To date, we have focused our attention on sapphire/YAG and related compositions sapphire/R-Al-O, where Y is replaced by a rare earth R = Gd, Dy, Ho, or Er. We have used the micro pulling-down technique [2] to grow eutectic fibers over a wide range of growth rates, from 0.045 to 28 mm/min. The strength of these materials is strongly dependent on their microstructure, which varies with both composition and pulling speed. The microstructure is of the Chinese script type, in which the two phases form a complex, continuous, interpenetrating network. The interface between domains, as studied by transmission electron microscopy, is atomically sharp. Especially for thin fibers, the mechanical properties, in addition to the oxidation and corrosion resistance, depend on the nature of the surface. We have used atomic force microscopy to characterize both the surface and the bulk microstructure of the fibers. The script microstructure extends to the surface, but there it differs from the bulk in both composition and domain size, exhibiting a larger sapphire fraction and smaller domains. The surface tends to approach the bulk properties as the growth rate increases. To better understand and control these characteristics, we have developed a computer model to simulate the eutectic solidification process, which yields insight into formation of the Chinese script microstructure. [1] Y. Waku, N. Nakagawa, T. Wakamoto, H. Ohtsubo, K. Shimizu, and Y. Kohtoku, Nature 389 (1997) 49. [2] A. Yoshikawa, B. M. Epelbaum, T. Fukuda, K. Suzuki, and Y. Waku, Jpn. J. Appl. Phys. 38 (1999) L55.

**F8.2**

**INSULATOR-METAL TRANSITION IN NANOSTRUCTURED Ni-Al THIN FILMS.** Hoi-Pang Ng, Alfonso H.W. Ngan, The Univ of Hong Kong, Dept of Mechanical Engineering, Hong Kong, PR CHINA.

The electrical resistance of Ni-Al alloy thin films prepared by dc magnetron sputtering process was found to be abnormally high at room temperature. However, when heated at elevated temperatures, the resistance dropped significantly, exhibiting a remarkable negative temperature coefficient of resistance (TCR). The phenomenon was found to be substrate-independent. Cross-sectional transmission electron microscopy revealed that the films were essentially particulate and porous in nature. Although quantum-mechanical tunnelling is generally regarded as the predominating transport mechanism in porous films, our results seem to suggest that localized charged carriers ejected by thermionic emission mechanisms are probably the effective conduction sources in our Ni-Al films at elevated temperatures. Analysis of the current density-electric field (J-E) characteristics yielded a satisfactory agreement with the space charge limited (SCL) and the Poole-Frenkel (PF) emission models, indicating an emission-based conduction process rather than tunnelling in the films. The negative TCR effect diminishes and the usual metallic resistance is restored in thicker films, probably due to reduction in particle separation and coalescence of neighbouring crystallites.

**F8.3**

**RAMAN SHIFT AND BROADENING IN STRESS-MINIMIZED GE NANOCRYSTALS IN SILICON OXIDE MATRIX.** Yixiong Jie, Alfred Huan, Andrews Wee, Zhe Xiang Shen, Dept of Physics, National Univ of Singapore, Kent Ridge, Singapore, SINGAPORE.

Ge<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> alloy films have been synthesized by co-sputtering Ge and quartz targets using an rf-magnetron sputtering machine. By intentionally lengthening the cooling time interval in the annealing process and reducing the temperature gradient in the annealing samples, the resulting Ge nanocrystals embedded in amorphous silicon oxide matrix have been found to be nearly spherical, well-dispersed in the matrix and nearly stress-free by means of XRD, HRTEM, EDX and temperature-dependent Raman scattering characterization. Significant Raman shifts ranging from 2.0 to 5.8 cm<sup>-1</sup> have been observed from samples annealed at different temperatures. A phonon confinement model with various weighting functions and dispersion relations have been used to fit room temperature Raman spectra from selected samples. The size-dependent shift and broadening is found to be in good agreement with Fauchet's phonon confinement mode together with the isotropical TO<sub>2</sub> phonon dispersion relation introduced by Sasaki et al. The Raman spectra can also be well-fitted using peaks calculated from the phonon confinement mode without any artificial treatment. The inhomogeneous Raman peak broadening from samples annealed at lower temperatures were attributed to the non-Gaussian size distribution of Ge nanocrystals. The irregular compressive stress reported in the literature may originate from Ge nanocrystals surface strain formed during a fast cooling process due to the mismatch of thermal expansion coefficients of the matrix and the Ge nanocrystals.

**F8.4**

**SYNTHESIS AND CHARACTERIZATION TWO NOVEL COBALT VANADIUM OXIDES AS CATHODES IN LITHIUM BATTERIES.** Fan Zhang, Peter Zavalij and M. Stanley Whittingham Materials Research Center and Chemistry Department State University of New York at Binghamton, Binghamton, NY.

There has been much interest in the last two decades in layered vanadium oxides and their intercalates because of their potential use as secondary cathode materials for advanced lithium batteries. Therefore, the already rich crystal chemistry of the vanadates with open framework was considerable replenished with many new structures. We report here two novel cobalt vanadium oxides, [N(CH<sub>3</sub>)<sub>4</sub>]<sub>0.12</sub>Co<sub>y</sub>V<sub>2</sub>O<sub>5.0.26</sub>H<sub>2</sub>O and [CH<sub>3</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>0.12</sub>Co<sub>y</sub>V<sub>2</sub>O<sub>5</sub>. The two compounds were synthesized by the hydrothermal reactions of vanadium (V) pentoxide, CoSO<sub>4</sub> or Co(COOH)<sub>2</sub>, with an organic templating cation, tetramethyl ammonium hydroxide or triethylmethylammonium at 170°C for 72 hours. The stoichiometry, phase, and structure of the compounds have been examined as a function of deposition conditions using XRD, DCP, TGA, FTIR, SEM and EDS. In these double sheet oxides, organic species do not appear to impede the incorporation of lithium. They readily react with butyl-lithium solutions. Galvanostatic cycling of composite electrodes based on these compounds revealed a high charge capacity and promising cyclability. Electrochemical properties and rate capabilities of the materials used as cathodes for lithium cells will be presented. Supported by the National Science Foundation.

**F8.5**

Abstract Withdrawn.

### **F8.6**

**NOVEL SYNTHESIS OF II-VI SEMICONDUCTOR NANOCRYSTALS.** Gregory A. Khitrov, Geoffrey F. Strouse, University of California Santa Barbara, Department of Chemistry, Santa Barbara, CA.

A long-standing goal in materials chemistry has been the synthesis of high quality II-VI semiconductor nanocrystals by wet chemical methods. Currently, the best nanocrystals are produced by lyothermal methods that require the use of organometallic precursors, which are expensive and need to be handled under an inert atmosphere. We present an alternative crystal seeding method using molecular precursors. The growth of nanocrystals from the precursors can in most cases be carried out at lower temperatures than used in lyothermal technology. Results of characterization by electronic absorption and emission spectroscopy, TEM, ESMS, and ICP-AES will be presented.

### **F8.7**

**ENCAPSULATION OF NANOPARTICLES IN CROSS-LINKED RESORCINARENE 'SKINS'.** Stephen V. Puzstay, Shouzhong Zou, Alexander Wei, Dept of Chemistry; Kevin B. Stavens, Ronald P. Andres, Dept of Chemical Engineering; Purdue University, West Lafayette, IN.

Neutral nanoparticles are metastable and require organic surfactants to prevent their irreversible aggregation in solution. This approach, however, has only been successful in stabilizing particles of a limited size range. We have developed a novel encapsulating procedure for stabilizing nanoparticles using resorcinarenes as surfactants, which can then be cross-linked to form permanent shell-like coatings. This organic 'skin' imparts remarkably stability to the nanoparticles, allowing them to withstand a wide range of chemical processes while retaining their dispersity in organic solvents. This has also allowed us to isolate the particles and to characterize them as discrete chemical entities. Characterization of these encapsulated nanoparticles includes GPC-HPLC, TEM and surface-enhanced Raman spectroscopy. Our resorcinarene-based system is able to stabilize neutral gold nanoparticles of at least 20 nm in diameter, and promises to be of general utility. The improved processability of the encapsulated nanoparticles should be useful for their directed self-assembly into arrays and other periodic structures for the development of nanoelectronic networks.

### **F8.8**

**STRUCTURE AND STABILITY OF NANO-SCALE PHASES IN MELT SPUN Mg-Ca-Zn ALLOYS.** P.M. Jardim and I.G. Solorzano, PUC-Rio de Janeiro; J.B. Vander Sande, MIT, Cambridge, MA; W.W. Park, KIMM, Kyungnam, KOREA.

Alloys, with six different compositions in the system Mg-Ca-Zn in the form of ribbons with approximately 70  $\mu\text{m}$  thick and 3mm wide, were produced by melt spinning under argon using a Cu-Be wheel with a speed of 30-50m/s. These alloys were analyzed by means of Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive Spectrometry (EDS). The phases stability is being studied by Differential Scanning Calorimetry. To correlate microstructure and mechanical properties, the ribbons are being tested by micro-indentation. TEM and field emission SEM have been proved to be essential tools to fully characterize the microstructure. The first technique, however, has demanded particular sample preparation procedure in order to obtain electron-transparent foils free of artifacts induced by electrolyte contamination. The combination of this procedure with dimpling polishing and ion-milling cleaning is described in the presentation. The result microstructure is presented as based on a nano-structured ( and, perhaps, amorphous ) matrix containing a rather copious population of precipitates mainly based on  $\text{Ca}_3\text{Zn}$  and  $\text{Ca}_2\text{Mg}_5\text{Zn}_{13}$ . All the six compositions have shown a microstructural gradient from the wheel contact side to the argon atmosphere side as a result of the differences in the solidification rate across the ribbons. Work is being planned in the direction of incorporating rare earth additions into the system. The phase stability and the microstructural evolution will be discussed based upon TEM and FEG-SEM observations.

### **F8.9**

**SILICON NANOPARTICLE FORMATION BY LASER ABLATION IN A LOW PRESSURE INERT GAS.** Nobuhiro Aya, Seisuke Kano, Takafumi Seto, AIST-MITI, Mechanical Engineering Laboratory, Tsukuba, JAPAN; Takehito Yoshida, Matsushita Research Institute Tokyo, Inc., Kawasaki, JAPAN; Nagaraja P. Rao, MicroTherm, LLC, Minneapolis, MN; Steven L. Girshick, Univ. of Minnesota, Dept. of Mechanical Engineering, Minneapolis, MN.

Laser ablation is a promising method for the synthesis of nanosized particles of a wide range of materials with no contamination. We have produced 1-20 nm-diameter silicon particles by laser irradiation on a

substrate in 1-20 Torr inert gas. It was found that the size, shape and structure of particles depend on the experimental conditions of laser irradiation and ambient gas. The size of primary particles or nanocrystalline grains, which is important for the expected application of Si nanoparticles for luminescence devices, increases as the ambient gas pressure is increased, and can be controlled by the pressure. Previously published simulations of particle growth using the classical theory of droplet formation in an expansion plume could not explain the experimental observations, e.g. the above-mentioned pressure-dependence of the particle size and also the reported observations of the atoms, ions and small clusters in the plume. We have described the clustering of silicon vapor with high kinetic energy and the evolution of particles in the free-molecule regime by a model which considers the effects of ion-induced nucleation and three-body recombination, and which uses a simplified expression for the temperature and density change in the plume with time. A comparison with the experimental results is shown and the validity of our approach is discussed.

### **F8.10**

**ATOMIC SCALE STUDY OF Pt NANOCCLUSERS ON  $\text{TiO}_2(110)$ .** Shupan Gan, Yong Liang and Donald R. Baer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Understanding the interaction of titanium dioxide with its supporting metals is important to photocatalytic applications.  $\text{TiO}_2(110)$  has two surface phases: (1x1) and (1x2). We have conducted a comparative study on the interaction of Pt with these two phases using scanning tunneling microscopy/spectroscopy (STM/STS), x-ray photoelectron spectroscopy (XPS), rutherford back scattering (RBS), and low energy electron diffraction (LEED). It has been found that Pt forms nanoclusters on  $\text{TiO}_2$  surfaces. On the (1x1) structure, Pt clusters randomly distribute on the surface at 300 K. In contrast, Pt predominantly adsorbs on step edges on the (1x2) reconstruction. Atomic resolution STM images reveal that these clusters are attached to bright spots at the end of atomic rows, with an average of 40  $\text{\AA}$  in diameter, and are 2.4  $\text{\AA}$  higher than the surrounding atomic rows at the Pt coverage of one monolayer. The electronic information of these clusters is examined by bias dependent images and scanning tunneling spectra. Further annealing of the surface to 450 K causes coalescence of some clusters. By the means of statistically analyzing STM images, the size distribution of Pt clusters is obtained as well as the diffusion length of Pt on  $\text{TiO}_2$  surfaces, which will be further discussed at the meeting.

### **F8.11**

**LOW DOSE HREM IMAGING OF SMALL ANGLE GRAIN BOUNDARIES AND DISLOCATIONS IN DCHD POLYDIACETYLENE NANOCRYSTALS II.** Christian Kuebel, Lawrence Drummy, and David C. Martin, The University of Michigan, Materials Science and Engineering, Ann Arbor, MI.

We have been examining the influence of specific grain boundary and dislocation defects on the microstructure and macroscopic properties of semiconducting, conjugated crystalline polymers. Low Dose HREM has been used to image the internal structure of DCHD polydiacetylene nanocrystals prepared by precipitation from dilute acetone solution into water. HREM images of several different crystallographic zones have been obtained with reflections in the FFT observed out to scattering vectors corresponding to a resolution of 0.19 nm. The lattice images reveal the internal perfection of the DCHD polymer nanocrystals, and provide evidence for dislocations, small angle grain boundaries, and lattice bending. Digital FFT's of the HREM images were used to obtain quantitative maps of the size and extent of the local structural variations. The beam stability of the organic DCHD nanocrystals was sufficient to facilitate the acquisition of a series of HREM images as a function of objective lens defocus.

### **F8.12**

**SYNTHESIS OF NANOSTRUCTURED TUNGSTEN CARBIDE FILMS BY LASER ABLATION OF MICROPARTICLE AEROSOLS.** Michael P. Beam, Michael F. Becker, James R. Brock, Dale E. Henneke, John W. Keto, Gokul Malayavanatham, William T. Nichols, University of Texas at Austin, Dept of Physics, Austin, TX.

Tungsten carbide (WC) coatings are prepared using a novel process, pulsed laser ablation of microparticle aerosols. The produced nanocrystallites are supersonically impacted onto glass, silicon wafers and stainless steel substrates. The influence of experimental parameters (laser fluence, pressure and impaction velocity) on the structure, composition and physical properties of the resultant particles and films are studied. It was found that stoichiometric, crystalline films could be grown at rates of nearly 1 micron per second under a wide variety of processing conditions. These films pass both the adhesive lift off and scratch tests. TEM investigations indicate that the laser ablation forms individual particles (2-10 nm) and small

aggregates of these particles. Adjustment of the gas pressure in the laser interaction cell was found to control the degree of aggregation while laser fluence had a slight effect on nanoparticle size. Upon impaction, the separate particles form dense, self sintering nanocrystalline films, with helium forming the most dense as determined from SEM images. However, at the high impaction velocities of helium, particle bounce off from the substrate occurred. An increase in the supersonic nozzle diameter was found to reduce this problem and increase deposition rates. This work was supported by the NSF (grant no. CTS-9530347), the Texas Advanced Technology Program (grant no. 3658-348) the Robert A. Welch Foundation and by an MRS Undergraduate Materials Research Initiative grant.

#### **FS.13**

##### **PREPARATION AND PROPERTIES OF COLLOIDAL PARTICLES. SILICA ON YTTRIUM IRON GARNET.**

**R.H.M. Godoi**, M. Jafelici, Jr., Joaquim Portillo\*, Sao Paulo State University- Chemistry Institute, Campus of Araraquara, BRAZIL and \*Seveis Cientifico Tecnicos, University of Barcelona, Barcelona, SPAIN.

Various properties of particles can be altered by coating them with a layer of different chemical composition. Specifically, yttrium iron garnet (YIG) has been coated with silica particles for the control of their sintering, corrosion resistance, and stabilization of magnetic properties. This cover was obtained by hydrolysis of tetraethylorthosilicate (TEOS) in 2-propanol. This material was characterized by transmission (TEM) electron microscopy, (XEDS) X-ray energy-dispersive spectrometry, (XPS) X-ray photoemission spectroscopy and (VSM) vibrating sample magnetometry. YIG was heterocoagulated by silica as indicated by TEM micrographies. The electron diffraction patterns for YIG and silica were obtained and the elements detected by XEDS. XPS measurements indicated that only binding energy for silicon and oxygen were found, on the silica shell, which confirms that the YIG was covered. The values of the saturation magnetization differ from the heterocoagulated system to well-crystallized YIG.

#### **FS.14**

##### **OPTICAL CHARACTERIZATION OF A SPHEROIDAL NANOPARTICLE ON A SUBSTRATE.**

**Carlos E. Roman-Velazquez**, Cecilia Noguez and Ruben G. Barrera Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico DF, MEXICO.

We developed a spectral representation for the effective polarizability of a spheroidal nanoparticle located at an arbitrary distance above a substrate. This representation allows systematic studies of the optical response of the system in terms of the excitations of optical modes, including multipolar contributions. As an example of its applicability, we study the optical response of potassium particles with different anisotropies, located at different distances above of substrates of different materials (Si, TiO<sub>2</sub>). We present results in terms of differential reflectance spectra that allow us for direct comparison with experimental measurements.

#### **FS.15**

Abstract Withdrawn.

#### **FS.16**

**NANOCRYSTALLINE THICK FILMS BY CHEMICAL VAPOR SYNTHESIS.** S. Seifried, M. Winterer, H. Hahn, Darmstadt University of Technology, Department of Materials Science, Thin Films Division, Darmstadt, GERMANY.

Crystalline ceramic films with thicknesses up to 150 microns and grain sizes below 30 nm are prepared by a modified Chemical Vapor Deposition (CVD) method, the Chemical Vapor Synthesis (CVS) on different substrate materials. A horizontal hot wall reactor is used for the pyrolysis of metalorganic precursors under helium flow using various precursor delivery techniques. The influence of process parameters, specifically reactor position and reactor temperature on the microstructure and phase evolution is examined. One dimensional gradients in concentration and porosity are obtained by variation of parameters during the process.

#### **FS.17**

**ON THE INFLUENCE OF SOME SYNTHESIS TECHNIQUES ON THE LOW TEMPERATURE SUPERPLASTIC DEFORMATION BEHAVIOUR OF NANOCRYSTALLINE YTTRIA STABILISED ZIRCONIA.** U. Betz, S. Rhee<sup>1</sup>, S.S. Bhattacharya<sup>2</sup>, N.S. Gajbhiye<sup>3</sup>

and H. Hahn, Department of Materials Science, Thin Films Division Darmstadt University of Technology, Darmstadt, GERMANY;

<sup>1</sup>Department of Technical Physics, Materials Science Division, Research Centre, Karlsruhe, GERMANY, <sup>2</sup>Permanent Address: Department of Metallurgical Engineering, IIT Madras, Chennai, INDIA, <sup>3</sup>Department of Solid State Chemistry, IIT Kanpur, INDIA.

It is now well established that nanocrystalline yttria stabilised

zirconia is capable of exhibiting superplastic deformation in tension and compression at relatively lower temperatures (less than half the absolute melting point or phase transformation temperature of the material). However, the influence of different techniques used for synthesis as well as processing of nanocrystalline powder have not been thoroughly investigated in terms of the mechanical deformation behaviour. In this study, nanocrystalline powder produced by several methods of synthesis: (a) two vapour phase condensation techniques - an Inert Gas Condensation (IGC) and a Chemical Vapour Synthesis (CVS) process, (b) a sol-gel method and (c) a laser ablation technique (procured through a commercial company) have been compared. In the case of the IGC process, nanocrystalline zirconia was separately synthesised and subsequently stabilised by physically mixing with the requisite quantity of nano yttria (also produced by an IGC process), whereas in the other three processes nanocrystalline yttria stabilised zirconia was directly synthesised by in-situ doping of yttria in zirconia. The powders synthesised from these different processes were separately consolidated and compacted to a green density of about 50%. A standardised sintering route was chosen for an optimal combination of high density and fine grain size (well within the nanometric range). The green compacts were sintered essentially in vacuum at 1423K with a holding time of 120 mins. The sintered specimens were then tested under compression for their deformation behaviour at a temperature of 1423 K. The difference in the low temperature superplastic deformation behaviour of the different powders is expressed in terms of some of the phenomenological constants of high temperature deformation. Microstructural characterisation was also carried out at each and every stage with a view to highlight the differences in the powders produced from the different synthesis techniques.

#### **FS.18**

##### **ARC DISCHARGE FOR THE SYNTHESIS OF MONOCLINIC Ga<sub>2</sub>O<sub>3</sub> NANOWIRES.**

**Young Chul Choi**, Dong Jae Bae, Seung Mi Lee, Young Soo Park, Young Hee Lee, Dept of Semiconductor Science and Technology and Semiconductor Physics Research Center, Chonbuk Natl Univ, Chonju, R.O.KOREA; Kyeong-Su Park, Analytical Engineering Laboratory, Samsung Advanced Institute of Technology, Suwon, R.O.KOREA; Won Bong Choi, Nae Sung Lee, Jong Min Kim, Display Laboratory, Samsung Advanced Institute of Technology, Suwon, RO KOREA.

Monoclinic gallium oxide ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>) nanowires were catalytically synthesized by electric arc discharge of GaN powders mixed with a small amount (less than 5%) of Ni and Co (1:1) under a pressure of 500 Torr (80%-Ar + 20 %-O<sub>2</sub>). Scanning electron microscope (SEM) and transmission electron microscope (TEM) images showed that the average diameter of the wires were about 30 nm and their lengths were as long as up to a few hundreds micrometers, resulting in extremely large aspect ratio. Selected area electron diffraction pattern was indicative of single crystalline nature of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> wire. High resolution TEM showed twin defects and jog dislocations. Some metal particles are enclosed within the wires. Both X-ray diffraction (XRD) patterns and Raman spectra of the wires identified the observed nanowires as monoclinic crystalline gallium oxides. Growth mechanism in conjunction with catalytic step growth will be further presented.

#### **FS.19**

**SYNTHESIS OF CUBIC AND RHOMBOHEDRAL PHASED NANOCRYSTALLINE SnO<sub>2</sub> DOPED In<sub>2</sub>O<sub>3</sub> ITO POWDERS WITH COPRECIPITATION METHOD.** Bong-Chull Kim, Jeong-Joo Kim, Kyungpook Natl Univ., Dept. of Inorganic Materials Engineering, Taegu, KOREA; Se-Hong Chang, KETI, PyungTaek, KOREA.

Nanocrystalline SnO<sub>2</sub> doped In<sub>2</sub>O<sub>3</sub> [ITO] powders were prepared by coprecipitation from homogeneous solutions and then calcination of these precipitates. Characteristics of precipitates were investigated with the controlling of coprecipitation conditions (pH, concentration of solution, and aging temperature, etc.). When the coprecipitation process were carried out in high pH, concentrated solution, and low aging temperature, the structure of precipitates was indium hydroxide [In(OH)<sub>3</sub>] with rod-like shape. On the contrary, indium oxide hydroxide [InOOH] with globular shape was formed in low pH, diluted solution, and high aging temperature condition. Furthermore, when the indium hydroxide [In(OH)<sub>3</sub>] and the indium oxide hydroxide [InOOH] were calcined at 600°C, each precipitates were transformed to the cubic and the rhombohedral ITO phase, respectively. Besides, the size and shapes of powders were preserved after calcination process.

#### **FS.20**

**SYNTHESIS, CHARACTERIZATION, AND UTILIZATION OF SINGLE CRYSTALLINE NANOPARTICLES OF SILVER.** Ziyi Zhong, Yadong Yin, Byron Gates, Younan Xia, University of Washington, Department of Chemistry, Seattle, WA.

We have demonstrated the use of Tollen's reaction in generating

monodispersed, single crystalline particles of silver with diameters in the range of 20-60 nm. The nucleation and growth of these nanoparticles was studied using UV-Vis spectroscopy and transmission electron microscopy (TEM). Upon exposure to alkanethiol molecules, the plasmon peak of these silver nanoparticles changed substantially in intensity and/or position. The potential use of this optical property in fabricating new types of optical sensors will be discussed.

#### **F8.21**

**SI NANOPARTICLES SYNTHESIZED BY BALL-MILLING A MIXTURE OF GRAPHITE AND SI DIOXIDE POWDERS.** C. Lam, Y.F. Zhang, Y.H. Tang, C.S. Lee, I. Bello, S.T. Lee, Centre of Super-Diamond and Advanced Films and Department of Physics and Materials Science, City University of Hong Kong, HONG KONG.

Since Canham reported intense visible photoluminescence (PL) from porous Si at room temperature, light emission from Si nanostructures has given rise to enormous interest in view of the potential applications in optoelectronics. Mechanical attrition by ball-milling is a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment, and applicability to essentially all classes of materials. However, normal mechanical milling technique produces Si nanostructures not by cluster assembly but by the structure decomposition. The sizes of the produced Si nanoparticles are normally too large to exhibit quantum confinement effects. Recently, we found that ultrafine Si nanoparticles can be synthesized by solid phase reaction of graphite and Si dioxide powders in ball-milling processes. The generated Si in solid phase assembled as nanoparticles in a wide spectrum of diameters. Intense multiple-peak structures in photoluminescence spectra of the Si nanoparticles are observed at room temperature. The peak energies are found to coincide well with the photoluminescence peak pinning energies previously reported in porous Si. Thus the fine structures of luminescence spectra could be attributed to the size quantization of Si nanoparticles formed during solid phase reaction processes of ball milling. In this paper, both the synthesis of Si nanoparticles by ball milling from mixtures of graphite and Si dioxide powders and the PL characteristics are presented.

#### **F8.22**

**PREPARATION OF NANOCRYSTALLINE BISMUTH-CONTAINING POWDERS THROUGH SOLUTION-PHASE REDUCTIONS.** Edward E. Foose, Alan D. Berry, Arthur W. Snow, and J. Paul Armistead, Naval Research Laboratory, Chemistry Division, Washington, DC.

Current studies into the chemical synthesis of soluble metal nanoparticles have focused primarily on the d-block elements, with little work examining the preparation of similar materials from the main group metals. Recently, in an attempt to both synthesize such materials and understand the fundamental chemistry behind their formation, we have begun to examine the preparation of nanocrystalline bismuth and bismuth/gold alloys through several straightforward solution methods. Nanocrystalline bismuth powders with approximate average particle sizes ranging from 15 to 30 nm have been prepared from the reduction of BiCl<sub>3</sub>. In addition, nanocrystalline Au<sub>2</sub>Bi powders of comparable dimensions have been obtained from a modification of the procedure used for the formation of gold nanoparticles. The alloy is produced from the reduction of a biphasic water/toluene mixture of HAuCl<sub>4</sub> and a BiCl<sub>3</sub>/HCl precursor, utilizing a phase-transfer reagent. Full details of the synthesis of these materials as well as their characterization through XRD and TEM will be presented.

#### **F8.23**

**MAGNETIC HARDENING OF MECHANICALLY ALLOYED SmFe<sub>11-x</sub>Co<sub>x</sub>Ti.** Lotfi Bessais and Catherine Djega-Mariadassou, CNRS, LCMTR, Thiais, FRANCE.

Mechanical alloying of ternary SmFe<sub>11-x</sub>Co<sub>x</sub>Ti ( $x = 0, 0.5, 1, 1.5, 2$ ) alloys was carried out under an Ar atmosphere, milled samples were annealed for 30 min in a vacuum at different temperatures  $T_a$  from 650°C to 1150°C. The effects of heat treatment on local structural changes have been investigated by means of X-ray diffraction (refined using the Rietvelt method), Mössbauer spectroscopy and differential sample magnetometer. Tetragonal ThMn<sub>12</sub>-type structure is observed for samples annealed at  $T_a > 900^\circ\text{C}$  (Curie temperature  $T_c = 408^\circ\text{C}$ , for  $x = 1$ , as an example). For  $650 < T_a < 800^\circ\text{C}$  the TbCu<sub>7</sub> type phase was identified as the unique phase ( $T_c = 327^\circ\text{C}$  for  $x = 0.5$ ). Between these two regions a mixture of TbCu<sub>7</sub> and ThMn<sub>12</sub>-type nanocrystalline phases is obtained with a maximum of the coercive field  $H_c$  ( $H_c > 5\text{kOe}$ ) and of the energy product  $(BH)_{max}$ . The Mössbauer spectra relative to the hexagonal phase show sextuplets broadened by the statistical occupancies of the iron sites. The relationship between the iron families of the hexagonal and the tetragonal phases can be deduced. The experiments with annealing temperature variation were repeated for all composition of alloys. An

enhancement of the magnetic properties results from the Co substitution.

#### **F8.24**

**ORDERING IN NANOCRYSTALLINE SmFe<sub>9</sub>.** Catherine Djega-Mariadassou and Lotfi Bessais, CNRS, LCMTR, Thiais, FRANCE.

Three samples of nominal atomic Sm composition consistent respectively with the theoretical stoichiometry 1/12, 2/17 and 1/7 were prepared by high energy ball milling of Fe and Sm powders and subsequent annealing at temperature  $T_a$  between 873 and 1473K. The X-ray analysis by the Rietvelt method, taking into account diffraction domain size and strain effects was coupled to Curie temperature  $T_c$  measurements and Mössbauer spectroscopy at room temperature. For all samples, at  $T_a$  between 873 and 1023K, the detected out-of-equilibrium phase is the hexagonal  $P6/mmm$  structure derived from TbCu<sub>7</sub> with the composition SmFe<sub>9</sub>. The increase of the 2e iron dumbbell site occupation along the  $c$  axis favors the displacement of Fe atoms in the 6l positions  $x\ 2x\ 0$ , the third iron site 3g being fully occupied. For  $T_a > 1023\text{K}$  the emergence of additional lines leads at 1273K to the  $R\bar{3}m\ 2/17$  structure. The Mössbauer experimental spectra of the samples annealed at  $T_a \geq 1273\text{K}$ , are similar to earlier works devoted to Sm<sub>2</sub>Fe<sub>17</sub>. The spectra assigned to SmFe<sub>9</sub> are explained by one hyperfine field attributed to the 2e dumbbell close to the value observed for the  $R\bar{3}m$  phase. The two remaining hyperfine fields broadened by a quadrupole split distribution are assigned to the two remaining Fe families. They are increased comparatively to the values shown by the derived atom families of Sm<sub>2</sub>Fe<sub>17</sub>, inducing a higher  $T_c$  for the SmFe<sub>9</sub> phase. For intermediate  $T_a$ , the reduction of the field broadening is centered on lower field values and leads, as a consequence, to a better resolution of the 2e dumbbell site. This result is connected, too, to a decrease of  $T_c$  explaining the wide spread of  $T_c$  values found in all previous works.

#### **F8.25**

**SIZE EFFECT IN GERMANIUM NANOSTRUCTURES FABRICATED BY PULSED LASER DEPOSITION.** K.M. Hassan, A.K. Sharma and J. Narayan, Department of Materials Science and Engineering, and NSF Center for Advanced Materials and Smart Structures, North Carolina State University, Raleigh, NC; J.F. Muth, C.W. Teng and R.M. Kolbas, Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, NC.

We have fabricated ten alternating layers of Ge nanostructures<sup>1</sup> buried in AlN and Al<sub>2</sub>O<sub>3</sub> matrices grown on Si(111) and sapphire by pulsed laser deposition (PLD) at the substrate temperature of 500°C. The characterization of these structures was performed using high resolution transmission electron microscopy (HRTEM), photoluminescence, Raman spectroscopy and transmission measurements. The HRTEM results show that the Ge islands are single crystal with a pyramidal shape. The average size of Ge islands was in the range ~5-20 nm for different laser deposition and substrate parameters. The Raman spectrum showed a peak of the Ge-Ge vibrational mode downward shifted upto 295 cm<sup>-1</sup> for the 15nm size nanodots which is caused by quantum confinement of phonons. Photoluminescence of the Ge dots (size ~15nm) was blue shifted by ~0.266 eV from the bulk Ge value of 0.73 eV at 77 K, resulting in a distinct peak at ~1.0 eV. The transmission measurements carried out at room temperature and 77K on different samples deposited on sapphire substrate showed shift of both E<sub>1</sub> and E<sub>2</sub> transitions in the absorption spectra toward higher energy as Ge dot size decreases in accordance with the quantum confinement effect. The size effect of Ge nanostructures on optical properties is discussed and the importance of PLD in fabricating novel nanostructures is emphasized in this paper. Reference: <sup>1</sup>K.M. Hassan, A.K. Sharma, J. Narayan, J.F. Muth, C.W. Teng and R.M. Kolbas, Appl. Phys. Lett. (in press 1999)

#### **F8.26**

**CHARACTERIZATION OF INCLUSIONS IN RUTILE NANOPARTICLES.** Shirley Turner, Surface and Microanalysis Science Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

The surfaces of rutile (TiO<sub>2</sub>) have been the subject of considerable study, in part because rutile can be used as a photocatalyst to dissociate water and organic compounds. Previous work showed that central inclusions (voids) are formed in some larger nanoparticles of rutile generated in a flame burner system. In this work, the morphology of the inclusions is more fully characterized and the effect of heating by the electron beam is described. The particles were observed using transmission electron microscopy (TEM) and characterized by bright and dark-field imaging, electron diffraction and high-resolution TEM. Inclusions were viewed in many orientations including down rutile [001] and in orientations perpendicular to [001]. The inclusions as formed are either ovoid or polygonal. Many of the polygonal inclusions have {110} faces that appear as squares with

rounded corners when viewed down [001]. Some of the particles with central inclusions have additional smaller inclusions. Upon heating in the electron beam, many of the ovoid and polygonal inclusions form facets. Upon further heating, the facets in some cases migrate or change size. Possible factors involved in the morphological changes to the inclusions upon heating will be explored.

#### **F8.27**

##### **THE ROLE OF BORON IN THE MECHANICAL MILLING OF TITANIUM -6% ALUMINIUM -4% VANADIUM POWDERS.**

**A.P. Brown**, R. Brydson, C. Hammond, Dept of Materials, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds, UK; A. Wisbey, T.M.T. Godfrey, Structural Materials Centre, Defence Evaluation Research Agency, Farnborough, Hants, UK.

Titanium -6% Aluminium -4% Vanadium (Ti-6-4) is widely used for commercial superplastic forming (SPF) and a reduction in grain size would lead to significant improvement in its SPF properties. Mechanical alloying (MA) of Ti-6-4 with a second phase is a possible route to producing a fine-grained, particulate reinforced material. Boron is an ideal choice for a second phase because on consolidation of the MA powders the boron will react with the titanium to form stable TiB reinforcing particles. Although boron has a low solid solubility in titanium it is expected that the MA process would at least lead to nanoscale mixing of boron. Furthermore boron is known to stabilise amorphous structures of alloys. It is therefore of interest to focus on the exact role boron plays in the MA process. The clean mechanical alloying of gas-atomised Ti-6-4 with 0, 2, 25 and 50 at.% boron powder has been carried out at the Defence Evaluation Research Agency (UK). The powder samples have been analysed using XRD, thermal analysis and analytical TEM (EDX and PEELS). The nanocrystalline nature of the powders is confirmed and the effect boron has on the evolution of their microstructures will be reported.

#### **F8.28**

##### **EFFECT OF SURFACE MODIFICATION OF NON-STOICHIOMETRIC CDS NANOPARTICLES ON THEIR LUMINESCENCE.** **Alex V. Isarov** and John Chrysochoos, Department of Chemistry, The University of Toledo, Toledo, OH.

Nanoparticles of II-VI semiconductors are of great interest as precursors of optoelectronic devices in general, and light emitting devices in particular. The luminescence emission of semiconductor nanoparticles depends upon both the size of the nanoparticles (quantum size effect) and the nature of their surface [1]. Surface modification of semiconductor nanoparticles may lead to: (a) enhancement of excitonic emission by eliminating surface traps responsible for radiationless transitions [2] or (b) formation of new emission bands, which are attributed to the luminescence of ultrasmall particles on the surface of initial nanoparticles (e. g. HgS/CdS [3]). In the latter case the intensity of the new luminescence band increases with increasing concentration of the modifier. Surface modification of nonstoichiometric CdS nanoparticles ( $[Cd^{2+}/S^{2-}] = 3$ ,  $E_g = 3.0$  eV) with copper(II) ions leads to the formation of a new red-shifted emission band. However, this band is observed only at very low concentrations of copper(II) ions (less than  $2 \times 10^{-6}$  M for  $2 \times 10^{-4}$  M CdS nanoparticles in 2-propanol) and its intensity decreases as the concentration of copper(II) ions increases. Such low concentrations of Cu(II) ions have no effect upon the absorption spectrum of the modified nanoparticles. The new emission band is attributed to the formation of isolated  $Cu^+$  ions onto the surface of CdS nanoparticles, resulting from the immediate reduction of adsorbed Cu(II) ions. These adsorbed Cu(I) ions create a new energy level in the bandgap of CdS at about 1.2 eV below the conduction band [4]. At higher concentrations of copper(II) ions ultrasmall particles of copper sulfide are formed on the surface of CdS nanoparticles at the expense of isolated copper ions. Such ultrasmall copper sulfide particles are nonluminescent, and therefore, the intensity of the new band decreases as the concentration of copper(II) increases. The formation of ultrasmall particles of copper sulfide can be controlled by using complexed Cu(II) ions instead of free Cu(II) ions [5]. The effect of surface modification of CdS nanoparticles upon its luminescent properties depends upon the number of adsorbed Cu(I) ions per CdS nanoparticle. An appropriate mechanism will be discussed.

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#### **F8.29**

##### **OBTAINING NANOSIZE POWDERS OF AMORPHOUS AND CRYSTALLINE IRON THROUGH QUANTUM CHEMICAL TECHNOLOGY.** **Razmik T. Malkhasyan**, Susanna L. Grigoryan,

Sergo G. Kamanchajyan, Scientific Production Enterprise ATOM, Ministry of Industry and Trade, Yerevan, ARMENIA.

The results of reduction of vibrationally excited to the third quantum level by hydrogen molecules of  $\alpha - Fe_2O_3$  and nano phase  $\gamma - Fe_2O_3$  oxides are presented. Due to nonequilibrium quantum-chemical reduction technology nonequilibrium phase of amorphous iron is obtained. The identification of amorphous phase of metals is determined through electron diffraction study on the transmitting electron microscope (TEM), x-ray diffraction and calorimetric method. The conditions of obtaining nano size powders of amorphous and crystalline metals are defined experimentally. Both amorphous and crystalline nano size metal powders have high activity. The preliminary results of chemical study indicated that amorphous metal reacts more actively with chemical reactors, as acids, alkalis, water, etc. While seeking a method of protection of obtained metal powders it was discovered that the nano size particles can dissolve in organic solvents.

#### **F8.30**

##### **SYNTHESIS AND OPTICAL PROPERTIES OF STABLE ORGANIC DISPERSIONS OF BISMUTH SULFIDE NANOPARTICLES.** **Datatri Nagesha**, Nicholas Kotov, Oklahoma State University, Chemistry Department, Stillwater, OK.

The synthesis of semiconductor nanoparticles with high chalcogen/metal ratio, such as bismuth sulfide, is compounded by the insufficient passivation of their surface when traditional Lewis base stabilizers such as thiols, amines, phosphates, etc., are utilized. Many of these materials have a bang gap in the near IR region, and therefore, a strong size-quantization effect is anticipated in the visible region of spectrum provided that the diameter of nanoparticles does not exceed a few nm. Two types of synthetic strategies were utilized to obtain nanoclusters of bismuth sulfide: 1) synthesis in acidic media in the presence of pyridine and 2) decomposition of a precursor in the presence of Sc surfactant. In both cases, the growth of nanoparticles is expected to be impeded by the reaction of Lewis acid centers of the stabilizers with chalcogen atoms located on the particle surface. Produced bismuth sulfide nanoparticles were characterized by TEM, XRD, mass-spectroscopy, ultracentrifugation, and optical spectroscopy. A sharp absorption onset has been observed between 550 and 650 nm depending on the method of synthesis, which is attributed to the variations of particle size. A strong luminescence peak was registered in the near-bang-gap region of  $Bi_2S_3$  nanoparticles, when protonated pyridine was used as a stabilizer.

#### **F8.31**

##### **HYSTERESIS LOOP SHIFTS IN MAGNETIC FIELD COOLED FeOOH NANOPARTICLES.** **M.S. Seehra** and **A. Manivannan**, Physics Department, West Virginia University, Morgantown, WV.

Recently, a number of reports on the structural, catalytic and magnetic properties of commercially available FeOOH nanoparticles have been published [1]. This material is a free flowing powder of average particle size  $\approx 30$  Å, with Fe being in  $Fe^{3+}$  state. Magnetic studies show that this material behaves as a superparamagnetic (SP) with a blocking temperature  $T_B \approx 65$  K. However the nature of the magnetic state below  $T_B$  is not understood since  $T_B$  does not scale with measuring time scale according to the predictions of SP. In this work, we report detailed investigations of the hysteresis loops observed below  $T_B$ , under field-cooled (FC) and zero-field-cooled (ZFC) conditions, in magnetic fields up to  $\pm 10$  kOe. Under ZFC, the hysteresis loop at 10 K is symmetric with coercivity  $\approx 500$  Oe and remanence  $\approx 0.9$  emu/g. But the loop remains open till 40 kOe with no indication of saturation. For the FC cases, the sample was cooled from 150 K to 10 K in  $H = 10, 15, 20$  and 30 kOe, followed in each case by measurements of the hysteresis loop at 10 K. The loop shifts rapidly for lower cooling fields but the shift saturates at 3500 Oe for cooling field above 20 kOe. These results suggest that uncompensated surface spins responsible for SP above  $T_B$  get frozen in a spin-glass-like state below  $T_B$  and the cooling field picks out one of the spin-configurations, resulting in a loop shift. These results will be discussed in terms of the anisotropy of the surface spins and their interaction with the core spins [2]. [1]. Feng et al, *J. Catal.* **143**, 510 (1993); Zhao et al, *Phys. Rev. B* **54**, 3403 (1996); Ibrahim et al, *Phys. Rev. B* **51**, 295 (1995). [2]. R.H. Kodama and A.E. Berkowitz, *Phys. Rev. B* **59**, 6321 (1999).

#### **F8.32**

##### **CADMIUM SELENIDE NANOPARTICLES SYNTHESIZED WITH FUNCTIONAL CAPPING GROUPS.** **Sebastian J. Norager**, Paul O'Brien, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK.

Semiconductor nanoparticles capped with Trioctylphosphine oxide (TOPO) have been of considerable interest in recent years. This is because the TOPO route offers narrow size-distribution, high degrees

of crystallinity, colloidal stability over time and robust surface passivation. These characteristics are very important as they directly influence the quality of photoluminescence exhibited by the nanoparticles, e.g. quantum yields and deep trap luminescence. Conversely, TOPO causes complications when the nanoparticles are integrated into devices as it is an insulating waxy solid. The conventional approach has therefore been to synthesise the nanoparticles in TOPO and then to replace the capping group by a more labile compound, often a liquid at room temperature, such as pyridines or thiols. However, there are drawbacks to this approach, as the particles are less stable after replacing the TOPO, resulting in the loss of qualities mentioned above. In this work we present CdSe nanoparticles synthesised directly in capping agents such pyridines, thiols and dithiols, and mixtures of these and Trioctylphosphine (TOP) or TOPO. Optical measurements such as UV and photoluminescence have been carried out. The particles have been characterised by X-Ray diffraction, Energy Dispersive X-ray Analysis (High Resolution) Transmission Electron Microscopy imaging. Emphasis has been put on surface functionalising the particles for specific uses during synthesis, so the particles can be reacted with surfaces or self assemble straight after.

### **F8.33**

**SYNTHESIS OF SELF CAPPED METAL SULFIDE NANOPARTICLES.** Michael R. Lazell, P. O'Brien, Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK.

Here we report the synthesis of self capped (where the precursor contains the capping group) metal sulfide nanocrystals from the thermolysis at a range of temperatures, 150 - 300 °C, in a dynamic vacuum, of the novel asymmetric metal dithiocarbamates, *bis*(N-methyloctadecyldithiocarbamate) cadmium(II), and zinc(II) [MS<sub>2</sub>CN(C<sub>18</sub>H<sub>37</sub>)(CH<sub>3</sub>)<sub>2</sub>] where M = Cd and Zn. The CdS quantum dots are cubic in phase when synthesised at temperatures of between 150 to 250 °C. However, when the temperature is increased to 300 °C there is a change in phase of the nanocrystalline CdS, from cubic to hexagonal, as evidence in the powder XRD patterns. The nanoparticles were soluble in pyridine and photoluminesce with a slight Stokes shift which decreases as the synthesis temperature increases, approaching that of band edge luminescence. The capping group is believed to be the amine [N(C<sub>18</sub>H<sub>37</sub>)].

### **F8.34**

**OPTICAL PROPERTIES OF NANOCRYSTALLINE SILICON FILMS WITH DIFFERENT DEPOSITION TEMPERATURE.** A.M. Ali, T. Inokuma, Y. Kurata and S. Hasegawa, Kanazawa Univ, Dept of Electronics, Kanazawa, JAPAN.

In these last years, a renewed interest for the growth of nanocrystalline Silicon (nc-Si) which has been demonstrated to have good properties for application in both passive and active electronic and optoelectronic devices. In our previous study [1], PECVD poly-Si films were deposited using SiH<sub>4</sub>-H<sub>2</sub> mixtures by varying the deposition temperature, T<sub>d</sub>, and the film thickness. The films crystallized at T<sub>d</sub> between 150 and 600°C and above 650°C. However, under a deposition temperature of 600-650°C, no crystallization for the film thinner than 0.2 μm was found independent of the surface morphology of substrates. This may be due to interference among growing grains with different textures. However, the crystallinity for films with T<sub>d</sub> below 300°C strongly depended on the conditions of the plasma treatments of substrates. Furthermore, in these films with T<sub>d</sub> = 600-650°C, no hydrogen incorporation was observed. In the present work, the optical properties (Optical band gap, E<sub>g</sub><sup>opt</sup>, and photoluminescence, PL) of PECVD nc-Si films with different T<sub>d</sub> (500-750°C) were investigated. The SiH<sub>4</sub> and H<sub>2</sub> flow-rates were 1.0 and 3.0 sccm, respectively. The film thickness were kept constant 0.2 μm by adjusting the deposition time. The rf power and gas pressure during film deposition were maintained at 20 W and 0.15 Torr, respectively. Results shown the E<sub>g</sub><sup>opt</sup> values were around 1.75 eV at 600-650°C which agree well with the data for amorphous silicon, a-Si, but at T<sub>d</sub> between 650 and 700°C the E<sub>g</sub><sup>opt</sup> values strongly increased around 2.1 eV due to small grains included in the films. Therefore, we have shown that the transition from amorphous-to-nanocrystalline easily occurs at T<sub>d</sub> of around 700°C using SiH<sub>4</sub>-H<sub>2</sub> mixture. (1) S. Hasegawa et al., J. Appl. Phys. 85 (1999) 3844.

### **F8.35**

**INFLUENCE OF DOPING ELEMENTS ON THE SINTERING AND MICROSTRUCTURE OF NANO ALUMINA.** Denis Autissier, CEA, Monts, FRANCE.

The final aim of this work is to correlate microstructural properties and electrical breakdown capability of doped nanoscaled aluminas. Main structural parameters studied are densities, porosities, grain size and shapes, dopants concentrations, valencies and localisation. Powders were synthesized through sol-gel methods, such as salts

precipitation, alkoxydes hydrolysis-condensation, peptisation. Seeding with alpha alumina has been used in order to promote the phase transitions which lead to corundum. Dopants (Mn, Cr) were introduced in the form of nitrates. Samples were cold isostatically pressed at 400 MPa and sintered in air around 1500 Celsius degrees. They were analyzed using X Ray diffraction, scanning electron microscopy, electron microprobe analysis in order to determine phases, grain sizes and shapes and to control dopants repartition. Chromium is uniformly soluble in the alumina matrix. Manganese precipitates in a spinel form. Isothermal and constant rate of heating dilatometry were performed to determine diffusion mechanism contributing to the neck growth stage, for pure and doped alumina. The two types of experiments provide complementary results. Chromium inhibits sintering while manganese increases densification. Pure alumina initial sintering is controlled by grain boundary diffusion of aluminium. Study of dopants influence on alumina sintering is disturbed by chemical reactions.

### **F8.36**

**INORGANIC FULLERENE-LIKE MATERIALS AND NANOTUBES (IF) FROM LAYERED COMPOUNDS.** Reshef Tenne, Yishai Feldman, Gitti Frey, Ella Zak, Moshe Homiyonfer, Weizmann Inst, Rehovot, ISRAEL.

Using the paradigm of carbon fullerenes, it was shown by Tenne and co-workers that nanoclusters of layered compounds, like MoS<sub>2</sub>, are unstable in the planar form and fold into hollow cage structures of various shapes: from spherical and polyhedral to nanotubes of a nm length and cross-section of 10-20 nm diameter (IF). Following this discovery a few methodologies for the systematic synthesis of large amounts of IF, were pursued. Recently, IF structures from various other layered compounds were synthesized. Intercalation of IF WS<sub>2</sub> rendered these nanostructures as stable suspensions in aprotic solvents and photoelectrochemical cells were subsequently prepared. Recently, the first MoS<sub>2</sub> octahedra having 572 Mo atoms, were reported. The structural, optical, electrochemical, and tribological properties of IF MoS<sub>2</sub> were investigated in some detail. It was found by Frey et al., that IF MoS<sub>2</sub> are semiconductors with a tunable bandgap which scales with the size of the nanoparticles. The 2H polytype structure is locally preserved in these nanoparticles. Few extra Raman lines observed in the IF suggest a reduced symmetry compared with the bulk (2H) predecessor. The tribological properties of IF was shown by Rapoport et al. to outperform the ubiquitous solid lubricants 2H-WS<sub>2</sub>. This suggests a large range of applications for these nanomaterials. Other applications will be briefly discussed.

### **F8.37**

**SYNTHESIS AND CHARACTERIZATION OF Mn DOPED CdS QUANTUM DOTS FROM A SINGLE SOURCE PRECURSOR.** M. Azad Malik, Paul O'Brien, N. Revaprasadu.

Nanoparticles of CdS and Mn-doped CdS capped with TOPO (tri-*n*-octylphosphine oxide) and close to mono-dispersed have been prepared by a single source route using *bis*(methyl(*n*-hexyl) dithiocarbamate)cadmium(II) and manganese dichloride as a precursor. The nanoparticles obtained show quantum size effects in their optical spectra and CdS nanoparticles exhibit near band-edge luminescence. Clear difference in photoluminescence results between CdS and CdS:Mn samples ESR spectra and ICP results confirm the presence of Mn in CdS quantum dots. The Selected Area Electron Diffraction (SAED), X-ray diffraction (XRD) pattern and Transmission Electron Microscopy (TEM) show the material to be of the hexagonal phase. The crystallinity of the material was also evident from High Resolution Transmission Electron Microscopy (HRTEM) which gave well-defined images of nanosize particles with clear lattice fringes.

### **F8.38**

**ELECTRICAL AND MAGNETORESISTANCE PROPERTIES OF GRANULAR THIN LAYERS FORMED BY METAL IMPLANTATION INTO SILICON.** S.P. Wong, W.Y. Cheung, M.F. Chiah, C.P. Li, K.Y. Lai, The Chinese University of Hong Kong, Department of Electronic Engineering, Shatin, N.T., Hong Kong, CHINA.

Various kinds of granular thin layers were formed by high dose metal ion implantation into silicon using a metal vapor vacuum arc ion source. Characterization of these thin layers was performed using Rutherford backscattering spectrometry, transmission electron microscopy, and electrical measurements. The ion species used include Co, Fe, and Ti and the granular thin layers consist of nanometer size crystalline metal silicide precipitates embedded in the Si substrates. It was found that these granular thin layers exhibit interesting electrical and magnetoresistance properties. For example, when prepared at appropriate implant doses, the Co and Ti implanted samples show a nearly-temperature-independent electrical resistance from 20K to 300K. Some of the Fe implanted samples exhibit a large positive

magnetoresistance at temperatures lower than about 50K. A magnetoresistance larger than 700% was observed for one sample at 30K. The temperature dependence of the electrical resistance and the magnetoresistance of these samples, and their variation with the processing conditions will be presented and discussed in conjunction with the results of other characterization techniques. This work is supported in part by the Research Grants Council of Hong Kong (Ref. No.: CUHK 374/96E).

#### **F8.39**

**OPTICAL AND ELECTRICAL CHARACTERIZATION OF A SYSTEM OF (110) ORIENTED SILICON NANOCRYSTALS FORMED BY EXCIMER LASER PULSES IN a-Si:H FILMS ON GLASS SUBSTRATE.** M.D. Efremov, V.A. Volodin, A.V. Vishnyakov, O.K. Shabanova, S.A. Kochubei, L.I. Fedina, Institute of Semiconductor Physics SB RAS, Novosibirsk, RUSSIA; V.V. Bolotov, Institute of Sensor Microelectronics SB RAS, Omsk, RUSSIA.

The optical and electrical studies of undoped and phosphorus doped a-Si:H films with silicon nanocrystals of various concentrations and sizes formed by pulse excimer laser treatments (ELTs) were carried out. The band gap of a-Si:H can reach 1.8 eV, band gap for crystal silicon is 1.16 eV, so, electrons can be localized in nanocrystals. Peculiarities connected with localized electron states within nanocrystals may be expected especially in the case of high concentration of nanocrystals, when a-Si barriers became tunnel thin. The average size (from 2 up to 10 nm) and concentration of nanocrystals were evaluated from Raman scattering and HREM data. Due to the presence of nanocrystals the dark conductivity becomes 2-3 orders greater. At low temperatures near 284K the sharp changes of the activation energy from 0.75 to 0.13 eV were observed in the case of a-Si films with 2 nm silicon nanocrystals. Anisotropy of Raman scattering intensity in different geometries versus angle between polarization vector of incident light and an axis lying in sample plane was experimentally discovered in system of Si nanocrystals in a-Si:H films. This effect can be interpreted as result of preferred (110) orientation and correlation of in-plane orientation of the nanocrystals formed by pulse ELTs. Appearance of the preferred (110) orientation in the case of excimer laser annealing of a-Si/glass structures was supported using HREM. It was calculated that the modulation of the intensities in different scattering geometries versus the above mentioned angle depends on part of self-oriented nanocrystals. According to Raman data it can be proposed that the part of (110) oriented nanocrystals was 90%, and the part of self-oriented nanocrystals was 33%. Deformation mechanism of the observed selforganization of nanocrystals is proposed.

#### **F8.40**

**CHEMICAL REACTIONS ON THE SURFACE OF SnO<sub>2</sub> NANOSIZED POWDERS AT THE ORIGIN OF THE GAS SENSING PROPERTIES: FTIR INVESTIGATION.** Marie-Isabelle Baraton, Spts-Umr 6638 CNRS, University of Limoges, Limoges, FRANCE; Lhadi Merhari, CERAMEC, Limoges, FRANCE.

The increasing demand for environment monitoring calls for gas sensors capable of detecting pollutants at sub-ppm levels. Such a high sensitivity can be reached by using nanosized particles in the fabrication of chemical gas sensors. The benefit of using nanoparticles is double. Firstly, their high surface-to-bulk ratio leads to a larger area exposed to the gases to be detected. Secondly, the grain size of the nanoparticles becomes comparable to the depth of the depletion layer. It is therefore expected that the sensitivity should be influenced by the particle size.

Besides, it has been proved that nanosized SnO<sub>2</sub>-based sensors have a maximum sensitivity toward CO at two different temperatures, one of them being close to the room temperature. To clearly understand the CO detection mechanism, the chemical reactions taking place at the surface of SnO<sub>2</sub>-based sensors have to be studied in close connection with the electrical conductivity variations. These surface chemical reactions inducing the sensor response have been demonstrated to be identical on the real sensor and on the original nanopowder constituting the sensing layer. A very relevant and convenient tool for this dual analysis of nanopowders is Fourier transform infrared (FTIR) spectrometry which allows the *in situ* investigation of the surface chemical species modifications under various environments, simultaneously with the measurement of the infrared energy transmitted by the sample directly related to the variations of the electrical conductivity.

In this paper, we present the FTIR study of two SnO<sub>2</sub> powders with different average grain sizes (13 and 8 nm). The formation of new chemical species when the SnO<sub>2</sub> surface is subjected to CO at different temperatures is described and the role played by oxygen in the CO detection mechanism is discussed. This work has been partially supported by the European Commission under the BRITTEURAM III program (BRPR-CT95-0002).

#### **F8.41**

**POLYMERIZATIONS FROM SILICA SURFACES USING TETHERED RUTHENIUM ALKYLIDENES.** Fatma Vatansever, Thomas A.P. Seery, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Modification of silica surfaces with rationally designed microstructures is important from both a scientific and a technological point of view. Polymerizations initiated from the surface allow us to grow layers of polymers directly from the substrate to be modified. One approach to Surface Initiated Polymerization (SIP) uses silane coupling agents to provide an initiator ligand for a transition metal catalyst. Ruthenium alkylidenes that catalyze ring opening metathesis polymerizations have been used to generate a variety of functionalized polymer layers in our laboratories. 'Layers' synthesized by this method can incorporate a wide range of functional groups and may be easily modified to provide both hydrophilic and hydrophobic surfaces. Characterization of surface polymerized layers must be performed on two levels. Chemical characterization is performed using IR and NMR spectroscopy. The physical structure of these materials is also of interest and we have employed TEM and thermal analysis as well as light scattering to study them.

#### **F8.42**

**MASS SPECTROMETRY: ANALYZING NANOMATERIALS A MOLECULE AT A TIME.** Jean-Jacques Gaumet, Geoffrey F. Strouse, University of California at Santa Barbara, Santa Barbara, CA.

Efforts in metal chalcogenide nano-material science at the 1-3 nm scale has opened new routes into materials that exhibit quantized physical properties. These materials can be synthesized as near-mono-disperse with controlled surface capping via lyothermal methods. Analysis of the structure and molecular-level interactions in these materials typically centers on solid state methods, such as TEM, X-ray diffraction, UV/Visible, and photoluminescence techniques. These methods are excellent tools for average analysis of an ensemble, however they do not specifically address the distribution in compositions and structure. We have developed methodology for exploring particle size and composition utilizing mass spectrometry. ESMS and MALDI ionization methods allow for the direct analyses of mixtures and solvated molecules without substantial fragmentation induced by either the ionization method. The analysis of positive and negative ion modes offers a unique opportunity to probe the fragmentation with direct observation of the parent ion in pseudo-positive mode. Correlation of the MALDI and ESMS methods provides substantial insight into composition, sample homogeneity, and thermodynamic stability. Analysis of these results provide insight into the applicability of ESMS methods to structure analysis, composition and stability of metal chalcogenide nano semiconductor materials at the 1-3 nm scale. We present MALDI and ESMS results for a series of metal chalcogenide samples at the 1-3 nm size regime. We have carried out a careful mass-spectroscopic analysis on a series of mono-disperse metal-chalcogenide clusters in which the substitution of the core and surface are carefully controlled. Analysis of the optical properties with respect to the structure of the cluster suggest the importance of surface derivatization on the lowest optical properties and electronic gap in these materials.

#### **F8.43**

**ULTRASONIC FORCE MICROSCOPIC CHARACTERIZATION OF NANOSIZED COPPER PARTICLES.** Edward J. Schumaker, Liming Shen, Mark J. Ruddell, Shamachary Sathish, Center for Materials Diagnostics, University of Dayton Research Institute, Dayton, OH; Terry Murray, Research Institute and Graduate Materials Engineering, University of Dayton, Dayton, OH.

Ultrasonic Force Microscopy (UFM) has been developed by modifying a Scanning Probe Microscope. Two function generators are employed to drive a piezoelectric transducer in a continuous wave (CW) mode or in an amplitude modulated mode (referred to as mechanical diode). The transducer is attached to the bottom surface of the sample and the elastic wave propagating through the sample is detected by an atomic force microscope tip. Two lock-in amplifiers are then used to measure the magnitude and phase of this elastic wave. In the CW mode, the tip is always in contact with the specimen during scanning. Images of ultrasonic properties can be simultaneously obtained with the topography images. The technique has been utilized to characterize nanoscale copper grains and copper nanoparticles deposited on a quartz substrate by ionized cluster beam deposition. Images of the same region obtained with atomic force microscopy (contact mode), lateral force microscopy, and ultrasonic force microscopy are compared. The origin of image contrast in ultrasonic force microscopy and its utilization for quantitative elastic property measurement of nanometer regions of the material are discussed.

#### **F8.44**

**SURFACE ENHANCED RAMAN SPECTROSCOPY; A TOOL TO**

INVESTIGATE ULTRATHIN FILMS AND NANOSTRUCTURES ON SURFACES. Giuseppe Compagnini, Dipartimento di Chimica, Università di Catania, Viale A. Doria, Catania, ITALY.

Surface Enhanced Raman (SER) is considered a promising technique to study the vibrational properties of nanostructures and ultrathin films onto suitable surfaces. In fact the giant enhancement makes this technique sensitive to even sub-monolayer amounts of adsorbate and gives an interesting tool for the study of nanostructures on surfaces. In this work I present some contributions to the understanding of SERS effect and to the application of SERS to the investigation of ultrathin films.

In particular, using alkanethiol self assembled monolayers (SAMs) of different length it is possible to study the distance dependence of SERS enhancement. Moreover, in the frame of the study of other molecules with the Enhanced Raman technique, alkanethiole SAMs can be used as spacer to avoid the direct metal-adsorbate interaction maintaining a good enhancement and preventing degradative reactions at the surface.

#### **F8.45**

MICROSTRUCTURAL AND MAGNETIC PROPERTIES ON GRAPHITICALLY ENCAPSULATED Ni NANOCRYSTALS AND PURE Ni NANOPARTICLES WITH NiO LAYER. Xiangcheng Sun<sup>a</sup>

and M. Jose Yacaman<sup>a,b</sup>. <sup>a</sup> Instituto Nacional de Investigaciones Nucleares (ININ), Mexico, MEXICO; <sup>b</sup> Instituto de Fisica, Universidad Nacional Autonoma de Mexico (UNAM), Mexico, MEXICO.

Graphitically encapsulated Ni nanocrystals [Ni(C)] and pure Ni nanoparticles [Ni(O)] coated with NiO layers have been synthesized via modified arc-discharge method in a methane and a mixture of H<sub>2</sub> and Ar atmospheres, respectively. The distinct morphological properties on two kinds of Ni nanoparticles surface were investigated by high resolution transmission electron spectroscopy (HRTEM), nanoarea electron diffraction (NED); and electron dispersive spectra (EDS). The magnetization measurements at different field and temperatures (2K<T<300K) for an assembly of two kinds of Ni nanoparticles were performed using superconducting quantum interface device magnetometer (SQUID). In contrast with Ni(C) particles, for Ni(O) particles, we observed a larger coercivity and remanence magnetization as well as a deviation between the zero field cooling (ZFC) and the field cooling (FC) magnetization at below a critical temperature T<sub>c</sub>. T<sub>c</sub> is a function of the applied magnetic field. This can be explained by the effect of exchange anisotropy interaction between the interfaces of the ferromagnetic region of Ni nanocrystals and the layer of antiferromagnetic NiO on the surface of Ni(O) particles. On the other hand, Ni(C) particles, exhibited nanocluster glass like behavior, depending applied magnetic fields. Moreover, the gradual decrease in saturation magnetization is attributed to the nanocrystalline nature of the encapsulated particles, coupled with possible carbon solution in Ni nanocrystals, and the reduced remnant magnetization and coercivity at room temperature is close one of the characteristics of superparamagnetism.

#### **F8.46**

TRANSPORT AND MAGNETIC CHARACTERISTICS OF MONODISPERSIVE Co<sub>0</sub>/CoO CLUSTER ASSEMBLIES.

Kenji Sumiyama, Dong Liang Peng, Takehiko Hihara, Saeki Yamamuro and Toyohiko J. Konno, Institute for Materials Research, Tohoku University, Aoba-ku, Sendai, JAPAN, and CREST of Japan Science and Technology Corporation, JAPAN.

We have fabricated CoO-coated monodispersive Co cluster assemblies with the mean cluster size of 13 nm at various oxygen gas flow rate, RO, by a plasma-gas-condensation type cluster beam deposition method. We have studied their electrical resistivity, magnetoresistance, MR, and magnetization between 5 and 300 K. For RO < 0.24 SCCM, the resistivity reveals a minimum and shows log T dependence at lower temperatures, probably due to the weak localization of conduction electrons in disordered thin oxide shells covering Co cores. A small negative magnetoresistance is observed in this regime. For RO > 0.3 SCCM, tunneling type temperature dependence of conductivity,  $\sigma$ , in the form of  $\log \sigma$  vs.  $1/T$  is observed between 7 and 80 K. This differs from the well-known temperature dependence of  $\log \sigma$  vs.  $T^{-1/2}$  for granular materials made via precipitation. MR is negative and its absolute value increases sharply with decreasing temperature below 25 K: from 3.5% at 25 K to 20.5% at 4.2 K. These temperature dependent behaviors are prominent co-tunneling effects in the Coulomb blockade regime, being ascribed to the uniform Co core size and CoO shell thickness in the present cluster assemblies. Since ferromagnetic Co cores are covered by antiferromagnetic CoO layers, Co/CoO cluster assemblies reveal marked exchange anisotropy effects at low temperatures.

#### **F8.47**

SPUTTERING EFFECTS AND TWO DIMENSIONAL ARRANGEMENT OF NANOPARTICLES IN INSULATORS UNDER

HIGH FLUX Cu<sup>-</sup> IMPLANTATION. N. Kishimoto, C.G. Lee, National Research Institute for Metals, Tsukuba, Ibaraki, JAPAN; N. Umeda, Tsukuba University, Tsukuba, Ibaraki, JAPAN; Y. Takeda, National Research Institute for Metals, Tsukuba, Ibaraki, JAPAN V.T. Gritsyna, Kharkov State University, Kharkov, UKRAINE.

Application of negative heavy ions, alleviating surface charging, enables us to conduct low-energy and high-flux implantation into insulating substrates. Negative Cu ions of 60 keV, at high dose rates, have generated metal nanocrystals in insulators, suitable for nonlinear optical devices. We have observed in substrates of amorphous(a-) and crystalline(c-) SiO<sub>2</sub> that nanospheres spontaneously grow and occasionally lead to a two-dimensional arrangement in a certain dose-rate range. In this paper, we focus on effects of surface sputtering on the two-dimensional nanocrystal formation. The Cu<sup>-</sup> implantation is conducted into a- and c-SiO<sub>2</sub> at various current densities up to 100  $\mu\text{A}/\text{cm}^2$ , fixing the total dose at  $3.0 \times 10^{16}$  ions/cm<sup>2</sup>. Surface- and nanoparticle morphologies are studied by tapping AFM and cross-sectional TEM, respectively. Optical absorption is measured in a photon range from 1.4 to 6.5 eV. With increasing dose rate ( $\sim 10 \mu\text{A}/\text{cm}^2$ ), nanoparticles grow larger and surface sputtering and texture gradually vary. Above 30  $\mu\text{A}/\text{cm}^2$ , flux-enhanced sputtering begins, the surface roughness rapidly increases and optical absorbance of the plasmon peak begins to drop. Coincidentally, the two-dimensional arrangement of nanoparticles occurs at a depth shallower than the projected range of ions. It is a contrast to the cases at the lower dose rates where nanoparticles follow a gaussian-like profile. The coincidence between the outer- and inner processes suggests that the mass transport via the surface influences the intra-solid precipitation of nanocrystals. Results of the nanoparticle statistics and the surface roughness will be presented and the possible correlation will be discussed.

#### **F8.48**

THERMOELECTRIC PROPERTIES OF THE X%BiJ<sub>2</sub>TeJ<sub>3</sub>-Y%SbJ<sub>2</sub>TeJ<sub>3</sub> COMPOUNDS BY MA-PULSE DISCHARGE SINTERING PROCESS. Rae-Eun Park, Yong-Ho Park, Toshihito Abe, Materials Engineering Division, Tohoku National Industrial Research Institute, AIST, MITI, Sendai, JAPAN.

The X%BiJ<sub>2</sub>TeJ<sub>3</sub>-Y%SbJ<sub>2</sub>TeJ<sub>3</sub> compounds with composition of useful thermoelectric cooling materials were prepared by mechanical alloying (MA)-pulse discharge sintering process. Effects of MA times and sintering condition on Seebeck coefficient, electrical resistivity, Hall coefficient, carrier mobility and thermal conductivity of the sintered materials. For typical specimens the temperature dependence of Hall coefficient and carrier mobility were measured over the temperature range from 80 to 350K and thermal conductivity at room temperature. A thermoelectric characterization of specimens of these p-type compounds is carried out as a function stoichiometric deviations. The figure of merit Z was found to be about  $3.0 \times 10^{-3} \text{K}^{-1}$  for the 25%BiJ<sub>2</sub>TeJ<sub>3</sub>-75%SbJ<sub>2</sub>TeJ<sub>3</sub> sintered at 618K using reduced MA-powders less than 75  $\mu\text{m}$ .

#### **F8.49**

ELECTRICAL RESISTIVITY AS A CHARACTERIZATION TOOL FOR NANOCRYSTALLINE METALS. J.L. McCreary, K.T. Aust, U. Erb, Univ of Toronto, Dept of Metallurgy and Materials Science, Toronto, Ontario, CANADA; G. Palumbo, Integran Technologies Inc, Toronto, Ontario, CANADA.

The electrical resistivity as a function of temperature (4K to 673K) of several electrodeposited nanocrystalline materials (Ni, Ni-Fe, Co) has been examined. The contribution of the grain boundaries to the electrical resistivity was quantified in terms of a specific grain boundary resistivity, which was found to be similar to previously reported values of specific grain boundary resistivity for copper and aluminum obtained from studies involving polycrystalline materials. In the high temperature range, the resistivity of the nanocrystalline samples was monitored as a function of time. The observed time dependence of the resistivity at elevated temperatures was correlated to microstructural changes in the material. The study has shown that electrical resistivity is an excellent characterization tool for nanocrystalline materials giving useful information regarding grain size and degree of thermal stability, as well as some insight into the grain growth kinetics at various temperatures.

#### **F8.50**

SIZE DISTRIBUTIONS, OPTICAL PROPERTIES, AND SURFACE CHEMISTRY OF NANOCCLUSERS STUDIED BY LIQUID CHROMATOGRAPHY. J.P. Wilcoxon, J.E. Martin, and P.P. Provencio, Nanostructures and Advanced Materials Chemistry Dept, Sandia National Labs, Albuquerque, NM.

We have been investigating the cluster size distributions, aging processes, optical properties, and surface chemistry of nanosize clusters of Au, Ag, Pt, and MoS<sub>2</sub> dispersed in organic solvents using

high pressure liquid chromatography (HPLC), dynamic light scattering (DLS), and transmission electron microscopy (TEM). The nanosize metals are formed by the inverse micelle synthetic process at room temperature in inert oils and range in diameter from 1-10 nm. HPLC is used to monitor the changes in cluster size distribution and average cluster size as a function of sample age, surface passivating agent, and metal type. This technique is sensitive enough to discern changes in hydrodynamic volume corresponding to only 2 carbon atoms of the passivating agent or metal core size changes of  $>4$  and we have determined how the total cluster volume (metal core + passivating organic shell) changes with the size of the passivating agent. At the same time we have measured the optical absorbance properties of these Au and Ag clusters and have demonstrated a significant blue shift and broadening of the plasmon absorbance as the Au cluster size is decreased. Remarkably, the smallest Au clusters also exhibit significant visible photoluminescence! It is found that the cluster size distribution in these surfactant-stabilized dispersions narrows with age and this redistribution of cluster mass occurs even in the presence of strongly binding surfactants like thiols or amines. The rate of mass redistribution is most rapid for metals with the lowest bulk melting temperatures (e.g. Au, Ag), and slowest for those with the highest values (Pd, Pt). It occurs most rapidly with the weakest surface-active agents (polyethers). The narrowing of the cluster size distribution and the preference for certain discrete sizes argues that special structural stabilities overwhelm the expected kinetically-broadened Ostwald ripening process historically observed for larger colloids (i.e.  $>10$  nm). We show how HPLC is particularly useful for studying the relative strength of binding of organic molecules to the nanocluster surface—a feature of paramount importance for catalytic applications. Acknowledgment This work was supported by the US Department of Energy under contract DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

#### **F8.51**

**STEADY-STATE PHASE DIAGRAM OF NANOPHASE BALL-MILLED Cu-Ag: A XRD, DSC AND ATOM PROBE STUDY.** Fang Wu, Pascal Bellon, Univ of Illinois at Urbana-Champaign, Dept of Materials Science and Engineering, Urbana, IL; Allan J. Melmed, Thomas A. Lusyby, Johns Hopkins Univ, Dept of Materials Science and Engineering, Baltimore, MD.

Mechanical alloying is widely used to synthesize nanostructured materials. This non-equilibrium processing route induces also compositional phase transformations: in the case of systems with positive heat of mixing, it is often possible to force a solid solution by low temperature milling, or to stabilize a nanocomposite by intermediate temperature milling, due to a fine scale decomposition. In order to gain insight on the fundamental understanding of these driven phase transformations, we have built a diagram of the steady-states reached by Cu-Ag powders milled at temperatures ranging from 80 to 450K, with nominal compositions from 35 to 75% Cu. X-ray diffraction, differential scanning calorimetry, and atom probe (AP) field ion microscopy are used. At liquid nitrogen temperature, a single solution is formed. When ball milled at 450K, two-phase coexistence is observed between a  $\text{Cu}_{97}\text{Ag}_3$  and a  $\text{Cu}_6\text{Ag}_{94}$  solid solutions. At intermediate temperatures,  $373 < T < 423\text{K}$ , and close to the equiatomic composition, two terminal solid solutions coexist with a solution near the nominal composition. Surprisingly, this three-phase coexistence disappears for compositions away from the equiatomic position, leading only to a two-phase coexistence between terminal phases. We have developed a new method for preparing FIM tips from ball milled powders, which makes it possible to obtain direct atomic scale information on the nanophases described above. Statistical analysis of the data shows in particular that room temperature milling produces a solid solution with short scale and large scale composition fluctuations. The latter inhomogeneities are likely to result from inhomogeneous plastic deformation. At higher milling temperatures, nanoscale decomposition is confirmed and AP data allows measurement of the scale of decomposition as a function of milling temperature. Such steady-state phase diagrams combined with detailed atomic information should help to select the best possible operating conditions to synthesize, by ball-milling, nanostructures with optimized mechanical or magnetic properties.

#### **F8.52**

**GLASS FORMATION AND NANOSTRUCTURE DEVELOPMENT IN Al-BASED ALLOYS.** Robert I. Wu, Gerhard Wilde, John H. Perepezko, University of Wisconsin-Madison, Dept of Materials Science and Engineering, Madison, WI.

Amorphous and nanostructured Al-based alloys have attracted much attention for their outstanding mechanical properties such as high tensile strength, hardness and corrosion resistance.  $\text{Al}_{92}\text{Sm}_8$  metallic glasses have been produced by rapid solidification processing (melt-spinning) and solid state amorphization (repeated cold rolling).

While the rapidly quenched samples showed a primary crystallization with an exotherm onset around  $170^\circ\text{C}$  in DSC and yielded a high density of Al nanocrystals in the glass transition range, the sample from repeated cold rolling showed a clear glass transition signal at  $172^\circ\text{C}$  and no evidence for a premature crystallization. The comparison of these amorphous samples obtained from different reaction pathways suggests that primary crystallization originates from quenched-in, pre-exist clusters. Moreover, the glass transition temperature ( $T_g$ ) has been assessed in  $\text{Al}_{92}\text{Sm}_8$  and  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  through the application of modulation calorimetry. It has been difficult to measure the glass transition temperature in alloy systems that exhibit primary crystallization since the thermal response of the primary crystallization often obscures the observation of the signal that corresponds to the glass transition. With the capability of modulation calorimetry to separate heat flow response signals of the reversible and irreversible reactions, the glass transition temperature can be readily measured. In addition, insoluble Pb has been incorporated into the  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  amorphous matrix during rapid solidification in order to develop a nanostructured material with an enhanced particle density ( $> 10^{22} \text{m}^{-3}$ ). It has been shown that after proper annealing, the nanocrystal density can be increased by an order of magnitude in the melt-spun samples with Pb addition. The incorporation of extraneous nucleation catalysts has provided insight into enhancing the nano-particle density in amorphous alloys and studying heterogeneous nucleation behavior of nanocrystals in metallic glasses. The support of the ARO (DAAG55-97-1-0261) is gratefully acknowledged.

#### **F8.53**

**DIRECT TRANSMISSION ELECTRON MICROSCOPY STUDY OF Au-Fe-Au AND GOLD-COATED IRON CORE SHELL NANOPARTICLES SYNTHESIZED USING REVERSE MICELLES.** W.L. Zhou, E.E. Carpenter, and C.J. O'Connor, Advanced Materials Research Institute, University of New Orleans, LA.

The Au-Fe-Au and gold-coated iron core shell nanoparticles were synthesized using reverse micelles. The core shell structure were observed by transmission electron microscopy (TEM). The X-ray energy dispersive analysis (EDAX) and selected-area diffraction pattern (SADP) also confirmed that the successful synthesis of the core shell structure. The average size of Au-Fe-Au and gold-coated iron were 9 nanometer and 8 nanometers, respectively. Shell structures with different thickness and shape were also observed. The outside shell lattice were easily observed in both nanoparticles. The magnetism of both kinds of nanoparticles were also characterized.

#### **F8.54**

**FORMATION OF FE-BASED NANOSTRUCTURED ALLOYS BY RAPID SOLIDIFICATION.** Q. Li, H.W. Kui, The Chinese University of Hong Kong, Dept of Physics, Shatin, N.T., Hong Kong, CHINA.

Recently, it [1, 2] was demonstrated that liquid phase spinodal decomposition can take place in undercooled molten eutectic alloy at large undercoolings defined as  $DT = T_l - T$ , where  $T_l$ : liquidus and  $T$ : temperature of the undercooled melt. At still higher  $DT$ , it turns out the wavelength  $l$  of the spinodal network can be  $\ll 100$  nm [3]. The morphologies of the liquid spinodal network can then be frozen by subsequent solidification. The as-prepared specimen is therefore a nanostructured/nanocomposite material. In this study, an attempt is made to synthesize Fe-based nanostructured alloys. References 1. C.W. Yuen and H.W. Kui, J. Mater. Res., 13, 3034 (1998). 2. W.H. Guo, C.C. Leung, and H.W. Kui, MRS Meeting, (1998). 3. W.H. Guo, L.F. Chua, and H.W. Kui, submitted.

#### **F8.55**

**PECULIAR TEMPERATURE DEPENDENCE OF THE RESISTIVITY OF GAS DEPOSITED NANOCRYSTALLINE GOLD FILMS.** J. Ederth, L.B. Kiss, G.A. Niklasson, C.G. Granqvist and E. Olsson, Dept of Materials Science, Uppsala University, SWEDEN.

Nanocrystalline gold films consisting of high quality particles show interesting properties below 20 K. For small grain size with narrow size distribution the influence of the truncated phonon spectrum yields an exponential decay of the phononic resistivity. For annealed films with larger grain sizes a  $T^5$  dependence is observed, indicating the existence of low angle phonon scattering.

#### **F8.56**

**CHARACTERIZATION AND SYNTHESIS OF BICONTINUOUS NANOPOROUS METALS.** Sean G. Corcoran, Virginia Tech, Dept of Materials Science and Engineering, Blacksburg, VA.

The preferential dissolution of one element in a binary alloy has been used to produce electrodes of nanoporous metal. The porous metal morphology can be thought of as a nanocomposite material consisting of a bicontinuous network of solid and void phases; both phases have length scales of order 20 nm. These materials have potential as high

surface-area electrodes in such applications as amperometric sensors. Despite the interest in these materials, very little is known about the physical phenomena that lead to their formation. The main difficulty has been in characterizing the 3-dimensional morphology of these materials. This talk will focus on the use of Small Angle Neutron Scattering (SANS) to characterize the 3-dimensional morphology of porous gold created during the selective dissolution of Ag from Ag-Au alloy foils. SANS was also used in situ to follow the morphological evolution of the porosity during synthesis. Over a 20-hour period, the average size scale of the metal phase was found to increase from approximately 7 nm to 20 nm as a result of room temperature coarsening. The resultant size scale and morphology of the porosity was found to be sensitive to the electrochemical environment.

#### **F8.57**

**PROTEIN SUPPORTED METALLIC NANOSTRUCTURES AS CATALYSTS.** Silke Behrens, Wilhelm Habicht, Nikolaos Boukis, Eckhard Dinjus, Institut für Technische Chemie, Forschungszentrum Karlsruhe, GERMANY; Marina Baum, Eberhard Unger, Institut für Molekulare Biotechnologie, Jena, GERMANY.

There is an increasing interest in nano-sized metal particles due to their new catalytic and electronic properties. With decreasing particle size the ratio of surface to volume increases continuously, so that the particle properties are more influenced by the surface atoms instead of the classic lattice atoms. The smaller and the more monodisperse the particles are, the better should be their catalytic activity. Particles in the nanometer size range reveal a great potential for heterogeneous catalysis. One disadvantage of such particles, however, is a certain tendency to aggregate that might be partly prevented by binding the particles to supporting surfaces. An aggregation can be basically avoided by subsequent particle nucleation and growth on a support. Highly oriented protein assemblies with characteristic nanometer-sized patterns are used as a template for the nucleation, growth and support of metallic nanoparticles. Following a bottom-up approach noble metal particles in the nanometer size range are obtained by the reduction of the corresponding metal salts in the presence of the protein assemblies. By reduction of an aqueous palladium salt solution, palladium particles (1 - 5 nm) could be nucleated and immobilised on the tubulin lattice of microtubules (that are hollow cylinders with outer diameters of 25 nm and lengths of several micrometers composed of 4 nm tubulin subunits). By a seed-growth mechanism, bimetallic Au/Pd-particles have also been linked to microtubules. The catalytic activity of the protein-supported particles is determined by hydrogenation reactions.

#### **F8.58**

**GRAIN BOUNDARY STRUCTURE IN Ni<sub>3</sub>Fe NANOCRYSTALS.** H.N. Frase, B. Fultz, California Institute of Technology, Pasadena, CA; J.L. Robertson, S. Spooner, Oak Ridge National Laboratory, Oak Ridge, TN.

We made small angle neutron scattering (SANS) and Mössbauer spectroscopy measurements on four Ni<sub>3</sub>Fe materials with an average grain size of 6 nm; nanocrystalline material prepared by mechanical attrition, nanocrystalline material after an exposure to 4 K, nanocrystalline material after temperature treatments of 100°C for 10 days, and a control sample composed of large crystals. The thermal treatments of the nanocrystalline materials caused changes in the intensity and the slope of the ln(I) vs. ln(Q) plot at large Q of both the nuclear and magnetic scattering profiles of the SANS measurements. The Mössbauer spectra of the nanocrystalline samples showed changes in the hyperfine fields associated with grain boundary atoms. The changes induced by cryogenic exposure and annealing at 100°C were somewhat different, but both were consistent with a sharper density gradient between the crystalline region and the grain boundary region. Some grain boundary atoms in mechanically attrited Ni<sub>3</sub>Fe are in high-energy positions, and shift into new positions during low temperature treatments. Since a subset of the unique properties of nanocrystalline materials originates from the high density of grain boundaries present in nanocrystalline materials, grain boundary atomic structure could have a large impact on the attributes of nanocrystalline materials. Possible evidence of the effects has been seen in previous phonon density of states (DOS) measurements on Ni<sub>3</sub>Fe nanocrystals. The room temperature phonon DOS of nanocrystals with an average grain size of 6 nm and a large grain boundary volume fraction of 20%, was different from the phonon DOS of the same powder after it had been exposed to 10 K or 350 K for 8 hr.

#### **F8.59**

**SHAPE-DEPENDENT THERMODYNAMIC PROPERTIES OF NANOCRYSTALS.** Z.L. Wang<sup>1</sup>, M. Mahade<sup>2</sup>, S. Link<sup>2</sup>, J. Petroski<sup>2</sup> and M.A. El-Sayed<sup>2</sup>, <sup>1</sup>School of Material Science and Engineering; <sup>2</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

The surface selectivity and activities of shape-controlled nanocrystals, such as platinum nanocrystals and gold nanorods, strongly depend on their sizes and shapes. Following the success of synthesis of Pt nanocrystals with controllable shapes [1,2], their thermodynamic properties, such as surface stability, shape transformation and melting behavior, are becoming interesting. The microstructures of the as-synthesized cubic, tetrahedral and truncated octahedral Pt particles have been studied by in-situ transmission electron microscopy (TEM) [3]. Our results indicate that the surface capping polymer is removed by annealing the specimen to a temperature of 180 - 250°C, while the particle shape shows no change up to ~350°C. In a temperature range of 350 to 450°C, a small truncation occurs in the particle shape but no major shape transformation. The particle shape experiences a dramatic transformation into spherical-like shape when the temperature is higher than ~500°C; the macroscopic melting occurs at ~600°C, much lower than the melting point of bulk Pt (1773°C). Gold nanorods of aspect ratio 3-7 have been synthesized by a reversal miscell technique. The thermodynamic property of the Au nanorods is interesting because the nanorods are enclosed by {100} and {110} facets. The presence of 110 facets, a high energy surface, is a unique characteristic of Au nanorods. In-situ TEM has revealed the surface diffusion, sublimation and growth of the nanorods of different sizes, clearly displaying the shape-dependent properties of nanocrystals. 1. T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein and M.A. El-Sayed, *Science*, 1996, 272, 1924. 2. Z.L. Wang, T.S. Ahmadi and M.A. El-Sayed, *Surface Sci.*, 1997, 380, 302. 3. Z.L. Wang, J. Petroski, T. Green and M.A. El-Sayed, *J. Phys. Chem. B*, 1998, 102, 6145. 4. Research was supported in part by NSF DMR-9733160.

#### **F8.60**

**COLD WELDING OF GOLD AND PLATINUM NANOPARTICLES.** Sang Lu, Nan Yao, Ilhan A. Aksay, Princeton Materials Institute and Department of Chemical Engineering, Princeton University, Princeton, NJ.

Cold welding (sintering) of nanosized gold and platinum particles has been observed at temperatures below 250°C; but, the mechanisms for this phenomena are still not clear. In our study, monodisperse 20 nm Au particles and 2 nm Pt particles were prepared via sodium citrate reduction of appropriate metal salts. The morphological changes of the particles at the contact regions and changes in chemical composition caused by sintering Au-Au, Pt-Pt, and Au-Pt nanoparticles under electron beam were investigated using transmission electron microscopy (TEM). Complete lattice alignment via atomic-level rearrangement was observed at the completion of the sintering of Au-Au or Pt-Pt particles. In contrast, frequent reorientation of lattices was observed during the sintering between Au and Pt particles. A curve-fitting of experimental data on the neck growth of Au particles revealed a linear relationship between the rate of neck growth and the inverse of the neck radius, agreeing with the mass transfer model for plastic deformation. The atomic concentration profile of the Au-Pt binaries revealed the absence of Pt in the Au phase but as much as 15 at% of Au in the Pt phase, contradicting the prediction by conventional binary phase diagram for bulk Au and Pt. This deviation from phase diagram is attributed to the formation of an amorphous Pt phase that accommodated more Au atoms.

#### **F8.61**

**LIQUID PHASE SYNTHESIS AND PROPERTIES OF DOPED NANOPARTICLES: BLUE-COLORED COLLOIDS ON N-DOPED SnO<sub>2</sub> NANOCRYSTALS.** T. Nütz, M. Haase, J. Rockenberger, U. zum Felde, H. Weller, Univ. of Hamburg, Dept. of Physical Chemistry, Hamburg, GERMANY; M. Tischer, L. Tröger, HASYLAB, DESY, Hamburg, GERMANY.

Blue-colored aqueous colloids of highly crystalline tin dioxide nanoparticles have been prepared hydrothermally either by doping the nanoparticles with antimony or by introducing oxygen vacancies into the SnO<sub>2</sub> lattice. Temperatures above 250°C during the synthesis are required to achieve blue-colored particles in the 4 to 9 nm size regime. The blue color corresponds to a broad absorption peak in the red and the IR region. Powders of blue colored SnO<sub>2</sub>:Sb nanocrystals exhibit an up to 10<sup>5</sup> fold increase in electrical conductivity as compared to the corresponding yellowish material obtained by the usual low temperature synthesis. For both, non-conductive yellowish nanoparticles as well as blue-colored conductive nanocrystals, the oxidation state and the coordination of antimony have been investigated by near edge x-ray absorption fine structure measurements (XANES) at the Sb L<sub>1</sub>-edge and by extended x-ray absorption fine structure measurements (EXAFS) at the Sb K-edge. Based on these measurements, a two-step reaction model for the formation of conductive antimony doped tin dioxide is proposed. In the absence of antimony, blue-colored colloids of SnO<sub>2</sub>-nanoparticles are obtained, if the hydrothermal synthesis is performed in a reducing atmosphere (and T > 250°C). In this case, the blue color vanishes slowly, if the colloid is exposed to oxygen,

indicating that oxygen vacancies have been introduced into the lattice during the synthesis. Based on these results, the IR-absorption band causing the blue color of the material is interpreted as a plasma excitation of free carriers in n-doped nanoparticles. For SnO<sub>2</sub> nanocrystals doped with 6% antimony, the peak position of the absorption band indicates an electron density of about  $5 \cdot 10^{20} \text{ cm}^{-3}$ , in accordance with literature values for conductive layers of the corresponding material prepared by sol-gel techniques.

#### **F8.62**

**FLOW STRESS OF Ni CONTAINING Al<sub>2</sub>O<sub>3</sub> AND NiO NANOPARTICLES: EXPERIMENT AND THEORY.** S.M. Myers, J.A. Knapp, D.M. Follstaedt, G.A. Petersen, Sandia National Laboratories, Albuquerque, NM.

We quantitatively investigated the extreme strengthening of Ni produced by hard-particle dispersions with particle sizes and separations in the nanometer range. Ion implantation of Al and O was used with annealing to form cubic-phase Al<sub>2</sub>O<sub>3</sub> or NiO particles at volume fractions of 10 or 15% with average sizes from 1.5 to 14 nm as observed by TEM. The intrinsic, substrate-independent elastic and plastic mechanical properties of the submicrometer alloyed layer were evaluated through nanoindentation testing in conjunction with finite-element modeling. Force-versus-depth data were analyzed using a Mises yield criterion with no work hardening in the precipitated zone, giving the flow stress and Young's elastic modulus. As expected, the influence of the nanoparticles on the elastic modulus was modest, being less than a factor of 1.5. Flow stress was increased far more with values ranging up to 4.6 GPa, as compared to 0.15 GPa obtained for untreated Ni at 0.2% plastic strain. Our results agree quantitatively with continuum dispersion-hardening theory for dislocation blocking by spherical particles: the experimental flow stresses vary in inverse proportion to particle spacing as predicted, and the absolute magnitudes of the experimental and predicted flow stresses agree within the combined uncertainty, which is about a factor of 1.4. Moreover, when the present findings for Ni are combined with our earlier results for strengthening of Al by Al<sub>2</sub>O<sub>3</sub> nanoparticles, the entire body of experimental information is quantitatively unified by the theory. This study demonstrates that nanoparticle strengthening of Ni can be extended to ~5 GPa, and that such strengthening is described by continuum hardening theory despite particle sizes and separations of only a few atomic spacings. Work supported by Office of Basic Energy Sciences, US DOE, under Contract DE-AC04-94AL85000.

#### **F8.63**

**DEFECT CHEMISTRY IN TiO<sub>2</sub> AND CeO<sub>2</sub> NANOCERAMICS.** P. Knauth, Université de Provence, Marseille, FRANCE; H. L. Tuller, M.I.T., Cambridge, MA.

The electrical and thermodynamic properties of titanium dioxide and cerium dioxide nanoceramics were examined by impedance spectroscopy and electrochemical methods. The data were analyzed with respect to interactions of point defects and dopants with interfaces. The influence of dopant segregation, reduction of defect formation and migration energies, enhanced interfacial diffusion and the existence of metastable phases on properties are discussed. The impact on applications, such as sensors, catalytic activity and oxygen storage capacity of nanoceramics is pointed out.

#### **F8.64**

**SOLUTION-BASED SYNTHESIS OF MAGNESIUM OXIDE NANORODS.** Qingqiao Wei, Harvard Univ., Dept of Chemistry and Chemical Biology, Cambridge, MA; Charles M. Lieber, Harvard Univ., Dept of Chemistry and Chemical Biology and Div of Engineering and Applied Science, Cambridge, MA.

A solution-based synthesis route was developed to produce large quantities of MgO nanorods. Hydrated basic magnesium chloride, which has needle-like crystal structure, was used as a precursor. A subsequent two-step transformation process with magnesium hydroxide as an intermediate product was able to preserve the crystal form of the precursor to yield magnesium oxide nanorods. Scanning electron microscopy, powder X-ray diffraction and energy dispersive X-ray spectroscopy show that the products are very pure (>95%) crystalline MgO nanorods with diameters from 40 nm to 200 nm and lengths 10 microns or longer. High resolution transmission electron microscopy and electron diffraction further reveal that these MgO nanorods are single crystalline and that the rod axis is along  $\langle 110 \rangle$  crystal direction. A model for the structural transformation from hydrated basic magnesium chloride to magnesium oxide has been developed and compared to our experimental results. This solution-based process can be easily scaled-up, and is a low-cost source of pure magnesium oxide nanorods needed in many industrial applications, for example, as reinforcing agents in matrix composites and as flux-pinning centers in high-T<sub>C</sub> superconductors.

#### **F8.65**

**UNEXPECTED PREPARATION OF NANOPHASIC FLUORIDE ION CONDUCTORS.** Georges Denes, Delphine Le Roux, M. Cecilia Madamba, Alena Peroutka, Josselin Vogel and Zhimeng Zhu, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

Fluoride ion conductors are materials that exhibit an unusually efficient motion of the fluoride ions over very long distances, well below the melting point of the material. The highest performance fluoride ion conductors have the fluorite type structure (beta-PbF<sub>2</sub>) or are derived from it by cell distortion and superstructures (PbSnF<sub>4</sub>). Amorphous or nanocrystalline phases are usually obtained either by prolonged milling, fast precipitation, or ultra fast-cooling from the gaseous or liquid states. We have discovered two new procedures that give tin(II) containing fluoride ion conductors that have the fluorite-type structure and are nanocrystalline. In these materials, covalently bonded tin(II) and the other metal M (M= Ca or Pb) are fully disordered on the M(+2) site. This is a highly unusual feature, considering the covalency of the Sn-F bonds in contrast with the M-F typically ionic bonds, and also considering that the tin and M coordinations are highly different. Nanocrystalline cubic gamma-PbSnF<sub>4</sub>, M(1-x)Sn(x)F<sub>2</sub>, and SrSn<sub>2</sub>F<sub>6</sub>H<sub>2</sub>O and Pb<sub>2</sub>SnF<sub>6</sub> have been obtained by ball-milling and leaching in aqueous solutions. Their preparation and study will be discussed.

#### **F8.66**

**EFFECT OF VAPOR PRESSURE OF H<sub>2</sub>O ON THE FORMATION OF NANO-CRYSTALLINE TiO<sub>2</sub> ULTRAFINE POWDERS.** Kang-Ryeol Lee, Sung Park, Myong Ji Univ, Dept of Ceramic Engineering, Yonjin; Jae Sung Song, KERI, Changwon; Sun Jae Kim, KAERI, Daejeon, ROK(Republic of Korea).

Mono-dispersed TiO<sub>2</sub> ultrafine particles with diameters 40-400nm were obtained from aqueous TiOCl<sub>2</sub> solution with 0.67M Ti<sup>4+</sup> concentration prepared diluting TiCl<sub>4</sub> by homogeneous precipitation process in the ranges of 17-230°C. With the spontaneous hydrolysis of TiOCl<sub>2</sub>, which means the natural decrease of pH value in the aqueous solution, all mono-dispersed precipitates were crystallized with the anatase or rutile TiO<sub>2</sub> phase. TiO<sub>2</sub> precipitate with the pure rutile phase was fully formed at the temperatures below 65°C, not involving the evaporation of H<sub>2</sub>O, and above 155°C, which were available by suppressing it. TiO<sub>2</sub> precipitate with rutile phase including a small amount of the anatase phase started to be formed in the intermediate temperatures above 70°C showing the full formation of the anatase above 95°C under the free evaporation of H<sub>2</sub>O. However, in the case of completely suppressing H<sub>2</sub>O evaporation at the temperatures above 70°C, TiO<sub>2</sub> precipitate with anatase phase was fully transformed with the reaction time into the precipitate with the rutile phase by the vapor pressure of H<sub>2</sub>O. Therefore, the formation of TiO<sub>2</sub> precipitates with the rutile phase around room temperature would be caused due to the existences of the capillary pressure between the agglomerated needle-shaped particles or the ultrafine clusters, together with the slow reaction rate.

#### **F8.67**

**SUPERPARAMAGNETIC FERRITES - REALIZATION AND PHYSICAL OBSTACLES.** Dieter Vollath, Eric Pellegrin, Dorothee V. Szabó Forschungszentrum Karlsruhe, Karlsruhe, GERMANY.

Superparamagnetic nanocrystalline ferrites have a high potential for application in high frequency systems such as cellular phones. In these materials, the change of the direction of magnetization is not associated with the movement of Bloch walls, but with thermal fluctuation of the magnetization vector. Therefore, the resonance frequency of the Bloch walls, found at frequencies below 200 MHz, is no longer limiting the maximum frequency for application. This new limit is given by the frequency of electron spin resonance in the gigahertz range. It was possible to verify this behavior with spinelle type ferrites, based on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Changing the composition of the spinelle changes the energy of magnetic anisotropy controlling the susceptibility and the maximum frequency for applications. It was possible to show that these superparamagnetic materials have their frequency limit beyond 2 GHz. In all cases the materials were nanocomposites made of ceramic or polymer coated nanoparticles produced by the microwave plasma process. The coating of the particles is necessary to reduce spin - spin coupling destroying superparamagnetism. Even when the susceptibility is in the range of today's commercial ferrites, the saturation magnetization is always found to be significantly smaller than the theoretically expected value. This phenomenon is - at least partly - clarified by measurement of the X-ray magnetic circular dichroism. These investigations show a significant orbital magnetic moment antiparallel to the direction of the spin moment in these ferrites. These moments that, according to Hund's rules, should quench, were found to be ca. 20% of the spin moment. Additionally, it was found that the amount of Fe<sup>2+</sup> ions is

larger than expected by thermodynamic data of bulk materials. Point defects that can be healed out at temperature below 300 °C lead to a further reduction of the magnetization.

#### **F8.68**

**NANOSIZED ALUMINA POWDERS VIA FLAME SPRAY PYROLYSIS: SYNTHESIS, CHARACTERIZATION, AND MICROSTRUCTURAL EVOLUTION.** T.R. Hinklin, R.M. Laine, University of Michigan, Dept. of Materials Science and Engineering, Ann Arbor, MI.

We recently described methods of producing various nanosized oxide powders by flame spray pyrolysis of novel alkoxide complexes. This scalable synthesis route provides reproducible, high purity multimetallic nanosized powders. We can currently make single crystal oxide powders (2-80 nm dia. and surface areas of 40-60 m<sup>2</sup>/g) at production rates in excess of 100 g/h. The flexibility of the FSP process also allows for the incorporation of dopant atoms in the as prepared powders. This presentation will focus on the effect of several dopants on the formation, sinterability and microstructural evolution of FSP d-alumina powders, 25 nm average particle size.

#### **F8.69**

**SINTERING BEHAVIOR OF NANOSIZED CERAMIC COATINGS.** J.Th.M. De Hosson, R.L.W. Popma, J.W. Hooijmans, Dept Applied Physics, Materials Science Center and Netherlands Institute for Metals Research, University of Groningen, Groningen, THE NETHERLANDS.

This paper concentrates on the sintering behavior of nano-sized ceramic coatings, e.g. silica and zirconia, produced with the sol-gel-processing route. Because the sintering behavior of the sol-gel coating is a crucial aspect the paper focuses on the microscopic mechanism of sintering of nano-sized ceramic coatings. The sintering takes place in a furnace and the results are compared with laser sintering. Especially, attention is paid to the densification behavior and the grain growth in the layer. Also the different crystal phases observed are addressed. Experimentally it was found that a green layer with a maximum thickness of about 350 nm could be attained. At greater thickness the green layer exhibited severe cracking. The samples were examined using ellipsometry and in-situ environmental scanning electron microscopy (FEG-ESEM-Philips XL30 and FEG-SEM-Philips XL30-S with a special electromagnetic lens). A high resolution TEM (JEOL 4000/II) was used to study the original sol-gel particles. With ellipsometry layer thickness and density in sol-gel derived zirconia layers could be obtained. Complete densification of the sol-gel-derived coatings was found at temperatures above 1000°C. The various stages of sintering were explained based on a viscous sintering regime and a crystalline sintering regime.

#### **F8.70**

**MESOSCOPIC SILICA FILMS GROWN AT THE AIR-WATER INTERFACE.** Nan Yao, Anthony Y. Ku, Horiyaki Nakagawa, Tu Lee, Dudley A. Saville and Ilhan A. Aksay, Princeton University, Princeton Materials Institute and Department of Chemical Engineering, Princeton, NJ.

We studied the structural evolution of mesoscopic silica thin films grown at the air-water interface under dilute, acidic (pH 0-2) conditions. Our transmission electron microscope observations reveal that the film is initially amorphous. Over time, mesoscopically ordered regions appear, and enlarge within this disordered film resulting in a film with hexagonally packed channels mainly parallel to the air/water interface. Scanning electron microscopy revealed structural evolution at larger length scales - including ribbons, protrusions, domain boundaries, microindentations and pits. Our work confirms previous reports of a disordered structure early in the process and shows that the film develops mesoscopic order through a solid-state crystallization of the amorphous structure. Our observations also suggest that the interface plays a determining role in the microscopic structural evolution of the films. Based on these observations and previous work, we extend the current understanding of the structural evolution of the film by providing a detailed mechanism for the transition to order.

#### **F8.71**

**CARBOXYLATE-ALUMOXANES: APPLICATIONS AS PRECURSORS FOR AN ALUMINA ULTRAFILTRATION MEMBRANE AND HETEROGENEOUS CATALYSTS.** Christopher D. Jones, Rice University, Department of Chemistry, Houston, TX; Andrew R. Barron, Rice University, Department of Chemistry and Department of Mechanical Engineering and Materials Science, Houston, TX.

Carboxylate-alumoxanes are organic substituted alumina nano-particles synthesized from boehmite in aqueous solution which are an inexpensive and environmentally benign precursor for the

fabrication of nano-, meso-, and macro-scale aluminum based ceramics. The purpose of this paper is to describe the applications of carboxylate-alumoxanes currently being researched our laboratory. The first application which will be discussed is the use of carboxylate alumoxanes as a precursor to alumina ultrafiltration membranes. It has been discovered that the calcined material exhibit very narrow pore size distributions with average pore sizes at the lower end of the meso-porous scale. Particle size and porosity can be controlled by chemical methodology. Pores in this range are normally very difficult to obtain by traditional sol-gel techniques. Another application that will be discussed is the use of carboxylate-alumoxanes as a precursor for heterogeneous catalysts. The ability to perform further chemistry on the organic part of the carboxylate-alumoxanes allow for attachment of catalysts. During calcination, the organic ligands are burned out, leaving behind the catalyst in a well dispersed manner. Characterization of the active catalyst site will be discussed.

#### **F8.72**

**SURFACE STRUCTURE OF NANOPHASE TITANIA.** Victor Luca, John Bartlett, Darren Attard, Jim Woolfrey, Materials Division, Australian Nuclear Science and Technology Organization, Menai, AUSTRALIA.

Anatase and rutile are the two most common polymorphs of titania and are widely used in applications such as catalysis, photocatalysis, and dye-sensitized photovoltaic cells. Nanocrystalline titania often exhibits unique electronic and/or surface chemistry, although the relationship between these properties and the structure of the surface is not well understood. To investigate the relationship between nanocrystallite dimensions and surface structure, a series of anatase and rutile nanopowders were prepared by sol-gel processing, with crystallite sizes of 20 to 130 Å. The corresponding fractions of surface Ti(IV) sites were ca. 60 to 10 percent for the anatase series, and 50 to 8 percent for the rutile series. The nanopowders were characterized by a wide range of techniques, including XAS, XRD, TEM, FTIR/Raman spectroscopy and TGA. The XANES spectra of the anatase nanoparticles, were strongly dependent on the crystallite dimensions and the observed changes can be interpreted in terms of the distortion of the initially octahedral Ti(IV) environment. No such size dependence was observed for the XANES spectra of rutile nanoparticles. EXAFS revealed that the average Ti(IV) environment (surface and bulk Ti(IV) sites) in the smallest anatase nanoparticles was distorted, with contracted Ti-O bonds and reduced Ti-O coordination numbers. The results suggest that the surface Ti(IV) sites in anatase are coordinatively unsaturated (presumably with five-fold Ti-O coordination), whereas the rutile surface sites exhibit six-fold Ti-O coordination.

#### **F8.73**

**NANOPOROUS ALUMINA FILMS PREPARED FROM COLLOIDAL SOLUTION.** Vladimir Petrovsky, Harlan U. Anderson, Tatiana Petrovsky, University Missouri-Rolla, EMARC, MO.

Nanoporous alumina films are of interest for such applications as high surface area catalyst support, interface layers for gas separation membranes on porous substrates, low dielectric constant planarization coatings, etc. Alumina films were prepared by spin coating and dip coating from water colloidal solutions of small (50nm) boehmite particles. Special components were used to stabilize solution, to improve wetting and adhesion. Platinum, silicon and alumina were used as the substrates. The resulting film thickness ranged from 1µm to 10µm. No cracking or separation from the substrate took place over the temperature region under investigation (up to 1000°C for Si substrate and up to 1500°C for alumina and Pt substrates). The phase transitions from boehmite to γ-alumina and then to α-alumina were investigated by XRD analysis. The quality of the depositions were evaluated by SEM and AFM. Roughness of the surface before deposition and after deposition of the films from different precursors was measured by the mechanical profilograph to characterize planarization effect. Ellipsometrical and spectrophotometrical measurements were used to characterize optical properties of coatings as well as to calculate the thickness and refractive index of the films. The resulting 50% dense films were optically smooth with pore size of about 50 nm, refractive index of 1.30 and dielectric constant less than 3. Such films were able to planarize substrates with roughness up to 10µm.

#### **SESSION F9: NANOWIRES AND NANOSPHERES**

Chairs: Jeffrey A. Eastman and Gar B. Hoflund  
Thursday Morning, December 2, 1999  
Salon F (M)

#### **8:30 AM F9.1**

**CHARACTERIZATION OF BISMUTH NANOWIRE ARRAYS BY TRANSMISSION ELECTRON MICROSCOPY.** Melissa Sander, U.C. Berkeley, Dept of Chemistry, Berkeley, CA; Yu-Ming Lin, M.I.T.,

Dept of Electrical Engineering and Computer Science, Cambridge, MA; Mildred S. Dresselhaus, M.I.T., Dept of Electrical Engineering and Computer Science and Dept of Physics, Cambridge, MA; Ronald Gronsky, U.C. Berkeley, Dept of Materials Science, Berkeley, CA.

Arrays of bismuth nanowires have attracted recent attention due to their interesting transport properties and potential for application as thermoelectric materials. In this study, transmission electron microscopy and electron diffraction have been employed to examine the nanostructure of these arrays. Samples were prepared by pressure injection of liquid bismuth into nanochannels in alumina templates, producing arrays with average wire diameters of 50-110nm. The orientation and structure of the bismuth wires have been determined. The composition and morphology at the wire-matrix interface have also been assessed.

#### 8:45 AM F9.2

STUDIES OF THE DIELECTRIC CONSTANT OF THIN FILM BISMUTH NANOWIRE SAMPLES USING OPTICAL REFLECTOMETRY AND ELECTRON ENERGY LOSS SPECTRA. Marcie R. Black<sup>a</sup>, P.C. Eklund<sup>d</sup>, Franck Ragot<sup>b</sup>, Bruce Dunn<sup>b</sup>, M.S. Dresselhaus<sup>a,c</sup>; <sup>a</sup>MIT, Department of Electrical Engineering and Computer Science, Cambridge, MA, <sup>b</sup>UCLA, Department of Materials Science and Engineering, Los Angeles, CA, <sup>c</sup>MIT, Department of Physics, Cambridge, MA, <sup>d</sup>University of Kentucky, Department of Physics, Lexington, KY.

Recently, 10 to 120 nm diameter single crystalline Bismuth nanowires have been formed inside amorphous sapphire. In a second set of samples, 50Å diameter Bismuth nanowires are embedded in silica dioxide. Since Bismuth has a small effective mass compared to other materials, quantum mechanical confinement is calculated to occur at the 50Å diameter dimensions. Using Fourier transform infrared reflectometry and visible / ultra violet reflectometry the optical properties over a wide range of energies are examined. Wires of several diameters are compared. Using these results, the dielectric constant as a function of wire diameter is studied. Electron Energy Loss experiments also give information on the plasma frequency and could be compared to the optical data to better insure correct interpretation of the band gap and plasma Frequency as a function of wire diameter. This paper will present the results of these studies on the dielectric function of Bismuth nanowires as well as the Brewster angle determination of light incident on a nanowire array. We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grant DMR-9400334, and the US Navy contract N00167-92-K0052.

#### 9:00 AM F9.3

SYNTHESIS OF SINGLE CRYSTAL BISMUTH-TELLURIDE AND LEAD TELLURIDE NANOWIRES. Qingqiao Wei, Harvard Univ, Dept of Chemistry and Chemical Biology, Cambridge, MA; Charles M. Lieber, Harvard Univ, Dept of Chemistry and Chemical Biology and Div of Engineering and Applied Sciences, Cambridge, MA.

Dimensionality can play an important role in determining the properties of materials. In the case of thermoelectric materials, it has been proposed that one-dimensional quantum wires or nanowires and two-dimensional superlattices could exhibit substantially higher efficiencies compared to the corresponding bulk, three-dimensional solids. To explore such predictions we have initiated a program directed towards the controlled growth of nanowires, and herein, we report the synthesis of single crystal Bi<sub>2</sub>Te<sub>3</sub> and PbTe nanowires by pulsed laser ablation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that Bi<sub>2</sub>Te<sub>3</sub> wires 80 nm to 200 nm in diameter and lengths exceeding 10 microns, and PbTe wires 25 nm to 60 nm in diameter and lengths to 2 microns can be readily produced by the laser ablation method. High-resolution TEM and electron diffraction show that the Bi<sub>2</sub>Te<sub>3</sub> nanowires are single crystals with wire axes along the < 110 > crystal direction. TEM and electron diffraction measurements also show that the PbTe nanowires are single crystals. The transport properties of these new nanowire materials will be discussed.

#### 9:15 AM F9.4

STRUCTURAL AND MAGNETIC PROPERTIES OF THE ELECTROCHEMICALLY DEPOSITED ARRAYS OF NICKEL NANOWIRES. H. R. Khan and K. Petrikowski, FEM Materials Physics Department, Schwaebisch Gmuend, GERMANY.

Ferromagnetic nanowires of cobalt show anisotropic magnetic properties (1). A series of arrays of nanowires of Nickel of diameters (18 to 78 nm) and lengths (0.5 - 5 μm) were fabricated by electrochemical deposition of Ni into the pores of anodic alumina obtained by anodic oxidation of AlMg1 (Al-1% Mg) substrates using sulphuric, phosphoric and chromic acid based electrolytes. X-ray diffraction investigations show that the Ni-nanowires consist of f.c.c. structure and the crystallite size varies between 30 and 60 nm. Ni-nanowires of 18 nm diameter and 5 μm length show a strong

magnetic and crystallographic anisotropy and the preferred magnetization direction is along the axis of the nanowires. The coercivity and ratio of the remanent magnetization (M<sub>r</sub>) to the saturation magnetization (M<sub>s</sub>), (M<sub>r</sub>/M<sub>s</sub>) of these nanowires are 770 Oe and 0.92 respectively. The magnetoresistance ratio [R(H)-R(0)]/R(0) of the nanowires measured in the CIP geometry shows an anisotropic magnetoresistance (AMR) behaviour. The magnetic and crystallographic anisotropy of the nanowires decreases with increasing diameter. The structural and magnetic behaviour of the Ni nanowires in relation to the diameter and length as well as to the Ni layer of 5μm deposited on the copper substrate using the same Ni-electrolyte will be discussed.

[1] H.R. Khan, O. Loebich and G. Rauscher, Thin Solid Films 275 (1996) 207 209.

This work is supported by Bundesministerium für Wirtschaft through Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. and grant no (AIF 11429 N).

#### 9:30 AM F9.5

PROCESSING OF MULTIWALLED CARBON NANOTUBES BY SHEAR MIXING. Fiona McKenzie, Rodney Andrews and Frank Derbyshire, Center for Applied Energy Research, University of Kentucky, Lexington, KY.

Recent developments have shown that the production of multiwalled carbon nanotubes (MWNTs), both cheaply and in large quantities, is a distinct possibility. We anticipate that the main challenge in bringing nanotube materials into the marketplace will not be production, but rather the problems in synthesizing these advanced nanotube-containing materials. In recent work, we have focused on the development of nanotube-polymer composites. To prepare thin polymer films containing MWNTs, an ultrasonic wand was used to disperse the nanotubes and solvents were employed to reduce viscosity as an aid to enhancing dispersion. This work has shown that the presence of MWNTs in polymers can produce dramatic improvements in conductivity and changes in mechanical properties. Industrial processing of MWNT-polymer mixtures would probably involve shear mixing followed by extrusion to form geometric shapes. Preliminary work suggests that the inclusion of relatively small quantities of MWNTs produces substantial changes in viscosity in both polymer and pitch systems and that these changes are very pronounced at low mixing speeds. In this study the viscosity of polypropylene compounded with MWNTs is measured for a range of die aspect ratios using a Haake PolyLab conical twin screw extruder with capillary rheometer. The rheological properties are studied as a function of temperature, MWNT concentration and the properties of the nanotubes (aspect ratio, length and diameter distribution) and the viscoelastic behavior of the mixtures described.

#### 9:45 AM F9.6

THE STRUCTURE DEFORMATION OF SINGLE WALL CARBON NANOTUBES AND THEIR FIELD EMISSION PROPERTY VARIATIONS IN FULLY SEALED FIELD EMISSION DISPLAY PANEL. I.T. Han, D.S. Chung, W.B. Choi, S.Y. Jung, S.N. Cha, H.Y. Kim, J.H. Kang, N.S. Park, J.M. Kim, Display Lab., Samsung Adv. Inst. of Technol., KOREA.

We report the field emission property variations of fully sealed single wall carbon nanotubes (s-CNT) field emission display (FED) panel by changing the ambient gases during FED panel packaging process. s-CNT powder were coated on cathode panel and it was assembled with phosphor coated anode panel. During sealing process at high temperature, the s-CNT was damaged by ambient gases. s-CNT protection was accomplished by using reductive ambient gas. The structure deformations of s-CNT cathode measured by electron microscope will be discussed with emission property changes.

#### 10:30 AM F9.7

VANADIUM OXIDE NANOTUBES: STRUCTURE AND PROPERTIES. F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, M. Reinoso, R. Nesper, Laboratory of Inorganic Chemistry, ETH Zurich, SWITZERLAND.

Vanadium oxide nanotubes (VO<sub>x</sub>-NTs) were obtained as the main product in a sol-gel reaction followed by hydrothermal treatment from vanadium(V) alkoxide precursors and primary amines (C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub> with 4 ≤ n ≤ 22) or α,ω-diamines (H<sub>2</sub>N[CH<sub>2</sub>]<sub>n</sub>NH<sub>2</sub> with 14 ≤ n ≤ 20) [1,2]. The amines act as structure-directing templates. This synthesis procedure provides an easy access to large quantities of a novel, tubular form of a vanadium oxide with mixed valency (V<sup>4+</sup>/V<sup>5+</sup>). TEM images show that the length of the tubes is up to 15 μm; their outer diameters range from 15 to 150 nm and their inner diameters from 5 to 50 nm. The tube walls consist of 2-30 crystalline vanadium oxide layers. The structure within the VO<sub>x</sub> layers gives rise to a square pattern of reflections (a ≈ 0.61 nm), which is the same in all tubes independent of the template molecule. On the other hand, the inter-layer distances (1.7-3.8 nm) increase with the alkyl chain length

of the template, indicating that the amine molecules are intercalated between the  $\text{VO}_x$  layers. Cross-sectional TEM investigations of  $\text{VO}_x$ -NTs reveal that a major fraction of the tubes has a serpentine-like morphology. Clear concentric tubular arrangements of layers like in carbon nanotubes are rarely present (< 1%). The scroll-like structure is highly flexible and permits to perform numerous exchange reactions without destructing the tubular morphology: the organic template can either be substituted by various metal cations or via proton exchange by diamines. The option to functionalize the tube walls by exchange reactions represents a promising approach for a tailoring of nanotube structures and thereby for a modification of their mechanical, electrical and chemical properties. [1] M.E. Spahr, P. Bitterli, R. Nesper, M. Müller, F. Krumeich, H.U. Nissen, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1263. [2] R. Nesper, H.-J. Muhr, *Chimia* **1998**, *52*, 571.

#### 10:45 AM F9.8

**SYNTHESIS OF TUNGSTEN DISULFIDE NANOTUBES AND THEIR USE AS TIPS IN SCANNING PROBE MICROSCOPY.** Aude Rothschild, Sidney Cohen, Reshef Tenne, Department of Materials and Interfaces, Weizmann Institute, Rehovot, ISRAEL.

Synthesis of various inorganic nanotubes from layered compounds has been described in the past. However, the synthesis of large amounts of a single phase of long inorganic nanotubes has not been reported yet. We have recently devised a method for growing a pure  $\text{WS}_2$  nanotube phase. The strategy of the synthesis and the growth mechanism will be discussed. Multiple wall nanotubes 3-10 micron in length were obtained. While most of the nanotubes have a cross section diameter of about 30 nm, about 20% of the total number are thicker (up to 100 nm). Amongst the applications, which are envisaged for these nanotubes, tips for scanning probe microscopy (SPM) is most tempting. Using a previously reported method the nanotubes have been affixed to a silicon cantilever of an SPM. Different types of surfaces have been examined with such tips. In particular, due to their robustness and passivity, they seem to be ideally suited for examining rough surfaces with high aspect ratio features.

#### 11:00 AM F9.9

**SILICON CARBIDE NANOWIRES GROWN BY HOT FILAMENT CHEMICAL VAPOR DEPOSITION.** Xintai Zhou, H.Y. Peng, N. Wang, S.T. Lee, City University of Hong Kong, Hong Kong, CHINA.

Silicon carbide nanowires have attracted a great deal of attention in recent years for their potential uses as a high-temperature semiconductor and a reinforcing element for nano-scaled composites. SiC nanowires were usually grown on carbon nanotubes, on carefully prepared silica xerogels or on active carbon as substrates. In present study, we grew SiC nanorods by a simple hot filament chemical vapor deposition method. A mixture of C and  $\text{SiO}$  solid powder was used as the reaction source. The deposition took place on the substrate heated up to 1257K. TEM observations together with electron diffraction analysis reveal that bulk-quantity SiC nanorods with diameter of 20 nm stand densely around the stem of SiC whiskers of 200 nm in diameter. The nanowires had random orientations with one other, while the whiskers were well aligned. High-resolution images of SiC nanowires showed that the nanowires grew mainly along < 111 > direction and had a lot of planar stacking faults on the basal plane. Both nanowires and whiskers possess spheres or rectangle clusters at their tips, which suggests a VLS growth process. EDX analysis of individual tips indeed showed that the tip contained W, Si and C.

#### 11:15 AM F9.10

**CHAINS OF SILICON NANOSPHERES SYNTHESIZED FROM MIXTURES OF SILICON AND SILICON MONOXIDE.** Ning Wang, H.Y. Peng, W.S. Shi, Z.W. Pan, S.T. Lee, City University of Hong Kong, Dept of Physics and Materials Science, Hong Kong, CHINA.

The bulk-quantity synthesis of silicon nanowires has stimulated great interest because of the potentially useful electronic and optical properties of nano-materials. Recently, a self-organized chain of crystalline-silicon nanospheres was fabricated via an extension of the vapor-liquid-solid (VLS) mechanism [1]. Here, we report a new synthesis of bulk quantity of chains of Si nanospheres of 20 nm in diameter through thermal evaporation of mixed Si and  $\text{SiO}$  powders. Notably, the present synthesis requires no metal catalyst, thus the growth mechanism is similar to the oxide-assisted nanowires synthesis recently reported by us [2] and is different from the VLS method. High-resolution TEM observations revealed that the silicon nanoparticles in the chains have no orientation relationship with respect to the growth direction of the chains. The amorphous connects between the nanoparticles have equal length around 20 nm. Electron energy loss spectrum analysis shows that the amorphous material is silicon oxide. The amorphous connects of the chain could be broken easily by a focused electron beam offering the possibility of fabricating individual Si quantum dots. The I-V characteristic and the photoluminescence of this one-dimensional array of quantum dots will

be discussed. [1] H. Kohno and S. Takeda, *Appl. Phys. Lett.* **73** (1998) 3144. [2] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, I. Bello and S.T. Lee, *Chem. Phys. Lett.* **299** (1999) 237.

#### 11:30 AM F9.11

**CONTROLLED GROWTH OF ORIENTED AMORPHOUS SILICON NANOWIRES VIA A SLS MECHANISM.** Q.L. Hang, Y.J. Xing, H.F. Yan, D.P. Yu, Z.G. Bai, J. Xu, H.Z. Zhang, Y. Ding, S.Q. Feng, Department of Physics, National Key Laboratory of Mesoscopic Physics, and Electron Microscopy Laboratory, Peking University, Beijing, CHINA.

Recently, much progress was achieved in the synthesis, characterization, and quantum confinement effect of silicon nanowires prepared by laser ablation, or by simple physical evaporation (1-8). In this report, we will present the experimental results on large-scale synthesis of oriented silicon nanowires which are completely amorphous (a-SiNW's). The a-SiNW's were grown on (111) silicon substrate which was deposited with a thin layer of catalysts. The a-SiNW's have average diameter around 20 nm, and length upto 1 micron, and grown perpendicular to the substrate. No other silicon source was used except the solid substrate. It was believed that the growth of the a-SiNW's is different from the conventional nanowire growth controlled by the well-known vapor-liquid-solid (VLS) model. Instead the a-SiNW's grow via a Solid-Liquid-Solid (SLS) mechanism, that is an analogy of the VLS. Exploration of possible novel physical property that the a-SiNW's may possess is under way, and the oriented a-SiNW's may find application in future nanoelectronics and optoelectronics. 1. D.P. Yu, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, J.S. Fu, H.Z. Zhang, Y. Ding, G.C. Xiong and S.Q. Feng: Direct evidence of quantum confinement evaluated from size-dependence of the photoluminescence of silicon quantum wires, *Physical Review B: Rapid communication* Vol. 59 (4) (1999) 2498-2501. 2. B.B. Li, D.P. Yu, and S.L. Zhang, "Raman Spectra with Excitation of Various Wavelength lasers on Silicon Nanowires", *Physical Review B*, 59(3), 1645-1648(1999). 3. D.P. Yu, C.S. Lee, I. Bello, X.S. Sun, Y.H. Tang, G.W. Zhou, Z.G. Bai, Z. Zhang and S.Q. Feng: Synthesis of Nano-Scale Silicon Wires by Excimer Laser Ablation at High Temperature, *Solid State Communications*, 105 (1998) 403-407. 4. D.P. Yu, Z.G. Bai, Y. Ding, Q.L. Hang, H.Z. Zhang, J.J. Wang, Y.H. Zou, W. Qian, H.T. Zhou, G.C. Xiong and S.Q. Feng: Nanoscale Silicon Wires Synthesized Using Simple Physical Evaporation, *Applied Physics Letters*, 72(1998) 3458-3460. 5. G.W. Zhou, Z. Zhang, Z.G. Bai, S.Q. Feng, D.P. Yu: Transmission Electron Microscopy Study of Si Nanowires, *Applied Physics Letters*, 73(1998) 677. 6. H.Z. Zhang, D.P. Yu, Y. Ding, Z.G. Bai, Q.L. Hang and S.Q. Feng: Dependence of the silicon nanowires diameter on the ambient pressure, *Applied Physics Letters* 73(23), 3396-3398 (1998). 7. D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong and S.Q. Feng: Amorphous silica nano wires: Intensive blue light emitters, *Applied Physics Letters*, 73(21), (1998) 3076. 8. N. Wang, Y.H. Tang, Y.F. Zhang, D.P. Yu, C.S. Lee, I. Bello, S.T. Lee: Transmission electron microscopy evidence of the defect structure in Si nanowires synthesized by laser ablation, *Chem. Phys. Letters*, 283(1998)368. 9. Y.F. Zhang, Y.H. Tang, N. Wang, D.P. Yu, C.S. Lee, I. Bello, S.T. Lee: Silicon nanowires prepared by laser ablation at high temperature, *Applied Physics Letters*, 72 (1998)1835-1837. 10. Guangwen Zhou, Ze Zhang, Dapeng Yu, "Growth morphology and micro-structural aspects of Si nanowires Synthesized by Laser Ablation", *J. Crystal Growth*, 197(1999)129-135.

#### 11:45 AM F9.12

**LARGE-SCALE SYNTHESIS OF AMORPHOUS SILICON NANOWIRES ON (111) Si SUBSTRATE.** H.F. Yan, Q.L. Hang, Y.J. Xing, D.P. Yu, Z.G. Bai, S.Q. Feng, Department of Physics, National Key Laboratory of Mesoscopic Physics, and Electron Microscopy Laboratory, Peking University, Beijing, CHINA; G. Zeng, H&G Technology Inc., Beijing, CHINA.

The nanostructured materials have been a focused research field due their peculiar structure, novel physical properties related to materials of low dimensionality, and potential applications in future nanodevices. Using (111) Si substrate coated with a thin layer of Ni, amorphous silicon nanowires (a-SiNWs) were prepared by heating the substrate in an atmosphere of Ar and  $\text{H}_2$  at 900°C. The a-SiNWs have average diameter around 40 nm, and length up to several micrometers. The growth mechanism of the a-SiNWs was found inconsistent with the well-known vapor-liquid-solid mechanism (VLS). Instead it was revealed that the growth of the a-SiNWs was controlled by a solid-liquid-solid (SLS) mechanism which is an analogy of the VLS model. Green-blue light emission was evidenced for the a-SiNWs. The physical origin of such a photoluminescence from the a-SiNWs is attributed to the oxidized surface of the nanowires.

SESSION F10: NANOPHASE METALS AND  
SIMULATION STUDIES

Chair: Felix Edelman

Thursday Afternoon, December 2, 1999

Salon F (M)

**1:30 PM F10.1**

**SYNTHESIS OF MONODISPERSE COBALT NANOCRYSTALS WITH CONTROL OVER THEIR SIZE, SHAPE, AND INTERNAL CRYSTAL STRUCTURE.** Dmitry P. Dinega, M.G. Bawendi, MIT, Dept. of Chemistry, Cambridge, MA.

The preparation of uniform magnetic nanoparticles with control over as many parameters as possible has always been attractive from both a scientific and technological point of view. Metallic particles due to their strong magnetic properties are of particular interest. Here we present a simple technique which enables such control. Thermal decomposition of dicobaltoctacarbonyl in solution in the presence of various coordinating ligands and stabilizing agents leads to the formation of cobalt nanocrystals with control over their size, shape, and internal crystal structure. The size distribution is further improved by size-selective precipitation, which yields nearly monodisperse spherical particles. The size of the particles may be varied in 3-13nm range by simply changing the relative concentrations of the reagents. The crystal structure, controlled by an appropriate coordinating ligand, can be changed from primarily fcc to *c*-cobalt. These nanocrystals can be dispersed in a variety of non-polar solvents forming stable colloidal solutions. A technique for assembling these nanocrystals into 2D and 3D supercrystals is also presented. The particles as well as their assemblies are characterized by X-ray and electron diffraction combined with structural simulations, transmission electron microscopy, and SQUID magnetometry.

**1:45 PM F10.2**

**STRUCTURAL CHARACTERIZATION OF MONODISPERSE COBALT NANOCRYSTALS.** Hugh Doyle, Shouheng Sun and C.B. Murray, IBM T.J. Watson Research Center, Yorktown Heights, NY.

High temperature, solution phase synthesis is coupled with size selective processing techniques to produce organically passivated nanocrystals with size distributions less than 5%. A series of small and wide angle x-ray scattering and electron microscopy studies are combined with detailed computer simulations to correlate structural and magnetic properties of cobalt nanocrystals. Studies are extended to the structural investigation of self-assembled nanocrystal superlattices are model systems in which to study the electronic coupling of neighboring particles. Procedures developed are not limited to Cobalt Nanocrystals but provide general methods for the dispersed nanocrystal and ordered nanocrystal structures from a variety of nanocrystal based materials.

**2:00 PM F10.3**

**SYNTHESIS AND CHARACTERIZATION OF RESORCINARENE-ENCAPSULATED NANOPARTICLES.** Alexander Wei, Stephen V. Puzstay, Kevin B. Stavens, Ronald P. Andres, Purdue Univ., Depts. of Chemistry and Chemical Engineering, West Lafayette, IN.

A novel class of surfactants based on the calix[4]resorcinarenes have demonstrated remarkable abilities to encapsulate and stabilize neutral gold nanoparticles in organic solution. These surfactants are several times more efficient at capturing aerosol-generated particles than alkanethiols, and are able to maintain nanoparticles of up to 20 nm in a dispersed state over a period of several months. Encapsulation is mediated by the chemisorption of multiple heteroatoms on the resorcinarene headgroup to the Au surface, as characterized by surface-enhanced Raman spectroscopy (SERS). Cross-linking the resorcinarenes enhances the robustness of the encapsulated system, enabling the particles to survive a wide range of chemical environments and processing conditions. Characterization by electron microscopy, gel permeation chromatography, and other physical methods will be discussed.

**2:15 PM F10.4**

**NOVEL ROUTES TO NANODISPERSED FUNCTIONALISED METALS.** Mark Green, Paul O'Brien, Dept. of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK.

Metal nanoparticles have potential applications as memory devices and catalysts. The preparation of monodispersed quantum dots of nickel, gold and chromium passivated by various Lewis base ligands is described. The dimensions of the passivating ligand appears to effect the final structural properties of certain nanoparticles. Specific metal and Lewis base capping agents have a propensity to induce nanowire formation, whilst other metal/capping agents systems form nanoparticles of various morphology and sizes. NMR and IR spectroscopies are used to investigate the passivating ligand, whilst

HRTEM and XRD are used to investigate the structural properties of the metal crystals. The organisation of monodispersed nanoparticles into superlattices (colloidal crystals) is discussed. The template effect of other organic species in the formation of colloidal crystals is discussed and the effect on the directional crystallisation is described.

**2:30 PM F10.5**

**DENDRIMER-ENCAPSULATED METAL NANOCCLUSERS: SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS TO CATALYSIS.** Richard M. Crooks, Mingqi Zhao, Victor Chechik, Li Sun, Texas A&M University, Department of Chemistry, College Station, TX.

In this talk we describe a general template-based method for preparing stable metal nanoparticles and demonstrate their use as homogeneous catalysts in aqueous and nonaqueous solvents. Our approach involves the use of polyamidoamine (PAMAM) Starburst dendrimers as both template and stabilizer. These dendrimers are nearly monodisperse, hyperbranched polymers, which are roughly spherical in shape, highly functionalized, sterically crowded on the exterior, and somewhat hollow on the interior. We have found that transition-metal ions, including Cu(II), Pt(II), Pd(II), Ru(III), and Ni(II), partition into PAMAM dendrimers where they are strongly complexed by interior functional groups. The number of complexed metal ions per dendrimer can be nearly monodisperse. Thus, by preloading a dendrimer nanotemplate with suitable metal ions and then chemically reducing this composite in situ, a dendrimer-encapsulated, zero-valent metal cluster results, which contains the same number of atoms as were loaded into the dendrimer as ions initially. These structures have high catalytic activity for hydrogenation of alkenes indicating that the metal-particle surfaces are active. Moreover, the dendrimer exterior can act as a nanofilter that admits exclusively linear isomers to the catalytic metal particle, resulting in selective catalysis. In addition to aqueous solvents, the dendrimer/metal-cluster nanocomposites can also be rendered soluble in nonaqueous solvents. This is accomplished by addition of a fatty acid to the nonaqueous phase. The fatty acids surround the dendrimers in a 1:1 stoichiometry to yield structures akin to monodisperse inverse micelles. In this configuration, the nanocomposites show interesting catalytic activity for a number of technologically important reactions, including the Wacker process. By lowering the pH of the aqueous phase, the dendrimer-encapsulated metal nanoparticles can be re-extracted into the aqueous phase.

**2:45 PM F10.6**

**SUPERSONIC CLUSTER BEAM SYNTHESIS OF NANOPHASE MATERIALS.** P. Milani, P. Piseri, E. Barborini, INFN-Dipartimento di Fisica, Universita' di Milano, Milano, ITALY; S. Iannotta, CEFSA-CNR, Povo di Trento (TN), ITALY.

We will present the principles and the characterization of supersonic cluster beam deposition as a viable technique for the synthesis of nanostructured films. The use of supersonic expansions can improve the deposition rate and favour a better control on cluster mass distribution, thus making this technique competitive compared to other synthetic methods. The cluster source is based on the condensation of the material removed from a target by a pulsed sputtering process. After the condensation the cluster are expanded into the vacuum to produce a supersonic expansion. With this source, intense and stable cluster beams can be produced allowing film deposition rates up to several tens of nm/min over large surfaces. Cluster mass distributions and kinetic energies of the clusters can be characterized prior to deposition by time-of-flight mass spectrometry. By separation effects typical of supersonic beams it is possible to select different mass distributions of neutral clusters in the beam, allowing the deposition of thin films with controlled nanostructure. Supersonic cluster beam deposition (SCBD) has been applied to produce nanostructured thin films of carbon and NiTi, structural characterization confirms that the films retain the memory of the precursor clusters thus presenting different properties. In view of nanostructured film applications in microelectronics and for the realization of sensors, the capability of SCBD of depositing patterns and free-standing microstructures with high lateral resolution will be demonstrated.

**3:15 PM \*F10.7**

**NEW PHENOMENA IN MODERN GAS-PHASE NANOTECHNOLOGY.** Laszlo B. Kiss, Claes-Goran Granqvist, Robert Vajtai, Uppsala Univ, The Angstrom Lab, Uppsala, SWEDEN; F. Einar Krus, Process- and Aerosol Measurement Technology, Dept of Electr Eng, Gerhard-Mercator-Univ, Duisburg, GERMANY; P.M. Ajayan, Rensselaer Polytech Inst, Dept of Mater Sci & Eng, Troy, NY.

When we try to understand key processes in modern nanotechnology, we often find that the satisfactory explanation of experimental findings requires a new way of thinking as compared to classical approaches. In this talk we discuss some examples. 1) How is it possible that the size distribution of gas condensed nanoparticles is

lognormal, even if coagulation is negligible during particle formation? 2) What should we do if we want particles with small mean size and narrow size distribution; large mean size and narrow size distribution; small mean size and wide size distribution; or large mean size and wide size distribution? 3) A new model which is able to explain the super-thermal-stability of gas deposited metal films. 4) A new model which, by a proper incorporation of stochastic forces into fluid dynamics, can answer the basic open questions of nanotube formation.

#### 3:45 PM F10.8

##### TIGHT-BINDING MOLECULAR DYNAMICS OF CERAMIC NANOCRYSTALS USING PC-BASED PARALLEL MACHINES.

Kenji Tsuruta, Hiroo Totsuji, Chieko Totsuji, Okayama Univ., Dept. of Electrical and Electronic Engineering, Okayama, JAPAN.

Tight-binding molecular dynamics (TBMD) simulations are performed to study atomistic and electronic structures of nanocrystalline ceramics [1] such as n-SiC. The simulations are based on the Fermi-operator expansion method (FOEM) [2]: The computational cost of the method scales linearly as the system size increases, and the code has been fully parallelized on our eight-node parallel PC cluster. Preliminary results on sintering of 460-atoms n-SiC show distorted local bonding in a grain-boundary region and associated localized gap states in the electronic density of states. Effective charges in the region deviate significantly from the bulk value. Effects of an external strain on local-bonding structures and electronic states in the grain boundary are investigated. Results on TBMD simulations of nanocrystalline oxide ceramics such as n-TiO<sub>2</sub> will also be presented. [1] K. Tsuruta et al., MRS Symp. Proc. vol. 457, 205 (1997). [2] S. Goedecker and L. Colombo, Phys. Rev. Lett. **73**, 122 (1994).

#### 4:00 PM F10.9

##### THE TRANSITION IN DEFORMATION MECHANISM OBSERVED IN COMPUTER SIMULATED NANOCRYSTALLINE FCC METALS: A DISCUSSION IN TERMS OF GRAIN BOUNDARY STRUCTURE. Helena Van Swygenhoven, Paul Scherrer Institute, Villigen, SWITZERLAND; A. Caro, Centro Atomico Bariloche, ARGENTINA; D. Farkas, Virginia Tech., Dept. of Materials Science, Blacksburg, VA.

We report molecular dynamics computer simulations on the plastic behavior of two model fcc metals, Ni and Cu, with different stacking fault energies, and average grain sizes in the range of 3-12 nm. We observe a transition in deformation mechanism: at the smallest grain sizes all deformation is accommodated in the grain boundaries. At higher grain sizes we observe intragrain deformation. Analysis of the atomic configurations shows that intrinsic stacking faults are produced by motion of Shockley partial dislocations generated and absorbed in the opposite grain boundaries. In Cu we observe the stacking faults at smaller grain sizes than in Ni (8 nm in Cu, 12 nm in Ni) which is attributed to the lower stacking fault energy. Shockley partial dislocations appear on slip systems that are not necessarily those favored by the Schmid factor. The dislocation emission process is discussed in terms of the role of grain boundary structure and of triple junctions in the nanocrystalline fcc samples.

#### 4:15 PM F10.10

##### PRESSURE-INDUCED STRUCTURAL TRANSFORMATIONS IN GaAs NANOCRYSTALS BY MOLECULAR DYNAMICS SIMULATIONS. S. Kodiyalam, R.K. Kalia, H. Kikuchi, X. Liu, A.

Nakano, F. Shimojo, P. Vashishta, P. Walsh, Concurrent Computing Laboratory for Materials Simulations, Dept. of Physics and Astronomy and Dept. of Computer Science, Louisiana State University, LA.

Motivated by experiments on pressure induced structural transformation in semiconductors, we have investigated this transformation in GaAs nanocrystals using parallel molecular dynamics (MD) simulations. Nanocrystals of different radii are studied by suspending them in a Lennard-Jones liquid and then isothermal-isobaric MD simulations are performed. It is found that the transformation from four-fold (zinc blende) to six-fold (rock salt) coordination is nucleated on the nanocrystal surface and proceeds inwards with increasing pressure. Inequivalent orientation of the rock salt phase at different nucleation sites on the surface lead to transformed nanocrystals having grains of this phase of different orientation separated by grain boundaries. Spatially resolved phonon densities of states correlate with local structure. Trends in the variation of the transformation pressure with nanocrystal radius will be discussed.

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#### 4:30 PM F10.11

##### VARIABLE-CHARGE MOLECULAR DYNAMICS STUDY OF SINTERING OF TiO<sub>2</sub> NANOCRYSTALS USING PARALLEL COMPUTERS. Shuji Ogata, Yamaguchi Univ, Dept of Applied

Sciences, Ube, JAPAN; Hiroshi Iyetomi, Niigata Univ, Dept of

Physics, Niigata, JAPAN; Kenji Tsuruta, Okayama Univ, Dept of Electrical and Electronic Engineering, Okayama, JAPAN; Rajiv K. Kalia, Aichiro Nakano, Fuyuki Shimojo, Priya Vashishta, Louisiana State Univ, CCLMS, Baton Rouge, LA.

Large-scale molecular dynamics (MD) simulations are performed to investigate microscopic mechanisms of sintering of TiO<sub>2</sub> nanocrystals in both rutile and anatase phases. The simulations are based on an interatomic potential that was developed recently [Ogata et al., The Journal of Applied Physics, Sept. 15 issue (1999), in press]. This interaction potential allows atomic charges to change dynamically on the basis of the generalized-electronegativity equalization principle. The potential reproduces the cohesive energy, lattice constant, elastic moduli, phonon density of states, the directionally dependent dielectric constants, and the surface relaxation of rutile. The interatomic potential is also applicable to anatase.

Through MD simulations of sintering, we elucidate the microscopic mechanism for the neck formation between TiO<sub>2</sub> nanocrystals. We find that the charge transfer in the neck region and inside the nanocrystals plays an important role in the initial stage of sintering. Results for structural correlations and dielectric properties of the sintered nanophase TiO<sub>2</sub> will also be presented.

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#### 4:45 PM F10.12

##### STRUCTURAL, MECHANICAL PROPERTIES, AND DYNAMIC FRACTURE IN NANOPHASE SILICA GLASSES: MULTIMILLION ATOM MOLECULAR DYNAMICS SIMULATIONS.

Hideaki Kikuchi, Timothy J. Campbell, Cindy L. Rountree, Fuyuki Shimojo, Aichiro Nakano, Rajiv K. Kalia, Priya Vashishta, Concurrent Computing Laboratory for Materials Simulation, Dept. of Astronomy & Physics, Dept. of Computer Science, Louisiana State University, Baton Rouge, LA; Shuji Ogata, Dept. of Applied Science, Yamaguchi University, JAPAN.

We have investigated structural correlations and mechanical behavior of nanophase silica glasses using large-scale parallel molecular dynamics simulations. During the sintering process, the pore sizes and distribution change without any discernible change in the pore morphology. The height and position of first sharp diffraction peak in static structure factor shows significant differences in nanophase silica glasses relative to the bulk system. The simulations show a power-law dependence of the elastic moduli of nanophase silica glass on the density relative to the bulk silica density. Results on fracture toughness, crack-tip speed and stress distributions will be presented. Work supported by NSF, DOE, AFOSR, ARO, USC-LSU MURI(DARP-AFOSR), NASA, PRF, LEQSF, and NSF USA-Japan International Grant.