

SYMPOSIUM V

Nanophase and Nanocomposite Materials IV

November 26 – 29, 2001

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SESSION VI: NANOCOMPOSITE MATERIALS

Chair: Sridhar Komarneni
Monday Morning, November 26, 2001
Back Bay C (Sheraton)

8:30 AM *V1.1

SEPARATE MULTIMODE, AND SINGLE MODE H FIELD AND E FIELD PROCESSES AT MICROWAVE FREQUENCIES FOR CREATING NANO DISORDER (GLASSINESS) DIRECTLY FROM CRYSTALLINE PHASES. Rustum Roy, J.P. Cgeng and D.K. Agrawal, The Pennsylvania State University, University Park, PA.

Contrary to the Warren-Zachariassen random network model, non-crystalline phases are nano-disordered at the 1 - 10 nm scale (in structure and/or composition). Crystalline phases (with very rare exceptions) can be transformed to noncrystalline ones, only via melting or vaporization and subsequent quenching. Very recently, Endo et al., showed the possibility of creating non-crystalline spinels by irradiating crystalline phases with 28 GHz multimode radiation. We report herein on a general process utilizing multimode and single mode 2.45 GHz radiation to convert a range of common unary and binary oxide solids into nanodisordered ("x-ray amorphous") phases in 30 seconds to 5 minutes. Radical differences between the E field and H field in effecting such changes will be described, and very tentative explanations offered.

9:00 AM V1.2

PROCESSING, DYNAMIC STUDIES AND PROPERTIES OF EXFOLIATED AEROSPACE EPOXY ORGANOCCLAY NANOCOMPOSITES. Chenggang Chen, University of Dayton Research Institute, Dayton, OH; David Curliss, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Polymer-layered silicate nanocomposites are new hybrid materials of polymers with nanometer-thickness layered silicates. Due to the unique nanometer-size dispersion of the layered silicates in the polymer matrix these materials generally exhibit improvements in properties such as mechanical performance, thermal stability, barrier performance, and flame retardancy, even at very low loadings of layered silicate. The challenge is to produce a layered silicate system compatible with a thermoset resin of high performance for aerospace structural applications. In this research effort organoclays such as the commercially produced I30E and in-house synthesized SC18 and SC16, were demonstrated to be very compatible with a high Tg aerospace epoxy resin (Shell Epon 862 and curing agent W). Investigation of the rheological characteristics showed that the addition of clay to the resin did not significantly alter the viscosity or cure kinetics and that the modified resin would still be suitable for liquid composite molding techniques such as resin transfer molding (RTM). DSC was performed to study the kinetics of the curing reactions in the modified resin. An in situ small-angle x-ray scattering (SAXS) experiment was used to try to understand the development of the layered-silicate morphology during cure. Based on the in situ SAXS data, morphological changes were monitored in real time during cure and analyzed. Results from wide-angle x-ray diffraction, SAXS, and transmission electron microscopy of the polymer-silicate nanocomposites were used to characterize the morphology of the layered silicate in the epoxy resin matrix. The glassy and rubbery moduli of the polymer-silicate nanocomposites were found to be greater than the unmodified resin due to the high aspect ratio and high stiffness of the layered silicate filler. The solvent absorption of several common solvents and the oxygen plasma erosion rates were also reduced for the polymer-silicate nanocomposites.

9:15 AM V1.3

THERMAL AND MECHANICAL PROPERTIES OF ALUMINA/POLYMETHYLMETHACRYLATE (PMMA) NANOCOMPOSITES. Benjamin Ash, Linda Schadler, Richard Siegel, Rensselaer Polytechnic Institute, MS&E Dept, Troy, NY.

Alumina/polymethylmethacrylate nanocomposites were synthesized by free-radical polymerization. The 39 nm diameter alumina nanoparticles used in the study were produced by a forced gas condensation method and were used as received, or coated to modify the interaction between the particles and the polymer matrix. Tensile testing, differential scanning calorimetry, and dynamic mechanical thermal analysis were used to determine the mechanical and thermal behavior of the resulting composites. At an optimum weight percent, composites made with uncoated nanoparticles showed an average of 600% increase in their strain-to-failure and the appearance of a well-defined yield point when tested in uniaxial tension. Concurrently, the glass transition temperature of the nanocomposites dropped by as much as 25°C, while the ultimate strength and the Young's modulus decreased by 20% and 15%, respectively. We investigate the role of the particle/polymer interface and the nanoparticles in altering the glass transition temperature and in changing the mode of deformation of the bulk polymer.

9:30 AM V1.4

ORGANIC/INORGANIC NANOCOMPOSITES FROM CUBIC SILSESQUIOXANES. Jiwon Choi, Ryo Tamaki, Chad Brick, Seunggyu Kim, Kyongwon Park, Richard M. Laine, Departments of MS&E, Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI.

Octasilsesquioxanes [(RSiO_{1.5})₈, cubes] have been studied extensively as nanobuilding blocks for constructing organic/inorganic hybrid composites with novel properties. Various functional groups including R = H, epoxy, methacryloyl, vinyl, aminophenyl, acetyl, have been successfully appended to these cubes and new hybrid composites have been prepared from them. Selected composites show excellent thermal/mechanical stabilities. Other composites offer well-defined nanostructure and nanoporosity of potential utility for applications ranging from electronics packaging materials to preconcentrators for MEMs gc analysis. High transparency suggests potential for photonics applications. We present here our latest effort to expand the library of the functionalized cubes and to develop hybrid nanocomposites.

10:15 AM *V1.5

MOLECULAR ENGINEERED POROUS CLAYS USING SURFACTANTS. Huai-Yong Zhu, G.Q. Max Lu, Dept of Chem Eng, The University of Queensland, Brisbane, AUSTRALIA.

Quaternary ammonium surfactants were used to control the pore structure of bentonite intercalated with a mixed hydro-sol of silicon and titanium. Porous clay heterostructures of alumina and laponite were prepared in the presence of polyethylene oxide (PEO) surfactants. Participation of the surfactants in the synthesis results in significant changes in the structure of porous clay products. Surfactants are involved in different mechanisms. In the case of bentonite, the mean size of the framework pores was directly proportional to the chain length of the quaternary ammonium surfactants. This indicates a molecular templating mechanism, similar to that observed in the synthesis of MCM41. However, in the case of laponite, the size and volume of the mesopores were related to the amount of PEO surfactants used. By using an appropriate surfactant we can obtain highly porous clays with various pore structures. Introducing surfactants during intercalation is an efficient strategy for the molecular engineering of porous clay adsorbents and catalysts.

10:45 AM V1.6

STUDY OF IRON-NICKEL INSULATOR NANOCOMPOSITES. Shiqiang (Rob) Hui, Y.D. Zhang, T.D. Xiao, Inframat Corporation, Farmington, CT.

In order to dramatically increase the electric resistivity of metallic magnetic alloys while retaining their excellent soft magnetic properties high saturation magnetization, high permeability, high Curie temperature, etc., Ni_xFe_{1-x}v/SiO₂1-v nanocomposites, where x denotes the atomic fraction of Ni in the Ni-Fe alloy phase and v denotes the volume fraction of the magnetic constituent in the composite, with 50 ≤ x ≤ 80 and 0.5 ≤ v ≤ 0.8 were synthesized using a wet chemical approach. The x-ray diffraction and TEM experiments show that the synthetic NiFe/SiO₂ is a two-phase composite system in that the Ni-Fe particle is coated by an amorphous insulating SiO₂ layer. The NiFe particle is in a fcc Ni-Fe alloy state. Its size can be controlled in a rather large range between 10 nm to 70 nm by adjusting the reaction parameters. Particular attention was paid to reduce the chemical reaction temperature so as to insure the smallness of the particle size. Our study reveals that the magnetic properties are very sensitively dependent on the packing density of the nanoparticles. A systematic study has been made to increase the packing density and correlate it with the electric resistivity and permeability.

Acknowledgments.

The work is supported by NASA Contract No. NAS3-01013. The authors would like to thank Profs. J.I. Budnick and W.A. Hines of the University of Connecticut for the use of the SQUID magnetometer and impedance meter.

11:00 AM *V1.7

INORGANIC QUANTUM DOT-ORGANIC POLYMER HYBRID NANOCOMPOSITES: A NEW PHOTOREFRACTIVE MEDIA. Jeffrey G. Winarz, Moataz Soliman, Paras N. Prasad, Institute for Lasers, Photonics and Biophotonics, The University at Buffalo, State University of New York, Buffalo, NY.

At the Institute for Lasers, Photonics and Biophotonics new generation nanostructured materials are being developed which will have a significant impact on telecommunications, high capacity data storage and bar code systems, as well as on the newly emerging field of biophotonics, a light wave based biotechnology. Our comprehensive program involves nanoscale synthesis and processing to produce nanoparticles and hybrid nanocomposites. The design on the nanoscale provides a judicious control of the excitation dynamics,

photoinduced charge transfer, charge migration and trapping to produce a specific optoelectronic response at a selected wavelength. This wavelength specificity will be demonstrated through the presentation of photoconductivity data, showing the ability to tune the photoresponse of the composite in the visible as well as the infrared portion of the spectrum. The applicability of this approach will be further established with the presentation of data exhibiting photorefractive behavior at relevant wavelengths including the communication wavelength of 1310 nm. In an effort to understand the charge-carrier dynamics associated with these novel hybrid inorganic:organic systems, we have conducted extensive studies of the charge carrier mobilities, the results of which will be presented. Also, with the goal of producing channel waveguides with photorefractive capabilities, we have begun work on the process development for producing free standing photorefractive films with waveguiding structure.

11:30 AM V1.8

NOVEL SYNTHESIS OF OXIDE NANOCOMPOSITES IN LAPONITE. G.Q. Max Lu, Huai-Yong Zhu, Dept of Chemical Engineering, Brisbane, AUSTRALIA.

Surfactants are widely used as templates or directing agents for the effective control of mesophase structures in nanomaterials synthesis. Here we report the first observation of surfactant-induced oriented growth of nano-crystallite in synthesis of mesoporous alumina. In the presence of polyethylene oxide surfactant lath-shaped nanocrystallites of γ -alumina of about 3-4 nm thick and 30-60 nm long formed from aluminium hydrate colloids. Such a structure exhibits strong resistance to heating at high temperatures. A sample retains a BET surface area of 68 m²/g, after being heated at 1200°C. These solids promise to be good substrates for catalysts of high thermal stability.

11:45 AM V1.9

PHOTOELECTROCHEMICAL PROPERTIES OF NANO-COMPOSITE THIN FILMS COMPOSED OF TiO₂ MATRIX AND NANO-SIZED NOBLE METAL. Jong-Won Yoon, Takeshi Sasaki, Naoto Koshizaki, Nanoarchitectonics Research Center, National Institute of Advanced Industrial Sci & Tech, Tsukuba, JAPAN.

Nanocomposite films based on coupling TiO₂ matrix with the nano-sized noble metal (Au, Pt) showed promising photoelectrode properties. The M/TiO₂ (M=Au, Pt) nanocomposite thin films were deposited on quartz and ITO glass substrates using co-sputtering method. TiO₂ in rutile form is a dominant crystalline phase for as-deposited nanocomposite films. Along with heat treatment up to 600°C, XRD peaks of rutile phase as well as those of noble metal increased in intensity and decreased in width, indicating the growth of crystallites. From the TEM observation, the platinum particle size ranged from 1 to 2 nm in as-deposited Pt/TiO₂ nanocomposite and increased to 5-10 nm by heat-treatment at 600°C. From the UV-VIS spectra for Au/TiO₂, strong absorption peak was observed around 600 nm, resulting from the surface plasmon resonance (SPR) of Au particles. On the other hand, Pt/TiO₂ film does not have clear absorption peak in visible light wavelength due to the small intensity of SPR in Pt nanoparticles. The nanocomposite electrodes of Au/TiO₂ and Pt/TiO₂ showed photocurrent response even in visible light range, which is quite different from pure TiO₂ electrode showing response mainly in UV light range. In the UV light region, the current density of Au/TiO₂ electrode was about seven times larger than those of Pt/TiO₂ and pure TiO₂. In the visible light region, the Au/TiO₂ electrode showed a photocurrent peak around 600 nm, even though the current density was less than 5 nA/cm². The photocurrent peak could be attributed to the SPR of Au particles. The photocurrent of Pt/TiO₂ electrode in visible light range was about one order of magnitude larger than pure TiO₂ and extended to around 700 nm. Probably, this is due to the surface states or impurity levels in the nanocomposite films.

SESSION V2: NANOSTRUCTURES I

Chair: Jun-Ichi Matsushita

Monday Afternoon, November 26, 2001

Back Bay C (Sheraton)

1:30 PM *V2.1

SELF-ASSEMBLY OF METAL NANOCCLUSERS IN BLOCK COPOLYMERS. Rina Tannenbaum, Georgia Inst. of Technology, Atlanta, GA.

The realization of the technological advantages offered by the size specificity and selectivity of nanoclusters relies on the fundamental understanding of the principles and methodologies for preparation and processing of cluster assembled materials, with high standards of size, structural, morphological and shape uniformity. Chemical synthesis and self-assembly of metal clusters offer a great deal of freedom in

manipulating a wide range of parameters, such as the oxidation state of the metals in the cluster and the reactivity of the metal clusters due to particle size variations, all within the bounds of the nanoscale cluster regime. Among the most promising chemical avenues, is the thermolysis of metal complexes in polymeric media, under controlled atmosphere, to form either zero-valent metallic particles or metal oxide clusters. Stabilization of metallic colloidal particles in a polymeric medium results in the adsorption of the polymer to the metal fragments to form a film, which separates the particles sufficiently to keep van der Waals forces below thermal energy levels. Multi-component polymers with self-organizing properties, such as block copolymers, are utilized to produce a controllable, predetermined, self-developing spatial arrangement of clusters. Selective phase separation of the metal nanoclusters is achieved by using blocks having different reactivities towards the metal fragments. The metal clusters aggregate primarily in the phases having the more reactive block, thus creating a patterned distribution, which coincides with the morphology of the block copolymer. A detailed study of these interactions provides the basis for the understanding of the various parameters affecting the phase separation process, the spatial confinement of the nanoparticles and the smoothness of the interfaces formed. Such a self-assembled three-dimensional structure is an ideal candidate for applications in the area of optoelectronics, as it allows the formation of an ordered domain structure, with domains having different refractive indices and dielectric constants.

2:00 PM V2.2

ENERGETICS OF NANOARCHITECTURED MATERIALS: TiO₂-ZrO₂ AND TiO₂-MoO₃. Mandar R. Ranade and Alexandra Navrotsky, UC Davis, Dept of Chemical Engineering and Materials Science, Thermochemistry Facility, Davis, CA; Scott H. Elder, Intel Corporation, Hillsboro, OR.

High temperature drop solution calorimetry in sodium molybdate solvent was performed on nanoarchitected materials using a Calvet type twin micro-calorimeter at 975 K. A series of nanocrystalline TiO₂-ZrO₂ samples (mesoporous structure) and a series of nanocrystalline TiO₂-MoO₃ samples (core-shell structure) were used in this study. The drop solution enthalpies and the transformation enthalpies to macroscopic stable crystalline phases have been calculated. The enthalpy of transformation from amorphous to m-ZrO₂, from this work, -50.08 ± 4.92 kJ/mol, is in good agreement with -58.60 ± 3.30 kJ/mol, determined by Molodetsky et al (2000). The enthalpy of transformation from amorphous to crystalline MoO₃ is derived from these data as -51.25 ± 2.01 kJ/mol. The energetics of both series, TiO₂-ZrO₂ and TiO₂-MoO₃, suggest that these materials constitute a nanoscopic two-phase mixture, with their energetics a weighted sum of end member enthalpies. Thermogravimetric analysis and differential thermal analysis (TG/DTA) results corroborate the proposed energetic model for these compounds. Thermodynamic stability issues of these nanoarchitected materials are discussed along with the structural aspects.

2:15 PM V2.3

PREPARATION OF CdS NANOPARTICLES IN SALT-INDUCED BLOCK COPOLYMER MICELLES. Hanying Zhao, Elliot P. Douglas, University of Florida, Dept of MS&E, Gainesville, FL.

The synthesis of semiconductor nanoparticles has attracted much interest due to their size dependent properties and great potential for many applications, especially as nonlinear optical materials. These applications result from their unique properties caused by quantum size effects and the large number of unsaturated surface atoms. We have developed a novel preparation method of CdS nanoparticles with controllable size and stability based on poly(styrene-block-2 vinyl pyridine) block copolymer. Upon addition of cadmium ions into polymer solution in THF, both single micelles and aggregates of single micelles, called compound micelles, are formed. Upon introduction of hydrogen sulfide gas into the solution CdS nanoparticles grow within the core of the single micelles. UV-Vis spectra, fluorescence spectra and transmission electron microscopy all indicate that with decreasing block copolymer initial concentration in THF, the size of CdS nanoparticles decreases, with diameter from 1.0 nm to 3.8 nm. The prepared CdS nanoparticles have excellent colloidal stability and thermal stability. We have also prepared nanoparticles in the corona region of micelles by dropping core-loaded CdS nanoparticles in THF solution into water with low pH values. TEM results, fluorescence spectra and UV-Vis spectra all show that the size of nanoparticles increases slightly after the transition. Accompanying the location change of nanoparticles from the core to the corona of micelles, there exists a transition of the micelles themselves, from compound micelles to single micelles.

3:00 PM *V2.4

GROWTH OF HIGHLY ORIENTED ZnO NANOWHISKERS BY CHEMICAL VAPOR DEPOSITION. Sai-Chang Liu, Jih-Jen Wu, Natl Cheng Kung Univ, Dept of Chemical Engr, Tainan, TAIWAN.

ZnO nanowhiskers were grown directly on fused silica substrates by a thermal CVD method using $Zn(C_5H_7O_2)_2$. SEM images show that a high density of well-aligned nanowhiskers with a diameter in the range of 60-80 nm was formed over the entire substrate. XRD analyses reveal only two peaks detected which are indexed as (000c) of the ZnO wurtzite structure, indicating the nanowhiskers are preferentially oriented toward the c-axis direction. Photoluminescence (PL) measurements show a strong emission at around 3.2eV which is corresponding to the near band-edge emission of the wide band gap ZnO. Further studies on the relationship between the substrate and the nanowhiskers by TEM as well as the mechanism of catalyst-free growth of the ZnO nanowhiskers will be discussed.

3:30 PM V2.5

SEMICONDUCTING OXIDE NANOBELTS. Z.L. Wang, Z.W. Pan and Z.R. Dai, Center for Nanoscience and Nanotechnology, School of MS&E, Georgia Institute of Technology, Atlanta, GA.

Ultra-long belt-like, quasi-one-dimensional nanostructures (so called nanobelts or nanoribbons) have been successfully synthesized for semiconducting oxides of zinc, tin, indium, cadmium and gallium, by simply evaporating the desired commercial metal oxide powders at high temperatures [1]. The as-synthesized oxide nanobelts are pure, structurally uniform, single crystalline and most of them free from defects and dislocations; they have a rectangular-like cross-section with typical widths of 30-300 nm, width-to-thickness ratios of 5-10 and lengths of up to a few millimeters. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. The nanobelts are an ideal system for fully understanding dimensionally confined transport phenomena in functional oxides and building functional devices along individual nanobelts.

[1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 291 (2001) 1947.

3:45 PM V2.6

NANO-CYLINDER STRUCTURE STUDIED BY X-RAY DIFFRACTION. Gu Xu, McMaster Univ, Dept of MS&E, Hamilton, CANADA; Zhechuan Feng, Axcelphotonics, Boston, MA; Zoran Popovic, Xerox Research Ctr of Canada, Mississauga, CANADA; Jianyi Lin, National Univ of Singapore, Dept of Physics, SINGAPORE; J.J. Vittal, National University of Singapore, Dept of Chemistry, SINGAPORE.

The study of the nano-cylinder structure has attracted much attention due to the application of multi-wall carbon nanotubes (MWCNTs). While some TEM observations indicate that they are formed by seamless concentric cylinders, other TEM and high pressure X-ray diffraction studies suggest that they look like scrolls of graphite sheets. Although many people now accept the concentric cylinder model, there has been no confirmation reported. On the other hand, this structural difference of MWCNTs plays a crucial role in determining the properties and suitability for future applications. For example the periodical boundary condition can only be imposed for cylinders, but not for scrolls. To resolve this issue, we employed high-resolution X-ray diffraction to measure detailed profiles of the Bragg peaks for high-purity MWCNTs. We then identified some unusual observations unique to the nano-cylinder structure, followed by the analysis of the structural difference in the Fourier transform between nanotubes formed by scrolls and concentric cylinders. The simulation results are then compared with the experimental data to reveal the structural details.

4:00 PM V2.7

THERMAL CHARACTERIZATION OF NANOWIRE ARRAY IN α - Al_2O_3 MATRIX. Diana-Andra Borca-Tasciuc, Gang Chen, Univ of California at Los Angeles, Mechanical and Aerospace Engineering Dept, Los Angeles, CA; Alexander Borschhevsky, Jean-Pierre Fleurial, Margaret A. Ryan, Jet Propulsion Laboratory, California Inst of Technology, Pasadena, CA; Yu Ming Lin, Mildred S. Dresselhaus, Massachusetts Inst of Technology, Dept of Electrical Engineering and Computer Science, and Dept of Physics, Cambridge, MA.

Classical size effects and quantum effects often lead to new, unique material properties in low-dimensional systems such as thin films and nanowire/ nanotubes. Theoretical modeling of transport properties in one-dimensional systems predicts an enhancement in the thermoelectric figure-of-merit due to the strong confinement of transport carriers. Characterization of thermoelectric properties of Bi_2Te_3 nanowires is of high interest and challenging. In this paper, we report on measurements of the thermal diffusivity of Bi_2Te_3 nanowires in α - Al_2O_3 (alumina) templates. A simple theoretical model is developed in order to extract thermal diffusivity of Bi_2Te_3 nanowires in the direction parallel to the nanowires from measured thermal diffusivity of the composite material.

4:15 PM *V2.8

FORMATION OF ORDERED SILICA-ORGANIC HYBRIDS BY SELF-ASSEMBLY OF HYDROLYZED ORGANOALKOXY-SILANES WITH LONG ORGANIC CHAINS. Kazuyuki Kuroda and Atsushi Shimojima, Dept of Applied Chemistry, Waseda Univ, Shinjuku-ku, Tokyo and Kagami Memorial Lab Mater Sci Technol, Waseda Univ, Tokyo, JAPAN.

Inorganic-organic hybrid systems are of current interest for the production of new materials with controlled structures, morphologies, and unique properties. We have been interested in constructing nanostructured materials composed of silica as the inorganic networks. Sol-gel processing using organoalkoxysilanes has been studied as a versatile route to prepare a wide variety of hybrid materials. We have recently demonstrated the formation of transparent and oriented thin films composed of alternating silica and organic layers with Si-C bonds in the interface. The method is based on co-hydrolysis and polycondensation of alkyltrialkoxysilane and tetraalkoxysilane mixtures. In this paper, we will present an overview of the systems that includes monoalkoxy- and dialkoxylalkylsilanes as well as alkenyltrialkoxysilane as the starting materials of alkylalkoxysilanes. Hybrid films thus obtained are a new class of materials and of great interest from a wide range of materials chemistry. The present approach is unique in utilizing the molecular self-assembly of organoalkoxysilane-tetraalkoxysilane system.

4:45 PM V2.9

POLYMERIZATION BY INVERSE MICROEMULSION: SYNTHESIS OF BIODEGRADABLE AND NON BIODEGRADABLE PARTICLES. France Lebon, Dipartimento di Scienze Biomediche e Biotecnologie, Univ di Brescia and INFN, Brescia, ITALY; Christian Grandfils, Interfacultary Biomaterial Centre, University of Liège, BELGIUM; Robert Jérôme, Center for Education & Research on Macromolecules (CERM), University of Liège, BELGIUM; Luciana Sartore, Dipartimento di Chimica e Fisica per l'Ingegneria e i Materiali, Univ di Brescia, Brescia, ITALY.

Production of nanoparticles with well-defined structure, properties and functions is a topic of continuous interest in the field of advanced materials. In this respect, polymerization in inverse microemulsions has potential for the preparation of crosslinked nanoparticles with functional groups on the surface. A first example of nonbiodegradable polyacrylamide nanoparticles will be discussed, with the purpose to produce stable monodisperse lattices to be used as enzymatic reactors or in diagnostic applications. The size was controlled in the 50 to 90 nm range, and a model enzyme (phosphatase alkaline) was physically immobilized. In another example, formation of monodisperse biodegradable nanoparticles of polyamidoamines with size ranging from 90 to 130 nm will be considered. The stability of the latex was studied in relation to the surfactant content and the nature of the macromonomer. This type of nanoparticles is envisioned for intravenous administration with an as low amount of non-metabolized material as possible and absence of toxicity.

SESSION V3: POSTER SESSION NANOPHASE AND NANOCOMPOSITE MATERIALS I

Chairs: Sridhar Komarneni, G. Q. (Max) Lu, Jun-Ichi Matsushita and Richard A. Vaia
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

V3.1

SELF-ENERGY CORRECTIONS TO DFT-LDA GAPS OF REALISTIC CARBON NANOTUBES. Guido Satta, Giancarlo Cappellini, Francesco Casula, INFN and Dept of Physics, University of Cagliari, ITALY.

Since their discovery[1] carbon nanotubes have attracted much interest for their peculiar electronic properties which go from metallic to semiconducting behaviour, depending both on diameter and chirality[2]. The exact value of their band gap is obviously a crucial point to be addressed because it enters in the nanotube application as microelectronic devices[3]. On the other hand DFT-LDA ab initio calculations which we have systematically performed on many nanotubes structures, by using both localized orbital(LO) and plane wave(PW) basis sets, while confirming previous theoretical results for what attains to stability and energetics, do not agree at all with available experimental data [4]. Corrections to LDA gaps are expected to be as large as 1eV. Actually by making use of an efficient GW scheme, previously tested on bulk systems[5], and by taking advantage of symmetry properties, as well as of a model screening function, we have been able to obtain excitation energies in better agreement with measured ones even for large unit cells as those of carbon nanotubes. References:

- [1] S. Iijma, *Nature* **354**, 56(1992).
 [2] N. Hamada et al., *Phys. Rev. Lett.* **68**, 1579(1992).
 [3] F. Leonard and J. Tersoff, *Phys. Rev. Lett.* **84**, 4693(2000).
 [4] J.W.G. Wildoer et al., *Nature* **391**, 59(1998).
 [5] G. Cappellini, S. Bouette-Russo, B. Amadon, C. Noguera, F. Finocchi, *J. Phys.: Condens. Matter* **12**, 3671-3688(2000).

V3.2
 COMPUTATIONAL MODELING OF THE DEFORMATION OF NANOSTRUCTURED MATERIALS. Ming Dao, Nuwong Chollacoop and Subra Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

When the grain size of a polycrystalline material becomes smaller than 100 nm, the grain boundary properties become increasingly important in determining the overall mechanical behavior. Detailed computational models, within the context of finite element discretization, are developed so as to study various possible deformation modes of the grain boundary phase in nanostructured metals and alloys. Grain boundary deformation and grain boundary sliding are explicitly modeled using mechanistic features that are predicated upon experimental observations. The model correctly captures the dependence on grain size of the initial flow stress, the saturation flow stress as well as the tension/compression asymmetry in a variety of nanostructured metals and alloys. Conditions governing the possible occurrence of an inverse Hall-Petch response are also identified using the model. The computational results based on continuum approaches are also found to agree, under appropriate conditions, with the trends predicted by molecular dynamics (MD) models, where grain boundary shearing and sliding were found to play the critical role in determining the macroscopic mechanical behavior. Implications of the present computational approaches to simulate the mechanical response of nanostructured ceramics are also addressed.

V3.3
 USING NANOCOMPOSITES IN THE DESIGN OF CASIMIR ENGINES. R. Esquivel-Sirvent, C. Villarreal and C. Noguez. Instituto de Fisica, UNAM, MEXICO.

Recent advances in micro and nanotechnology have shown that Casimir forces can inhibit the performance of MEMS and also it has been proposed that these forces can be used to drive micro-devices. This was first considered by Pinto (F. Pinto, *Phys. Rev. B*, **60**, 14 740 (1999-I)), who proposed an optoelectronic vacuum transducer. In this work we present a theoretical calculation that shows that Casimir forces can be modulated using nanocomposite materials, in particular those that will present a Mott transition as a function of temperature (e.g. VaO_2 implanted in SiO_2). The transition induces a change in vacuum mode density that affects the magnitude of the Casimir force. For this purpose we first present a calculation of the optical properties of the nanocomposites involved. The thermodynamic cycle and efficiency of an idealized system are discussed as well as potential technological applications.

V3.4
 CHARACTERIZATION OF ORDER-ANNEALING OF NANOSTRUCTURED IRON-PALLADIUM BASED FERROMAGNETIC THIN FILMS. Huiping Xu, Adam T. Wise, Jorg M.K. Wiezorek, Dept. of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA; Timothy J. Klemmer, Seagate Technology, Pittsburgh, PA.

$L1_0$ -ordered alloys of FePt, CoPt, MnAl and FePd are of interest as active ferromagnets in thermally stable high-information density thin film data storage media. Their attractive properties, e.g. high crystalline anisotropy $\sim 10^7$ - 10^8 ergs/cc, derive from their tetragonal ordered $L1_0$ crystal structure. Here magnetron sputtering has been used to deposit FePd based thin films on Si-substrates with various metallic under- and cap-layers. Sputtering produces disordered FePd with the FCC crystal structure, which necessitates post-deposition order-annealing to obtain the desired ordered tetragonal $L1_0$ -FePd. The development of optimized processing strategies for these nanostructured materials systems requires a basic understanding of the microstructural response of as-deposited thin films to annealing. Chemical, compositional and structural changes occurring during annealing at temperatures between 400-500°C have been investigated by a combination of X-ray diffraction and Transmission electron microscopy experiments. Mechanisms and pathways for the microstructural evolution of the nanoscale films have been identified and are discussed with respect to process optimization.

V3.5
 NANOSTRUCTURED NICKEL-FERRITE SOFT MAGNETIC MATERIAL. Zongtao Zhang, Y.D. Zhang, T.D. Xiao, Inframatt Corporation, Farmington, CT.

$NiFe_2O_4$ is an important high frequency soft magnetic material due to

its ultra high resistivity, but its initial permeability is rather low. Conventionally magnetic ferrites are manufactured through ceramic processing. In the effort to explore innovative approaches in fabricating ferrite materials for improved performance, we have carried out a study of fabricating nanostructured $NiFe_2O_4$ using wet chemical approaches. The synthetic $NiFe_2O_4$ precursor was synthesized by citrate reaction method followed by calcinating at various temperatures. Systematic studies concerning the crystallographic structure, the nanostructure and morphology of the particle, the phase homogeneity, the conditions for chemical reaction completion, the electric and magnetic properties have been carried out using x-ray diffraction, transmission electron microscopy, thermogravimetry analysis, electric and magnetic measurements. Our work shows that by using a citrate reaction approach, pure phase and stoichiometric $NiFe_2O_4$ can be fabricated easily, and the particle size can be controlled in a nanometer scale even at high calcination temperatures. In addition, a comparative study of the $NiFe_2O_4$ fabricated by the conventional ceramic processing and this new citrate processing will be presented.

Acknowledgments:
 The work is supported by US Air Force Contract No. F29601 01-C-0141. The authors would like to thank Profs. J.I. Budnick and W.A. Hines of the University of Connecticut for the use of the SQUID magnetometer and impedance meter.

V3.6
 NOVEL FORMS OF NANOPOROUS CARBON. Michael A. Smith, Raul F. Lobo, Department of Chemical Engineering, University of Delaware, Newark, DE.

Among the unique and useful forms of carbon are fullerenes and carbon nanotubes - the later have been offered as potential quantum wires - and carbon molecular sieves, which are used as catalysts and separations agents. Novel carbon structures have been created by templating appropriate carbon precursors (for example, polyfurfuryl alcohol, sucrose, or simpler species like propylene) on inorganic substrates such as clays and zeolites. Of interest as templates here is the mesoporous silicates SBA-15, this material has pore sizes in the mesopore range from 20 to 300 Angstroms, and the pore size and geometry can be controlled by varying the synthesis conditions. In this study we develop a variety of carbon structures in and on the pore walls of SBA-15, with the intent to control the size and structure of resulting carbon by control of template geometry. The silica is removed and the resulting carbon product characterized. Characterization using X-ray diffraction, nitrogen adsorption and transmission electron microscopy suggest acetylene vapor deposition results in layers on the interior pore surface about one monolayer thick. Templated carbons produced by pyrolysis of sucrose show ordering that mirrors the original template structure, but this is contingent on the original calcination temperature of the SBA-15 template.

V3.7
 PROTON CONDUCTING POLYANILINE/ V_2O_5 HYBRID MEMBRANE. Hua Zhang, Allan J. Jacobson, Univ of Houston, Dept of Chemistry, Houston, TX.

Solid state proton conductors which are mainly acidic or hydrous inorganic compounds, polymers, oxide ceramics and intercalation compounds, can be applied in many devices, such as fuel cells, some types of sensors and in hydrogen separation. Most of them can only work below 150°C or above 700°C either because the proton transport depends on the water content or on high temperature. It is of interest to develop proton conducting materials possessing sufficiently high conductivity at medium temperature. Organic-inorganic hybrid materials have been a topic of recent interest because of their unusual properties. It is well known that polyaniline can be inserted in $V_2O_5 \cdot nH_2O$ xerogel by in situ oxidative polymerization/intercalation of aniline in air. This work is devoted to polyaniline/ V_2O_5 hybrid membranes that may be applicable above 150°C. The influence of synthesis conditions have been studied and properties of the bronze are given. The proton transfer in polyaniline/ V_2O_5 bronze is also discussed.

V3.8
 MULTI-SCALE TEMPLATING SYNTHESIS OF HIERARCHICALLY ORDERED CERAMIC MATERIALS BY THE MINERALIZATION OF BIOLOGICAL CELLULAR STRUCTURES. Yongsoon Shin, Li-Qiong Wang, Jeong Ho Chang, William D. Samuels, Gregory J. Exarhos, Pacific Northwest National Laboratory, Richland, WA.

Considerable effort has been made to develop synthetic materials with multiscale structural ordering which mimic that of living biological systems. In this presentation, the synthesis of hierarchically ordered ceramic materials produced by in-situ mineralization of ordered wood cellular structures with surfactant-templated sol-gel solutions will be

discussed. In acidic solution, acid-soluble lignins and hydrolyzed hemicelluloses are leached out and replaced by silicate solution to form a positive replica, while in neutral solution the precipitating silica particles clog the cells and pit structures to form a negative replica of wood. The micelles formed by the surfactant produce ordered fibrous nanopores in the cell walls. This idea can be applied to prepare other hierarchically ordered metal oxides and metal phosphates for catalysis, separation, and environmental remediation. This research is supported by the Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the Department of Energy.

V3.9

DYNAMIC FRACTURE MECHANISMS IN NANOSTRUCTURED SILICA GLASSES MILLION-ATOM MOLECULAR DYNAMICS SIMULATIONS. Laurent Van Brutzel, Cindy L. Routree, Rajiv K. Kalia, Aichiro Nakano, Priya Vashishta, Concurrent Computing Laboratory for Materials Simulations, Biological Computation and Visualization Center, Department of Physics and Astronomy, Department of Computer Science, Louisiana State University, Baton Rouge, LA.

Parallel molecular dynamics simulations are performed to investigate dynamic fracture in bulk and nanostructured silica glasses at room temperature and 1,000K. In bulk silica the crack front develops multiple branches and nanoscale pores open up ahead of the crack tip. Pores coalesce and then they merge with the advancing crack-front to cause cleavage fracture. The calculated fracture toughness is in good agreement with experiments. In nanostructured silica the crack-front meanders along intercluster boundaries, merging with nanoscale pores in these regions to cause intergranular fracture. The failure strain in nanostructured silica is significantly larger than in the bulk systems.

V3.10

A NON-TRADITIONAL VAPOR-LIQUID-SOLID METHOD FOR BULK SYNTHESIS OF SEMICONDUCTOR NANOWIRES. Shashank Sharma, Mahendra K. Sunkara, University of Louisville, Department of Chemical Engineering, Louisville, KY; Guoda D. Lian, Elizabeth C. Dickey, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY.

In a conventional Vapor-Liquid-Solid (VLS) method to synthesize silicon nanowires, a transition metal such as gold is used, which forms a molten alloy with silicon. This alloy catalyzes the decomposition of Silyl radicals at the vapor-liquid interface. In our technique using non-catalytic metal gallium, the microwave plasma containing hydrogen and nitrogen radicals seems to selectively mediate the kinetics at Vapor-Liquid interface. We have synthesized silicon and gallium oxide nanowires at temperatures lower than 400°C. Gallium forms eutectic with certain other elements at temperatures as low as 30°C. In this regard, this technique has the potential to work at temperatures lower than 100°C. In addition, gallium exhibits extremely low solubility and low miscibility for various elemental semiconductors, enabling bulk nucleation and growth of nanometer scale wires from large gallium droplets thus eliminating the need for creation of quantum sized droplets as in the traditional transition and noble metal catalyzed VLS routes. Because of the fact that multiple wires nucleate and grow from the same droplet, this technique offers control on the absolute size and on the size distribution of resulting nanowires. In this presentation, we will discuss our results with synthesis of silicon nanowires less than 20 nm in diameter and the resulting nanowire size distribution. Characteristics such as crystallinity and composition were determined using high-resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDX).

We acknowledge partial support from National Science Foundation through CAREER grant (CTS 9876251) and an Infrastructure grant.

V3.11

NANOSCALE MEASUREMENTS OF THE THREE-DIMENSIONAL CHEMISTRY AND MORPHOLOGY OF COMPLEX NANOCOMPOSITES USING FIB/SIMS TECHNIQUES. Alan J. Kubis, Robert Hull, Univ of Virginia, Dept of Materials Science and Engineering, Charlottesville, VA; Derren Dunn, IBM Microelectronics, Hopewell Junction, NY.

Many techniques exist to study the structure and chemistry of nanophase and nanocomposite systems, but very few are able to produce three-dimensional representations of these materials. We show how sputtering, secondary electron imaging and secondary ion mass spectrometry (SIMS) in the Focused Ion Beam (FIB) system allow 3D morphology and chemistry to be investigated with spatial resolution of tens of nanometers. A 30 keV Ga⁺ focused ion beam is rastered over a surface and secondary electrons, secondary ions and neutral atoms are produced. The secondary electrons are used to image the materials surface with a resolution of 10 nm while the secondary ions can be mass filtered to create elemental maps. These

images or maps are obtained at increasing depths in the sample as it is sputtered and can be used to reconstruct the 3D structure and elemental distribution in the material via linear or shape-based interpolation techniques. A challenge in elemental reconstructions using SIMS maps is the low number of ions detected. This is due to a combination of the small amount of material sputtered, the geometry of the commercial FIB/SIMS system and the low ionization efficiency of the primary Ga⁺ beam. We have measured the collection efficiency for a wide range of elements and explored several techniques for increasing sensitivity. Approaches explored include reactive gas introduction, varying sample orientation and biasing the sample. Together these techniques have yielded an order of magnitude improvement for some materials. We are currently interfacing an F₂ laser for post ionization of sputtered neutrals. This offers the possibility for several orders of magnitude improved sensitivity. Results from a Nickel Based Superalloy, complex metallic precipitates and a semiconductor via structure have been developed to show the utility of this technique for understanding the three-dimensional nanostructure and gaining insight into the properties of materials.

V3.12

MAGNETIC PROPERTIES OF AN ARRAY OF HIGH-ANISOTROPY MAGNETIC NANOPARTICLES. Korey D. Sorge, James R. Thompson, Tony E. Haynes, Stephen P. Withrow, John D. Budai, C.W. White and Lynn A. Boatner, Oak Ridge National Laboratory, Oak Ridge, TN; Alkiviathes Meldrum, University of Alberta, Alberta, CANADA.

Highly-anisotropic ferromagnetic nanoparticles of FePt and CoPt have been formed in the near-surface region of single-crystal Al₂O₃ and yttria-stabilized zirconia (YSZ) as well as in the amorphous host SiO₂. These nanoparticles were formed by implanting overlapping profiles of constituent ions in the host and using thermal processing to precipitate the alloy particles. These single-domain, single-crystal particles align themselves with the host matrix (if crystalline) to create a thin, nanocomposite layer of crystallographically oriented nanoparticles. For FePt in Al₂O₃, Fe was implanted at an energy of 350 keV to an areal dose of 1×10¹⁷ ions/cm²; then Pt was implanted at 910 keV to an areal dose giving the desired alloy compositions (25–52 at. % Pt). Typical dimensions for the particle size and layer thickness are 5–30 nm and 50 nm, respectively, providing a volume filling fraction near 10% as measured by RBS, TEM, and XRD. Magnetic properties of these arrays (including retentivity, coercivity, and saturation magnetization) were measured with a SQUID magnetometer for temperatures of 5–400 K and applied fields up to 65 kOe. Extraordinary behavior was observed. For example, coercivities of FePt nanoparticle arrays are as high as 20 kOe at room temperature, more than 100 times the coercivity of similarly-prepared, similarly-sized Fe nanoparticle arrays. Also, the saturation magnetization falls off more rapidly than expected with temperature. FePt in Al₂O₃ has a T^{3/2} spin-wave dependence to temperatures as high as 400 K (more than half of the bulk Curie temperature, T_c). This enhanced temperature dependence would normally not be expected much above 0.1 T_c (or 75 K). Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

V3.13

OVERVIEW OF THE “NANOTECHNOLOGY MATERIALS PROGRAM” AT NEDO. Shinji Koike, Kiyotaka Ueno, Shosei Fukaya, Yukio Ito, Yoshihiro Sugai, Masayoshi Kubota, Yoshihisa Ohashi, Akihito Yokohata, Yuki Yoshimura, Masanori Kobayashi, Yoshiteru Sato and Kyohei Nishida, Key Technology Development Dept, New Energy and Industrial Technology Development Organization (NEDO), Tokyo, JAPAN.

New Energy and Industrial Technology Development Organization (NEDO) initiated the “Nanotechnology Materials Program” this year. The program consists of 8 projects, namely, Nanostructure Polymer Project, Nanotechnology Glass Project, Nanotechnology Metal Project, Nanotechnology Particle Project, Nanostructure Coating Project, Synthetic Nano-Function Materials Project, Nanotechnology Material Metrology Project, and Systematization of Nanotechnology Materials Program Results Project. These are planned as 5- to 7-year projects, financially supported by the Ministry of Economy, Trade and Industry and managed by NEDO.

The purpose of the program is to develop nanoscale science and technology of material fields that will influence progress in an extraordinary wide range of fields, such as physics, chemistry, materials science, biology and engineering, which are related to special functions and processes with much lower energy and environmental costs. Those fields also directly relate to our secure existence. We will present the details of the program and projects, including the aims, targets, plans, and organization. The policy and the expected results and achievements of the program will be discussed.

V3.14

ONE-STEP SYNTHESIS OF CORE-SHELL SEMICONDUCTOR NANOPARTICLES IN LAYERED DOUBLE HYDROXIDE MATRIX.

Alexey A. Vertegel, Andrey A. Eliseev, Alexey V. Lukashin, Yury D. Tretyakov, Moscow State Univ, Dept of Materials Science, Moscow, RUSSIA; S.V. Kalinin, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA; Oleg I. Lebedev, Gustav Van Tendeloo, Univ of Antwerpen, EMAT, Antwerpen, BELGIUM.

Design of core-shell semiconductor nanoparticles is an important challenge because of the possibility to tune up their physicochemical properties. Due to recent advances in colloidal chemistry, synthesis of core-shell nanostructures has been successfully performed in many research groups. However, colloidal chemistry routes are rather complicated and thus obtained nanoparticles are not stable enough to be suitable for many applications. We report a one-step preparation of core-shell PbS/S nanoparticles in inorganic matrix via decomposition of lead thiosulphate complex intercalated into hydrotalcite-type layered double hydroxide (LDH). LDHs have a general formula $M'_{1-x}M''_x(OH)_2(\text{anion})^{x+}_x/n \bullet mH_2O$, where M' and M'' are metals in the oxidation state 2 and 3, respectively, and anionⁿ⁻ 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. During decomposition of anions in the interlayer space, reaction zone is spatially constrained by the rigid hydroxide layers, giving rise to the conditions similar to those in 2D nanoreactors. Decomposition of $[Pb(S_2O_3)_2]^{2-}$ intercalated between the hydroxide layers is performed under UV-irradiation at 77 K and is not accompanied by destruction of the layers. Core-shell PbS/S nanostructures are formed in one step as a result of the simultaneous formation of PbS and elemental sulfur from $[Pb(S_2O_3)_2]^{2-}$. Nanoparticles are stabilized inside the matrix and show unusual optical properties, including the presence of excitonic peaks in absorption spectrum and high quantum yield of photoluminescence. This work is supported by RFBR grant 00-03-32579.

V3.15

CATALYTIC GROWTH OF LARGE-SCALE Ga₂O₃ NANOWIRES.

Ko-Wei Chang, Sai-Chang Liu, Liang-Yih Chen, Franklin Chau-Nan Hong, and Jih-Jen Wu, National Cheng Kung University, Department of Chemical Engineering, Tainan, TAIWAN.

Large scale gallium oxide nanowires were synthesized on catalyst-coated Si substrates using gallium and H₂O vapor in an 800°C furnace. The nanowires with diameters of 20-70 nm were characterized as single crystals with predominantly monoclinic phase (β -Ga₂O₃). The preliminary results show that the substrate temperature is crucial for the growth of Ga₂O₃ nanowires on the catalyst-coated Si substrates through the vapor-liquid-solid (VLS) method. SiO_x nanowires instead of Ga₂O₃ nanowires were formed preferentially on the Ni-coated Si substrate as the temperature was increased to 900°C. Nanowire-structured SiO_x-Ga₂O₃ heterojunctions could be prepared by a two-stage growth method with a simple temperature programming. Detailed characterizations and property studies of the β -Ga₂O₃ nanowires will be presented in this paper.

V3.16

GRAIN SIZE DEPENDENT MAGNETIC PROPERTIES OF NANOCRYSTALLINE Sm₂Co₁₇/Cu.

Lotfi Bessais, Catherine Djega-Mariadassou, Junxiang Zhang, Valérie Lalanne, and Annick Percheron-Guégan.

New core-shell structure as Sm₂Co₁₇/Cu presents a great interest in the magnetic recording field. High-density storage material requires small magnetically independent particles above their super-paramagnetic critical volume. Thus the powder coating process seems to be an appropriate way to obtain isolated ferromagnetic particles. This study deals with the elaboration of the core Sm₂Co₁₇ particles by soft co-milling of mechanically alloyed Sm-Co particle with Cu nanoparticles, which have been produced by cryogenic melting technique. The evolution of both micro structural and magnetic properties, of the obtained powder, is studied as a function of co-milling time. The average grain size was determined by transmission electron microscopy coupled with x-ray diffraction using the Rietveld method. The particle shape and chemical distribution were investigated by elemental mapping, using wavelength dispersive x-ray analysis with microprobe microscopy. The coercivity evolution shows that an optimum value of 0.5 T is obtained after 5 h co-milling. The microstructure analysis indicates that both materials are well mixed in nanometer scale. This technique appears as a potential route to synthesize nanocrystalline Sm₂Co₁₇ isolated by non-magnetic metal Cu.

V3.17

MULTI-FUNCTIONALIZATION OF Si BY NANOPARTICLES THROUGH A PLUG AND PLAY APPROACH.

Kuniyil Prabhakaran, Toshio Ogino, NTT Basic Research Laboratories, Atsugi, JAPAN; K.V.P.M. Shafi, A. Ulman, Polytechnic University, NY.

In this paper, we demonstrate a "Plug and Play" approach, whereby externally synthesized nanoparticles of desired functions and size are incorporated into the semiconductor, followed by the manipulation of surface chemical bonds in order to achieve multiple functionality. Sonochemically synthesised Fe₂O₃ nanoparticles were introduced onto device quality Si wafers. On annealing the particle-treated Si wafer in ultra high vacuum, oxygen changes the bonding partner from Fe to Si and desorb as SiO at ~760°C, leading to the formation of uniform sized Fe nanoparticles (size ~6-8 nm) on the surface and the sample shows ferromagnetic behaviour. More importantly, the particle treated Si exhibits light emission at wavelengths 1.57, 1.61 and 1.65 microns (full width at half maximum ~20 meV). Emission in this wavelength range is crucial for optical communications and is highly desired from a Si based material. Further, oxidation of this material leads to the formation of a selective capping layer of SiO₂. Thus, by manipulating the surface chemical bonds, we are able to introduce optical, magnetic, metallic and insulating functions to Si. Additionally, the particles exhibit self-assembly on a patterned Si surface. We believe that this approach is universal and the material developed here is compatible with the planar Si technology, bringing us closer to realization of Si based monolithic electronics.

V3.18

SYNTHESIS AND PROPERTIES OF POLYIMIDE-SILICA HYBRID OPTICAL THIN FILMS.

Chao-Ching Chang and Wen-Chang Chen, Dept of Chemical Engineering, National Taiwan Univ, Taipei, TAIWAN.

In this study, two series of polyimide-silica hybrid optical thin films were prepared by aminoalkoxysilane capped poly(amic acids) with tetramethoxysilane, followed by spin coating and multi-step baking. The poly(amic acids) of PMDA-ODA and 6FDA-ODA were used as the precursors. The FE-SEM study suggests the nano-size domain of the silica moieties in the hybrid thin films. The AFM diagrams show excellent planarity of the prepared hybrid thin films. Highly transparent hybrid thin films were obtained at the silica content of 0-55 wt%. The prepared hybrid thin films have the thermal decomposition temperature higher than 530°C. The optical properties can be controlled by the silica content as well as the polyimide segment. The refractive indices of the prepared PMDA-ODA/silica and 6FDA-ODA/silica films at 633 nm decrease linearly from 1.659 to 1.532 and 1.568 to 1.517 with increasing the silica content, respectively. The abbe numbers and the birefringence of the hybrid thin films show the opposite trend with the refractive indices since the optical dispersion and anisotropy are resulted from the polyimide moieties. The lower refractive indices, birefringence, and extinction coefficients of the 6FDA-ODA/silica films than those of the PMDA-ODA/silica films are due to the fluorine content and the orientation of the polyimide structures. The prepared hybrid thin films show an excellent transparency in the visible region. Low loss optical waveguides were obtained from the prepared hybrid thin films.

V3.19

STEP ENERGY BARRIERS AND MORPHOLOGY CHANGES IN SMALL FACETED PARTICLES.

Brian W. Sheldon and Janet Rankin, Brown University, Division of Engineering, Providence, RI.

Shape changes that occur during processes such as particle synthesis, coarsening, and sintering are traditionally described in terms of surface curvature. This paper presents results from in situ TEM investigations which show that morphology changes in small particles are better understood in terms of the energetics and motion of atomic steps. While curvature-based descriptions are sometimes equivalent to those based on steps, the work presented here demonstrates that curvature approximations do not provide an accurate assessment of many of the experimental observations. In particular, shape changes can be strongly influenced by the step energy barrier associated with adding or removing additional atomic planes from a faceted surface. This barrier can cause particle shapes that differ from those predicted by traditional equilibrium considerations (i.e., the Wulff construction). It can also limit or alter kinetic processes (e.g., particle growth during coarsening, etc.). In addition to the experiments, thermodynamic and kinetic models of these phenomena will also be presented.

V3.20

FUNDAMENTAL ELECTRONIC PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES.

Min Ouyang, Jinlin Huang, Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

Single-walled carbon nanotubes (SWNTs) are ideal systems for understanding the fundamental low-dimensional physics and for building novel nanodevices. This presentation will focus on recent atomically resolved scanning tunneling microscopy (STM) studies of fundamental electronic properties of SWNTs. Our data show that the electronic properties of nanotubes depends not only on radius and chirality but also on finite curvature and local environment. Based on a graphene sheet model, SWNTs with indices $(n,n,3q)$ (q is an integer) should behave as metallic quantum wires. However, tunneling spectroscopy measurements made on "metallic" zigzag tubes showed energy gaps with magnitudes depending inversely on the square of the tube radius, whereas isolated armchair tubes do not have energy gaps and are truly metallic. In addition, armchair SWNTs in bundles exhibit pseudogaps at the Fermi energy, which show an inverse dependence on tube radius. Lastly, experimental studies of the unique one-dimensional (1D) energy dispersion of SWNTs will be presented. Analysis of energy and position dependent tunneling spectroscopy data has enabled the determination of the linear energy band dispersion near the Fermi energy for the first time. The implications of studies on our understanding of the electronic properties of SWNTs and related carbon based nanoelectronic devices will be discussed.

V3.21

SOL-GEL PROCESSING OF POROUS SILICA THIN FILMS FOR LOW K INTERCONNECTS. Deok-Yang Kim, Henry Du, Stevens Inst Tech, Dept of Chemical, Biochemical, and Materials Engineering, Hoboken, NJ; Suhas Bhandarkar, Bell Labs, Lucent Technologies, Murray Hill, NJ; David W. Johnson, Jr., Agere Systems, Murray Hill, NJ.

Tetramethyl ammonium silicate (TMASi) has been known as structuring agent in zeolite synthesis for a long time. We will report the first use of TMASi to prepare porous silica films for low k applications. TMASi 18.7 wt. % solution (from Aldrich) was spin coated on Si substrates with a 3,000 Å thick thermal oxide and was heat-treated at 450°C to obtain porous silica thin film. The films, deposited by merely using as-received TMASi solution, have a moderate porosity value of 10%. The addition of gelling agent, Methyl Lactate, significantly increased porosity and improved control of pore size distribution. For example, 50% porosity and uniform pore size distribution (average pore size ~ 40 Å) has been achieved with proper amount of gelling agent. Dielectric constant of the nanoporous film is around 2.5.

V3.22

MICROMAGNETIC PROPERTIES OF CoFe_2O_4 /BLOCK COPOLYMER NANOCOMPOSITE FILMS. Georgia C. Papaefthymiou, Villanova University, Dept. of Physics, Villanova, PA.

Oxidic spinels are of interest both for fundamental studies in magnetism and for technological applications. In particular, ferrite spinels exhibit combined electrical and magnetic properties that have found numerous applications in high-frequency devices, memory cores and magnetic recording media. Currently, the properties of nanometer size ferrites are under intense investigation due to the broad range of magnetic behavior that may be engineered into such structures. In this investigation the micromagnetic properties of CoFe_2O_4 nanoparticles (ca. 9 nm diameter) self assembled within diblock copolymers via a novel room temperature synthesis procedure [1] have been examined by Moessbauer spectroscopy. Collective magnetic excitations observed below the blocking temperature give values for sublattice saturation magnetic hyperfine fields $H_{hf}^s(A) = 502$ kOe and $H_{hf}^s(B) = 527$ kOe, where A and B denote magnetic sublattices with tetrahedral (A) and octahedral [B] cation coordination of the spinel structure. Within a cubic anisotropy model, superparamagnetic relaxation processes give an effective particle magnetic anisotropy density $K_{eff} = 43 \times 10^5$ erg/cc. Deviations of the above parameters for the nanocomposite from those of bulk CoFe_2O_4 are discussed in terms of finite-size effects and particle-support interactions.

[1] S.R. Ahmed and P. Kofinas, MRS Abstracts, Fall 2000, p. 699.

V3.23

FABRICATION OF SIZE-GRADED SILICON NANOPARTICLES BY PULSED LASER ABLATION. Don O. Henderson, Marvin H. Wu, Richard R. Mu, Akira Ueda, Fisk University, Chemical Physics Laboratory, Department of Physics, Nashville, TN.

Pulsed laser irradiation of Si (100) targets was performed at: 532 nm, 40 ps pulse, laser spot size of 100 μm , and an energy of 100 μJ . The target and the substrates used are Si (100) wafers. All ablation experiments were performed under a vacuum of 10^{-7} torr; the target to substrate distance was fixed at 2 cm. Under these conditions a layer of quantum dots covered a circular area with a radius, $r = 10$ mm. AFM images obtained in tapping mode of Si quantum dots that were fabricated by pulsed laser irradiation show that most Si particles are in a size range comparable to that of the exciton (3 nm) and are

therefore in the regime of strong to intermediate quantum confinement. Optical absorption spectra were collected by placing a 1 mm aperture before the sample, and translating the sample at 2 mm steps. The spectra show a blue shift in the band edge absorption at increasing distances from the plume center. This trend indicates that there is a continuous decrease in the quantum dot size with increasing distance from the plume center. This observation is consistent with the density of the plume profile, which has a greater density near the center and a decreasing density on the edges. These results demonstrate that size-graded quantum dot structures are readily fabricated by laser ablation. The size gradation accounts for the increasing band edge absorption, which is due to quantum confinement of the exciton.

V3.24

HARD NANO-CRYSTALLINE CHROMIUM NITRIDE FILMS.

G.C.A.M. Janssen, J.-D. Kamminga, W.G.M. Sloof, Materials Science Dept., Delft University, NETHERLANDS.

Polycrystalline chromium nitride films with composition ranging from pure Cr to CrN were prepared by reactive sputter deposition in an argon/nitrogen plasma. The overall composition of the films was assessed by EPMA. The hardness was determined from nano-indentation. The microstructure of the films was studied by X-ray diffraction. The bcc Cr phase was obtained for compositions up to CrN_{0.35}. Compositions from CrN_{0.40} to CrN_{0.65} yield hcp Cr₂N. Compositions above CrN_{0.70} yield fcc CrN. For a composition of CrN_{0.43}, i.e. chromium rich Cr₂N, a maximum in hardness of 18 GPa was obtained. XRD line broadening yields a minimum in crystallite size for this composition. A crystallite size of 8 nm was estimated. A second but lower maximum in the hardness of 9 GPa was obtained at a composition of CrN_{0.73} i.e. chromium rich CrN. In this case the film consisted of nano-crystalline CrN. In contrast the hardness of stoichiometric Cr, Cr₂N, and CrN films is only 5, 7 and 4 GPa respectively. No bcc Cr was observed in the CrN_{0.43} films indicating the absence of Cr crystals. Assuming that the excess Cr in these films is located at the grain boundaries, we calculate the thickness of the chromium at the grain boundaries to be less than one atomic layer. Apparently, during deposition the mobility of the excess chromium is so small that this growth mode prevails over the growth of a two phase mixture, thereby forcing the growth of a nanocrystalline material. In conclusion it is stated that the hardness of chromium nitride is a consequence of the nano-crystallinity of the material.

V3.25

FORMATION OF GOLD NANOCRYSTALS ON MgO SURFACES.

Akira Ueda, Vanessa Saunders, Thurston Livingston, Richard Mu, Marvin Wu, Don Henderson, Fisk University, Chemical Physics Laboratory, Department of Physics, Nashville, TN; Vera L. Arantes, FEAU-Universidade do Vale do Paraiba, Sao Jose Campos, SP, BRAZIL.

Electron beam evaporation of gold is used for the fabrication of gold nanocrystals on usual MgO $\langle 100 \rangle$ and highly stepped MgO $\langle 100 \rangle$ surfaces. Atomic force microscopy (AFM) is used to image the evolution of gold deposited on the MgO surfaces due to subsequent annealing in an oxidizing atmosphere. The highly stepped MgO $\langle 100 \rangle$ surfaces are produced by polishing $\langle 100 \rangle$ surfaces at an inclined angle 0.5° toward (110) direction. Annealing the samples show that gold nanocrystals preferentially grow on the $\langle 100 \rangle$ surface of micron size MgO islands, which are imperfections produced by polishing. The islands on the highly stepped $\langle 100 \rangle$ surfaces with an inclined angle 0.5° have an anisotropy, which are elongated along the steps. Annealing the samples deposited on the highly stepped $\langle 100 \rangle$ surfaces show that gold nanocrystals preferentially grow on the $\langle 100 \rangle$ surface of micron size MgO islands. Polarized optical absorption has been carried out to detect the difference in absorption between polarization parallel and perpendicular to the steps. The polarized optical absorption spectra show that the surface plasmon band is shifted by 4 nm, and indicate that the gold nanocrystals are aligned along the step direction of MgO, while the islands on the usual MgO $\langle 100 \rangle$ surfaces have no anisotropic effects on the polarized absorption measurements.

V3.26

SOLVOTHERMAL SYNTHESIS ON ELECTROCHEMICALLY ACTIVE NANOCRYSTALLINE LiTiO SPINEL. Dina Fattakhova, Petr Krtil, J. Heyrovsky Institute of Physical Chemistry, Prague, CZECH REPUBLIC; Valery Petrykin, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Nanocrystalline materials play an important role in design of new electrochemical energy related applications namely in development of new rechargeable batteries or photoelectrochemical cells. The use of nanocrystalline materials allows one to improve both the size and quality, of the electrode electrolyte interface as well as to shorten significantly the characteristic diffusion lengths. LiTiO spinels are

usually prepared by solid state reaction at 800 C; an alternative route leading to nanocrystalline material is room temperature TiO₂ reduction with butyllithium and subsequent annealing of the formed precursor at temperatures above 500 C. In this paper we describe a solvothermal synthesis of LiTiO spinels by a reaction of TiO₂ in lithium containing water and ethanol based alkaline solutions at temperatures below 200 C. This reaction proceeds via dissolution precipitation mechanism and its course is not sensitive to crystal structure of TiO₂ used in synthesis. Product of the hydrothermal synthesis has cubic rock salt type structure. Heating to temperatures above 300 C leads to water removal and recrystallization to Li₄Ti₅O₁₂ spinel with Fd3m symmetry. Solvothermal reaction in ethanol leads directly to a product with spinel structure without need for annealing. Both products are active for Li insertion; the electrochemical activity of the phase prepared in ethanol is superior to that of the phase prepared in water.

SESSION V4: SYNTHESIS AND CHARACTERIZATION I

Chair: G. Q. (Max) Lu
Tuesday Morning, November 27, 2001
Back Bay C (Sheraton)

8:30 AM *V4.1

HOLOGRAPHIC PHOTOPOLYMERIZATION-BASED SUB-MICRON TEMPLATING OF NANO-SIZED PARTICLES. T.J. Bunning, B.J. Gadzecki, C.L. Dennis, V.P. Tondiglia¹, L.V.

Natarajan¹, D.W. Tomlin², R.A. Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH. ¹SAIC, Dayton, OH. ²TMCI, Dayton, OH.

We have successfully templated on a sub-micron periodicity nano- and meso-particles using holographic photopolymerization. The spatially varying intensities caused by constructive and destructive interference of coherent writing beams result in a modulation of polymerization conditions. This anisotropy was used to template clay sheets, gold nanoparticles, and polystyrene beads on large length scales. Aspect ratios greater than 100 were observed. The spatially periodic polymerization conditions cause the nano-particles to segregate from the polymer during polymerization with the periodicity dictated by the holographic overlap of the curing laser. We present HRSEM and TEM results and the corresponding diffractive properties of these films. Good agreement with general diffraction theory is observed. We examine the causes of the observed phenomena by solving the coupled mass transport equation for a non-reactive particle in a reactive fluid. A mutual diffusion coefficient term is used and the resulting patterns are shown to be very dependent on the balance of the monomer and particle diffusivities.

9:00 AM V4.2

METAL-SEMICONDUCTOR PHASE TRANSITION IN NANOSCALE VANADIUM DIOXIDE PRECIPITATES FORMED IN SILICA AND SAPPHIRE BY ION IMPLANTATION.

Rene Lopez, Leonard C. Feldman, Richard F. Haglund, Vanderbilt Univ, Dept of Physics and Astronomy, Nashville, TN; Lynn A. Boatner, Tony E. Haynes, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

The study of solid-state phase transitions at the nanometer length scale provides new insights into the effects of material size on the mechanisms of structural transformations. Such research also opens the door to new applications, either because materials properties are modified as a function of particle size, or because the nanoparticles interact with a surrounding matrix material, or both. For applications such as optical memory, the hysteresis characteristic of the phase transition is especially relevant. In this paper, we describe the formation of vanadium dioxide precipitates in silica and sapphire substrates by stoichiometric ion implantation and thermal processing. We observe 10-100 nm size vanadium dioxide nanoparticles with varying shapes from spheroids to needles. The metal-semiconductor-transition of the precipitates shows different features in each substrate. The effects on the phase transition of nanocrystal morphology, nanocrystal size and the interaction with the host are characterized by transmission electron microscopy, x-ray diffraction, Rutherford backscattering, infrared optical measurements and doping experiments. Of particular interest are the enhanced size-dependent hysteresis and the surface plasmon resonance induced by dielectric confinement when the particles reach the metallic state. This resonance amplifies the optical contrast in the range of near-infrared optical communication wavelengths. The vanadium dioxide nanoparticles in sapphire present a round and non hysteric transition, while the nanoparticles embedded in silica exhibit a sharper transition with up to 50 K of hysteresis, one of the largest values ever reported for this transition. This hysteresis and the transition temperature seem to be correlated with the size of the

precipitates. In other hand, doping the particles with such ions as tungsten and titanium gives insight into the mechanics behind these features, together with a capability to tailor the transition temperature and the hysteresis over a wide range of values.

9:15 AM V4.3

NON LITHOGRAPHIC FABRICATION OF DENSE Sn NANOWIRE ARRAYS. Regina Ragan, Vanessa Sih, and Harry A. Atwater, California Inst of Technology, Pasadena, CA.

Fabrication of nanowires in diamond cubic alpha-Sn can enable the zero direct energy band gap to be opened via quantum confinement to tune the energy bandgap in the infrared via engineering of the wire radius. It has also been shown theoretically that quantum confinement can enhance the performance of thermoelectric devices.¹ Bandstructure calculations indicate that quantum confinement can open the bandgap yielding a group IV direct energy bandgap semiconductor. Tight binding energy band calculations performed for diamond cubic Sn indicate for wires of 40 nm diameter, the band gap is 0.4 eV, which corresponds to an absorption edge wavelength of 3 microns and for wires of 10 nm diameter, the bandgap is 2.5 eV and the absorption edge is predicted to be 500 nm. We have fabricated Sn nanowires with 12:1 aspect ratios (40 nm diameter and 500 nm length) by high pressure injection (1400 psi) of molten Sn in porous alumina templates fabrication by electrochemical anodization of Al foil. Anodically-synthesized alumina templates with pore sizes less than 10 nm and densities of 10¹¹ cm² are achievable with this non-lithographic anodization technique.² Structural, optical and electrical characterization of these dense arrays of Sn nanowires will be discussed.

¹ L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B 47, 12727 (1993).

² A.P. Li et. al., J. App. Phys. 84, 6023 (1998).

9:30 AM V4.4

NANOSTRUCTURED MATERIALS CHARACTERIZATION BY X-RAY AND NEUTRON SCATTERING TECHNIQUES: FROM POLYMER AND METAL TO CLAY NANOPARTICLES.

Kwanwoo Shin, Sushil K. Satija, NIST, Gaithersburg, MD; Benjamin Ocko, BNL, Upton, NY; Miriam Rafailovich, John Sokolov, SUNY at Stony Brook, NY.

The rapid developments in nanotechnology require advanced techniques to explore individual structures on the nanoscale. In this study, high-resolution depth-profiling techniques of X-ray and neutron scattering were used to probe the nanoparticle structures of polymeric, metallic, and inorganic nanostructures at interfaces. The results show that the combined study of X-ray and neutron scattering can be an effective investigative method for nanotechnology, which allows i) in-situ measurement of morphological evolution; ii) characterization abilities covering large surface area of the various nanostructured materials and iii) detailed information of individual structures.

10:15 AM *V4.5

MICROWAVE-HYDROTHERMAL SYNTHESIS OF NANOPHASE MATERIALS. Hiroaki Katsuki, Saga Ceramics Research Laboratory, Saga, JAPAN; Sridhar Komarneni, The Pennsylvania State Univ, Materials Research Laboratory, University Park, PA.

Microwave-hydrothermal(M-H) synthesis has been shown to be superior to conventional-hydrothermal(C-H) synthesis at least in three ways, i.e., the M-H process leads to (1) very rapid heating to temperature of treatment, (2) extremely rapid kinetics of crystallization by one to two orders of magnitude compared to C-H process and (3) formation of new phases. The objective of this paper is to show the rapid synthesis of nanophase hydroxyapatite(HAp) and hematite particles via a M-H process. HAp crystals were synthesized from gypsum powder with 0.5M diammonium hydrogen phosphate solution via a M-H process. Gypsum powder could be completely converted to fine HAp particles of 30-300 nm length at 100°C in 5 min. Compared to the formation of HAp crystals via a C-H treatment, M-H treatment led to increased rate of formation (by two orders of magnitude). Spherical red hematite particles of 100-180 nm in diameter were preferentially formed at 100°C after 24 hrs via a C-H treatment, but hematite particles of 30-66 nm in diameter could be formed in 2 hrs from 0.018M FeCl₃ solution at 100°C. The formation kinetics of hematite via M-H treatment increased with increasing reaction temperature, as expected. Furthermore, some hematite particles were prepared from 0.18 and 1.8M FeCl₃ solutions and 2MFeCl₃ 8MNaOH solution via M-H treatment at 100-180°C and the formation kinetics and some properties of these particles will also be reported.

10:45 AM V4.6

IN SITU ANALYSIS OF CHEMICAL VAPOR SYNTHESIS BY AEROSOL MASS SPECTROMETRY. In-Kyum Lee, Markus Winterer, Horst Hahn, Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERMANY.

An Aerosol Mass Spectrometer (AMS) was constructed. It is a combination of a Quadrupole (QMS) and a Partikel Mass Spectrometer (PMS) and enables the in-situ analysis of gasphase processes to generate nanoparticles. Mass distributions of ultrafine particles in the range of 1e4 amu to 1e8 amu are measured in the PMS. At the same time measurements of molecular species up to 300 amu can be detected in the QMS. Aerosols containing nanocrystalline silicon carbide particles produced from tetramethylsilane by pyrolysis are analyzed by the AMS as a function of process parameters to elucidate the formation and growth mechanism.

11:00 AM V4.7

GRAIN-SIZE-DEPENDENT THERMAL TRANSPORT PROPERTIES IN NANOPHASE YTTRIA-STABILIZED ZIRCONIA. H.-S. Yang, J.A. Eastman, L.J. Thompson, and G.-R. Bai, Argonne National Laboratory, Materials Science Division, Argonne, IL.

Understanding the role of grain boundaries in controlling heat flow is critical to the success of many envisioned applications of nanophase materials. This presentation will describe the thermal transport behavior of nanophase yttria-stabilized zirconia (YSZ) coatings prepared by metal-organic chemical vapor deposition. A strong grain-size-dependent reduction in thermal conductivity is observed at all temperatures from 6480 K. Since the highly defective nature of the YSZ crystal structure results in an extremely short phonon mean-free-path-length even in single crystals, the behavior is understood in terms of the interfacial (Kapitza) resistance to thermal transport. In response to the application of heat to a material, interfacial resistance results in a small temperature discontinuity at every grain boundary, an effect that is magnified in nanophase materials because of the large number of grain boundaries. The observed behavior in YSZ will be compared with predictions derived from a diffuse-mismatch model. Implications for the possible development of improved thermal barriers based on nano-layered structures with large interfacial thermal resistance will be discussed. This work is supported by the U. S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38.

11:15 AM V4.8

SURFACE PHENOMENA IN NANOCRYSTALLINE MATERIALS. Geoffrey F. Strouse and Robert W. Meulenberg, University of California, Santa Barbara, CA.

We report findings of quantum dot size dependent pressure coefficients that are modulated by a surface-to-volume ratio dependence seen in dimensionally restricted materials. Using pressures below the critical limit for structural phase transitions (< 1 GPa), we show that pressure induced perturbation of coupling between core electronic levels by surface states exhibit two regimes in quantum dot materials. The size dependent coupling exhibits a $1/r$ scaling law due to the large the surface-to-volume ratio in these materials.

11:30 AM V4.9

OPTICAL PATTERNING OF PHOTSENSITIVE THIN-FILM SILICA NANOSTRUCTURES AND NANOCOMPOSITES. Dhaval A. Doshi, Department of Chemical and Nuclear Engineering, Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM; Nicola Huesing, Institute of Inorganic Chemistry, Vienna University of Technology, Vienna, AUSTRIA; Adam Cook, Timothy Stachowiak, Shawn Coffee, Hongyou Fan, Darren Dunphy, Sandia National Laboratories, Albuquerque, NM; C. Jeffrey Brinker, Department of Chemical and Nuclear Engineering, Center for Micro-Engineered Materials, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

Co-operative self-assembly of surfactant and silica resulting in mesostructured materials is important for various applications such as photonics, sensors, fluidics, membranes etc. In the past decade various pathways have been explored to access a wide spectrum of mesostructured materials with a variety of macro and micro structures. Their spatial definition has been patterned via various soft lithographic techniques, ink-jet printing, micro-pen writing and selective de-wetting. Recently, we reported multi-functional patterning of photosensitive thin-film silica mesophases. By incorporating photoactive compounds such as photoacid generators or photoresists in a solution of silica, alcohol, water, and surfactant we have combined self-assembly with optical lithographic procedures. This allows us to control structure and function on various length scales. Preferential solvent evaporation during dip/spin coating concentrates the system in surfactant thereby promoting thin-film mesophase formation. During this assembly the hydrophobic core of the surfactant micelle acts as a nano-container for the photoactive compounds yielding a photosensitive nanocomposite. This incorporation allows optical patterning of refractive index, pore size, mesostructure, wetting behavior, open versus closed pores in the thin

films. Results of these patterning schemes and their application for photonics, sensors and fluidics will be discussed.

11:45 AM V4.10

LOW TEMPERATURE SINTERING OF TIN DOPED INDIUM OXIDE NANOPARTICLES. A. Hultáker, A. Hoel and C.G. Granqvist, Dept of Materials Science, The Ångström Laboratory, Uppsala University, SWEDEN; A. van Doorn and M.J. Jongerius, Philips CFT, Eindhoven, THE NETHERLANDS; D. Burgard Nanogate GmbH, Saarbrücken, GERMANY.

Thin transparent and electrically conductive films of tin doped indium oxide (ITO) were spin-coated from a nanoparticle dispersion. The films were heat-treated at temperatures in the $300^{\circ}\text{C} \leq T_A \leq 800^{\circ}\text{C}$ range. Optical and electrical properties were studied as well as microstructure, the latter by using scanning electron microscopy and X-ray diffraction. We found that the films have a transmittance of 90% in the visible for $T_A \leq 650^{\circ}\text{C}$. A maximum conductivity of $1 \cdot 10^{-2} \Omega\text{cm}$ was obtained for $T_A = 800^{\circ}\text{C}$. The sintering behaviour of the nanoparticles was compared with theoretical models of grain growth.

SESSION V5: SYNTHESIS AND CHARACTERIZATION II

Chair: Sridhar Komarneni
Tuesday Afternoon, November 27, 2001
Back Bay C (Sheraton)

1:30 PM *V5.1

EPITAXIAL ELECTRODEPOSITION OF ORDERED NANOSTRUCTURES OF METAL OXIDE SEMICONDUCTORS. Run Liu, Thomas A. Sorenson, Hiten M. Kothari, and Jay A. Switzer, University of Missouri-Rolla, Dept. of Chemistry and Materials Research Center, Rolla, MO.

We have been using electrodeposition to produce epitaxial films of bismuth oxide, cuprous oxide, zinc oxide, and magnetite onto single crystals such as gold, silicon, and indium phosphide. The films are all deposited from aqueous solution at or near room temperature. In addition to having in-plane and out-of-plane order that is induced by the substrate, the materials often grow as nanostructures. Zinc oxide deposits as hexagonal nanopillars on gold. Cuprous oxide and copper metal deposit as a layered nanostructure in an electrochemical system that undergoes spontaneous potential oscillations. Cuprous oxide deposits during the positive spikes in the electrode potential, while a composite of copper metal and cuprous oxide deposits during the more negative plateau region of the oscillation. The resulting nanostructures act like tunnel diodes, with sharp negative differential resistance (NDR) features. Finally, nanometer-scale cross-hatched patterns of cuprous oxide are produced at pH 12 on Au(100) following a transition from the thermodynamically-controlled [100] orientation to the kinetically-controlled [110] orientation. This transition occurs at a critical thickness of about 20 nm.

2:00 PM V5.2

SOL-GEL SYNTHESIS AND CHARACTERIZATION OF NEODEMIUM DOPED TITANIA. A. Burns, S. Ismat Shah, W. Li, and C. Baker, Univ of Delaware, Newark, DE.

The focus of this paper is the chemical and structural characterization of Nd-doped nanostructured TiO_2 films synthesized via the sol-gel method. Films were synthesized on single crystal Si and quartz substrates. The effects of calcination temperature and time on particle size were analyzed by X-ray diffraction (XRD). The morphology of the nanostructured film was studied by atomic force microscopy (AFM). The optical absorption measurements were carried out on the films and the shift in the band edge as a result of Nd doping was measured. Addition of Nd resulted in a red shift. X-ray Photoelectron Spectroscopy was carried out to measure the chemical composition of the films as well as the oxidation states of the cations, Ti and Nd. The results on the effects of doping and particle size on Ti oxidation states will be presented.

2:15 PM V5.3

MICROENCAPSULATION OF SEMICONDUCTOR NANOCRYSTAL QUANTUM DOTS (QDs) AND THEIR PHOTOLUMINESCENCE. Jinwook Lee, MIT, Dept of Materials Science and Engineering; Neal K. Devaraj, Brent R. Fisher, Mouni G. Bawendi, Dept of Chemistry; Klavs F. Jensen, Dept of Chemical Engineering, Cambridge, MA.

Microspheres of semiconductor nanocrystal quantum dots (QDs), where the QDs are uniformly embedded in polymers, have potential applications as active fluorescent units in flat panel displays and luminescent labels in biological detection. Chemically synthesized

semiconductor QDs exhibit a nearly monodisperse size distribution and controlled optical properties as a function of their size due to strong quantum confinement effects. Of particular interest are their narrow emission profiles that can be delicately tuned, combined with a high density of absorption states. While the synthesis of the QDs has been well established with a narrow size distribution, their practical use is dependent on their assembly into well-defined superstructures and on stable packaging technology. We report here the demonstration of ZnS-overcoated-CdSe QD encapsulated in microcapsules consisting of a liquid core and a polymer shell. The stable dispersion of the QDs in the organic liquid core allows QDs to be stored without aggregation. Furthermore, the protective polymer shell prevents oxidation and contamination of the core materials from the environment. Surface derivatization of these capsules allows them to attach to surfaces as well as assemble into 3D structures. The photoluminescence of the microcapsules was characterized by exciting the QDs using CW and pulsed light sources. The quantum efficiencies of the QD microcapsules were estimated from emission lifetime measurements and compared to those of QDs prior to encapsulation.

3:00 PM *V5.4

INSIGHT THE FORMATION OF ULTRAFINE NANOSTRUCTURES IN BULK AMORPHOUS $Zr_{54.5}Ti_{7.5}Al_{10}Cu_{20}Ni_8$. Andre Heinemann, Albrecht Wiedenmann, Hahn-Meitner-Institute Berlin, GERMANY; Helmut Hermann, Hans-Dietrich Bauer, Norbert Mattern, Uta Kühn, Institute for Solid State and Material Research Dresden, GERMANY.

Bulk amorphous $Zr_{54.5}Ti_{7.5}Al_{10}Cu_{20}Ni_8$ is investigated by means of small-angle neutron scattering (SANS), differential-scanning calorimetry (DSC), high-resolution electron microscopy (HREM) and other methods. A formation of ultrafine nanostructure in the glassy phase is observed and explained by a new model. Structural fluctuations of randomly distributed partially ordered domains grow during annealing just below the glass transition temperature by local re-ordering. During annealing the DSC gives evidence for a increasing volume fraction of the locally ordered domains. At high volume fractions of impinging domains a percolation threshold on the interconnected domain boundaries occurs and enhanced diffusion becomes possible. At that stage SANS measurements lead to statistically significant scattering data. The SANS signals are analyzed in terms of a model taking into account spherical particles surrounded by diffusion zones and interparticle interference effects. The mean radius of the particles is 1.3 nm and the mean thickness of the depletion zone is 2.6 nm. The upper limit for the volume fraction after annealing at 653 K for 4 hours is 12%. Electron microscopy confirms the size and shows that the particles are crystalline.

3:30 PM V5.5

SUPERSONIC NANOCRYSTAL DEPOSITION FOR NANOSTRUCTURED MATERIALS. William T. Nichols, Daniel T. O'Brien, Gokul Malyavanatham, Michael F. Becker, John W. Keto, University of Texas at Austin, Dept. of Physics, Austin, TX.

We experimentally demonstrate the large scale production and controlled collection of metal nanocrystals by laser ablation of microparticles entrained at high density in a flowing aerosol. Produced nanocrystals exhibit bi-modal, log-normal size distributions. Mean particle sizes are controlled from 3-16 nm by varying the type and pressure of carrier gas as well as laser fluence. A micronozzle orifice ($d = 200$ microns) supersonically accelerates nanocrystals into a low pressure chamber for deposition onto a room temperature substrate. Two regimes of deposition are described which depend on the nanocrystal's energy per atom on impact. Soft landings ($E \ll 1$ eV/atom) preserve the individual particle properties such as size and shape. By adjusting impaction parameters such as substrate distance, particles can be inertially sorted during deposition. Narrow nanocrystal size dispersions, 10-20%, are demonstrated using this technique. At high particle impaction velocities ($E = 1$ eV/atom) nanocrystals exhibit self sintering upon contact. At high mass densities, adherent, conductive lines are formed from metal nanocrystals. Silver nanostructured line widths of 80 microns are directly written onto substrates using a 200 micron nozzle orifice diameter. Applications of soft impacted metal nanocrystals to optoelectronic devices and hard impacted metal nanocrystals to conductive thick film circuits will be discussed.

3:45 PM V5.6

NOVEL SYNTHESIS OF LUMINESCENT HYBRID ORGANIC/INORGANIC NANOMATERIALS. Fatma Vatansever, Richard A. Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Inorganic core-shell nanoparticles with organic corona provides uniquely tailored photo- and electroluminescent properties for LEDs and other electronic devices. CdSe/ZnS and related core-shell inorganic nanoparticles are synthesized in solution by sequential

addition of selenium to organometallic precursors within TOPO, followed by controlled growth of ZnS shell. Organic corona, incorporating well-defined conjugated chromophores, is subsequently grown from the core-shell particle by ring-opening metathesis polymerization (ROMP). The ruthenium alkylidene catalyst for ROMP enables polymerization 'initiated from the surface' without disturbing the chromophoric structures. Living polymerization provides controlled conjugation length and desired chemical compositions; thus allowing fine-tuning of electronic energy levels. Tailoring of the organic corona will provide control of electron and hole transport around the active inorganic nanoparticle, enabling one-layer devices. Synthesis, spectroscopy and structural characterization will be discussed.

4:00 PM V5.7

Abstract Withdrawn.

4:15 PM V5.8

PMR-POLYIMIDE/LAYERED SILICATE NANOCOMPOSITES. Sandi Campbell, NASA Glenn Research Center, Cleveland, OH.

The nano-scale reinforcement of polymers with a layered silicate is becoming an attractive means of improving polymer properties and stability. This approach has been successfully demonstrated with low temperature resins, such as epoxies and nylons. In this work, PMR type polyimides have been investigated as a nanocomposite matrix, and properties such as modulus and thermal stability are investigated. While improvements in properties are observed with these materials, this research also seeks to understand the synthesis-processing-structure relationships. Systematic variation of synthetic parameters, such as silicate modification, is shown to yield differences in prepolymer viscosity and crosslink density. An understanding of the polymer/silicate interactions will allow the design and property control of these nanostructured materials.

4:30 PM V5.9

PRODUCTION AND MAGNETIC PROPERTIES OF NANOCOMPOSITES MADE OF FERRITES AND CERAMIC OXIDES* A. Huerta, Y. Acosta, V. Cruz, H.A. Calderon, Depto. Ciencia de Materiales ESFM-IPN, Mexico D.F., MEXICO; M. Umemoto, Dept. Production Systems, Technical University of Toyohashi, JAPAN; K. Cornett, Motorola Inc., Plantation, FL; *Work supported by CONACYT (28925-U), Motorola and COFAA-IPN.

This investigation deals with the production of materials containing a dispersion of magnetic nanoparticles in an insulating matrix. The systems under investigation include magnetite precipitates (Fe_3O_4) in a wstite matrix (Fe_xO) and magnesioferrite precipitates ($MgFe_2O_4$) in a magnesia matrix MgO. Additionally other systems have been investigated including Ni-ferrite ($Ni_xZn_{(1-x)}Fe_2O_4$) and hexagonal ferrites type M ($[Ca(CoTi)_xFe_{(12-2x)}O_{19}]_{96}[La_2O_3]_4$) and Y ($Ba_2Ni_{(2-x)}Zn_xFe_{12}O_{22}$). The combination of an isolating matrix and magnetic particles is interesting due to the expected magnetic and physical properties e.g. electromagnetic wave absorption. The spatial and size distribution of precipitates can affect the nanocomposite properties. In addition, the effect of the nanosized grains is documented in order to study the relationship between nanostructure, magnetic and physical properties in oxide ceramics. Mechanical milling is used together with spark plasma sintering for production of the materials. Measurement of magnetic properties of indicates the transformation sequence during milling of the as-milled powders and the nature of the phases formed after sintering. These measurements are supported by other experimental techniques e.g. Mössbauer spectroscopy, X-ray and electron diffraction.

4:45 PM V5.10

MICROSTRUCTURAL AND PROPERTY COMPARISON OF CHEMICALLY SYNTHESIZED, LOW THERMAL EXPANSION-HIGH CONDUCTIVITY Ag-Fe-Ni AND Cu-Fe-Ni NANOCOMPOSITES. Jonathan D. Stolk, Franklin W. Olin College of Engineering, Needham, MA; Michael Gross, Bucknell University, Department of Chemical Engineering, Lewisburg, PA; Arumugam Manthiram, University of Texas at Austin, Texas Materials Institute, Austin, TX.

Nanocrystalline Ag-Fe-Ni and Cu-Fe-Ni powders were produced by ambient-temperature reduction of aqueous metal ion solutions with sodium borohydride. The nanoscale Ag-Fe-Ni and Cu-Fe-Ni precipitates were processed to form fine-grained alloys that offer attractive thermal, electrical, and mechanical properties. Phase evolution and microstructure of the ternary alloys were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM); compositions were determined by wavelength dispersive x-ray spectrometry (WDS) and energy dispersive x-ray spectrometry (EDS); thermal, mechanical, and electrical properties were characterized via thermomechanical analysis, microhardness measurements, and electrical conductivity measurements; and thermal conductivity was

estimated using the Wiedemann-Franz law. Alloys of the Ag-Fe-Ni and Cu-Fe-Ni systems exhibited similar phase evolution and microstructures, and two-phase materials consisting of a higher conductivity phase and a low thermal expansion Invar phase were produced in both systems. The chemically synthesized and heat treated Ag-Fe-Ni alloys exhibited homogeneous, fine-grained microstructures with excellent conductivity and good mechanical properties. The electrical and thermal conductivities of the Cu-Fe-Ni alloys were relatively low due to high solubility of Fe and Ni in the Cu-rich phase; aging heat treatments were shown to improve the conductivity of the ternary Cu-Fe-Ni alloys. The relatively simple chemical synthesis methods used in this study combined with the excellent properties exhibited by many of the ternary alloys may make these materials attractive candidates for a variety of thermal, electronics, and magnetic applications.

SESSION V6: POSTER SESSION
NANOPHASE AND NANOCOMPOSITE
MATERIALS II

Chairs: Sridhar Komarneni, G. Q. (Max) Lu,
Jun-Ichi Matsushita and Richard A. Vaia
Tuesday Evening, November 27, 2001
8:00 PM

Exhibition Hall D (Hynes)

V6.1

A MECHANICAL PROPERTIES AND USAXS STUDY OF THE MORPHOLOGY OF PMMA-BARIUM SULFATE NANOCOMPOSITES. Mary Beth Turell, Anuj Bellare, Department of Orthopedic Surgery, Brigham & Women's Hospital, Harvard Medical School, Boston, MA; Robert E. Cohen, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Particulate barium sulfate of 8-10 weight % is commonly added to polymethyl methacrylate (PMMA) based bone cement for orthopedic surgeons to monitor cement fracture using x-ray radiographs. Uniform dispersion of barium sulfate is necessary for improved fracture toughness of the resulting PMMA-barium sulfate composites. In this study, the morphology and mechanical properties of PMMA containing various amounts of barium sulfate particles of 1 micrometer, 100nm and 50 nm was investigated. A twin screw extruder was employed to disperse various volume fractions of the particulate barium sulfate into PMMA melts. The resulting PMMA-barium sulfate micro- and nano- composites were injection molded into mechanical test specimens as well as specimens for morphological characterization. Ultra-small angle x-ray scattering (USAXS) was performed on all specimens at the UNICAT beamline of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL. Low voltage scanning electron microscopy (LVSEM) was used as a complementary morphology characterization technique and performed on freeze fracture cross sections of all PMMA-barium sulfate composites. The effect of dispersion of the barium sulfate fillers on the macroscopic properties of the PMMA-barium sulfate micro- and nano-composites will be presented.

V6.2

SILICON-QUARTZ INTERFACE: MOLECULAR DYNAMICS SIMULATION OF THERMAL CONDUCTIVITY. Sebastian von Alftan, Antti Kuronen, Kimmo Kaski, Laboratory of Computational Engineering, Helsinki University of Technology, HUT, FINLAND.

One of the most important interfaces in electronic devices is the silicon-quartz interface. Due to the continual decrease in device size the atomic structure of this interface becomes more and more important. In this work, the structure of the interface between silicon and quartz is studied using molecular dynamics simulations and semiempirical potentials. Different semiempirical potential models for silicon and quartz are used to simulate the interface and different ways of mixing the potential models for silicon and quartz are studied. The long range Coulombic interactions are calculated using the distributed parallel multipole tree algorithm (DPMTA). The structure of the interface and the influence of the chosen potential model on the structure is examined. The main interest of this study is conduction of heat in nano-structures. The effect of the small spatial dimensions and the silicon-quartz interface on the thermal conductivity in nano-structures are investigated using the above mentioned methods and results are compared with those of bulk materials.

V6.3

IRON/SILICA OXIDE NANOCOMPOSITE SOFT MAGNETIC MATERIALS. Shiqiang (Rob) Hui, Y.D. Zhang, T.D. Xiao, Inframat Corp, Farmington, CT.

In the effort of exploring high resistive soft magnetic materials,

Fe/SiO₂ nanocomposite materials with various Fe volume fractions have been synthesized using a wet chemical reaction approach in which the precursor complex were annealed at various temperatures. The crystallographic structure, nanostructure, morphology, and magnetic properties of the synthetic Fe/SiO₂ particles were studied by x-ray diffraction, transmission electron microscopy, thermogravimetry, and magnetic means. The experimental results show that in this system the α -Fe particles are coated with amorphous silica oxide. The reaction completion, the purity of Fe/SiO₂ in the synthetic powder, and the Fe particle size are very sensitively dependent on the annealing temperature. By adjusting the annealing temperature, the particle size can be controlled from about 10 nm to 70 nm. For the synthetic powder system with Fe particle size smaller than 15 nm, there exists a superparamagnetic behavior with the blocking temperature significantly below room temperature; while for larger particle size, the ferromagnetic behavior is dominant up to room temperature. Based on these studies, optimum synthesis conditions for Fe/SiO₂ nanocomposites have been determined.

Acknowledgments:

The work is supported by NSF Contract No. DMI-0060158. The authors would like to thank Profs. J.I. Budnick and W.A. Hines of the University of Connecticut for the use of the SQUID magnetometer and impedance meter.

V6.4

PREPARATION OF OPTICALLY TRANSPARENT FILMS OF POLY(METHYL METHACRYLATE) (PMMA) AND MONTMORILLONITE. Elena Vasiliu, Department of Chemical and Materials Engineering, University of Dayton, Dayton, OH; Chyi-Shan Wang, University of Dayton Research Institute, Dayton, OH; Richard A. Vaia, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Preparation of optically transparent films of PMMA through a solution mediated approach amenable to spray or dip coating is discussed. Two organically modified montmorillonites (OMM), Cloisite 6A and Cloisite 15A, ion-exchanged with dimethyl dihydrogenated allow at different milliequivalent ratios were examined. The PMMA composite films were prepared by mixing the OMM with the polymer in different solvents, to form a transparent solution, followed by evaporation of the solvent. Wide-angle x-ray scattering revealed intercalated structures. The d-spacing of Cloisite 6A did not change much after it was dispersed in PMMA, while the d-spacing of Cloisite 15A was increased, both to 4 nm. It also showed that the montmorillonite platelets were uniformly dispersed in the PMMA films, with the plane of the platelets oriented in the plane of the films. Preliminary optical transmission measurements indicated that the composite films containing 10 wt% of the organophilic montmorillonite had an optical transparency about 75% of that of neat PMMA film in the visible light region (480nm). Barrier and hardness characteristics will be discussed.

V6.5

Abstract Withdrawn.

V6.6

MORPHOLOGICAL CHARACTERIZATION OF NANOPARTICLES BY TRANSMISSION ELECTRON MICROSCOPY. Shirley Turner, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

Determination of the morphology of nanoparticles is important in many applications. For example, different facets in catalytic material have different efficiencies for promoting reactions. In pigment nanoparticles, certain morphologies are more desirable for durability of paint. Characterization of morphology and identification of facet type of nanoparticles is possible using transmission electron microscopy but challenging, in part, due to difficulties with particle manipulation. In many cases, it is desirable to rotate a nanoparticle around a specific crystallographic axis to best determine the particle morphology. Using conventional single tilt, double-tilt or rotate-tilt holders, the microscopist is limited by the random orientation of the axis of interest relative to the holder tilt axes. One approach to obtaining a suitably oriented particle is to survey a large number of particles to find one that is, by chance, satisfactorily oriented. In this work, advantages and limitations of a double-tilt, rotate holder applied to nanoparticle manipulation and morphology determination will be delineated.

V6.7

Abstract Withdrawn.

V6.8

A NEW EFFECTIVE APPROACH FOR THE LOW TEMPERATURE SYNTHESIS OF DIAMOND AND CUBIC BORON NITRIDE UNDER HIGH PRESSURE USING NANOSTRUCTURED DIAMOND. Igor M. Starchenko, Institute of

The idea of the work is the application of specially prepared powders of the nanostructured diamonds as the initiators for the synthesis of superhard materials (SH₁). The nanostructured diamonds crystals introduced into the mixture serve as the crystal nuclei of diamond or c-BN for synthesis. In this way the most energy consuming process of forming the nuclei are excluded. The approach employed was exceptionally fruitful. The synthesis temperature for diamond and c-BN with the use of the specially prepared nanostructured diamonds crystals varied from 600 to 700 C, that is 800-1000° lower than the catalytic synthesis temperature of these materials. This brings about a number of dramatic changes in the existing methods of the synthesis: (1) the possibility of replacing the high pressure apparatuses, made of the high-price hard-alloy by cheaper apparatus made of steel; (2) the stages of preparing the catalysts, mixtures, crushing the mixture and the chemical purification of the starting materials are excluded. This not only greatly reduces the price of the synthesis processes, but also makes these processes ecologically safe. The yield of the SH₁ product comes to 90-97% as opposed to 15-20% when the catalytic synthesis is used; (3) the synthesized SHM chips have approximately identical sizes, which strongly depend on requirements of synthesis (temperature and time). It allows to eliminate stages of partitioning the SH₁ particles on the sizes; (4) in this approach the synthesis of SH₁ occurs simultaneously with the processes of the powder sintering in the unified technological cycle. The latter allows one to exclude the technological processes of forming of the compacts and coating of the diamond instruments; (5) the adaptation of the new methods does not require replacement of the existing equipment. This brings up many questions for discussion about the present theoretical opinions of catalytic synthesis of diamond and cubic boron nitride too.

V6.9
PREPARATION OF COPPER ALUMINIUM OXIDE BY SPRAY PYROLYSIS. Ji Youn Rim, Shin Ae Song, Seung Bin Park, Korea Advanced Institute of Science and Technology, Dept. of Chemical Engineering, Taejon, KOREA.

Copper aluminum oxide (CuAlO₂) is known to be a promising p-type transparent conducting oxide (TCO) and is prepared by the solid-state reaction of Cu₂O and Al₂O₃. This conventional method requires Cu⁺ precursor, which is less stable under oxygen environment. In this work, the spray pyrolysis is proposed to prepare the copper aluminum oxide particles and the optimal preparation conditions are determined to produce phase-pure CuAlO₂. By changing the anion types of Cu and Al and the temperature of post-heat treatment ranging from 800 to 1300°C, the crystal phase of the prepared copper aluminum oxides is monitored by X-ray diffraction (XRD). The spray pyrolysis produces CuAlO₂ of delafossite phase, which is transparent and conducting phase, at the post-heat treatment temperature of 1100°C when Cu(NO₃)₂ and Al(NO₃)₃ are used as the precursors for copper and aluminum, respectively. At other combinations of the precursor types and the post-heat treatment temperatures, CuAlO₂ of pure delafossite phase is not obtained. The key conclusion of this report is that the spray pyrolysis produces the CuAlO₂ particles of pure delafossite phase when using Cu²⁺ precursor (Cu(NO₃)₂), whereas, the conventional solid-state reaction method does not produce the CuAlO₂ when using Cu⁺ precursor.

V6.10
RAMAN SCATTERING, LUMINESCENCE, AND ABSORPTION OF CeO_{2-y} NANOPARTICLES. Jonathan E. Spanier, Richard D. Robinson, Feng Zhang, Siu-Wai Chan, and Irving P. Herman, Columbia University, Materials Research Science and Engineering Center and Columbia Radiation Laboratory, New York, NY.

The combined effects of strain and phonon confinement were found to explain the shift of the 464 cm⁻¹ Raman peak of CeO_{2-y} nanocrystals to progressively lower energies and to broader and more asymmetric lineshapes as the nanoparticle size was decreased. The most important factor for these changes was the increasing lattice constant measured for decreasing particle sizes. Comparison of the temperature dependence of the Raman lineshape in the nanoparticles and the bulk showed that phonon coupling was no faster in the nanoparticles, so size-dependent phonon coupling does not contribute to the large nanoparticle peak red shifts and broadening at room temperature. Photoluminescence (PL) of these particles was unusual, in part because the PL emission depended nonlinearly on excitation laser intensity and the onset of PL was accompanied by changes in Raman scattering. The broad (FWHM > 200 nm) PL emission centered around 700 nm is thought to be caused by defect sites in the particles. The PL observations are linked to UV/VIS absorption spectra of these particles taken during synthesis. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-9809687.

V6.11
IN-SITU OBSERVATIONS OF SHRINKAGE OF NANOCAVITIES IN C-Si DURING ELECTRON BEAM IRRADIATION. X.F. Zhu and I.M. Robertson, Frederick Seitz Materials Research Laboratory, Univ of Illinois at Urbana, IL; J.S. Williams, Dept of Electronic Materials Engr, Research School of Physical Sci and Engr, Australian Natl Univ, Canberra, AUSTRALIA.

Structural changes and evolution of nanocavities embedded in crystalline silicon during electron beam irradiation were in-situ studied on a JEOL-4000 EX transmission electron microscope. An electron beam with energy of 300keV was employed for the irradiation, which can cause displacement damage in silicon. There are three types of structural changes and evolution of nanocavities observed due to different degree of passivation of the cavities by impurities. The most striking change is that the round shaped and less passivated cavities shrink without any addition of materials during electron beam irradiation. During this kind of shrinkage, it is also surprising that the cavities always keep their round shape. However, there are another two cases, which were also observed. That is, this shrinkage was interrupted and the shape of cavities changed due to a possible preferential melting around the cavities if initial size of cavities is small and the cavities are heavily passivated or the shrinkage was just stopped if initial size of cavities is large and the cavities are heavily passivated. Such instabilities of nanocavities in silicon associated with impurity passivation and interaction of energetic electron beam with such an open volume nanostructure were discussed.

V6.12
WEAR OF PET/CERAMIC NANOCOMPOSITES. Praveen Bhimaraj¹, Kevin Freudenberg², Jason Action², Linda Schadler¹, Gregory Sawyer², Gregory Toney³, Richard Siegel¹.
¹Rensselaer Polytechnic Inst, Troy, NY. ²Univ of Florida, FL. ³Albany International.

In this study, Alumina/ PET nanocomposites were prepared by melt mixing. Sliding wear tests were conducted using a reciprocating tribometer. This poster will report the effect of particle size and volume fraction on the wear rate and coefficient of friction. In addition, the wear properties will be related to the hardness and the elastic modulus. The morphology of the wear surface will be characterized using electron microscopy.

V6.13
STRUCTURE-PROPERTY RELATIONSHIPS OF ORGANICALLY MODIFIED SILICATE/THREMOSET NANOCOMPOSITES. Derrick Dean, Shamika Rucker, Kenya Clayton, Pele Bhembe, Lisa Austin and Hassan Mahfuz, Tuskegee University.

We have developed a series of layered silicate/thermoset nanocomposites using epoxies and vinyl ester resins and several organically modified layered silicates. Wide angle X-ray diffraction indicated that intercalated morphologies were obtained for the cases studied. The glass transition temperature has been found to vary as the organic modifier and its amount is varied. For samples dispersed with Cloisite 30B, a commercially available nanoclay, the Tg increased by twenty degrees upon addition of as little as 2% by weight clay. The viscoelastic behavior of these materials has also been investigated using dynamic mechanical analysis. A modest increase in the glassy storage modulus was obtained as the amount of nanoclay increased, with a significant increase in the plateau modulus. Additionally, master curves have been generated using time-temperature superposition, allowing further analysis of the effect of the nanoclay on the relaxation behavior. Activation energies calculated from Arrhenius plots increase as the clay contents increase. These effects will be discussed in the presentation. Current efforts to quantify the effects of the nanoclays on the crosslink topology and its relation to fracture toughness data is underway. We have also investigated the rheology of these systems with the goal of developing a processing window for fiber reinforced composites. The rheology as well as the mechanical properties of the fiber reinforced systems will be discussed.

V6.14
FIELD-FLOW FRACTIONATION OF SINGLE-WALLED AND MULTI-WALLED CARBON NANOTUBES. John P. Selegue, Bailin Chen, Mark S. Meier, Zhongwen Wang, Department of Chemistry, University of Kentucky, Lexington, KY; Rodney Andrews, David Jacques, Center for Applied Energy Research; Robert C. Haddon, Mark A. Hamon, Hui Hu, Department of Chemistry, University of California, Riverside, CA.

Field-flow fractionation is used to determine the effects of chemical treatment on both single-walled and multi-walled carbon nanotubes. Optimization of FFF conditions (surfactant, membrane and normal vs. steric mode) as well as post-fractionation sample analysis will be discussed. FFF-derived size distributions are compared with Photon

Correlation Spectroscopy results. Both single-walled and multi-walled carbon nanotubes are substantially shortened by subjecting them to oxidants such as potassium permanganate in sulfuric acid.

V6.15

INTERFACIAL DISSOCIATION IN NANOGRAINED THIN FILMS.

D.L. Medlin, D. Cohen, and G. Lucadamo, Sandia National Laboratories, Livermore, CA; S.M. Foiles, Sandia National Laboratories, Albuquerque, NM.

It is well appreciated that the nature of grain boundaries and related topological defects is particularly important in nanophase materials because of the large volume fraction of material associated with these defects. In this presentation, we consider the grain boundary structural relaxations that occur in nanograin, [110]-textured Au films. Our HRTEM observations and atomistic simulations show that boundaries between 90 degree-related grains in this system dissociate to form a layer of material, approximately 1 nm wide, with close-packed planes arranged in the 9R stacking sequence (i.e., abc/bca/cab). Formation of this non-FCC layer can be understood by considering the distribution of Shockley partial dislocations that are intrinsic to the interface: separation of the pure-edge (90 degree) and mixed character (30 degree) dislocations, which are present in a ratio of 2:1, produces a stacking fault every third plane and a characteristic local plane bending. Analogous relaxations appear to be a common feature for other orientations as well. We discuss how the interfacial dislocation content and resulting fault distribution can be related to grain orientation, and compare this analysis to HRTEM observations of Au boundaries for different [110] rotations. This work is supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000 in part by the Office of Basic Energy Science, Division of Materials Science.

V6.16

ERBIUM LUMINESCENCE FROM SILICON DIOXIDE EMBEDDED WITH SILICON AND GERMANIUM NANOCRYSTALS.

Myo Thaik, Mengbing Huang, Dept. of Physics, Univ. at Albany-SUNY, NY.

Erbium doped silicon dioxide is an important material used for optical fiber amplifiers. In this work, we studied effects of semiconductor nanocrystals embedded in SiO₂ on the 1.5-um luminescence from Er. Si or Ge nanocrystals of 1-10 nm in size were first formed in SiO₂ via ion implantation followed by thermal annealing at 1000°C. Er atoms were then incorporated into the nanocrystal encapsulated SiO₂ by ion implantation. Following thermal annealing to activate Er optical centers, photoluminescence (PL) measurements using an argon laser was conducted to monitor light emission from Er and nanocrystals under various conditions (e.g. nanocrystal size and density). The 1.5-um luminescence from Er was enhanced by Si or Ge nanocrystals in SiO₂, suggesting efficient energy transfer from nanocrystals to Er atoms. The shape of nanocrystals was examined by transmission electron microscope (TEM) before and after Er incorporation into SiO₂, in order to understand different mechanisms for coupling of Er atoms and semiconductor nanocrystals. The different effects caused by Si and Ge nanocrystals on Er luminescence, are discussed in terms of difference in quantum confinement between Si and Ge nanostructures.

V6.17

Abstract Withdrawn.

V6.18

SYNTHESIS OF CoPt NANOPARTICLES IN Al₂O₃ AND SiO₂.
S.P. Withrow, C.W. White, J.D. Budai, L.A. Boatner, K.D. Sorge, J.R. Thompson, Oak Ridge National Laboratory, Oak Ridge, TN; R. Kalyanaraman, Agere Systems, Murray Hill, NJ and Oak Ridge National Laboratory, Oak Ridge, TN; A. Meldrum, The University of Alberta, Alberta, CANADA.

Ion implantation and thermal processing have been used to synthesize CoPt nanoparticles in crystalline Al₂O₃ and amorphous SiO₂ matrices. In Al₂O₃, the nanoparticles are produced using high-temperature (500°C) implantation of overlapping profiles of Co (360 keV) and Pt (910) ions. Subsequent thermal annealing in a reducing environment leads to precipitation and nanoparticle formation. The atomic fraction of Pt in the alloy [Pt/(Co Pt)] can be changed over a wide range by controlling the relative doses of implanted Co and Pt. For compositions near 50% Pt, annealing at 1100°C/2 h results in the creation of CoPt nanoparticles with the tetragonal L1₀ structure. These nanoparticles exhibit multiple orientations within the crystalline Al₂O₃ matrix, but they have a low order parameter and a very low magnetic coercivity. Additional annealing for 120 h at 700°C (below the order/disorder transition temperature of CoPt) greatly improves the coercivity to ~1 Tesla (at 5K). For samples with Pt atomic fractions near 75%, x-ray measurements suggest the cubic L1₂ CoPt₃ phase is formed. Implantation and annealing is also being used to form ferromagnetic

CoPt nanoparticles in SiO₂. For alloy compositions near 50% Pt, the nanoparticles have a coercivity in excess of 0.5 Tesla following room temperature implantation and extended annealing at 750°C. Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

V6.19

TEMPERATURE DEPENDENCE OF ELECTRORESISTIVITY,

NEGATIVE AND POSITIVE MAGNETORESISTIVITY OF CARBON NANOPARTICLES. Anatoly I. Romanenko, Olga B. Anikeeva, Alexander V. Okotrub, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; Vladimir L. Kuznetsov, Yuriy V. Butenko, Andrew L. Chuvilin, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA.

The result of measurements of electrical resistivity and magnetoresistivity of carbon nanoparticles with different graphitization degrees prepared by vacuum annealing of nanodiamond at various fixed temperatures are presented. Intermediate samples contain particles with a diamond core covered by closed curved graphitic shells (graphite/diamond nanocomposites). The temperature dependence of electrical resistivity of these structures was measured by the four-probe method in the range of temperature 4.2-500 K. The magnetoresistivity was measured in the field (H) range 0 - 5.5 T at temperature 4.5 K using a model MPMS-5 SQUID. The electrical resistivity is characteristic for the systems with localized electrons and variable hopping-length hopping conductivity. The magnetoresistivity is negative at the range of field 0 < H < 2 T, and is positive at H > 2 T. The conduction carrier concentration n for the samples was estimated in the framework of the theory of negative magnetoresistance in semiconductors in the hopping conduction region using the fitting parameters of magnetoresistivity. Really, the value n is 8*10²¹ cm⁻³ for a sample annealed at 1800 K in comparison to 3*10²¹ cm⁻³ for a sample annealed at 2140 K. The estimation of a length of free path l at temperature of liquid helium from the data on positive magnetoresistivity gives the value: l ~ 1.2 nm for a sample annealed at 1800 K and l ~ 1.8 nm for a sample annealed at 2140 K. Thus, on the basis of obtained data we may to draw a conclusion about presence special type of defects in our carbon nanoparticles which result in decrease of l and to increase of n.

The work was supported by the Russian scientific and technical program "Fullerenes and atomic clusters" (Projects No. 5-1-98), the Russian Foundation of Basic Research (Grant No. 00-02-17987) and the INTAS (Project Nos. 97-1700, 01-237).

V6.20

RECENT PROGRESS WITH NANOSCALE CHARACTERISATION OF MATERIALS USING 3-D ATOM PROBE TECHNIQUES.

George Smith, Alfred Cerezo, Terence Godfrey, Richard Hardwick, Min Huang, Paul Warren and Yuan Zhang, Dept. of Materials, Oxford University, Oxford, UNITED KINGDOM.

The experimental technique of three dimensional atom probe microanalysis is now advancing rapidly. This paper will summarise new developments in high-rate ion detection and identification; new instrument geometries for the study of surfaces and thin films on the atomic scale; and some new applications in nanostructure characterisation. Examples presented will include the observation of the primary crystallisation process in melt-spun amorphous aluminium - transition metal - rare earth alloys, and characterisation of the role of alloy elements in refining the nanoscale microstructure of ultra-high strength steels.

V6.21

HETEROGENEOUS OXIDATIVE DEHYDROGENATION OF ETHANE. Yee San Su, William H. Green, and Jackie Y. Ying, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Within the petrochemical industry, a sizeable economic incentive exists for the upgrading of low-value, small molecular weight alkanes. For instance, the dehydrogenation of ethane to ethylene is of considerable interest due to ethylenes use as a polymeric and chemical precursor. Traditionally, ethylene is produced via steam pyrolysis of ethane. Unfortunately, the endothermic nature of this approach requires reactor temperatures in excess of 800°C for favorable thermodynamics. Moreover, coke deposition on reactor walls requires periodic shutdowns. Partial oxidation provides an attractive alternative to standard pyrolysis methods for alkane to alkene conversion. In contrast to pyrolysis, partial oxidative routes are largely unaffected by coke formation. Moreover, they have the added benefit of being exothermic. With the inclusion of oxygen as a reactant, however, numerous additional reaction pathways exist. Among these, the presence of parallel and consecutive reaction channels to CO_x products are of major concern. For this reason, previous efforts to create selective partial oxidation catalysts with high activity have typically fallen below economic feasibility requirements. Recently, we

have synthesized highly homogenous, zirconia-based nano-composites via chemical precipitation and sol-gel methods for the oxidative dehydrogenation of ethane. Various techniques have been applied toward characterizing the role of the various catalyst components. Through careful selection of secondary phases, superior catalytic activity has been achieved with selectivities as high as 92%. Thus, this represents one of the first economically viable examples of heterogeneous oxidative dehydrogenation, providing for excellent yields of ethylene conversion via a non-energy-intensive route.

V6.22

ALIGNED CARBON NANOTUBES GROWN BY NICKEL, IRON AND COBALT. Zhongping Huang, Dezhi Wang, Jianguo Wen, Shaoxian Yang, Michael Sennetta, Heidi Gibson, and Zhifeng Ren, Dept of Physics, Boston College, Chestnut Hill, MA; Material Science Team, U.S. Army Soldier Biological & Chemical Command, Research, Natick Soldier Center, Natick, MA.

Pure nickel, cobalt and iron films on silicon were used to investigate the effect of different catalysts on aligned nanotube growth by plasma-enhanced hot filament chemical vapor deposition. The study shows that the catalyst has a strong effect on the diameter, length, and growth rate. Ni gives the highest growth rate and the biggest tube diameter, whereas Co yields the slowest growth rate and smallest diameter, and Fe is just in between. The mechanisms behind these are discussed.

V6.23

RAPID-SOLIDIFICATION EFFECT ON MAGNETOSTRICTION IN IRON-BASED FERROMAGNETIC SHAPE MEMORY ALLOYS. Yasubumi Furuya, Takeshi Kubota, Teiko Okazaki, Hirosaki Univ, Faculty of Science and Technology, Hirosaki, JAPAN.

Ferromagnetic shape memory alloy (FSMA) is recently known as a new type of magnetic-driven solid state actuator material which has large strain as well as a quick response by the mechanism of re-arrangement of martensite twins under changing external magnetic field. Rational material design of microstructures and grain/twin interfaces will be very essential for us to get more high performance FSMAs. In this study, rapid-solidification technique of melt-spinning method has been adopted to change the crystallographic microstructures of two FSMAs, i.e. Fe-Pd and Fe-Pt alloys. The thin foils of about 30-60 nm thickness was made by melt-spinning methods with single and twin rolls, and these samples have very fine columnar grains with strong textures. We have investigated the thermo-magneto-mechanical properties of these samples. As a result, it showed strong anisotropy and larger magnetostriction, = 600-800 x10⁻⁶ strain at perpendicular direction to its plate surface at room temperature. The strain vs. temperature, T curve had a maximum at 370K/400K, then decreased steeply with increasing T, which seems to correspond to the inverse transformation point of As Af of this alloy. In the case of Fe-Pt alloy, the magnetostrictive strain remarkably increases in the rapid-solidified foil samples by five to ten times in comparison with the conventional hot-worked bulk material with randomly oriented grains. These improvements as well as the mechanism of magnetostrictions of the tested two FSMA alloys are also discussed based on the features of X-ray diffraction and magnetization curves.

V6.24

Abstract Withdrawn.

V6.25

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE, CHIRAL CONDUCTING POLYMER NANOCOMPOSITES. Hsing-Lin Wang, Patrick A. McCarthy, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM.

We report the template-guided synthesis of water-soluble chiral conducting polymer nanocomposite. This synthetic route is facile and can easily be prepared in large scale. Synthesis of water-soluble polyaniline nanocomposite is achieved by carefully control the experimental parameters such as; acid concentration, ionic strength, monomer/template ratio, total reagent concentration, and order of reagent addition. Here, we show that a chiral polyaniline nanocomposite can be synthesized by incorporating a chiral inducing agent (chiral acid) prior to polymerization, and that the helicity can be controlled by the addition of the (+) or (-) form of the chiral acid. Further, we show that varying the chiral acid and salt content has a dramatic impact on the degree of chirality in these nanocomposites. TEM micrograph revealed the as-synthesized nanocomposite has a rice grain shape with 100 nm in size. After repeated doping and dedoping cycles, the chirality of the nanocomposite remains the same. This result suggests that the polyaniline conformation is robust, presumably stabilized by the presence of the template.

V6.26

NANOSCALE COMPOSITIONAL CHANGES ALONG FAST ION

TRACKS: A COMPUTER SIMULATION OF ULTRA-FAST SOLIDIFICATION AND THERMO-MIGRATION IN SOLID SOLUTIONS. E.M. Lopasso¹, A. Caro¹, E. Ogando², and M. Caro¹.

¹Centro Atomico Bariloche - Instituto Balseiro, Bariloche, ARGENTINA. ²Elektrika eta Elektronika Saila, Bilbo, SPAIN.

Using molecular dynamics of an Embedded Atom Model system we determine the role of both thermo-migration (Soret effect) and redistribution during solidification across liquidus-solidus lines in a thermal spike that follows the energy deposition induced by an irradiation with an energetic ion. These are two of the thermodynamic forces that may affect the mass transport under the extreme conditions of time, temperature and length scales characteristics of a heat spike following the interaction of an energetic ion beam with a solid. By studying first heat spikes in liquid alloys we are able to isolate the Soret effect and measure the magnitude of the heat of transport Q^* . We find that this effect can give rise to an increase or a decrease of solute content in the core of a spike. We show the particular case of the Au-Ni system (complete solubility in the high temperature solid and in the liquid phases) in which Ni as solute in Au has a tendency to move towards the hot core of the spike, while the opposite is true for Au as solute in Ni. This effect appears in a system whose initial condition before irradiation is the equilibrium thermodynamic phase predicted by the phase diagram of the model potential, and therefore no solute motion is expected as a consequence of the irradiation. We then study the heat spike on an initially solid sample; we analyze the combined effect of thermo-migration in the liquid as well as the redistribution of solute induced by crossing the two-phase field delimited by the liquidus and solidus lines. Depending upon the system under consideration and the energy density of the spike, thermo-migration and redistribution can reinforce or cancel each other, providing eventually an experimental mean to modulate the composition of a solid solution along a track.

V6.27

DEPOSITION OF ULTRA THIN FILMS ON NANOPARTICLES BY PLASMA POLYMERIZATION AND THEIR APPLICATIONS. Donglu Shi, Peng He, Wim van Ooij, Dept. of MS&E, University of Cincinnati, Cincinnati, OH; Lumin Wang and Shixin Wang, Dept. of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI.

The current trend of developing nanophase materials has motivated an increasing need for nanometer-scale structures in a variety of applications. To achieve unique mechanical, physical, chemical, and biomedical properties, it is necessary to develop novel synthesis routes by which an entirely new nanostructure can be developed. This presented work deals with the deposition of ultrathin films (1-2 nm) on nanoparticles by a plasma polymerization method. An ultrathin film of pyrrole was deposited on alumina nanoparticles using a plasma polymerization. High Resolution Transmission Electron Microscopy (HRTEM) experiments showed that an extremely thin film of the pyrrole layer (2 nm) was uniformly deposited on the surfaces of the nanoparticles. In particular, the particles of all sizes (10-150 nm) exhibited equally uniform ultrathin films indicating well-dispersed nanoparticles in the fluidized bed during the plasma treatment. Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) experiments confirmed the nano-surface deposition of the pyrrole films on the nanoparticles. Several novel applications involving surface coating of nanoparticles will be discussed including ion exchange in metal removal from water, pen display, and low-temperature consolidation.

V6.28

DIRECT SYNTHESIS OF METAL NANOPARTICLE DISPERSED IN MESOPOROUS SILICA FOR CATALYST APPLICATION. Edson R. Leite, N.L.V. Carreño, L.P.D. Santos, E. Longo, Department of Chemistry, Federal University of São Carlos-UFSCar, SP, BRAZIL; P.A. Paskocimas, Institute of Chemistry, UNESP, Araraquara, SP, BRAZIL; A. Valentini and L.F.D. Probst, LABOCATH, Department of Chemistry, UFSC, Florianópolis, SC, BRAZIL.

The development of metal nanoparticles holds a fundamental interest in catalysts for inorganic and organic chemical reactions. However, it is well known that the cluster agglomeration tendency increases as the particle size decreases. To avoid the particle agglomeration several approaches have been adopted. With the advent of the mesoporous molecular sieves new possibilities to stabilize metal nanoparticles have arisen. These nanostructured materials present a well-defined pore structure and high-surface area, which make them excellent supports for heterogeneous catalysis and other applications. Here we report a new synthesis process and catalytic characterization of Nickel (Ni), Platinum (Pt) and Palladium (Pd) nanoparticles dispersed in SiO₂ mesoporous materials where the mesoporous support and particle were prepared simultaneously in a direct process. The general idea consists in processing a mesoporous amorphous SiO₂ matrix with metal nanoparticles well dispersed in this matrix in a direct process

without hydrogen atmosphere during the heat treatment. Mesoporous silica with narrow porous size distribution and high surface area with metal nanoparticles (particles in the range of 3-41 nm) were obtained in a direct process at low pyrolysis temperature ($T < 600^{\circ}\text{C}$). Preliminary results showed that the nanocomposite materials present excellent potential for catalytic application, including methanol and methane oxidation for hydrogen generation.

V6.29

SYNTHESIS AND CHARACTERIZATION OF METALLIC NANOWIRES. Yugang Sun, Younan Xia, Dept. of Chemistry, University of Washington, Seattle, WA.

We have demonstrated a solution-phase approach to the large-scale synthesis of metallic nanowires that had lateral dimensions between 30-100 nm, and lengths up to hundreds of micrometers. In a typical process, metal salts were reduced with a mild reducing agent with the presence of an appropriate amount of surfactant molecules. The surfactant could control the growth of these metal nanostructures into nanowires along a preferential crystalline orientation. A number of metals have been tested, including Au, Ag, and Pd. In this presentation, we will discuss the growth mechanism, as well as the electrochemical properties of these metallic nanowires.

V6.30

HYDROGENATION OF AMORPHOUS AND NANOSTRUCTURED MULTICOMPONENT Zr-BASED ALLOYS WITH HIGH GLASS-FORMING ABILITY. Ulrike Wolff, Nahla Ismail, Margitta Uhlemann, Jürgen Eckert, Annett Gebert, IFW Dresden, Institute for Metallic Materials, Dresden, GERMANY.

Zr-(Ti)-Cu-Al-Ni metallic glasses exhibit a high thermal stability corresponding to a wide undercooled liquid region before the crystallisation of multiple intermetallic equilibrium phases. Depending on their composition, the formation of metastable intermediate phases, such as a quasicrystalline phase is possible[1]. These alloys consist of a combination of early and late transition metals (ETML/LTM) which makes them very interesting regarding their interaction with hydrogen.

Amorphous ribbons of the compositions $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$, $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ and $\text{Zr}_{59}\text{Ti}_3\text{Cu}_{20}\text{Al}_{10}\text{Ni}_8$ were prepared by melt spinning in an argon atmosphere. The microstructure was checked by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and the thermal behavior was studied by differential scanning calorimetry (DSC) at a constant heating rate. The cathodic reactivity in 0.1 M NaOH of alloy samples at different microstructural states and after pre-etching in 0.1% HF was investigated applying potentiodynamic polarisation techniques at different scan-rates. Hydrogen-charging was performed galvanostatically at $i = -1 \dots 20 \text{ mA/cm}^2$. Hydrogenated samples were characterized by XRD, DSC, TEM and thermal desorption analysis (TDA).

Electrochemical measurements on amorphous $\text{Zr}_{59}\text{Ti}_3\text{Cu}_{20}\text{Al}_{10}\text{Ni}_8$ samples revealed an increase in capacity by two orders of magnitude after pre-etching which mainly results from the removal of air-formed surface oxides. Furthermore, compared to the corresponding crystalline alloy counterpart, the cathodic hydrogen reduction takes place at significantly lower overpotentials.

At room temperature, the Zr-based alloys can absorb hydrogen up to $\text{H}/\text{M} = 1.65$ while keeping the amorphous structure. Already small amounts of hydrogen cause a significant decrease of the thermal stability, i.e. a reduction of the supercooled liquid region, and a complete change in the crystallisation sequence. They hydrogen desorption, investigated by TDA measurements, is a two-stage process: 1, ($< 623 \text{ K}$) hydrogen desorption from high interstitial-site energy levels and 2, ($> 623 \text{ K}$) zirconium hydride formation and subsequent transformation under effusion of hydrogen[2]. Hydrogen was found to suppress the oxygen-triggered formation of metastable quasicrystalline phases upon heating and to support a primary copper segregation. At very high H/M ratios, severe zirconium hydride formation causes an enrichment of Cu, Ni and Al in the residual amorphous phase resulting in the crystallisation of new stable intermetallic compounds[3].

[1] J. Eckert, N. Mattern, M. Zinkevitch, M. Seidel, Crystallization Behaviour and Phase Formation in Zr-Al-Cu-Ni Metallic Glass Containing Oxygen. Mater. Trans. JIM 1998; 39 (6): 623-632.

[2] N. Ismail, M. Uhlemann, A. Gebert, J. Eckert, Hydrogenation and Its Effect on the Crystallisation Behaviour of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ Metallic Glass. J. Alloys Comp. 2000; 298: 146-152.

[3] N. Ismail, A. Gebert, M. Uhlemann, J. Eckert, L. Schultz, Effect of Hydrogen on $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ Metallic Glass. J. Alloys Comp. 2001; 314: 170-176.

V6.31

SYNTHESIS OF NANOSIZED LITHIUM MANGANATE FOR LITHIUM-ION SECONDARY BATTERIES. Chung-Hsin Lu, Hsien-Cheng Wang, Yueh Lin and Ming-Chang Wen, Department of Chemical Engineering, National Taiwan Univ, Taipei, TAIWAN ROC.

Nowadays, the demand for rechargeable batteries with high energy density and high voltage has increased rapidly due to the advancement and popularity of portable electronic devices. Lithium manganese oxide (LiMn_2O_4) is a promising cathode material for lithium ion batteries, because of its low cost and lower toxicity compared with the layered oxides LiCoO_2 and LiNiO_2 . For the consideration of practical application, it is important to produce LiMn_2O_4 powders with excellent capacity and cyclability. The electrochemical properties of LiMn_2O_4 strongly depend on its synthesis process. In order to reduce the particle size and control the morphology of LiMn_2O_4 powders, a new microemulsion process has been developed in this study. Transparent and thermodynamic stable microemulsion has been obtained by mixing the oil phase, water phase, and surfactants with proper volume ratio. The microemulsion with different concentration in aqueous phase have been prepared. The spinel LiMn_2O_4 powders with nano-sized, well-dispersed, and phase-pure powders were successfully prepared at low temperatures. The effects of the concentration in aqueous phase on the microstructure and electrochemical properties of LiMn_2O_4 powders were studied. The particle size of LiMn_2O_4 powders were found to play an important role in determining the electrochemical properties. The high-temperature performance of the LiMn_2O_4 powders prepared by the microemulsion process were also investigated in this study.

V6.32

DISTRIBUTION OF SILVER NANOPARTICLES EMBEDDED IN SiO_2 THIN FILMS: THE ROLE OF AGEING. Luisa D'Urso, Giuseppe Compagnini, Orazio Puglisi, Catania Univ, Dept of Chemical Science, Catania, ITALY.

Silver nanoparticles (10-20 nm) embedded into silica-like thin films were prepared in one step by a chemical route. Nanostructured thin films with thickness of 500-600 nm were prepared on glass and silicon substrates by spin coating of a spin-on-glass solution containing silver metallorganic molecules ($\text{Ag}(\text{hfa})$ tetraglyme), followed by thermal annealing at temperatures above 400°C . A spectroscopic (IR absorption and Raman spectroscopy) and microscopic (Atomic Force Microscopy), investigation of the obtained thin films gives a way to control the particle distribution inside the films as function of the ageing and annealing treatment. In particular the distribution of silver clusters into the silica matrix was observed to depend on the time elapsed between the thin film deposition and the annealing treatment.

V6.33

NANOSTRUCTURED MATERIALS BASED ON ORGANIC-INORGANIC HYBRIDS (II) -SYNTHESIS OF ZERO- AND ONE-DIMENSIONAL NANOMATERIALS IN ORGANIC-INORGANIC SYSTEMS. Yuko Tabuchi, Masahiro Rikukawa, Kohei Sanui, Sophia Univ, Dept of Chemistry, Tokyo, JAPAN; Keisuke Asai, Univ of Tokyo, Graduate School of Engineering, Tokyo, JAPAN.

Organic-inorganic perovskite-type materials have been known to self-organize into low-dimensional quantum confinement structures. Generally, organic-inorganic perovskites comprised of alkylamines and lead halides naturally form two-dimensional structure. The inorganic semiconductor part comprised of $[\text{PbX}_6]^{4-}$ octahedral is located at the body center, while the organic ammonium ions $[\text{RNH}_3]^+$ reside the eight corner of the cube being shared by eight unit cells. The dimension of the inorganic part can be easily controlled by changing the size or shape of organic amines. Thus, PbX-based perovskite compounds have enormous variety, which may be inherent to these materials. In this study, we attempt to fabricate low-dimensional quantum confinement structures using cyclic amines as the organic parts. The optical properties afforded by the quantum confinement structures are also investigated.

V6.34

TEM STUDIES OF COARSENING AND REDISPERSION OF NANOSIZE PLATINUM AND PALLADIUM PARTICLES. Jitendra Kumar, Indian Institute of Technology, Materials Science Programme, Kanpur, INDIA; Rakesh Saxena, Oil and Natural Gas Commission, Panvel, Mumbai, INDIA.

Platinum and palladium nanosize particles (diameters 4-12nm) dispersed over carbon and alumina support films have been studied by transmission electron microscopy and diffraction with regard to coarsening, redispersion and cause(s) for deterioration of their catalytic properties on prolonged usage in oxidising and reducing atmospheres at elevated temperatures. It is shown that, for platinum, coarsening of nanosize particles occurs in both air and hydrogen ambient. Also, it is accompanied by the formation of a number of oxides, e.g., PtO , (PtO_2) and (Pt_3O_4) , in air and a new cubic hydride phase (composition (Pt_3H_4) and lattice parameter $a = 0.310 \text{ nm}$) in hydrogen. On the other hand, in palladium system, while coarsening takes place in hydrogen following emergence of $(\text{PdH}_x \text{ (} x < 1))$, exhibiting a NaCl-type structure with $a = 0.401 \text{ nm}$, and (Pd_3H_4)

simple cubic phase with $a=0.299\text{nm}$, redispersion is observed in air through the formation of PdO (tetragonal $a=0.303\text{nm}$, $c=0.532\text{nm}$). Also, evidence is advanced for the Ostwald ripening mechanism to be operative, rather than particle migration and subsequent coalescence on collision (i.e., sintering process), for growth of particles. It is further demonstrated that the deactivation of supported platinum and palladium catalysts is determined not just by coarsening of nanosize particles but also by their reactions with the prevailing atmosphere during usage, i.e., reactive coarsening/redispersion. Finally, it is shown that the supported metal catalysts can be rejuvenated by treatment in hydrogen and oxygen if the deactivation is caused by oxidising atmosphere (through oxide formation) and reducing ambient (via pronounced coarsening and hydride formation), respectively.

V6.35

CATALYST DISPERSION TECHNOLOGY USING A PARTIAL REDUCTION REACTION. Seichi Suenaga, Miho Maruyama, Takayuki Fukasawa, Yasuhiro Goto, Toshiba Corporation, Corporate Research & Development Center, Kawasaki, JAPAN.

A new catalyst dispersion technology is proposed. Ni/(Ni,Mg)O composite was produced by partial reduction of a (Ni,Mg)O solid solution. Ni nanoparticles, whose diameters ranged from 10 nm to 100 nm, were segregated over the (Ni,Mg)O surface. Ni particle size was uniform and increased with increasing Ni content of the solid solution. The performance of these Ni/(Ni,Mg)O composites as catalyst for two types of reaction was investigated. First the methane reforming reaction of carbon dioxide was studied. A porous body of the Ni/(Ni,Mg)O composite was applied as a methane reforming catalyst system. The experimental process was as follows; first, the (Ni,Mg)O porous body, prepared by reaction sintering, was partially reduced so as to segregate the Ni nanoparticles over the inner surface. During the reforming experiment, the rate of methane conversion was constant and coking of the catalyst insignificant, particularly for the low Ni composition sample. In addition, the morphology of porous body was maintained after the reforming experiment. Secondly, the effect on carbon nanofiber synthesis was investigated. Carbon nanofibers, with diameters 10 nm to 100 nm, were grown over the surface of the Ni/(Ni,Mg)O from the catalytic decomposition of methane. The diameter of the nanofibers was found to be proportional to the diameter of the catalyst particles. Using a high Ni composition sample, fine, straight carbon nanofibers were observed over the solid solution surface. These nanofibers were not grown on the Ni particles, but on the (Ni,Mg)O solid solution surface. Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

V6.36

PREPARATION AND CHARACTERIZATION OF NANOSCALE CRYSTALLINE OPTICAL MATERIALS. BaoPing Wang, L.L. Isaacs, CCNY and CUNY Graduate Ctr, Dept of Chemical Engr; A.B. Bykov, R.R. Alfano, Dept of Physics, New York, NY.

Optical composites can be constructed by combining mono-dispersed nano-sized particles of Cr (IV) doped olivines (forsterite or cunyite) with a glass (inorganic or polymeric) matrix. They have the potential to provide amplification, for multi-thousand-channel wavelength division multiplexing (WDM) systems, in the near infrared spectral range of 1100-1600 nm. The sol-gel technique was used to produce sub-micron and micron-sized particles of the olivines. Scanning electron microscopy indicated a broad particle size distribution and an agglomeration tendency of the sub-micron particles from the sol-gel process. Several techniques are under investigation to narrow both the size distribution and to overcome the agglomeration problem.

V6.37

VISIBLE CATHODOLUMINESCENCE FROM MECHANICALLY MILLED GERMANIUM. E. Nogales, Dept. Física de Materiales, Facultad de Físicas, Univ. Complutense, Madrid, SPAIN; A. Montone, F. Cardellini, ENEA-INN-NUMA, CR. Casaccia, Roma, ITALY; B. Méndez, J. Piqueras, Dpt. Física de Materiales, Facultad de Físicas, Univ. Complutense, Madrid, SPAIN.

Mechanical milling has been extensively used to prepare nanocrystalline and small particle size metallic materials. To a lesser extent the method has been applied to some semiconductors as Si and Ge and some properties of the milled materials have been explained by the presence of nanocrystals. In this work the luminescence of ball milled germanium has been investigated by cathodoluminescence in the scanning electron microscope. The samples investigated were Ge powder, Ge wafer and GeO₂ powder. The untreated Ge powder shows a luminescence band centered at about 2.48 eV, at 90 K, which is also observed in untreated GeO₂. The same band is observed in the Ge wafer material after milling. This emission of Ge is attributed to the presence of oxides in the powder. After high energy ball milling the luminescence band of GeO₂ at 90 K appears at 2.25 eV while in the Ge powder the milling causes the appearance of a band peaked at

about 3.1 eV. Other authors have reported luminescence at this energy for samples containing Ge nanocrystals in an oxide matrix. The relationship of the observed visible luminescence of milled Ge and the structure of the samples is studied by XRD and TEM.

V6.38

COHESION IN STRUCTURAL INTERMETALLICS: A SYSTEMATIC MULTISCALE STUDY OF ADDITIVE EFFECTS. B.R. Cooper, D. Djajaputra, Dept. of Physics, West Virginia University, Morgantown, WV.

The presence of atomic impurities in intermetallic alloys, e.g. transition metal aluminides such as NiAl, induces a wide range of consequences to its cohesion. Some impurity atoms, e.g. boron, act as a cohesion enhancer which can improve the cohesion substantially; while some other atoms, e.g. oxygen, can destroy the cohesion, even when present in minute concentration. Due to its efficiency, the tight-binding method is a method of choice for studying systematically the effects of atomic impurities on the alloy cohesion. The challenge is to obtain tight-binding parameters that can have comparable accuracy to ab-initio methods. We have developed a method to extract accurate tight-binding parameters directly from a full-potential linear muffin-tin orbital (FP-LMTO) method. These parameters have been used as input to a local Green's function (recursion) calculation. Using this combined method, we systematically study the effects of atomic additives from boron to oxygen.

V6.39

CERIUM DIOXIDE NANOPARTICLES: SIZE-SELECTIVE FORMATION AND STRUCTURE ANALYSIS. Feng Zhang, Siu-Wai Chan, Jonathan E. Spanier, Ebru Apak, Qiang Jin, Richard D. Robinson, Irving P. Herman, Department of Applied Physics and Applied Mathematics and Materials Research Science and Engineering Center, Columbia University, New York, NY.

Nanoparticles of cerium oxide with a narrow size distribution ($\pm 15\%$) are prepared by mixing cerium nitrate solution with an ammonium reagent. High resolution transmission electron microscopy (TEM) indicates that over 99% of the synthesized particles are single crystals without boundaries. Light absorption and TEM are used to monitor particle size. Peaks from X-ray diffraction are broadened by particle-size effect. The systematic shift of the peaks to lower angles indicates that the lattice parameter increases with decreasing particle-size up to 0.45% at 6 nm. Raman scattering shows the shifting and the asymmetric broadening of the Raman peak at 464cm^{-1} with decreasing particle size. These Raman results are in agreement with the phonon confinement effect and the concomitant increased lattice expansion associated with decreasing particle-size. The lattice expansion is associated with surface effects and/or increased concentrations of oxygen vacancies and cerium (III) ions with decreasing particle-size.

SESSION V7: APPLICATIONS AND PROPERTIES I

Chair: Richard A. Vaia
Wednesday Morning, November 28, 2001
Back Bay C (Sheraton)

8:30 AM *V7.1

INORGANIC NANORODS: SYNTHESIS, PROPERTIES, APPLICATIONS. Paul Alivisatos, Univ of California, Berkeley, Dept of Chemistry, Berkeley, CA.

Inorganic nanocrystals with well-defined shapes are important for understanding basic size-dependent scaling laws, and may be useful in a wide range of applications. Methods for controlling the shapes of inorganic nanocrystals are evolving rapidly. This talk will focus on a strategy that involves pyrolysis of organometallic precursors in mixtures of hot organic surfactants. The surfactant mixtures can be used to control the growth rates of different facets of the nanocrystals, allowing for wide tunability of shape. This will be illustrated with CdSe and Co nanocrystals. Both of these materials show pronounced variation of fundamental properties with aspect ratio. The nanorods can be aligned in a variety of ways. For instance, monolayers of surfactant coated rod-like nanocrystals of these materials display a very rich phase diagram, analogous to the phases of liquid crystals. Block copolymers can be used to orient the rods. Finally, very special inorganic structures, tetrapods consisting of four rods at the tetrahedral angle, will always spontaneously align perpendicular to a surface. The possible application of these aligned nanorods in biological detection, photovoltaics, and light-emitting diodes will be described briefly.

9:00 AM V7.2

TIN-OXIDE BASED NANOCOMPOSITES FOR GAS SENSOR APPLICATIONS. Justin T. McCue, Jackie Y. Ying, Department of

Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

The use of gas sensors for detecting chemical species is important for numerous industrial and consumer processes. Dramatic improvements in industrial process control have been made with the aid of gas sensors. With increasing use of automation, the market size for gas sensors is expected to increase significantly over the next few years. Conventional gas sensors are limited by poor long-term stability, response reproducibility, gas selectivity and response time. The development of highly selective and thermally stable semiconductor oxide gas sensors is the focus of our research. Novel tin oxide-based semiconductor nanocomposites have been designed and synthesized via wet-chemical approaches. These new sensor materials display superb thermal stability and sensitivity to ppm levels of CO and NO_x. By controlling the nanocomposite microstructure and composition, and by introducing active dopants, sensors with excellent selectivity for CO and NO_x have been successfully attained and optimized.

9:15 AM V7.3

Abstract Withdrawn.

9:30 AM V7.4

ADVANCES IN THE FIELD OF GRAPHITE NANOFIBERS: PAST, PRESENT, AND FUTURE. Paul E. Anderson, Terry K. Baker, and Nelly M. Rodriguez, Catalytic Materials, Holliston, MA.

There is currently a concerted effort to control the chemical, physical, and morphological aspects of nanostructured carbon materials. Since the mid 1980s, countless studies have dealt with the creation, purification, and tailoring of these materials. In retrospect, as early as 1953 and through the 1970s, fuel and catalytic chemists were performing the first experiments investigating carbon deposition. These studies were designed to further understand the detrimental process of carbon deposition in brick linings of blast furnaces and on metal catalyst surfaces. With the advent of controlled atmosphere electron microscopy (CAEM), investigators were able to directly observe the formation of graphite nanostructures in real time and a comprehensive mechanism was put forth that involved decomposition of the carbon-containing gas on the catalyst, diffusion of carbon through the metal particle, and precipitation of graphite and/or other types of carbon. More recent investigations using high resolution transmission electron microscopy and other pertinent techniques showed the chemical and physical properties of graphite nanofibers (GNF) to be extremely sensitive to reaction conditions such as temperature, catalyst composition, flow rates of gases, and feed gas components. By tailoring the reaction conditions, one can now obtain large amounts of pure GNF species falling into such morphological categories as 'platelet', 'tubular', 'herringbone', or 'ribbon'. This talk revisits the mechanism of nanofiber growth central to the creation of these unique nanostructures and presents some pertinent refinements and findings which helps to provide an insight into the extraordinary performance of GNF in a number of vastly different applications. Additionally, real-time videos of nanotube-like and GNF growth from CAEM studies will be shown, and a comprehensive characterization and nomenclature system to aid in the cataloging of the structures will be presented.

10:15 AM V7.5

NANOSTRUCTURED HYDROXYAPATITE COATINGS FOR IMPROVED ADHESION AND CORROSION RESISTANCE FOR MEDICAL IMPLANTS. Zongtao Zhang, Matthew F. Dunn and T.D. Xiao, Inframat Corporation Antoni P. Tomsia and E. Saiz, Lawrence Berkeley National Laboratory.

Hydroxyapatite, coatings on medical implants have been used in commercial applications for several decades. The coating, currently made by thermal spray method, functions as an intermediate layer between human tissues and the metal implant. The coating can speed up early stage healing after an operation, but the life-span is limited by low interfacial bond strength, which comes from the dissolution of amorphous HA in human body fluid during its service. This amorphous phase is formed in a coating process under high temperature. To overcome these problems, Inframat has developed a novel room temperature electrophoretic deposition process to fabricate nanostructured HA coating. This nanostructured HA coating significantly improved bond strength up to 50-60 MPa, 2-3 times better than the thermal sprayed HA coating. The nanostructured HA coating also has corrosion resistance 50-100 times higher than the conventional HA coating. X-ray diffraction shows that all the HA coating is fully crystallized. It is expected that the implants with the nanostructured HA coating will have much longer service life. Other benefits derived from this process include room temperature deposition, the ability to control the coating microstructure, and low cost for production.

Acknowledgement: This project is supported by National Institute of Health, Contract No.1R43AR47278-01.

10:30 AM V7.6

NANOSTRUCTURED ELECTRODE MATERIALS FOR HIGH PERFORMANCE RECHARGABLE ENERGY STORAGE DEVICES. Amit Singhal, Ganesh Skandan, Nanopowder Enterprises Inc., Piscataway, NJ; Glenn Amatuucci, Telcordia Technologies, Red Bank, NJ.

Small rechargeable energy storage devices are being used in increasing number to power portable equipment such as, power tools, uninterruptible power supplies (UPS), computers, camcorders and wireless communication devices, and hybrid electric vehicles. There is an immediate need for rechargeable Li-ion batteries with high energy density (~250 Wh/kg) and hybrid devices with fast rate capabilities (charge and discharge in less than 6 minutes) for a variety of applications. Nanostructured materials for both cathode and anode will lead to significant enhancement in energy density and rate capabilities of energy storage devices. Vapor phase processes were used to synthesize nanopowders of V₂O₅, Sn-based alloys, and TiO₂. TiO₂ was the precursor used for producing nanostructured particles of Li₄Ti₅O₁₂. Li_xV₂O₅ and Sn-based alloys are candidate cathode and anode materials, respectively, in Li-ion batteries. Li₄Ti₅O₁₂ is an anode material for an asymmetric hybrid device. The Combustion Flame-Chemical Vapor Condensation (CF-CVC) process was used to synthesize V₂O₅ nanostructured powders with a metastable structure. These powders have 30% higher retention capacity than their coarse-grained counterparts, for the same number of cycles. The retention capacity of Sn-base alloys is increased significantly on partially oxidizing nanoparticles of these alloys. Unlike macrocrystalline powders, nanocrystalline Li₄Ti₅O₁₂ showed exceptional retention capacity at high enough discharge rates in Li/Li₄Ti₅O₁₂ cells. Structural and electrochemical characterization results are presented in this paper.

10:45 AM V7.7

CHARACTERIZATION OF SELF-ASSEMBLED LAYERS OF SnO₂ NANOPARTICLES FOR FABRICATION OF A HIGH SELECTIVITY MICRO-GAS SENSOR. R.C. Ghan, Y. Lvov, R.S. Besser, Institute for Micromanufacturing and Department of Chemical Engineering, Louisiana Tech University, Ruston, LA.

This paper deals with the novel growth of SnO₂ nanoparticle layers using the technique of layer-by-layer self-assembly. We are currently investigating the self-assembly of SnO₂ nanoparticles on various substrates, its characterization issues and its future application as a sensing element for gas sensing applications as well as supramolecular structures of alternately assembled SiO₂ and SnO₂ nanoparticles. Moreover, we believe this is the first report of SnO₂ layers grown by the layer-by-layer self-assembly technique. We have successfully grown layers of SnO₂ nanoparticles of size 10-15 nm on QCM (Quartz crystal microbalance) resonator using self-assembly technique. Alternate layers of SnO₂ and SiO₂ nanoparticles were deposited using the same technique thereby achieving a variety of nanocomposite supramolecular structures, which we believe will assist in improving the selectivity of our proposed sensor. The self-assembly technique is a method of organization of ultra-thin films by layer-by-layer (interlayer) electrostatic attraction. The thickness and mass of the self assembled layers can be characterized using the Quartz crystal microbalance, which works on the principle of detecting the change in the frequency of the quartz crystal resonator after nanolayers are deposited on it. The change in frequency is related by empirical equations, to the mass and thickness of the deposited films. The SnO₂ nanolayers deposited reported a self-terminating behavior and the process was found to be independent of time of immersion in the SnO₂ colloidal nanoparticle solution. The next phase of our project is to characterize the electrical behavior and details of the film nanostructure which we plan to include in the conference presentation. This data will be useful in fabricating a high-selectivity micro-gas sensor for detecting carbon monoxide.

11:00 AM V7.8

FLUORESCENCE FROM COATED OXIDE NANOPARTICLES. D. Vollath, D.V. Szabo, Forschungszentrum Karlsruhe, Institut fuer Materialforschung III, Karlsruhe, GERMANY.

In many cases, coated nanoparticles behave like isolated ones. Using the microwave plasma process it is possible to produce oxide nanoparticles with ceramic or polymer coating. Coating the particles has the additional advantage that, by proper selection of the coating, it is possible to suspend the particles in distilled water without using any colloid stabilizer. From quantum dots made of GaAs or CdSe, it is well known from literature that fluorescence depends strongly on the coating of the kernels. In the case of CdSe, the kernels are coated with CdS. Within this study, similar phenomena are found with coated oxide nanoparticles having sizes of ca. 6 nm in a very narrow particle size distribution. The coating consisted of a second ceramic phase or a polymer. Both influence fluorescence in a different way. Obviously, the

type of coating is a tool to modify fluorescence. This behavior is demonstrated on kernels consisting of Al_2O_3 , ZrO_2 , HfO_2 , ZnO etc. The coating consisted of PMMA, Teflon, or Al_2O_3 . In most cases, the fluorescence consisted of broad bands. In some cases, such as ZnO , additionally, a sharp emission line in the UV appears. It is interesting to note that coatings made of Fluor containing polymers quenched any fluorescence. In the case of the broad emission bands, the decay time constant is in the range of 45 μs , whereas for the isolated lines in the uv-range a decay time constant of ca. 50 μs was determined. The observed spectra are equivalent whether the powder is in aqueous suspensions or dry on a quartz glass carrier.

11:15 AM V7.9

NANOCOMPOSITE ELECTRODES FOR ADVANCED LITHIUM BATTERIES. Shoufeng Yang, Yanning Song, Peter Y. Zavalij, M. Stanley Whittingham, Chemistry Dept. and Institute for Materials Research, SUNY at Binghamton, Binghamton, NY.

Advanced lithium batteries for energy storage are in need of improved electrodes. The present anodes use lithium graphite intercalation compounds, which are unsafe in larger sizes, and so several tin based compounds are under investigation. Such compounds include Sn_2Mn and SnBi_y . Both have large initial capacities, but on cycling, phase separation occurs forming a nanocomposite. So long as this nanocomposite structure can be maintained, the electrochemical capacity is maintained. However, the tin phase has a tendency to grow in size on continued cycling resulting in loss of capacity. On the cathode side, LiFePO_4 /carbon composites show the most promise. This cathode can preferentially be formed by a solvothermal reaction, with the coke coating added. Capacities in excess of 140 Ah/Kg have been obtained at 0.2 mA/cm².

This research is being supported by the BATT program of DOE.

11:30 AM V7.10

CONJUGATION OF LUMINESCENT QUANTUM DOTS WITH ANTIBODIES USING AN ENGINEERED ADAPTOR PROTEIN: NOVEL REAGENTS FOR FLUOROIMMUNOASSAYS.

Ellen R. Goldman, George P. Anderson, Phan T. Tran, Hedi Mattoussi, and J. Matthew Mauro; U.S. Naval Research Laboratory, Center for Bio/Molecular Science and Engineering and Division of Optical Sciences, Washington, DC.

We describe the preparation and characterization of bioinorganic conjugates made of highly luminescent semiconductor nanocrystals (CdSe-ZnS core-shell quantum dots, QDs) bound to antibodies and their use in fluoroimmunoassays. The conjugation strategy employs an engineered molecular adaptor protein, attached to the QDs via electrostatic/hydrophobic self-assembly, to link the inorganic QDs with antibodies. In this method, the number of antibodies conjugated to a single luminescent nanocrystal can be varied. In addition, we have developed a simple purification strategy based on mixed composition conjugates of the molecular adaptor and a second two-domain inert protein, which allows the use of affinity chromatography to purify the QD-antibody conjugates. We will show that the prepared QD-antibody conjugates can be successfully used in fluoroimmunoassays for detection of low levels of a protein toxin (staphylococcal enterotoxin B) and a small molecule analyte (2,4,6-trinitrotoluene). We will also explore the use of QD-antibody conjugates in schemes for multi-analyte detection.

11:45 AM V7.11

MAGNETISM OF DIPOLAR NANOCOMPOSITES.

James E. Martin, Eugene Venturini, Sandia National Laboratories, Albuquerque, NM.

We have investigated the magnetism of Dipolar Nanocomposites consisting of field-structured superparamagnetic nanoparticles in a solid matrix. These nanocomposites are of two types: magnetic nanoparticles structured into chains by aligning the dipoles with a uniaxial field ("positive" dipole interactions); and magnetic nanoparticles structured into sheets by applying an audio frequency rotating field ("negative" dipole interactions). Particles in these configurations have dipolar interactions that tend to add, creating extremely large local fields not found in random particle composites. The strong collective interactions cause large enhancements in the magnetic susceptibility along the chains and in the plane of the sheets, and a susceptibility reduction along the orthogonal axes. The blocking temperature of these field-structured nanocomposites is anisotropic as well. These experimental observations are shown to be in good agreement with Brownian dynamics simulations, and the susceptibility anisotropy is shown to be stronger than that observed in field-structured composites of micron-size, soft magnetic particles.

SESSION V8: APPLICATIONS AND PROPERTIES II

Chair: John C. Parker

Wednesday Afternoon, November 28, 2001

Back Bay C (Sheraton)

1:30 PM *V8.1

NANOCOMPOSITE COATINGS AND CATALYSTS APPLICATIONS AND PROPERTIES. Roger H. Cayton, M. L. Kullberg, Dan Coy, and R.W. Brotzman, Jr., Nanophase Technologies Corporation, Romeoville, IL.

Nanometer size materials produced by gas phase condensation have novel characteristics including chemical reactivity, composition, morphology, and processing advantages. These materials are commercially available and have been engineered for several nanocomposite applications including transparent coatings and catalysts.

The structure of nanocomposites is important because often multiple physical properties are desired, i.e., electrical conductivity or abrasion resistance with transparency. In effect, the composite structure is selected for the desired physical property from uniform surface distribution of nanoparticles for abrasion resistance to connected nanoparticle structures for electrical conductivity.

Dense, crystalline nanoparticles have been formulated into organic materials and processed to form transparent coatings. Particle size, material composition, and surface treatments are manipulated to control composite properties and structure. The nanoparticles provide beneficial properties for wear and scratch resistant coatings, thermal spray coatings, radiation absorbing coatings, tailored refractive index coatings, and conductive coatings. The unique functional properties of the resultant coatings will be discussed.

Unique nanocrystalline oxygen-storage catalyst compositions and morphologies have been developed. Oxygen-storage capacity characterizes the ability of a material to facilitate oxidation reactions. The application and properties of these materials will be detailed.

2:00 PM V8.2

ULTRAVIOLET ZnO NANOWIRE NANOLASER. Haoquan Yan, Peidong Yang, Dept of Chemistry, UC Berkeley, Berkeley, CA.

ZnO nanowires were successfully synthesized by a simple vapor transport and condensation process. Based on the growth mechanism, the control of position, orientation and diameter was achieved. Room temperature ultraviolet lasing behavior has been demonstrated in these single crystalline ZnO nanowires. Grown in a preferred direction $\langle 0001 \rangle$, these wide band-gap semiconductor nanowires form natural resonance cavities with diameters varying from 20 to 150 nm and lengths up to 40 μm . Under optical excitation, surface-emitting lasing action was observed at a near-UV wavelength of 385 nm with emission line width < 0.3 nm. These room temperature UV nanolasers can be used for high-density information storage and microanalysis.

2:15 PM V8.3

VANADIUM OXIDE NANOTUBES: CHARACTERIZATION AND ELECTROCHEMICAL BEHAVIOR. Arthur Doble, Katana Ngala, Shoufeng Yang, Samuel T. Lutta, Peter Y. Zavalij, and M. Stanley Whittingham Chemistry Dept. and Institute for Materials Research, SUNY at Binghamton, Binghamton, NY.

The mechanism of vanadium oxide nanotube formation has been studied and their stability and reactivity have been ascertained. Organic free manganese vanadium oxide tubes have been synthesized. These tubes of manganese intercalated vanadium oxide have been synthesized by a hydrothermal process followed by ion exchange. The tubes, consisting of $\text{Mn}_{0.8}\text{V}_7\text{O}_{16} \cdot n\text{H}_2\text{O}$, have a tetragonal unit cell with $a=6.157$ (3) \AA and $c=10.52$ (3) \AA . These nanocomposites readily incorporate lithium ions into their structure, which makes them interesting candidates as cathode materials in lithium batteries. The compound intercalated 3.4 lithium ions per molecular formula, and exhibited a capacity of 139 Ah/Kg when cycled in a lithium cell. Characterization of the manganese intercalated vanadium oxide nanotubes has been done with X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy, electron microprobe, thermogravimetric analysis, and electrochemistry. This work was supported by NSF grant DMR9810198.

3:00 PM *V8.4

NEW CERAMIC MATERIALS WITH NOVEL NANOSTRUCTURE AND PROPERTIES. Koichi Niihara, The Institute of Scientific and Industrial Research (ISIR), Osaka, Univ, JAPAN.

ABSTRACT NOT AVAILABLE

3:30 PM V8.5

NANOSCALE METALS AS STORAGE ELECTRODES FOR LI-ION BATTERIES. Pimpa Limthongkul, Yet-Ming Chiang, Massachusetts

Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA.

Nanoscale metals have high potential as anode materials for rechargeable lithium ion batteries. The three desired characteristics for a Li-ion battery anodes are high storage capacity and low voltage relative to Li (for high energy density) and good cyclability. Li-metal alloys have been investigated as alternatives to carbon as anode materials due to their superior energy density. However, experimental devices constructed with bulk metal anodes exhibit poor cyclability, i.e. capacity fade after only a few charge/discharge cycles. This drop in capacity can be attributed to mechanical failure of bulk metal particulates due to the high volume change during alloying and de-alloying with Li. More recently, anodes fabricated with nanoscale metals have exhibited improved cyclability (i.e. capacity retention) relative to their bulk counterparts, ostensibly due to their greater resistance to mechanical failure when subjected to alloying and de-alloying volumetric strains. It has been suggested that a critical minimum particle size may exist, below which mechanical failure is fully suppressed and cyclability is unaffected by further particle size reduction. In this investigation, we combine electron microscopy and electrochemical techniques to examine the following: 1) the effect of particle size (down to the nanometer scale) on resistance to mechanical failure during alloying and dealloying of various metals including Al, Sn and Sb 2) the effect of such mechanical response on the electrochemical behavior during cycling.

3:45 PM V8.6
MECHANICAL SPECTROSCOPY OF NANOSTRUCTURED NICKEL. W.M. Yin, S.H. Whang, Polytechnic University, Department of Mechanical Engineering, Brooklyn, NY.

When the grain size in nanostructured metals decreases to near single digit nano-sizes, a considerable viscoelastic deformation has been observed probably due to a significant volume fraction of intercrystalline components. To understand the viscoelasticity in nanostructured nickel, its mechanical response has been investigated by dynamic mechanical analyzer to determine storage modulus, loss modulus and tangent delta as function of frequency (0.01-200 Hz) and temperature (300K-473K). Experimental results showed enhanced damping in nanostructured nickel compared to polycrystalline nickel for the given temperature range. It is found that as-prepared nanostructured nickel exhibited an internal friction peak in the first run of temperature scan test at 0.02 Hz while the peak disappeared in the second run. In addition, a viscoelastic recovery was observed from the interrupted creep test at 373K. The results showed that the viscoelastic strain of nanostructured nickel recovered very slowly after removing the applied stress, i.e. interrupting the steady state creep. The viscoelastic behavior in nanostructured nickel will be discussed in terms of grain boundary deformation.

4:00 PM V8.7
RELATIONSHIP BETWEEN SYNTHESIS, STRUCTURE AND MECHANICAL PROPERTIES OF SOL-GEL DERIVED MESOPOROUS MATERIALS. Hang-Shing Ma, Princeton Univ, Dept of Chemical Engineering, Princeton, NJ; Jean-H. Prévost, Princeton Univ, Dept of Civil and Environmental Engineering, Princeton, NJ; Rémi Jullien, Univ Montpellier II, Laboratoire des Verres, Montpellier, FRANCE; George W. Scherer, Princeton Univ, Dept of Civil and Environmental Engineering-Princeton Materials Institute, Princeton, NJ.

Sol-gel transition creates mesoporous network with nanoscale structure. Aerogel is derived from the sol-gel process and has potential applications ranging from low-dielectric material for semiconductors to thermal insulation. However, aerogel is usually too compliant to process and handle, and the underlying physics is not clearly understood. Computer modeling was performed to study the processing, structure and mechanical properties relationship of gels, using the diffusion-limited cluster-cluster aggregation (DLCA) with dangling bond deflection model and the finite element method (FEM). The results can be summarized by the architectural "blob-and-link" model, which depicts that gel network is made up of rigid blobs of small, aggregated cyclic structures, interconnected by tenuous polymeric chains as links. The links are responsible for most of the strain imposed on the network because they are more compliant to deform than the blobs. Since they are intrinsically compliant and represent only a small fraction of the total mass, gel network is mechanically much less efficient than what the open-cell foam model predicts. When the network is compressed beyond its yield point, its modulus drops initially due to the breakage of the links. Then the blobs begin to squeeze against each other, and the modulus rises with increasing strain. The scaling relationships between modulus and density of the aerogels measured under linear elastic and densification hardening conditions are reproduced by the simulation. The "blob-and-link" model suggests that a stronger network structure can be achieved by redistributing the mass from the blobs to the links to

increase the modulus. One possible method of homogenization is to vary the reactivity of the ligands of the gel precursors, so that linear polymerization is favored before cross-linking takes place. Preliminary results show that the hybrid TMOS-TEOS gels possess higher moduli than the pure TMOS or TEOS gels with similar porosity and reaction conditions.

4:15 PM V8.8
SEMICONDUCTOR NANOWIRES AS OPTOELECTRONIC BUILDING BLOCKS: FROM FUNDAMENTAL PHYSICS TO DEVICES. Mark S. Gudiksen, Jianfang Wang, Charles M. Lieber, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

Semiconductor nanowires can function as active device elements as well as interconnects for the transport of excitons and charge carriers, and thus represent exciting building blocks for electronic and optoelectronic devices. Realization of this potential requires fundamental exploration of the properties of these materials. To this end, we have studied the photoluminescence (PL) properties of individual, isolated indium phosphide (InP) nanowires at both room temperature and 7 K. PL measurements conducted on nanowires of different diameters show that the emission maxima systematically shift to higher energy with decreasing diameter, consistent with the concept of quantum confinement. Furthermore, polarization-sensitive PL studies reveal a striking and unprecedented polarization anisotropy in which the emission essentially turns from 'on' to 'off' as the polarization vector is rotated from parallel to perpendicular. This huge polarization anisotropy arises from the large dielectric contrast unique to these free-standing nanowires. Significantly, this anisotropy has been exploited to create nanoscale polarization-sensitive photodetectors, which may prove useful in integrated photonic circuits or near-field imaging applications. Lastly, recent results using single nanowires to create nanoscale light-emitting diodes will be discussed along with prospects for various applications, such as 'lab-on-a-chip' nanoscale light sources.

4:30 PM V8.9
FORMATION OF NOVEL ORGANIC-INORGANIC ELECTROACTIVE COMPOSITES. Jason H. Rouse, Zoubeida Ounaies, ICASE, NASA-Langley Research Center, Hampton, VA; Emilie J. Siocli, Joycelyn S. Harrison, Peter T. Lillehei, Advanced Materials Processing Branch, NASA-Langley Research Center, Hampton, VA.

In an effort to form materials that display an electroactive response and have stability towards oxidative environments, a series of organic-inorganic composites have been synthesized. Composites were produced from the hydrolysis and condensation of silicate precursors containing dipole moieties in the presence of various templating and polymeric agents. By varying the amount of polymeric material present within these composites it was possible to form materials with various levels of stiffness. The effect of the orienting environment on the electric, magnetic, or optical responses, as well as microstructure of these materials was also studied.

4:45 PM V8.10
CERIA-BASED NANOCRYSTALS AS IMPROVED OXYGEN STORAGE MATERIALS. Jason T. Sweeney, Neeraj Sangar, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA; Mark Stoykovich, University of Wisconsin, Dept. of Chemical Engineering, Madison, WI; Jackie Y. Ying, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

With more stringent regulations on mobile source emissions, there has been an increasing need for improved pollutant control in catalytic converter technology. Catalytic converters utilize an oxygen buffering material that has the ability to provide oxygen during reducing conditions and remove oxygen during oxidizing conditions, thereby maintaining a balanced gas atmosphere for the simultaneous treatment of NO_x, hydrocarbons and CO. Ceria, which can undergo significant lattice reduction without phase transformation, has proved quite effective at modifying the redox potential for high-temperature exhaust streams as an oxygen buffering material. However, it has a high activation temperature, which limits its ability to catalyze the oxidation of hydrocarbons and CO during an engine warm-up cycle. It also suffers from low oxygen storage capacity and thermal stability, which constrain its performance at low temperatures and after thermal aging. These issues can be addressed by introducing a secondary metal oxide into the ceria lattice to provide both improved activity and stability. Highly homogeneous, doped ceria nanocrystalline materials have been synthesized using chemical precipitation to achieve grain size < 20 nm upon calcination to 800°C. Through careful dopant selection, a reduction in activation temperature to < 350°C and a ~5-fold improvement in oxygen availability at 800°C have been achieved. By improving upon the

oxygen storage capacity, thermal stability and low-temperature activity of ceria-based systems, a more effective catalytic converter device can be achieved for automotive exhaust treatment.

SESSION V9: POSTER SESSION
NANOPHASE AND NANOCOMPOSITE
MATERIALS III

Chairs: Sridhar Komarneni, G. Q. (Max) Lu, Jun-Ichi Matsushita, Richard A. Vaia and John C. Parker
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

V9.1

CREATING MORPHOLOGICAL NANOCOMPOSITES: SILICA-COLLOID-MODIFIED SILICA GELS. Debra R. Rolison, Catherine A. Morris, Karen E. Swider-Lyons, Elizabeth J. Osburn-Atkinson, Celia I. Merzbacher, Naval Research Laboratory, Washington, DC.

The functionality of aerogels (gels dried so as to retain all or most of the free volume of the wet gel) can be markedly extended by the synthesis of composite aerogels in which the sol "nanoglues" solid guests into the network during the sol-to-gel transition. A related type of composite aerogel is a guest-silica composite in which the guest differs morphologically, rather than compositionally, from the silica sol that forms the solid network. The bulk structure and morphology of a composite silica gel (and ultimately an aerogel) can be defined and retained as colloidal (i.e., transparent) and monolithic via base-catalyzed sol-gel chemistry while the surface character of the nanoscale gel network can be modified to an acidic, silanol-rich character. This approach melds bulk and surface properties by grafting a pre-formed, acid-catalyzed silica sol onto a base-catalyzed gel to create silica-modified silica nanocomposites. Allowing an acid-catalyzed silica sol to gel onto a base-catalyzed silica gel creates morphological composite gels-in-gels that retain high porosity (>85%), yet which permit noncovalent entrapment of molecules at the base-catalyzed interface under conditions in which they would otherwise freely diffuse out of the gel or aerogel structure. Grafting acid-catalyzed silica colloids to a dye-modified base-catalyzed silica gel provides insight into the site heterogeneity of silanols in silica gels. In addition, non-silica sols (e.g., titania) can also be grafted to a base-catalyzed silica gel to create mechanically rugged titania-modified silica nanocomposites.

V9.2

NANOSTRUCTURED ALLOYS FOR CREEP RESISTANT, LOW TEMPERATURE BONDING. Hareesh Mavoori, Sungho Jin, Agere Systems/Lucent Technologies, Bell Labs, Murray Hill, NJ.

Dimensional stability the resistance to gradual changes in dimension/position caused by factors such as creep, microstructural changes, or mechanical instabilities during service is becoming an important factor in the design of bonding materials and device structures. In optoelectronic packaging, the need for dimensional stability in bonds is self-evident because of the need to maintain very precise, micron-scale optical alignment between components (e.g., active components, such as lasers and light-emitting diodes, and passive components, such as lenses and optical fibers) over extended periods of time. Low melting point bond materials are often preferred for ease of device assembly and for minimizing thermal stresses; however, they are susceptible to creep-related dimensional instabilities. Here we report the development of new composite bonding materials with low melting point yet high creep-resistance. An example is the commonly used Sn-Pb eutectic solder (melting point 183C), the microstructure of which is substantially modified by incorporating nano-sized, non-reacting, non-coarsening oxide dispersoids to create nanoscale grain structure. The new solders exhibit a dramatically enhanced creep resistance by ~3 orders of magnitude. The well-known thermal instability problem with ultrafine-grained structure appears to have been overcome in these solder alloys and the microstructure was seen to be quite stable upon high homologous temperature exposure (e.g. 120C). This is attributed to the presence of the nano-dispersoid particles which impede grain boundary sliding and dislocation movement. The new solders also exhibit improved ductility under high strain rate deformation and improved strength (4-5 times higher) at low strain rates. It is demonstrated that with a dispersion of ~5nm TiO2 particles, the Pb-Sn eutectic solder with a melting point of 183C can be made more creep-resistant than the 80Au-20Sn eutectic solder with a much higher melting point of 278C. These creep-resistant solders have potential use in optical and optoelectronic packaging requiring dimensional stability of the assembled structures.

V9.3

ENERGY TRANSFER IN CDSE NANOCRYSTALS ASSEMBLED WITH OLIGO-(P-PHENYLETHYNYLENE DIBENZYLTHIOL) SCAFFOLDS. Artjay Javier, C.S. Yun, G.F. Strouse, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

CdSe nanocrystals (NC) are assembled with a bridging ligand, composed of an oligo-(p-phenylethyne-dibenzylthiol-dipropyl-ether) ligand (OPE), to produce amorphous solids. Photoluminescence studies indicate long-range resonant energy transfer from the conjugated bridge (OPE) to the NCs. Assembly with different NC sizes then tunes the rate of energy transfer, through the spectral overlap integral $\langle J \rangle$. OPE exhibits excimer formation in solution, J-aggregate formation on NC surfaces, as well as photo-induced luminescence-detected melting transitions. Potential applications for LEDs will be discussed.

V9.4

MICROSTRUCTURE AND MAGNETIC PROPERTIES OF FERROMAGNETIC NANOCRYSTALS PRODUCED BY ION IMPLANTATION. K.S. Beatty, A. Meldrum, The University of Alberta, Edmonton, AB; K. Sorge, J.R. Thompson, The University of Tennessee, Knoxville, TN; C.W. White, S.P. Withrow, J.D. Budai, and L.A. Boatner, Oak Ridge National Laboratory, Oak Ridge, TN; S. Honda, Osaka University, JAPAN.

Ion implantation coupled with annealing is a versatile and flexible approach to creating ferromagnetic near-surface nanocomposites that represent a wide range of particle/host combinations. In previous work Co was implanted into amorphous SiO₂ or crystalline Al₂O₃ hosts. Subsequent thermal processing induced the precipitation of the implanted material to form a thin layer of nanocrystals embedded a few tens of nanometers below the specimen surface. We used ion implantation to create layers of Co nanoparticles in a sapphire host that were subsequently irradiated with Xe, Pt, or Pb in order to systematically modify the magnetic properties of the composites. Transmission electron microscopy was used to carry out a detailed characterization of the microstructure of the resulting near-surface composites whose magnetic properties were determined using SQUID magnetometry. The shape of the hysteresis loops depends on the composition, size, crystallographic orientation, and microstructure of the nanoparticles. These composites exhibited magnetic hysteresis, with coercivities ranging from near zero (i.e., superparamagnetism) up to almost 2 kG, depending on the composition and microstructure. This paper emphasizes alteration of the physical and magnetic properties of the Co particles subsequent to heavy-ion irradiation with Xe, Pt, and Pb. The results suggest ways to pattern the magnetic properties of these composites, and demonstrate means whereby the magnetic properties of nanocomposites produced by ion implantation can be tailored for specific applications - potentially including magnetic recording.

V9.5

NANOPHASE ELECTROLYTE FOR RECHARGEABLE LITHIUM ION BATTERY. R.E. Melgarejo, M.S. Tomar and A. Hidalgo, Univ. Puerto Rico, Phys. Dept., Mayaguez, PR; R.S. Katiyar, Univ. Puerto Rico, San Juan, PR.

Nanocomposites based of polymer and wide gap materials such as TiO₂ and MgO are important as solid state electrolyte for Li-ion batteries. We synthesized polymer-TiO₂ nanocomposite and its structural, charge transport, and impedance studies were carried out. The study suggests that this solid nanophase material could be a suitable electrolyte with lithium intercalation cathode material.

V9.6

MULTISCALE SIMULATION OF THE DEVELOPMENT AND COALESCENCE OF 3-DIMENSIONAL GRAIN STRUCTURES. Max O. Bloomfield, Ottmar Klaas, Vinay Prasad, Jing Lu, Antoinette M. Maniatty, and Timothy S. Cale, Focus Center-New York, Rensselaer Polytechnic Institute, Troy, NY.

We have created a finite-element based, multiple level-set code to model the evolution and coalescence of islands during thin film growth. Our software tool can simulate the evolution of N grains or atomic-scale proto-grains. Grain boundaries are represented implicitly by a set of N 1 scalar fields, $\phi_i(r, t)$ expressed on an unstructured mesh, subject to the condition that $\phi_i(r, t) = 0$ for all r on the boundary of grain i at time t [1]. By extracting the zero contour, we can recover the grain boundaries at any time. Because each grain is associated with its own scalar field, properties such as lattice orientation can be easily retained on a grain-by-grain basis. The evolution of each grain is computed separately using the usual level set equation. We use an explicit positive coefficient scheme for this evolution. Level sets representing different regions are then reconciled to bring the them into agreement. To address distortions in the scalar fields, we implement a "redistancing" algorithm that corrects these

distortions. This step stabilizes the evolution, allowing for simulations that include the coalescence of proto-grains and islands into complex grain structures. Demonstrations of this code are presented, including applications within a multiscale framework. Reactor scale simulations of reactant transport are performed using an FEM code. Reactant data are passed to this scale from the grain scale in the form of boundary conditions. This allows us to establish concentration fields of reactant both on the scale of 0.1 μm , and using local refinement, on the 0.1 mm scale. The reactor-scale simulation passes reactant data back down to a grain-scale level set simulation. This allows us to show the interaction of phenomena such as reactor-scale reactant depletion on the resulting grain structure.

1. S. Osher, and J.A. Sethian, *J. Comput. Phys.* 79, 12 (1988).

V9.7
INNOVATIVE AND COST-EFFECTIVE MICROFABRICATION OF NANOCERAMIC COMPONENTS. Balakrishnan Nair, Ceramatec Inc., Salt Lake City, UT.

An innovative and cost-effective casting technique has been developed at Ceramatec Inc for microfabrication of ceramic components with very high dimensional tolerance. The materials system is a proprietary nanophase composition called CERANAM (CERamatec C A stable N ANo Material). Scanning electron microscopy revealed that CERANAM components can be fabricated with dimensional tolerance as high as plus or minus 2 micron for surface features on the die of dimensions about 1 mm. The process can also be modified to fabricate nanoporous ceramic components with very high surface areas. Components with surface areas as high as 7.4-9.2 sq.m/g have been obtained from starting alumina powders of 11 sq.m/g (67-85% retention). The fabrication process does not involve a high-temperature sintering step, which eliminates loss of surface area from high temperature sintering. It is anticipated that microcomponents fabricated with specific microstructures and properties will have applications in the optical fiber industry as interconnects, in the packaging industry and the chemical industry.

V9.8
SiO₂ SOL-GEL FILMS DOPED WITH NICKEL OXIDE NANOCUSTERS FOR OPTICAL GAS SENSOR APPLICATIONS. A. Martucci, N. Bassiri, M. Guglielmi, Dip. Ingegneria Meccanica S. Materiali, Univ di Padova, ITALY; M. Post, ICPET, National Research Council of Canada, Ottawa, CANADA; L. Armelao, S. Gross, CNR - CSSRCC, Univ di Padova, ITALY; J.C. Pivin, CSNSM, IN2P3-CNRS, Orsay Campus, FRANCE.

Recently, nanocomposites with sensor function are becoming a new area of interest in the field of optical gas sensors. In fact, the optical transmittance of nano-particles or thin films has been reported to be changed by exposure to certain gas atmospheres [1,2]. In particular it was found that NiO, Co₃O₄ and Mn₃O₄ thin films showed a reversible decrease in the Vis-NIR absorption when exposed to CO at temperatures around 250-350°C [2]. The aim of this work is the synthesis and characterization of SiO₂ sol-gel glass films doped with NiO nanocrystals. Films of composition (100-X)SiO₂-XNiO with X=10, 20, 40, were obtained by mixing a matrix solution of Si(OC₂H₅)₄ (TEOS) and CH₃Si(OC₂H₅)₃(MTES) as SiO₂ precursors, with a doping solution containing NiCl₂ as a precursor for NiO particles. 3-Aminopropyltriethoxysilane (3-APTES), bearing an amine group capable of coordinating the Ni ions and hydrolysable siloxane groups for anchoring the metal complex moiety to the silicate matrix, was used as bifunctional ligand. Transmission electron microscopy (TEM) pictures showed a uniform distribution of round shaped nanoparticles with a mean diameter of 2.5 nm in a film heated at 500°C. The crystal size increases with the heating temperature as observed by XRD and UV-Vis absorption measurements. The film composition evaluated from Rutherford backscattering spectrometry (RBS) was in good agreement with the nominal one. The film density (mol cm⁻³) was measured by combining the thickness data (cm) obtained from profilometer and the film dose (mol cm⁻²) from RBS data. The density of the films heated at 1000°C is much higher than the density of the film heated at 500°C. This difference can be mainly ascribed to the residual porosity present in films heated at lower temperatures. Fourier transform infrared (FTIR) spectra also confirmed the presence of residual porosity in the films heated at 500°C. Experiments to evaluate the optical transmittance (UV-Vis), sensor functionality and sensitivity of the nanocomposite materials to CO are in progress.

1. K. Yasumoto, N. Koshizaki, K. Suga, in: J.D. Mackenzie (ed.), *Proc. SPIE* vol. 1758 (1992) 604. 2. M. Ando, T. Kobayashi, M. Haruta, *Catalysis Today* (1997) 135.

V9.9
ORGANIC NANOCRYSTALS GROWN IN BULK GEL-GLASSES AND THIN FILMS FOR PHOTONIC APPLICATIONS. Estelle Botzung, Julien Zaccaro, Irene Wang*, Patrice L. Baldeck*, Alain Mosset, Alain Ibanez, Laboratoire de Cristallographie, CNRS,

Grenoble FRANCE and *Laboratoire de Spectrométrie Physique Université J. Fourier, CNRS, Saint Martin d'Heres, FRANCE.

We have prepared a new type of nanocomposites organic-inorganic materials, bulk and thin films. These hybrid materials are composed of organic nanocrystals grown in gel glasses. Our simple and generic method is based on the control and nucleation and growth kinetics in the pores of the gel matrices. The confined nanocrystallization is obtained through an instantaneous nucleation followed by a reduced growth of the nuclei due to the gel viscosity (weak solute diffusion). In addition, the gel matrix avoids the crystal coalescence while its pores act as nanometer-sized reactors of growth in solution. For bulk samples, transparent and isotropic samples are obtained after drying: organic crystals (12 - 24 nm in diameter) are randomly dispersed in the gel-glasses. In order to demonstrate the reproducibility of this process, various organic molecules were selected particularly for luminescence and optical power limiting properties. To obtain quadratic nonlinear optical properties we have oriented the nanocrystals under high magnetic field (16T) through their diamagnetic susceptibility. We have extended this method to the preparation of stable organic nanocrystals in sol - gel coatings using the spin-coating method. We have prepared thin films, around 1mm thick, containing well-embedded organic nanocrystals (30-200nm in diameter depending on the experimental conditions) which are easily characterized by electron and optical confocal microscopies. Presently, the mainly targeted properties of the thin films are luminescence for chemical or biological sensors. But we are also optimizing in these nanocomposite thin films the orientation of organic nanocrystals by electric fields for electro-optics and the spatial control of the nucleation sites of organic nanocrystals for optical storage devices. Finally, this field of research is actually extended to the preparation and characterization of inorganic nanocrystals grown in sol-gel thin films for optical amplifiers in integrated optics.

V9.10
PROCESSING EFFECTS ON THE MORPHOLOGY OF HYDROTHERMALLY DERIVED NANOCRYSTALLINE LEAD TITANATE. Zhiyuan Ye, Elliott B. Slamovich, and Alexander H. King, School of Materials Engineering, Purdue University, West Lafayette, IN.

Nanocrystalline lead titanate was synthesized by reacting nanocrystalline titanium oxide in aqueous solutions of potassium hydroxide and lead acetate at 200 degrees C. X-ray diffraction (XRD) and TEM studies suggest that the initial KOH concentration influenced the nucleation and growth behavior of the lead titanate nanoparticles. Powders were processed in aqueous solutions containing 0.10 M lead acetate and a Pb:Ti ratio of 1, with varying concentrations of KOH. Powders processed in 0.01 M KOH were composed of irregularly shaped particles 50-100 nm in size, processing in 0.10 M KOH produced particles with finger-like morphology and broader particle size distribution, and processing in 1.0 M KOH resulted in anisometric plates with (001) facets, and 100-200 nm in size. XRD studies have shown systematic variations in the position and symmetry of reflections with a l component as a function of particle size. Modeling of the XRD data along with TEM studies indicate that the c/a ratio of lead titanate increases with decreasing nanoparticle size.

V9.11
NANOCOMPOSITE BASED ON SEMICONDUCTOR OXIDES SnO₂/WO₃. M.N. Rumyantseva, M.N. Boulova, D.A. Chareev, L.I. Ryabova, B.A. Akimov, A.M. Gaskov, Moscow State University, Chemistry Dept, Moscow, RUSSIA

Nanocrystalline SnO₂ and WO₃ and nanocomposite SnO₂/WO₃ with Sn:W ratio 1:9, 1:1, 9:1 were prepared by co-precipitation of a-stannic and tungstic acids with subsequent thermal annealing. Microstructure was studied by SEM. Phase composition and average crystallite size (2-15 nm for SnO₂ and 20-50 nm for WO₃) were determined from XRD data. Presence of second component results in the enhancement of thermal stability of major oxide in nanocomposite. Conductivity of nanocomposite was studied in static electric fields up to 5 V in the temperature interval 200-300 K. For the most of the samples the current-voltage (I-V) curves are non-linear, and current instabilities are observed. I-V curves character was interpreted in terms of electrochemical capacitor recharge. The effect of the charge accumulation may be related to ionic component of charge transport existing in addition to electronic conductivity. The estimation of the resistance R obtained for the nanocomposite in identical conditions at low field region are in good correlation with the change of the grain dimensions of the dominating oxide. A pronounced increase of R was observed for the samples with equal quantities of SnO₂ and WO₃ in nanocomposite. The temperature dependence of R reveals its activation character.

V9.12

NANOSTRUCTURED MAGNETIC NANOCOMPOSITE THIN FILMS. Honghui Zhou, A. Kvit, D. Kumar, T.K. Nath and J. Narayan, Department of Materials Science and Engineering and NSF Center for Advanced Materials and Smart Structures. North Carolina State University, Raleigh, NC.

Textured and epitaxial Ni nanodots have been produced by pulsed laser deposition technique (PLD). By controlling the deposition time, three-dimensional Ni nanodots were formed on the TiN matrix, which is epitaxially grown on Si (100) substrate. TEM study showed that these nanodots are single crystal with two kinds of epitaxial orientation relationship. One is cube on cube, where $\langle 001 \rangle$ Ni // $\langle 001 \rangle$ TiN. The dots grown via this orientation have a rectangular shape. The other involves a 90° rotation with respect to $[110]$ of TiN matrix, where $[2 -2 0]$ Ni // $[0 0 2]$ TiN and $[110]$ Ni // $[110]$ TiN. The dots grown via this orientation have a triangular shape. The mechanism of forming these two orientation relationship is still not well understood and needs to be further studied. STEM Z-contrast image showed that the interface between Ni / TiN / Si is sharp, which indicates that no significant interfacial reaction occurred. Superconducting quantum interference device (SQUID) was used for magnetic measurements, which shows that both blocking temperature and coercivity of Ni nanodots grown on epitaxial TiN matrix are significantly higher than that obtained in previous research for Ni nanodots grown on amorphous Al_2O_3 matrix layer. The higher value of coercivity is possibly associated with the stronger tendency of crystallographically oriented dots to retain its magnetic moments in the presence of a reversing magnetic field.

V9.13

PREPARATION AND CHARACTERIZATION OF NANOPARTICLES FOR APPLICATION TO HIGH-TEMPERATURE FUEL CHEMISTRY. Christopher E. Bunker, Barbara A. Harruff, Sophie M. Rozenzhak, David W. Tomlin, Donald K. Minus, Air Force Research Laboratory, Propulsion Directorate, WPAFB, OH; Daniel A. Zweifel, Ya-Ping Sun, Dept of Chemistry, Clemson University, Clemson, SC.

The U. S. Air Force is actively involved in understanding the chemistry of gas turbine aviation fuels (complex mixtures of aliphatic, olefinic, and aromatic hydrocarbons) under high-temperature, high-pressure conditions. Chief among our concerns are ways to eliminate or significantly mitigate the effects of such processes as autoxidation, pyrolysis, and pollution and particulate formation. Nanoparticles, as materials with extremely high surface areas, increased reactivity, and potentially novel chemistries, offer a new approach to fuel additization. The use of nanoparticle materials as additives provides several advantages over current formulations: 1) the nanoscale dimensions of the particles ensures complete access to all parts of an aircraft fuel system, 2) the ability to suspend or solvate nanoparticles (including organic, inorganic, and organometallic materials) in hydrocarbon solvents makes available new classes of compounds normally incompatible with the hydrocarbon fuel environment, and 3) inorganic based materials will likely out perform the current organic additives with respect to self-thermal stability. Initial efforts in our laboratory have been to exploit nanomaterials as fuel-chemistry additives. Our research has focused on understanding the correlations between preparation environment, particle physical characteristics, and particle reactivity. Model nanoparticles have been prepared using the well-established sonochemical and reverse-micelle methods and quantitatively characterized by various methods. The nanoparticles were then evaluated based on their impact on high-temperature fuel chemistry.

V9.14

OXIDATIVE STEAM REFORMING OF METHANOL. Steven E. Weiss, Jackie Y. Ying, MIT, Cambridge, MA.

Significant research has been directed towards designing autothermal reformers for on-demand hydrogen production. This reaction scheme utilizes internal oxidation of fuel to provide energy to drive the endothermic reforming reactions. The traditional reforming catalyst is nickel impregnated on alumina. Impregnation produces catalysts with large grains and poor metal dispersion. Our approach is to design a nanocrystalline combustion catalyst, which can be reduced in situ to produce highly dispersed nickel species. Specifically, LaNiO_3 -based perovskites are investigated for activity in oxidative steam reforming of methanol. These materials are synthesized by coprecipitation with ultrafine grain sizes and high surface areas. The reducibility of the catalyst is altered by doping and is investigated using temperature-programmed reduction. X-ray photoelectron spectroscopy is used to characterize the oxidation state of nickel along the length of the reactor bed. Careful study of this system reveals that 80% of the activity of this system occurs in the initial 20% of the catalyst bed, where the catalyst decomposes to lanthanum carbonate. The remaining nickel is not detectable by X-ray diffractometry and must

have a grain size less than 2 nm; evidence demonstrates that this highly dispersed nickel is responsible for the catalyst's activity. Thus, we are able to produce nanoclusters of various transition metal oxides via in situ decomposition of nanocrystalline perovskite s. Results show that nanocrystalline LaNiO_3 is extremely active for the oxidative steam reforming of methanol. It is even more active than expensive palladium-based partial oxidation catalysts. Furthermore, the perovskite bed is less than half the volume of the palladium catalyst bed, which translates into a more compact reformer.

V9.15

POLYMER SILICATE NANOCOMPOSITES FOR HIGH-ENERGY DENSITY, RECHARGEABLE THIN FILM BATTERIES. Mary E. Galvin, Mary Kurian, Department of Materials Science and Engineering, University of Delaware, Newark, DE; Patrick E. Trapa, Anne M. Mayes, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

The current project focuses on the development of a new type of lithium polymer battery (LPB), which is an attractive option for portable electric power. Our work involves the development and characterization of polymer-clay nanocomposite (PCN) materials for use as electrolytes in LPBs. The incorporation of Li cation-exchanged nanoscale clay sheets into the polymer matrix is expected to impart enhanced tensile strength, heat resistance and gas impermeability to the electrolyte, while significantly reducing polarization attributable to the electrolyte. Techniques such as X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, thermo gravimetric analysis, Fourier Transform Infrared spectroscopy and conductivity measurements, are used to characterize the PCN electrolytes.

V9.16

THERMAL AND STRUCTURAL CHARACTERIZATION OF NANOCOMPOSITE IRON NITRIDE - ALUMINA AND IRON NITRIDE - SILICA PARTICLES. A.M. Viano, Dept of Physics, Rhodes College, Memphis, TN; S.R. Mishra, Dept of Physics, The University of Memphis, Memphis, TN.

Nanocomposite iron nitride based powders are known to have enhanced magnetic and other physical properties. To further explore their potential for application in various fields, we have performed a systematic study of the iron-alumina and iron-silica systems. Iron nitride powder of composition Fe_xN ($2 < x < 4$) was mechanically milled, using a high energy ball-mill, with Al_2O_3 or SiO_2 powder for 4, 8, 16, 32, and 64 hours at the following compositions; $(\text{Fe}_x\text{N})_{0.2}(\text{Al}_2\text{O}_3)_{0.8}$, $(\text{Fe}_x\text{N})_{0.4}(\text{Al}_2\text{O}_3)_{0.6}$, $(\text{Fe}_x\text{N})_{0.6}(\text{Al}_2\text{O}_3)_{0.4}$, $(\text{Fe}_x\text{N})_{0.2}(\text{SiO}_2)_{0.8}$, $(\text{Fe}_x\text{N})_{0.6}(\text{SiO}_2)_{0.4}$. Thermal transformations and structural studies of these samples are reported in this work. Differential thermal analysis was performed to investigate thermally induced transitions from 100°C to 1500°C . Four irreversible exothermic transitions are observed in the low temperature (100°C - 700°C) region. As the milling time is increased, the lowest of these transitions are enhanced while the peak corresponding to the pure Fe_xN powder is diminished. A reversible endothermic transition occurs near 1400°C . These transitions are correlated with X-ray diffraction patterns for the as-milled samples and for samples heated at 700°C . All XRD peaks broaden as a function of milling time, corresponding to smaller particle size. The nanocomposite powders are composed of several iron phases, the exact combination of which depends on both composition of the starting materials and milling time.

V9.17

PREPARATION OF GOLD NANOPARTICLES FROM POLYELECTROLYTE COMPLEX (PEC) SOLUTIONS OF TERTHIOPHENE AMPHIPHILES. Ji Ho Youk, Jason Locklin, Chuanjun Xia, Mi-Kyoung Park and Rigoberto Advincula, Dept of Chemistry, Univ of Alabama-Birmingham, Birmingham, AL.

The synthesis and characterization of gold nanoparticles have attracted great attention due to their potential applications in optoelectronics, electronics, catalysis, and other areas. Oligothiophenes have attracted much interest as promising organic materials for electronic devices such as light emitting diodes, transistor, and materials for photoelectric conversion. In this study, we report for the first time, the preparation of gold nanoparticles in aqueous solutions using a polyelectrolyte that possesses pendant reducing oligothiophene groups. Polyelectrolyte complex (PEC) with water-soluble terthiophene derivative was used for the reduction of HAuCl_4 to gold nanoparticles. A number of parameters including solution concentration, percentage of complexation, solvent, reaction time, etc. were investigated in order to determine the extent of the reduction and nanoparticle formation (size, size distribution, etc.). In principle, the technique opens up the possibility of combining electro- and optically-active materials with inorganic metal nanoparticles prepared in-situ.

V9.18

SYNTHESIS AND STUDY OF Co AND Cu DOPED CdSe QUANTUM DOTS. Khalid M. Hanif, Robert W. Meulenberg, Geoffrey F. Strouse, Univ. of California Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

Doped semiconductor quantum dots (QD) have been shown to have potential applications as phosphors, magnetic-recording media and sensors. We have synthesized monodisperse $Cd_{1-x}Co_xSe$ and $Cd_{1-x}Cu_xSe$ quantum dots that have been doped with 1- 23% Co and Cu in the core of the particles. In these materials, the site occupation of the dopant atoms can substantially influence the properties of the QD host lattice. We report the concentration dependent PM to AFM phase transition in Co doped QDs. Inspection of the observed optical and magnetic data provides insight into the lattice site occupation in these materials. Analysis of these compounds has been performed using Raman Spectroscopy, XRD, TEM, Superconducting Quantum Interference Device (SQUID), Atomic Emission spectroscopy, Photoluminescence Spectroscopy, and UV-Vis Absorption to verify site and concentration of dopant ions.

V9.19

STRUCTURE AND NANOCRYSTALLITES IN Ni AND NiO THREE-DIMENSIONAL ORDERED MACROMESHES. W.L. Zhou, L. Xu, and J.B. Wiley, Advanced Materials Research Institute, Dept. of Chemistry, University of New Orleans, LA; A.A. Zakhidov, R.H. Baughman, Honeywell Int., Corporate Technology, Morristown, NJ.

The fabrication of macro- and mesoporous mesh and bead arrays of both metal and polymer has recently been reported by several groups. Potential applications of these materials include photonics, catalysis and magnetics. Recently we reported on the use of inverse opals as templates to generate opal bead arrays from various functional materials such as metals. It is crucial to study the structure and nanocrystallites in such inverse membranes to understand their growth mechanism and control the fabrication. Three-dimensional Ni and NiO inverse opal macroporous arrays were characterized by scanning electron and transmission electron microscopies. The cubes and tetrahedra of the inverse Ni mesh were found to mostly grown as single crystals. Some NiO nanocrystals with size about 5 nm were formed on the surface of inverse Ni opal membrane during etching away silica spheres. The oxidation of Ni mesh by annealing at 600°C turned it into NiO with grain size about 20 nm. The nanocrystalline NiO mesh is suitable for further fabrication of three-dimensional nanobeads. By annealing the meshes at 700°C, the NiO nanograins grew to the size about 70 nm. The mesh with high temperature treatment has constant structure for photonics application.

V9.20

SUBSTRATE DEPENDENCE IN THE GROWTH OF THREE-DIMENSIONAL GOLD NANOPARTICLE SUPERLATTICES. Seiichi Sato, Naoki Yamamoto, Hiroshi Yao, Keisaku Kimura, Himeji Institute of Technology, Dept of Materials Science, Hyogo, JAPAN.

Three-dimensional (3D) superlattices of nanoparticles represent a class of promising new electronic materials whose band structure may be engineered through control of core sizes, of the surface coverage thickness, and of packing arrangements for the nanoparticles. In this study, we generated hydrophilic nanoparticles which assembled into superlattices on various substrates in aqueous suspension. Gold (Au) nanoparticles with 3.5-nm radii whose surfaces were modified with mercaptosuccinic acid were used as the component particles. The acid surfactant affects the dispersion of Au nanoparticles in aqueous suspensions at low ionic concentration. After the Au nanoparticles were dispersed in distilled water, acid was then added into the suspension. This process induced self-assembly of the nanoparticles. This is a result of the added protons suppressing ionization of the surfactants and hence, weakening the repulsive interactions among the nanoparticles. Various metal, semiconductor, and insulator substrates were immersed in the suspension, and nanoparticle self-assembly into superlattices on those substrates was observed. Growth of superlattices was found to be strongly dependent upon the nature of the substrates. Nanoparticle growth on silver (Ag) substrates proceeded through the formation of a number of islands. After sufficient growth, the islands reached widths of several micrometers, and they formed clear facets, indicating the formations of the desired superlattices. In contrast, no growth was found on hydrogen terminated silicon, silicon oxide, and alumina substrates. To explain the observed substrate dependence, van der Waals interactions between nanoparticles and substrates through water were calculated using the Lifshitz theory. Through use of this theory experimental results could be fully explained, assuming the conduction electrons in the Au nanoparticles behaved not as relaxator systems, but as oscillator systems with an eigenfrequency equal to the surface plasmon frequency of Au.

V9.21

Abstract Withdrawn.

V9.22

TOPOLOGY AND ELECTRONIC STRUCTURE OF ONION-LIKE CARBON AND GRAPHITE/DIAMOND NANOCOMPOSITES. Lubov G. Bulusheva, Alexander V. Okotrub, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; Vladimir L. Kuznetsov, Andrew L. Chuvilin, Yuriy V. Butenko, Borekov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA; Malkom I. Heggie, School of Chemistry, Physics and Environmental Science, University of Sussex at Brighton, UNITED KINGDOM.

Annealing of nanodiamond at moderate temperature makes it possible to produce structures being intermediate in the carbon transformation from sp³- to sp²-state (graphite/diamond nanocomposites) and onion-like carbon (OLC). Electron microscopy shows such structures involve cage shells with a spacing close to graphite. X-ray emission spectroscopy has been applied to examine the electronic structure of OLC and diamond/graphite nanocomposites. The CK-alpha spectra of OLC produced in the temperature range of 1600-1900 K were found to be markedly different from the spectrum of particles formed at 2140 K and characterized by better ordering of graphitic shells. The latter spectrum was shown to be very similar to the CK-alpha of polycrystalline graphite, while the former ones exhibited a significant increase of high-energy maximum that might be caused by the defect structure of graphitic networks forming at the intermediate temperatures. The experimental spectra were compared to the theoretical ones plotted by the results of quantum-chemical semiempirical AM1 calculation on a few models: fullerene molecule C₂₄₀ having icosahedral structure, C₂₄₀ incorporating a greater number of non-hexagonal rings, and a holed structure formed by removing pentagons from the icosahedral molecule. The density of high-energy electronic states in the valence band of graphitic cage was found to be practically invariant to a change in ring statistics but to significantly increase due to localization of electrons on the zigzag sites of a hole boundary.

This work was supported by the INTAS (Project Nos. 97-1700, 01-237), the Russian scientific and technical program "Actual directions in physics of condensed states" on the "Fullerenes and atomic clusters" (Project No. 98055), the Russian Foundation for Basic Research (Project No. 00-03-32463a).

V9.23

MECHANICAL PROPERTIES OF UNSATURATED POLYESTER/MONTMORILLONITE COMPOSITES. Ulku Yilmazer, Ali Baran Inceoglu, Middle East Technical University, Dept of Chemical Engineering, Ankara, TURKEY.

Nanocomposites composed of unsaturated polyester as the matrix and montmorillonite as the filler were synthesized. The process involved mixing the unsaturated polyester and layered silicate powders that have been modified with hydroxyl terminated quaternary ammonium salt. During mixing, the polymer chains diffuse from the bulk polymer into the van der Waals galleries between the silicate layers. After the synthesis, the tensile, flexural, impact and thermal properties of the nanocomposites were analyzed and discussed in terms of mixing procedures, surface treatment and montmorillonite content. The best mixing was obtained by mechanical mixing followed by application of ultrasound. It was found that adding only 3 montmorillonite improved the flexural modulus of unsaturated polyester about 35%. Most properties exhibited a maximum with respect to the montmorillonite content.

V9.24

POLYMER-METAL NANOCOMPOSITES: MECHANICAL AND ELECTRICAL PROPERTIES OF THE HDPE/CU AND LDPE/Cu SYSTEMS. A. Concha, R. Quijada, Dept Ing Quimica, Universidad de Chile, Santiago, CHILE; N. Beltran, Dept Ing Electrica, Universidad de Chile, Santiago, CHILE; V.H. Poblete, Comision Chilena de Energia Nuclear, Santiago, CHILE; M.E. Pilleux, IDIEM, Universidad de Chile, Santiago, CHILE.

The mechanical and electrical conduction properties of metal-filled polyethylene nanocomposites were studied. The nanocomposites were made of HDPE and LDPE filled with nanosized copper (≈ 80 nm diameter). The results were compared with similar polymeric materials filled with micron-sized Cu particles ($\approx 10 \mu\text{m}$) and with the unfilled polymer. Stress-strain curves were performed and the Young's modulus was derived. The conductivity and percolation threshold for the nanocomposites was measured as a function of the copper volume content and the morphology was investigated using scanning electron microscopy. The conductivity of the nanocomposite was ohmic and in the order of 0.62 S/m. The experimental percolation limits found were compared to the theoretical 3-D limit of the system.

V9.25

MICROWAVE PLASMA CVD OF SILICON NANOCRYSTALLINE AND AMORPHOUS SILICON AS A FUNCTION OF DEPOSITION CONDITIONS. Jin-Hyuk Jeung, Hak-Gyu Lee, Lihong Teng and W.A. Anderson, SUNY at Buffalo, Electrical Engineering, Buffalo, NY.

Using the ECR-CVD (electron cyclotron resonance-chemical vapor deposition), we can make amorphous-silicon (a-Si) and nanocrystalline (nc-Si) thin films. We are looking forward to improve the photo/dark conductivity ratio (σ_p)/(σ_d) by measuring the photo and dark current-voltage (I-V). In the ECR deposition, there are several factors which we can control and adjust for the improved results, such as the amounts of silane and argon, the vacuum, and the temperature of the substrate. These become the critical factors for ECR deposition in order to make better films. Input gases consist of Ar, 2%SiH₄ in He and H₂. In the process, SiH₄ is decomposed into SiH_x. A residual gas analyzer (RGA) gives composition in the plasma. Because Ar possibly etches the substrate and Si is to be deposited, the best RGA signal is obtained with low Ar. This work serves to correlate process conditions, RGA signals and electrical data. The best RGA signal occurs for 5 mTorr Ar, 60 mTorr SiH₄:He, and power of 600 W. Best value of dark conductivity (σ_d) was $1.53 \times 10^{-9} (\Omega \cdot \text{cm})^{-1}$ and $1.58 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$ for photo conductivity (σ_p). High value of (σ_p) and low value of (σ_d) indicate material with fewer defects. Applications to heterojunction solar cells and thin film transistors will be reported.

V9.26

DISPERSION OF FUNCTIONALIZED NANOCCLAY PLATELETS IN EPOXY SYSTEM. D. Raghavan, A. Emekalam, D. Yebassa, and D. Ibetoh, Polymer Division, Department of Chemistry, Howard University, Washington DC; G. Holmes, Polymer Division, National Institute of Standards & Technology, Gaithersburg, MD.

Nanocomposites are a relatively new class of materials obtained by dispersing montmorillonite clay in polymer matrix. Evidences from literature suggest that clay platelet dispersion during nanocomposite preparation and clay-matrix adhesion are major technical issues that needs to be addressed in order to achieve the desired property enhancements in polymer-clay hybrid nanocomposites. We have studied the interaction of the organically functionalized silicate with the epoxy resin by including along the chain structure functional groups that will facilitate interaction with the resin. Through some conventional routes, functional and nonfunctional molecules have been synthesized and deposited on to the clay surface. Both the functionalized and nonfunctionalized clay has been analyzed using X-ray diffraction (XRD), thermo gravimetric analysis (TGA), atomic force microscopy (AFM), and fourier transform infrared spectroscopy (FTIR). The dispersion of functionalized nanoclay platelets in amine cured epoxy system has been studied using XRD and transmission electron microscopy (TEM).

V9.27

SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY INVESTIGATIONS OF IRON CORE MULTIWALL NANOTUBES. J. Liu, B. Foley, R. Czerw, A. Rao, D.L. Carroll, Dept. of Physics, Clemson Univ. Clemson, SC.

Tunneling microscopy and spectroscopy was used to investigate Fe core multiwalled carbon nanotubes (mwnts) grown by chemical vapor deposition (CVD). The mwnts show surprising variation in both topology as well as electronic structure near the tube ends as compared to the tube bodies that we attribute to interactions with the Fe catalysts typically found in the ends of CVD grown tubes. Combined with TEM studies, the effects of synthesizing conditions has been investigated. Growth mechanisms for these tubes along with simple models for core-tube interactions will be discussed.

V9.28

SURFACE PASSIVATION EFFECTS OF DEPOSITED Ge-NANOCRYSTAL FILMS PROBED WITH SYNCHROTRON RADIATION. C. Bostedt, T. van Buuren, J. Pitzko, T. Willey, L.J. Terminello, Lawrence Livermore National Laboratory, CA.

Clusters and nanocrystals represent a new class of materials that exhibit promising novel properties. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation often not possible in other growth modes. The clusters are condensed out of supersaturated Germanium-vapor that is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surface is then subsequently passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. The clusters are spherical in shape and their sizes are determined by atomic force

microscopy (AFM) and confirmed by transmission electron microscopy (TEM). X-ray absorption spectroscopy (XAS) was performed on thin films of Germanium (Ge) clusters. We find that the passivating agent strongly alters the electronic structure of the clusters. In general the absorption edge shifts to significantly higher energies compared to cluster films without surface passivation. This can be explained with a stronger confinement effect in the passivated films compared to unpassivated ones due to a reduction of the cluster-cluster interactions.

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V9.29

A SIMPLE MODEL FOR THE STRUCTURE NANOPOROUS CARBONS. Michael A. Smith, Raul F. Lobo, University of Delaware, Department of Chemical Engineering, Newark, DE.

Neutron scattering studies show the structure of nanoporous carbon to be locally ordered but globally amorphous. In addition electron micrographs show a tortuous array of parallel channels. Models of nanoporous carbon structure typically describe them as a disordered series of graphite-like layers with weak interlayer correlations; however, the precise nature and atomic origin of the disorder remains unknown. Here we present a structural model of a nanoporous carbon that contains only two simple, chemically reasonable disorder elements and show that calculated radial distribution of resulting structure captures all of the important features in the radial distribution function of experimental carbons.

V9.30

ENERGY TRANSFER IN DYE-DOPED MESOSTRUCTURED NANOCOMPOSITES. Brian J. Scott, Dept. of Chemistry, University of California-Santa Barbara, Santa Barbara, CA; Michael H. Bartl, Gernot Wirnsberger, Dept. of Chemistry, Karl-Franzens-University Graz, Graz, AUSTRIA; Galen D. Stucky, Dept. of Chemistry, University of California-Santa Barbara, Santa Barbara, CA.

The acid catalyzed synthesis and evaporation induced co-self-assembly of dye/silica/block-copolymer nanocomposites to produce ordered mesostructured materials is an emerging area in optical materials. The simultaneous co-assembly leads to improvements in optical characteristics by allowing high doping concentrations while at the same time maintaining high dye dispersion to avoid concentration quenching. These composites have previously shown to be high gain materials that display low threshold amplified spontaneous emission (ASE) in fibers, films, and patterned waveguides. Further, optically pumped lasers were achieved by patterning into structures that provide resonate feedback, e.g. microring and distributed feedback. Results will be presented on improvements in lasing properties obtained by efficient energy transfer between co-assembled dyes.

V9.31

CARBON NANOSTRUCTURES SYNTHESIS BY MEANS OF EXCIMER LASER ABLATION. N. Braidy and M.A. El Khakani, INRS-Énergie et Matériaux, Varennes, Québec, CANADA; G.A. Botton, Materials Technology Laboratory-CANMET, Ottawa, Ontario, CANADA.

We report on novel carbon nanostructures resulting from the excimer laser ablation of a Co/Ni doped graphite target at a laser intensity of $\sim 10^9$ W/cm². The laser ablation of the target was carried out in a flowing argon gas atmosphere at three different temperatures (25, 800 and 1150°C). The carbon deposits were investigated by various techniques, namely SEM/TEM, HRTEM, EELS and micro-Raman spectroscopy. At a microscopic level, regardless of the furnace temperature, the carbon deposits were found to be composed mainly of a foam-like mesoporous interconnected nanoparticulates having a diameter of about 10 nm. Along with this three dimensional network of almost spherical beads, SEM and TEM observations have revealed the presence of cabbage-like arranged features (with 0.1-1 μm diameter) and needle shaped structures ($\sim 1-2 \mu\text{m}$ long and 0.1-0.2 μm diameter). At the nanoscopic scale, the carbon features were composed of different graphitic based nanostructures, namely, (i) various arrangements of about 10 to 20 graphitic stacked sheets and (ii) single- or double- shell graphitic structures with a curled shape (i.e. nanocurls of ~ 1.2 nm diameter). At the highest temperature, not only the nanocurls were found to be more abundant but nanotubes and nanohorns were also observed. EELS analysis have confirmed the graphitic nature of all the carbon nanostructures. On the other hand, Raman spectra of the deposits presented two broad lines peaking at around 1570 cm⁻¹ and 1350 cm⁻¹, which are characteristic of graphitic structures and disordered carbon, respectively. Moreover, at the highest temperature (1150°C), a weak broad band centred at around 170 cm⁻¹ is also present in the spectra, which is thought to be related to the presence of nanotubular structures. The abundance,

size and misorientation of the obtained carbon nanostructures will be discussed on the basis of the intensity ratio of the disorder and graphitic Raman-active peaks.

V9.32

GRAIN GROWTH KINETICS OF NANOCRYSTALLINE Ni PREPARED BY CRYOMILLING. J. Lee, F. Zhou, K.H. Chung, and E.J. Lavernia, Dept of Chemical Engineering and Materials Science, University of California, Irvine, CA.

Grain growth kinetics of nanocrystalline Ni powders with an average grain size of ~ 22 nm prepared by cryogenic mechanical milling (or cryomilling) was investigated by X-ray diffraction (XRD), and transmission electron microscopy (TEM). A dispersion of NiO and Ni₃N particles with a size less than 5 nm was formed in the cryomilled powders. At 0.56 homologous temperature (T/T_M), Ni grains were retained at ~ 150 nm even after long annealing times (e.g., 4 hours). For 0.45 to 0.62 T/T_M , the time exponent (n) was 0.16 \sim 0.32, tending towards 0.5 as T/T_M increased. The activation energy for grain growth in the Ni sample was determined to be 113 kJ/mol, which is close to the activation energy (115 kJ/mol) for grain boundary self-diffusion in polycrystalline Ni. The growth kinetics of nanocrystalline Ni was compared with that of nanocrystalline Al and Fe. It was concluded that the observed high grain size stability was attributed primarily to a grain boundary pinning mechanism arising from the nanoscaled NiO particles as well as impurity segregation.

V9.33

COMBUSTION SYNTHESIS OF NANOSTRUCTURED CARBON MATERIALS. Michael Diener, J.M. Alford, TDA Research, Wheat Ridge, CO.

The fundamental problem in developing technologies based on fullerenes and nanotubes is the small quantities and great costs of the materials, results of energetically inefficient syntheses with low yields. A sooting flame is the most economical method for synthesizing carbon products at larger than laboratory scales, due to inexpensive hydrocarbon precursors, yields that improve with increasing scale, and continuous processing. However, the basic equipment is more challenging to operate at the laboratory scale than comparable arc technologies. Here we trace the development of fullerene combustion synthesis, and discuss both the fullerene formation chemistry in flames and the chemistry of nanotube formation in flames. Of particular interest for both products are the trends in yield and distribution as a function of hydrocarbon precursor.

V9.34

ATOM PROBE FIELD ION MICROSCOPY CHARACTERIZATION OF NANOSTRUCTURED POWDER MATERIALS. Fang Wu, Prajna Bhattacharya, Pascal Bellon, Dept. of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL; Dieter Isheim, David Seidman, Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL.

The structural and chemical characterization of nanostructured materials is an important step in the control of processing conditions in order to optimize the properties of these materials. Such a characterization, however, is quite challenging because of the very small characteristic length scales involved, typically ranging from 1 to 20 nm. While analysis methods such as x-ray diffraction (XRD), transmission electron microscopy (TEM) or scanning TEM are quite useful, they do not yield the full three dimensional structure with a nanometer or sub-nanometer resolution. The atom probe field ion microscopy (APFIM) is a unique technique to explore the spatial distribution of chemical species at that length scale. So far, its use has been limited, partly because of the difficulty in preparing sharp tip specimens, especially from powder materials. In this work, we take advantage of a new method that we devised to prepare sharp tips from powder materials, and APFIM is used to characterize nanostructured Cu-Ag and Ni-Ag powders prepared by high-energy ball milling. In particular we focus on milling conditions leading to the stabilization of nanocomposite materials. Statistical analysis methods, including power spectra, Fourier transform and filtering are used to extract the information of the amplitude and the length scale of the composition variations. For the Cu-Ag system, we show that by increasing the milling temperature from 80 to 453K, the steady-state obtained changes from a nearly random solid solution to 2-phase nanocomposites with length scales ranging from 10 to 30 nm. Three-dimensional atom probe is also used to study the connectivity and the shape of the Cu-rich precipitates of these nanocomposites. For the Ni-Ag system, we study the distribution of the Ag when the composition exceeds the nonequilibrium solubility limit. Segregation of Ag at nanograin boundaries is proposed to rationalize the formation of nanocomposites with low Ag content (10%). Other techniques, such as TEM, XRD, and nano-indentation are also used to obtain a comprehensive characterization of these powders.

V9.35

NO DECOMPOSITION PROPERTY OF ELECTROCHEMICAL CELL WITH NANO STRUCTURE CONTROLLED OXIDE LAYER. Kazuyuki Matsuda, Sergei I. Bredikhin, FCRA, Synergy Ceramics Laboratory, Nagoya, JAPAN; Masanobu Awano, AIST, Synergy Materials Research Center, Nagoya, JAPAN; Kunihiro Maeda, FCRA, Synergy Ceramics Laboratory, Nagoya, JAPAN.

The NO decomposition activity of electrochemical cells composed of yttria-stabilized zirconia (YSZ) solid electrolyte, Pt electrodes and a oxide nanocomposite layer, which covered the surface of the cathode, was evaluated in the presence of excess oxygen. The mixed oxide layer that consists of NiO and YSZ was sintered at 1723 - 1773 K. The layer was dense and included nanoscale continuous pore. The one-compartment cell was used for studying the electrochemical promotion of the NO decomposition by DC electrolyses. The NO decomposition behavior was measured on electrochemical cells by applying DC voltage in the temperature range from 823 to 973 K. It was found that covering of Pt cathode by mixture of oxygen ionic conductor, YSZ, and electronic conductor, NiO, increased the NO decomposition activity even in the presence of oxygen. In the presence of oxygen, the electrochemical cell without the oxide nanocomposite layer required a high current density to decompose NO. It is assumed that the existence of nanoscale pore in the dense nanocomposite layer promoted the NO decomposition. The relation between the microstructure and the NO decomposition activity will be discussed. Research supported by METI, Japan, under the Synergy Ceramics Project, part of the work supported by NEDO.

V9.36

INORGANIC - CARBON NANOTUBE MATRIX COMPOSITES. J. Ballato, Jeffrey R. DiMaio, Stephen Rhyne, School of Materials Science and Engineering, Clemson Univ., Clemson, SC; Richard Czerw, Scott Webster, David L. Carroll, Dept. of Physics, Clemson Univ., Clemson, SC.

Using an acid-catalyzed sol-gel approach, large optically transparent monolithic silica glasses containing well dispersed, isolated, carbon nanotubes have been created. The SiO₂ glass matrix has 80% theoretical density and exhibits a uniform distribution of nanotubes throughout. Rare earths such as Eu³⁺ have been used as an emissive probe dopant to examine the local dielectric properties of the glass - nanotube composites. A clear indication of dipole coupling between the emissive probe species and the nanotubes has been observed. Further, the strong optical nonlinearities of the composite suggest a number of exciting applications of these "hybrid" materials.

V9.37

STM STUDIES OF BORON DOPED SINGLE WALLED CARBON NANOTUBES. Jiwen Liu, Richard Czerw, David L. Carroll, Dept. of Physics, Clemson Univ., Clemson, SC; Pulickel M. Ajayan, Dept. of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Boron-doped SWNTs have been created using arc-discharge growth techniques. TEM investigations show significant differences in bundle morphology and length of B-doped materials as compared to pure materials grown under similar conditions. Atomic resolution STM imaging shows that these nanotubes exhibit a variety of chiralities unlike multiwalled nanotubes which are believed to be all zig-zag. Further, tunneling spectroscopy indicates that the "BC₃ island" formation reported for the B-doped MWNT does not occur in the SWNT case. This implies, not unexpectedly, that a very different incorporation mechanism is responsible for placing B into the SWNT lattice vs. the MWNT lattice during arc growth and provides insight into nanotube growth mechanisms overall.

V9.38

USING ION BEAMS TO MODIFY NANOCRYSTALLINE COMPOSITES. A. Meldrum, K.S. Beaty, University of Alberta, Dept of Physics, Edmonton, AB, CANADA; R.A. Zuhr, C.W. White, L.A. Boatner, Oak Ridge Nat'l Lab, Solid State Div, Oak Ridge, TN.

Ion irradiation is an established and widely used technique for modifying and controlling the microstructural and electronic properties of thin films. Generally, the injected ions pass through the film, creating defects but no intrinsic chemical changes. In recent years, several investigations have used ion irradiation as a means of controlling or patterning film properties - frequently in order to modify the magnetic hardness. In contrast, the effects of ion irradiation on nanocrystalline composites have not been extensively investigated despite over 50 years of radiation damage studies on bulk materials. As in the case of thin films, ion irradiation may be expected to radically alter the microstructural and electronic properties of such composites, as well as their overall strength and hardness. These effects may be particularly important where nanocrystalline materials are planned for use in high-flux environments (e.g., space flight).

Furthermore, ion irradiation offers an excellent opportunity to create or pattern materials with novel properties. In this work, a number of nanocrystalline composites were synthesized by ion implantation or by chemical precipitation. Specimens were irradiated with noble gas ions and microstructural changes were investigated by transmission electron microscopy. Magnetic or optical properties of some of the composites were measured before and after irradiation. The results demonstrate that ion irradiation can create many unusual microstructures and can be readily employed to modify or pattern the material properties of interest. We also find that, in some cases, the response of nanophase precipitates to ion irradiation can be strikingly different than that of the corresponding bulk phase.

V9.39

FUNCTIONALIZED OCTAPHENYLSILSESQUIOXANES AS PRECURSORS TO NANOCOMPOSITE MATERIALS. C. Brick, R. Tamaki, J. Choi, S. Kim, K. Park and R.M. Laine, Departments of MS&E, Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI.

Functionalized octaphenylsilsesquioxanes [(C₆H₅SiO_{1.5})₈, cubes], with their high thermal stabilities and rigid inorganic cage structure, have been sought after building blocks for nanocomposite materials. We report here the synthesis of several derivatives of octaphenylsilsesquioxane, incorporating functional groups such as amino, acetyl, bromo, and sulfonyl chloride. Selected derivatives have shown potential for application in inorganic/organic hybrid nanocomposites, opto-electronic materials, or chelating materials.

V9.40

NEW PRECURSOR APPROACH TO COLLOIDAL TiO₂ NANOPARTICLES. Anjana Devi, Harish Parala, Raghunandan Bhakta, Urmila Patil, Jurij Weiss, Roland A. Fischer.

New precursors of Ti namely [Ti(OPri)₂(deae)₂] 1 and [Ti(OPri)₂(deap)₂] 2, (where deae = diethylaminoethanol and deap = diethylaminopropanol) were used as Ti sources to grow colloidal TiO₂ nanoparticles using hexadecylamine (HDA) and trioctylphosphine oxide (TOPO) as coordinating or capping ligands. Modified alkoxides of Ti such as [Ti(OPri)₂(thd)₂] which have an increased coordinative saturation at the metal centre relative to Ti(OPri)₄, have been successfully investigated as alternative precursors in liquid injection MOCVD. We have developed novel Ti precursors using functionalized alkoxide ligands for CVD purposes and in the process have successfully used these precursors (1 and 2) to grow TiO₂ colloids using a non-aqueous route which will be reported. The colloidal TiO₂ nanoparticles were characterised by UV-Vis spectroscopy, photoluminescence spectroscopy, TEM, HRTEM analysis and X-ray diffraction. The particle size distribution was studied using laser light scattering.

SESSION V10/AA8: JOINT POSTER SESSION
SELF ASSEMBLY OF NANOPHASE AND
NANOCOMPOSITE MATERIALS
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

V10.1/AA8.1

NANOSIZED PARTICLES AS BUILDING BLOCKS FOR NOVEL POWDERS. Heinrich Hofmann, Nathalie Jongen, Marcel Donnet, Jaques Lemaitre, Paul Bowen Material Science Department, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND.

Nanostructured materials can be manufactured using very different methods, for examples crystallisation of amorphous metals, severe plastic deformation, self-assembling of supramolecules with or without templates or using nanosized particles. Regarding nanoparticles, beside classical processing routes like ceramic powder processing or coating with suspension, in the last few years an increasing interest regarding the assembling of nanoparticles could be observed. Applications like nanolithography, medical devices, devices for diagnostic etc. needs a very well controlled array of monosized particles with a well controlled shape in one, two as well as in three dimensions. In this presentation, some fundamental aspects regarding the required properties of the particles, the synthesis of such nanoparticles and the important forces and mechanisms dealing with the formation of arrays by self-assembling of nanosized particles will be discussed. If the crystallite size and shape of nanosized particles is very homogeneous, the agglomeration of these crystallites to dense particles with a controlled shape is possible. Our investigations show that with surface modification of the crystallites using organic molecules precipitated nanocrystallites can be agglomerated to spherical, cubic or rod like particles. In this paper, a thermodynamic approach which will explain the mechanisms of particle formation by

controlled self-organising of nanocrystallites will be developed. Beside surface energy and interactions of hydrophilic/hydrophobic nature, depletion forces combined with other entropic effects will be taken in consideration. With this example of molecular to micron scale control one can envisage the next step being microstructure control using the micron sized particles as the next building block ending with a well defined and organised macrostructure from the molecular level. Finally some interesting (potential) applications will be shown.

V10.2/AA8.2

SILVER-POLYIMIDE NANOCOMPOSITE FILMS GIVING SELF-ASSEMBLED HIGHLY REFLECTIVE SILVERED SURFACES. Robin E. Southward, Structures and Materials Competency, Langley Research Center, National Aeronautics and Space Administration, Hampton, VA; D.W. Thompson, C.J. Dean, J.L. Scott, S.T. Broadwater, Dept. of Chemistry, College of William and Mary, Williamsburg, VA.

Highly reflective and/or surface conductive flexible polyimide films have been prepared by the incorporation of soluble silver(I) complexes with the 1,1,1-trifluoro-2,4-pentanedionate and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ligands into dimethylacetamide, diglyme, and dimethylformamide solutions of the poly(amic acid)s and polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride/1,3-bis(aminophenoxy)-benzene, (6FDA/1,3(3)-APB), and 6FDA/2,2-bis[4-(4-aminophenoxy)hexafluoropropane, 6FDA/4-BDAF. Thermal curing of silver(I)-poly(amic acid) films ca. 20 mil in thickness leads to cycloimidization with concomitant silver(I) reduction yielding a reflective and conductive surface-silvered film for silver concentration from 2-13 weight percent. The films are cured to a final temperature of 300 C for several hours. The metallized 6FDA-based films retain the essential mechanical properties of undoped films and have good thermal stability particularly in nitrogen atmospheres. The bulk of the polymer contains nanometer-sized silver particles and is not electrically conducting. Transmission electron microscopy establish that films have surface layers of silver from ca. 20-200 nm in thickness. In general, films prepared with the silver(I)-1,1,1,5,5,5-hexafluoro-2,4-pentanedionate complex are reflective but not conductive, where as films prepared with the silver(I)-1,1,1-trifluoro-2,4-pentanedionate complex are both reflective and electrically conductive, particularly for silver concentration above 10 weight percent. Films prepared from the soluble fully imidized form of the 6FDA-based polymers rather than from the amic acid were in general less reflective and less regular in surface morphology than those prepared from the poly(amic acid). The metallized films were characterized with respect to conductivity, reflectivity, surface morphology, thermal, chemical, and mechanical properties.

V10.3/AA8.3

ANTI-STOKES LUMINESCENCE OF DYE-DOPED MESOSTRUCTURED SILICA THIN FILMS. Michael H. Bartl, Brian J. Scott, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA; Gernot Wirnsberger, Alois Popitsch, Karl-Franzens-Univ of Graz, Dept of Chemistry, Graz, AUSTRIA; Galen D. Stucky, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

Recently, materials showing efficient anti-Stokes luminescence are attracting interest with respect to possible applications such as laser cooling and temperature sensors. Here we report on very efficient anti-Stokes luminescence of the xanthene laser dye Rhodamine 101 incorporated into 2-d hexagonally ordered mesostructured silica thin films prepared by a combination of weakly acidic sol-gel chemistry and block-copolymer templating. Owing to their nanoscopic organic/inorganic phase separation as-synthesized mesostructured compounds are excellent solid host for organic dyes. While the inorganic silica phase gives a rigid porous framework comparable to sol-gel glasses the organic surfactant phase provides an ideal environment for organic dye molecules resulting in high quantum efficiencies comparable to that in liquid solutions. By excitation of the Rhodamine 101 dye doped mesostructured films with the 632.8 nm line of a He-Ne laser several unusual observations associated with the dye luminescence were made. Both the energy position of the emission intensity maximum and the average energy of the emitted photons are higher than the energy of the exciting photons. By varying the intensity of the laser output we found a linear dependence of the sample emission intensity on the power of excitation. This observation is attributed to an up-conversion process involving direct single-photon hot band absorption. Although the mesostructured films were doped with rather high amounts of Rhodamine 101 (ranging from 0.05 to 1.0 wt%) quantum efficiencies as high as 0.84 were obtained.

V10.4/AA8.4

STRUCTURAL INVESTIGATIONS OF SELF-ASSEMBLED NANOPOROUS ALUMINA. Guangwen Zhou, Judith C. Yang, Dept

of Materials Science & Engineering; Hong Koo Kim, Dept of Electrical Engineering, Univ of Pittsburgh, Pittsburgh, PA.

Anodic porous alumina is known to be a typical self-ordered nanochannel material. The density difference and volume expansion at the metal/oxide interface leads to compressive stress in the oxide layer, and this usually results in formation of a densely packed pore array of hexagonal symmetry. Highly regular arrangement of pores, however, occurs only for a small process window, and the domain size is usually limited to a micrometer scale. Recently we have fabricated nanoscale pore arrays on aluminum substrates using an anodic process. Within domains, hexagonal pore arrangements with the same orientation of the pore lattice are observed. We have examined the structure of the nanoporous alumina by SEM as well as by planar and cross-sectional TEM, and will present the results of our structural investigations.

V10.5/AA8.5

LOW TEMPERATURE HYDROTHERMAL SYNTHESIS OF NANOCRYSTALLINE CERIA-BASED SOLID SOLUTIONS WITH IRON DOPANTS. Guangshe Li, R.L. Smith Jr., H. Inomata, Tohoku Univ, Sendai, JAPAN.

Ceria-based solid solutions have several important applications such as fuel cells and sensors. The design of new electrolytes depends primarily on an understanding of conductivity for the dopants with a wider ionic size range. However, it is failed to prepare ceria-based solid solutions with a much smaller iron dopant by solid state reactions. This work reports on the crystallization of ceria-based solid solutions with iron dopants. It is found that under low temperature hydrothermal conditions, single phase fluorite ceria-based solid solutions containing trivalent iron ions could be obtained within the nano-meter scale in a compositional range of 0.00 to 0.20. These nanocrystals showed superparamagnetic behavior. The extremely low concentration of oxygen vacancies for these solid solutions was explained in terms of a structural model of substitutional and interstitial dopings.

V10.6/AA8.6

INVESTIGATING CATALYTIC PROPERTIES OF COMPOSITE NANOPARTICLE ASSEMBLIES. Mathew M. Maye, Yongbing Lou, Jin Luo, Laura Moussa, Wei-Ben Chan, Chuan-Jian Zhong, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Composite nanoparticles such gold and alloy particles in the nanometer-sized range are explored as candidates for highly effective catalysts. The nanoparticles are assembled as interfacial thin films. A key challenge is the effective isolation of the nanosized properties while retaining the nanoscale catalytic properties. Core-shell nanoparticles provide an intriguing pathway because the encapsulating structure enables tailoring of core size and enhancement of stability of nanosized catalysts against aggregation propensity. This presentation reports the results of an investigation of the catalytic activation of the nanoparticle assemblies towards CO and methanol oxidation using a number of techniques including electrochemical, electrochemical quartz crystal nanobalance, scanning probe microscopy and infrared reflection spectroscopy. It is demonstrated that the catalytic activity depends on a number of factors including core size, shape, composition, interfacial mass transport and potential-induced oxidation-reduction of surface oxygenated species. The findings will be discussed along with the core-shell tailoring strategies of the nanosized catalytic properties.

V10.7/AA8.7

SURFACTANT TEMPLATED HIGH QUALITY HEXAGONAL MESOSTRUCTURED CHALCOGENIDE SEMICONDUCTORS. P.N. Trikalitis, K.K. Rangan, M.G. Kanatzidis, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Ordered nano-materials with intimately mixed organic and inorganic components are a special class of nanocomposites that are expected to display novel electronic properties. We are particularly interested in metal chalcogenide porous frameworks with enhanced transport and optical properties. The organic part is typically surfactant molecules with special head groups and may play a role in the properties of these materials beyond merely serving as templating agents. The framework pores of these materials are ordered in the mesoscale regime with sizes of 20-50 Å. We will present our efforts in this area and our synthetic strategy to generate broad classes of these materials. We will also describe several semiconducting solids with hexagonal pore arrangement formed by linking adamantane clusters $[\text{Ge}_4\text{Q}_{10}]^{4-}$ (Q=S, Se) and $[\text{Sn}_4\text{Se}_{10}]^{4-}$ as well as simpler $[\text{SnSe}_4]^{4-}$ and $[\text{Sn}_2\text{Se}_6]^{4-}$ anions with square planar Pd^{2+} and Pt^{2+} ions in the presence of alkylpyridinium surfactant molecules, $\text{C}_n\text{PyBr}\cdot x\text{H}_2\text{O}$

(n=12, 14, 16, 18). The use of these ions as the linkage metal has a huge influence of the self-assembly reaction, and gives rise to highly ordered hexagonal mesostructures based on $[\text{Ge}_4\text{Q}_{10}]^{4-}$ (Q=S, Se) and $[\text{SnSe}_4]^{4-}$. The degree of hexagonal order in these materials rivals or exceeds that of the highest quality MCM-41.

V10.8/AA8.8

CYCLIC MICROHARDNESS BEHAVIOR OBSERVED IN CRYOMILLED NANOCRYSTALLINE Zn. Xinghang Zhang, Haiyan Wang, Jagdish Narayan, Carl C. Koch, North Carolina State University, Dept of Materials Science and Engineering, Raleigh, NC; Magdy Kassem, Suez Canal University, Dept of Materials and Metallurgical Engineering, Suez, EGYPT.

Nanocrystalline Zn has been prepared by a cryomilling technique. Large numbers of small grains (2~6nm) have been found in the very early stages of cryomilling as revealed by transmission electron microscopy (TEM) along with larger grains up to several hundred nanometers. Dynamic recrystallization was used to explain the observed phenomena. Microhardness of cryomilled Zn exhibits cyclic behavior with milling time. The microhardness changes are very reproducible and large changes in microhardness of factors of two are observed. Detailed TEM and HRTEM are carried out for samples milled at critical times with regard to the cyclic hardness. Evidence from XRD and DSC measurements is also used to explain these results. Possible explanations include differences in grain size distribution, dislocation densities within the grains, and activation of non-basal plane slip.

V10.9/AA8.9

STUDIES OF INTERSUBBAND TRANSITIONS IN ARRAYS OF BISMUTH NANOWIRE SAMPLES USING OPTICAL TRANSMISSION. M.R. Black^a, S.B. Cronin^b, Y.M. Lin^a, M. Padi^b, M.S. Dresselhaus^{a,b}, ^aMIT, Department of Electrical Engineering and Computer Science, Cambridge, MA; ^bMIT, Department of Physics, Cambridge, MA.

When a porous anodic alumina template is filled with bismuth, the bismuth forms a self-assembled array of aligned single crystalline bismuth nanowires, which exhibit unusual optical properties. If the diameter of the wires is small enough, for example 49(17)nm at 77K(293K), the bismuth nanowires are quantum confined in two dimensions and hence are one-dimensional conductors. The quantum confinement in the nanowires causes subbands in the electronic band structure to form. Electronic transitions between these subbands give rise to optical absorption features. Using Fourier transform infrared absorption, in an energy range where intersubband transitions are predicted (0.05 to 0.5 eV), intersubband transitions in arrays of bismuth nanowires have been measured. The experimental results are compared to theoretical simulations. The energy of the intersubband transitions as a function of wire diameter and n-type carrier doping are reported.

V10.10/AA8.10

CONTROLLING NANOSCALE ORDERING IN METAL OXIDE THIN FILMS TEMPLATED BY AMPHIPHILIC BLOCK COPOLYMERS. Ryan C. Hayward¹, Peter Alberius-Henning², Karen L. Frindell², Galen D. Stucky², Bradley F. Chmelka¹, Edward J. Kramer^{1,3}. ¹Department of Chemical Engineering, ²Chemistry Department, ³Materials Department, University of California, Santa Barbara, CA.

Templating with amphiphilic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers is a convenient route for the production of metal oxide films with regular nanostructural ordering. These films are promising for applications ranging from optical, electronic and photovoltaic devices, to membranes and sensors. To realize such applications it is important to exercise control over the phase structure adopted by the self-assembled organic/inorganic composite materials. Past studies have frequently focused on the production of one particular phase with a given polymer, despite the rich phase behavior exhibited by these polymeric species in aqueous systems. We will discuss how to exercise rational control over nanoscale morphology in thin films by mapping onto the polymer-water binary phase diagram. By systematically varying the polymer content in the composite films, materials with well ordered lamellar, 2D hexagonal, and cubic morphologies have been prepared using the same organic structure-directing agent. One- and two-dimensional small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) have been used to characterize the nanoscale morphology, domain size, and orientational ordering within the thin films. We focus on the characterization of composite silica/block copolymer films and demonstrate the apparent generality of the method for titania/block copolymer films as well.

V10.11/AA8.11

SYNTHESIS AND CHARACTERIZATION OF GRAPHITE NANOFIBERS FROM THE DECOMPOSITION OF CO/H₂ USING POWERED FeCu CATALYSTS. O. Carneiro, Northeastern University, Dept of Chemistry, Boston, MA; P.E. Anderson, Catalytic Materials Ltd, Holliston, MA; M.S. Kim, Myong Ji, University, Dept of Chemical Engineering, Seoul, KOREA; R.T.K. Baker, Catalytic Materials Ltd, Holliston, MA; N.M. Rodriguez, Catalytic Materials Ltd, Holliston, MA.

The formation of graphite nanofibers from the catalytic decomposition of carbon containing gases interacting with small metal particles continues to generate immense interest in the research community. The unique structure and chemical properties of these novel carbon materials are now at the forefront of aggressive research for potential electrochemical applications and as catalyst supports. In the present investigation the properties of graphite nanofibers formed from the decomposition of CO/H₂ interacting with powered FeCu catalysts in the temperature range of 550 to 650°C were studied. The surface area of the graphite nanofibers was determined using the BET equation and detailed characteristics of the graphite nanofibers are being investigated by a combination of High-Resolution Transmission Electron Microscopy (HR-TEM), Temperature Programmed Oxidation (TPO) and X-ray diffraction. It has been found that the composition of the catalyst, the reaction temperature and the CO/H₂ reactant gas ratio have a direct impact on the yield of the solid carbon formed, as well as the structural characteristics exhibited by the nanofibers.

V10.12/AA8.12

THE ROLE OF THE INTERFACES IN THE OPTICAL EFFECTS OF LARGE-SIZED SiC_xO_{1-x}N NANOCRYSTALLITES. K.J. Plucinski, Mil. Univ. of Technology, Dept of Electronics, Warsaw, POLAND, H. Kaddouri, Universite du Perpignan, Lab. LP2A, Perpignan, FRANCE, I.V. Kityk, Institute of Physics, WSP Czistochowa, POLAND.

The main goal of the present work was to study the transparency of large-sized (10-25) nm nanocrystallites (NC) of SiC_xO_{1-x}N (0.96 < x < 1.06), both experimentally, as well as theoretically. The band energy structure was investigated using different band energy approaches, as well as modified Car Parinello molecular dynamics simulations of interfaces. In particular, we investigated the influence of nanocrystallite size and carbon excess on the optical absorption of the SiC_xO_{1-x}N nanocrystallites, the contribution of the reconstructed near-interface states to the visible absorption of the NC and the contribution of the carbon sheet interfaces to the absorption spectra observed. Among the many possible NC materials, SiC_xO_{1-x}N crystallites were chosen because the technology for their manufacture with the sizes needed is well developed, the energy gap of SiC_xO_{1-x}N may be manipulated within the large spectral ranges (2 - 4.5 eV), depending on polytype kinds, and because SiC_xO_{1-x}N is substantially more stable than other SiON materials, when external mechanical and thermo-treatments are applied. A thin carbon sheet (of about 1 nm) appears, covering the crystallites. This sheet leads to substantial reconstruction of the near-the-interface SiC_xO_{1-x}N crystalline layers. Electron microscopy, NMR, X-ray diffraction, IR absorption and Raman data were applied in order to gain a full understanding of the structural properties and the optical absorption spectra of both the carbon sheets and the reconstructed SiC_xO_{1-x}N close to the particle surfaces. Numerical modeling shows that these NC may be treated as quantum dot-like SiC_xO_{1-x}N reconstructed crystalline surfaces, covering SiC_xO_{1-x}N crystallites. All band energy calculation approaches (semi-empirical pseudopotential, fully augmented plane waves and norm-conserving self-consistent pseudopotential approaches) predicted the experimental spectroscopic data obtained. In particular, it was shown that the near-the-surface carbon sheet plays a dominant role in the behavior of the reconstructed band energy structure. Independent evidence for the important role of the dot-like crystalline layers are the excitonic-like states, which are not dependent on the particular structure of the SiC_xO_{1-x}N, but are sensitive to the thickness of the carbon layer.

V10.13/AA8.13

REVERSIBLE CHARGING EFFECTS ON OPTICAL PROPERTIES OF POROUS SILICON. Vivechana Agarwal, J.E. Lugo and J.A. del Rio, UNAM, Temixco, MEXICO.

An effective medium approximation predicted that the effect of introducing charge is to decrease the dielectric response of the material. In this work porous silicon samples have been charged and depending on the current intensity, the PLE response can be tuned in the energy range 1.5-2.6 eV. A decrease in the emission intensity with an increase in charging current has been observed. This effect is reversible and the recovery time is found to be in the range of 4-6 min. The variation of charging effect with thickness of porous silicon layer has also been studied. An increase in the lowering of the intensity with an increase in thickness has been observed.

V10.14/AA8.14

FLAME SYNTHESIS OF Fe CATALYZED SINGLE-WALLED CARBON NANOTUBES AND Ni CATALYZED NANOFIBERS: GROWTH MECHANISMS AND CONSEQUENCES.

Randy L. Vander Wal, Lee J. Hall, Gordon Berger, The National Center for Microgravity Research, The NASA-Glenn Research Center, Cleveland, OH.

Flame synthesis of single-walled carbon nanotubes catalyzed by Fe and nanofibers catalyzed by Ni is demonstrated using a pyrolysis flame configuration. Fe reacts preferentially with CO/H₂/He mixtures to produce SWNTs. In contrast, Ni reacts preferentially with C₂H₂/H₂/He mixtures to yield nanofibers. Both catalyst metals exhibit a high level of size dependent reactivity towards these reactant gas mixtures. A 'yarmaluke mechanism' [Dai et al.] and a carbon solvation/diffusion/precipitation [Baker et al.] account for the different catalyzed products; SWNTs and nanofibers. The consequences of these mechanisms are discussed for a) catalyst particle size evolution, b) catalyst particle deactivation/inertness and c) SWNT and nanofiber structure and morphology.

V10.15/AA8.15

DENDRIMER NANOCOMPOSITES: SYNTHESIS, PROPERTIES AND APPLICATIONS. Lajos Balogh, Dept. of Medicine, Univ of Michigan, MI.

Dendrimer nanocomposites (DNC) are recently developed nanosized inorganic/organic hybrid materials (Chemical Innovation, March 2000, pp. 19-26) displaying unique physical and chemical properties. The primary goal of this presentation is to present the synthesis concept and the unique potential of these nanocomposites and engineered DNC nanostructures to make photonic and other materials. DNCs are synthesized as atomic/molecular level mixtures of organic and inorganic atoms as constituents with no covalent bonds between the components. They can be made in a controlled composition, in a predetermined and uniform size, with adjustable surface functionalities and in various morphologies. Both macromolecular and materials properties are present on this nanoscopic scale, which results in many interesting and unique features. A great variety of these nanocomposites can be built. The uniform DNC building blocks can be further organized into ordered structures, such as 0-D (quantum dots), 1-D (chains), 2-D (ultrathin multilayers) and 3-D nanostructures. These nanomaterials and nanostructures offer numerous application opportunities for photonic materials, optics, electronics, sensors, catalysis, environmental cleanup, bioengineering and medicine just to list a few.

SESSION V11: MODELING AND THEORY

Chair: Simon R. Phillpot

Thursday Morning, November 29, 2001
Back Bay C (Sheraton)

8:30 AM *V11.1

INTERCALATIVE ROUTE TO HETEROSTRUCTURED NANOHYBRIDS. Jin-Ho Choy, School of Chemistry and Molecular Engineering, Seoul National University, Seoul, KOREA.

Inorganic-inorganic, organic-inorganic and bio-inorganic nanohybrids have been demonstrated by applying an intercalation technique for Bi-based cuprate superconductors, Bi₂Str₂Ca_{m-1}Cu_mO_y (m = 1, 2, and 3; BSCCO), and for layered double hydroxides (LDHs). The molecular hybridization between two different compounds is of high importance in terms of basic understanding of intercalation reactions and of its practical applications. The organic-inorganic hybrids were achieved via intercalative complexation, where the pre-intercalated metal halide in Bi-based cuprate superconductors reacts with the organic salt of Py-C_nH_{2n+1}I (Py = pyridine). We also achieved superconducting colloidal suspension from the organic-intercalates, from which the fabrication of high-quality superconducting thin film could be realized. The intercalative complexation adopted in this work is expected to be a new route to the nanocomposite with unique structure and property unattainable by various conventional methods. We were also able to demonstrate that the biomolecules such as CMP, AMP, GMP, even DNA and FITC can be hybridized with an inorganic layer compound like LDH, giving rise to nanohybrids which consist of biomolecular layer and inorganic hydroxide one alternatively. And it was found that the biomolecules stabilized in the interlayer space of LDH retain their chemical and biological integrity. If necessary, LDH, as a reservoir, can be intentionally removed by dissolving it in an acidic media. On the other hand, interlayer biomolecules can also be deintercalated via ion-exchange reaction in an electrolyte which offers a way of recovering the encapsulated biomolecules. In addition, we also found that the hydroxide layers could protect the intercalated DNA very efficiently from DNase degradation, and also tailored the

DNA molecule with an appropriate size or length depending on the particle size of LDH. It is, therefore, concluded that the inorganic LDH can act as a good host lattice for a gene reservoir or carrier.

9:00 AM V11.2

WHAT XENON NANOCRYSTALS IN ALUMINUM TEACH US ABOUT MATERIALS SCIENCE. C.W. Allen, R.C. Birtcher, Argonne Natl Lab, Materials Science Div, Argonne, IL; U. Dahmen, LBNL, Berkeley, CA; K. Furuya, M. Song, NIMS, Tsukuba, JAPAN; S.E. Donnelly, Salford Univ, Joule Lab, Manchester, UNITED KINGDOM.

Noble gases are generally very insoluble in solids. Xe implantation into Al at 300 K, for example, results in a fine dispersion of Xe crystals, stabilized by the Laplace pressure due to precipitate/matrix interface tensions which are expected to be practically identical to matrix surface tensions. For known surface tensions, we show that the Laplace pressure on the largest possible equilibrium Xe precipitate which can exist at a given temperature is accurately predicted from bulk isothermal compression data for Xe at that temperature. Furthermore, it is suggested that this fact may be employed to determine unknown surface tensions of a solid matrix from the size and shape of such maximal precipitates of a noble gas element.

9:15 AM V11.3

EXAMINING THE INFLUENCE OF "NEGATIVE" TRIPLE JUNCTION ENERGY. Gaurav Gupta, Alex King, Purdue University, School of Materials Engineering, West Lafayette, IN.

Triple junctions are lines along which three phases or regions meet. Srinivasan, Cahn and Kalonji have suggested that "negative triple junction energy" is possible, meaning that the energy at triple junctions is smaller than that of the grain boundaries to which they are connected. "Negative" triple junction energy might have consequences on structural stability and on growth kinetics at small length scales. We have modeled two- and three-dimensional nanocrystalline solids, with varying triple junction energy and observe its effects on the overall system energy. At fine grain sizes, the volume fraction of the intercrystalline region becomes dominant and as the grain size decreases into the nanometer scale, triple junctions and quadruple points account for an increasing fraction of the intercrystalline material, and the overall microstructure. The negative slope of the total system energy with respect to grain size represents the global driving force for grain growth. It is mathematically possible for the system energy curve to exhibit minima, representing locally stable microstructures. Assigning reasonable, but differing values to the grain boundary, triple junction and quadruple point energies, including "negative junction energies," we find that this slope of the system energy with respect to the mean grain diameter is always negative, although it may exhibit inflection points. This means that negative junction energy, on its own, cannot be responsible for microstructural stabilization.

Work supported by the National Science Foundation, grant number DMR 0096147

9:30 AM V11.4

SYNTHESIS OF A MAGIC FAMILY OF ULTRABRIGHT Si NANOPARTICLES. G. Belomoin, J. Therrien, R. Twesten, S. Chaieb, and M. Nayfeh, Dept of Physics, and Dept of Theoretical and Applied Mechanics, Univ of Illinois at Urbana-Champaign; L. Wagner and L. Mitas, Dept of Physics, North Carolina State Univ, NC.

We demonstrate, using direct imaging, excitation, and emission spectroscopy, and colloidal crystallization that electrochemically etched, hydrogen capped Si_n clusters with n larger than 20 exhibit magic numbers. Particles classify into a family of spherical sizes that includes ~ 1.0 (Si_{29}), 1.67 (Si_{123}), 2.15, 2.9, and 3.7 nm diameter, with HUMO-LUMO gap of 3.44, 2.64, 2.39, and 2.11 eV, and emission band centered in the blue, green, yellow, and red for the smallest four. Density functional approaches confirm the sizes and the band gaps.

10:15 AM *V11.5

HYDROTHERMAL SYNTHESIS OF DESIGNER PARTICULATES. R.E. Riman, Dept of Ceramic and Matls Engr, Rutgers University, Piscataway, NJ.

Designer particulates are powders with controlled physical and chemical characteristics. With the growing interest in nanopowders, there is a growing need to have rational engineering strategies for cost-effective production. Our research is focused on hydrothermal methods for powder production using a rational approach for process development. Thermochemical computations for aqueous-solid heterogeneous systems are used to define phase space as a function of temperature, composition and if necessary, pressure. The defined phase space can be used to design robust processes as well as identify reaction variable regimes where opportunities for controlled size and morphology are possible, as we will show for broad range of materials.

10:45 AM V11.6

SIMULATION OF FORMATION AND VIBRATIONAL STATES IN GOLD NANOPARTICLES. Yoshiaki Kogure and Masao Doyama, Teikyo University of Science & Technology, Yamanashi, JAPAN.

Formation of gold nanoparticles and vibrational states in the particles are investigated by means of molecular dynamics simulation. The number of atoms in the particles ranges 100 and 10000. The EAM potential for Au developed by the present authors are adopted to express the interaction between atoms in the simulation. The potential function is expressed by exponential and power functions and contains five parameters, which are determined uniquely from the experimental values of the lattice parameter, the cohesive energy and the elastic constants. The nanoparticle is formed in a computer by cooling the molten state slowly and then by annealing the particle. Several methods of annealing procedure are tried to obtain a configuration with minimum energy. Surface morphology of the nanoparticles are investigated in relation to surface energy. It is related to the thermal stability of the nanoparticles. The atomistic structure in the particles are visualized through the potential energy difference and the local crystalline order, which distinguishes a fcc atom from the atoms of hcp or other crystal structures in nearest neighbor configuration. From the motion of atoms consisting particles at elevated temperatures, the vibrational density of states are calculated as a function of particle size. The generations of surface vibration and surface roughness at elevated temperatures are also observed in the simulation. Final purpose of the present study is to find the fundamental mechanisms of self organization in the nanoparticles.

11:00 AM V11.7

MECHANISMS OF HEAT FLOW IN SUSPENSIONS CONTAINING NANO-SIZED PARTICLES (NANOFLUIDS). Liping Xue, P. Keblinski, Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy NY; S.R. Phillpot, J.A. Eastman, Materials Science Division, Argonne National Laboratory, Argonne IL; S. U.-S. Choi, Energy Technology Division, Argonne National Laboratory, Argonne IL.

Recent measurements on stationary suspensions of nanosized solid particles in heat-transfer liquids (so-called nanofluids) have demonstrated that the thermal conductivity increases with decreasing grain size, even for stationary fluids. However, such increases cannot be explained by theories derived within the continuum description of matter under the assumption of diffusive heat transport in both liquid and solid phases. We explore four possible explanations for this anomalous increase: (i) the Brownian motion of the particles, (ii) molecular-level layering of the liquid at the liquid-particle interface, (iii) the nature of heat transport in the nanoparticles, and (iv) the effects of nanoparticle clustering. Analysis of the above factors and the results of atomic-level molecular-dynamics simulations, indicate that the key factors in understanding thermal properties of nanofluids are the ballistic rather than diffusive nature of heat transport in the nanoparticles combined with direct or fluid mediated clustering effects providing paths for rapid heat transport.

11:15 AM V11.8

CHEMICAL VAPOR SYNTHESIS OF NANOCRYSTALLINE SILICON CARBIDE: A REACTION-COAGULATION-SINTERING MODEL. Markus Winterer, Institute of Materials Science, Darmstadt University of Technology, Darmstadt, GERMANY.

Among the most recent developments in the theoretical description of gas to particle conversion processes is the simultaneous modeling of precursor decomposition, coagulation and sintering processes in the aerosol, originally reported by Koch and Friedlander (1990). A simple, monodisperse model has been developed by Kruijs et al. 1993. In the Chemical Vapor Synthesis process (CVS, Klein et al. 1998) particles pass through the complete temperature profile of a hot wall reactor together with the gas stream. This creates a highly non-isothermal temperature history for the particles. Therefore, we extended the model of Kruijs et al. 1993 by explicitly including the decomposition reaction as source term for the aerosol and the heat exchange and heat production to remove the restriction to isothermal conditions and applied the model to CVS of silicon carbide from tetramethylsilane (TMS). The inclusion of the total aerosol surface area and volume ensures mass conservation and enables the modeling of the CVS process with a time dependent source term. Primary and agglomerate particles are distinguished through the development of the volume and surface area of the agglomerates. A stationary, ideal, one-dimensional plug flow, without axial dispersion is used. The results of the numerical simulations and comparison with experimental results (Klein et al. 1998) as a function of process parameters (hot wall temperature, total pressure, precursor mass flow and reactor length and diameter) will be presented.

References:

S. Klein, M. Winterer, and H. Hahn, Chem. Vap. Dep. 4 (1998), 143

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F.E. Kruijs, K.A. Kusters, S.E. Pratsinis, and B. Scarlett, *Aerosol Sci. Techn.* 19 (1993), 514.

11:30 AM V11.9

OPTICAL CHARACTERIZATION AND MODELING OF S-INCORPORATED NANOCRYSTALLINE CARBON (n-C: S) THIN FILMS. S. Gupta, Univ. of Puerto Rico, Dept of Physics, PR; B.R. Weiner, Univ. of Puerto Rico, Dept of Chemistry, PR; G. Morell, Univ. of Puerto Rico, Dept of Physical Sciences, PR.

S-assisted nanocrystalline carbon (n-C: S) thin films were grown by hot-filament chemical vapor deposition (HFCVD) using a mixture of methane (CH₄), hydrogen sulfide (H₂S) and hydrogen (H₂). The films were deposited on molybdenum substrates at various substrate temperatures and with several H₂S concentration. They were optically examined using ex situ spectroscopic phase-modulated ellipsometry (SPME) from near IR to UV region (1.5-4.5 eV). The ellipsometry data (D(li), y(li)) were modeled using Bruggeman effective-medium approximation (EMA) and the dispersion relations for the amorphous semiconductor such as Forouhi and Bloomer Model (FB) and Tauc-Lorentz (TL) models. By performing these simulations using least-square regression analysis we obtained the dielectric function of our n-C: S material, along with the optical bandgap (E_g), film thickness (d), bulk void fraction (fv), and roughness layer (s). We also discuss the physical interpretation (s) of the modeling parameters. Results from micro-Raman spectroscopy, profilometry and atomic force microscopy (AFM) are also presented, which were used to guide and validate the fitted values.

11:45 AM V11.10

ANALYSIS OF THE ATOMIC-SCALE DEFECT CHEMISTRY AT INTERFACES IN FLUORITE STRUCTURED OXIDES BY ELECTRON ENERGY LOSS SPECTROSCOPY. Yasuo Ito, Northern Illinois University, Dept of Physics, DeKalb, IL; Yuanyuan Lei, Nigel D. Browning, University of Illinois at Chicago, Dept of Physics, Chicago, IL; Terry J. Mazanec, BP Amoco Chemicals, Naperville, IL.

Gd³⁺ doped Ce oxides are highly attractive candidates as electrolytes for solid oxide fuel cells operating at ~500°C. For their successful practical application, a full understanding of the defect chemistry in the bulk and at grain boundaries is essential. In particular, the contribution of the grain boundaries to the total ionic conductivity through such effects as the segregation of impurities, dopants and vacancies is of crucial importance. Here the effect of the atomic structure on the local electronic properties, i.e. oxygen coordination and cation valence, at grain boundaries of the fluorite structured Gd_{0.2}Ce_{0.8}O_{2-x} ceramic electrolyte is investigated by a combination of atomic resolution Z-contrast imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). In particular, O K-, Ce M₄₅- and Gd M₄₅-ionization edges were acquired from defined locations across several grain boundaries. The EELS analyses reveal that the majority of the grain boundaries exhibit segregation of Gd and oxygen deficiency. The Ce M₄₅-edge also shows a dramatic change in the M₅/M₄ white line ratios and the chemical shift of 1.5 eV in the Ce M₄₅-edge between the bulk and grain boundary, indicating a decrease of the valence state. Observation of the O K-edge near-edge fine structure also indicates changes in local atomic environment between the bulk and the boundary. The interplay between oxygen vacancies and dopant distribution on the atomic scale will be discussed in the presentation. The results from the GdCeO_{2-x} will also be compared from those from yttria stabilized zirconia grain boundaries.

SESSION V12: NANOSTRUCTURES II
Thursday Afternoon, November 29, 2001
Back Bay C (Sheraton)

1:30 PM V12.1

NANOCRYSTALLINE PEROVSKITES FOR CATALYTIC COMBUSTION AND MEMBRANE REACTIONS. Neeraj Sangar, Jackie Y. Ying, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Catalytic combustion of methane is an attractive alternative to gas-phase homogeneous combustion, since it can stabilize flames at lower fuel-to-air ratios, thereby lowering flame temperatures and significantly reducing NO_x emissions. Our research objective is to develop complex perovskite-based catalysts with high catalytic activity for methane oxidation and good hydrothermal resistance. Nanocrystalline perovskites (La_{1-x}A_xMn_{1-x}B_xO₃) were synthesized with high surface areas and ultrafine grain sizes using chemical co-precipitation. The precipitation conditions were controlled to obtain powders with correct chemical stoichiometry and excellent

phase purity at lower calcination temperatures. The catalytic activity for methane oxidation was investigated for different A and B site substitutions. These novel catalysts allowed for 10% conversion of a stream of 1% CH₄ in air (60,000 h⁻¹) at around 350°C, which is comparable to traditional PdO-based catalysts, with full conversion at around 550°C, and exhibit superior activity at higher temperatures and in the presence of water. The trends in catalytic activity were explained by characterizing the nature and amount of chemisorbed oxygen species on the catalyst surface using temperature-programmed desorption/reduction, X-ray photoelectron spectroscopy, and oxygen vacancy measurements. The perovskite systems have also been studied as oxide-conducting membranes for oxygen separation and selective methane oxidation. Our objective is to develop membranes with high oxygen flux and stability under operating conditions. We have investigated the effects of oxygen vacancy concentration and crystal structure (unit cell volume and oxygen vacancy ordering) on oxygen flux and stability for Ba_{1-x}Sr_xCo_{1-y}B_yO₃ system. An oxygen flux of ~3.5 cc(STP)/min/cm² was achieved at 900°C, which is substantially higher compared to conventional materials (0.5-2.5 cc(STP)/min/cm²). These membranes have been successfully synthesized as dense perovskite films (~50 nm) on porous supports by electrophoretic deposition to study the effect of decreasing membrane thickness on oxygen flux and separation selectivity.

1:45 PM V12.2

SEMICONDUCTOR NANOWIRES AS BUILDING BLOCKS FOR NANOTECHNOLOGIES: NANO-ELECTRONICS AND NANOSENSORS. Yi Cui, Qingqiao Wei, Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA.

Semiconductor nanowires represent critical building blocks for nanotechnologies, such as nanoelectronics and nanosensors, since their properties can be precisely defined. Herein we present results addressing key aspects of the synthesis, doping, electronic properties and applications of semiconductor nanowires with an emphasis on silicon-based materials. Silicon nanowires with monodisperse diameters can be prepared using our previously established catalytic growth mechanism. Electrical transport measurements are used to demonstrate that both n-type and p-type nanowires can be controllably prepared by introducing dopants during growth, and moreover, that individual wires function as well-defined field-effect transistors. The n-type and p-type nanowires also have been assembled into other key functional nanoelectronic devices including p-n junctions, complementary inverters and bipolar transistors that exhibit current rectification, voltage inversion and current gain, respectively. In addition, we show that these well-defined building blocks can function as ultrasensitive, real-time electrically-based sensors for chemical and biological species. Amine and oxide functionalized silicon nanowires show linear pH-dependence of conductance over a large dynamic range, suggesting that nanowires could function as good pH-sensors. Biotin-modified nanowires demonstrate a sensitive detection of streptavidin down to at least pM range, and real time detection of reversible antibody-antigen binding. The significance and important application of our work for nanoelectronics and nanosensors will be discussed.

2:00 PM V12.3

SYNTHESIS AND HEAT TREATMENT OF LARGE AREA ALIGNED CARBON NANOTUBES AND NANOSHEETS BY MICROWAVE ECR-CVD. Chao Hsun Lin, Hui Lin Chang, Ming Her Tsai and Cheng Tzu Kuo, Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, TAIWAN.

A novel microwave ECR-CVD process was developed to grow large area (4-inch in diameter) aligned carbon nanotubes and other nanostructures on p-type Si wafer with CH₄ and/or H₂ as source gases. The advantage of this process is to grow the aligned CNTs without using template as reported in literature. Effects of catalysts (including Co and Ni), substrate bias and other deposition conditions on nanotube deposition were examined. The SEM, TEM, and Raman spectroscopy characterized the deposited nanostructures. The preliminary results shown that the main parameters to grow different nanostructures include substrate temperature and bias, catalyst, and CH₄/H₂ flow ratio. For examples, the combinations of higher temperature (>550J), negative bias, optimum CH₄/H₂ ratio and catalyst are favor conditions to grow the well-aligned multi-walled carbon nanotubes. Formation of the seaweed-like "carbon nanosheets" is more favor without applications of bias and catalyst. The preliminary results also indicate the hydrogen in the source gases can act as an etching media to depress the nanosheet formation or to obtain the cleaner tubes, which is similar to the function in diamond deposition to remove graphite and leave diamond particles. The nanostructures heat treatment under Ar atmosphere shows that the nanosheets and the CNTs from Ni catalyst are more temperature resistance than the CNT from Co catalyst. The possible deposition mechanisms, structures and the range of deposition conditions of

various nanostructures will be discussed. Keywords: Carbon nanotubes, Carbon nanosheets, ECRCVD, Catalyst, Raman spectroscopy.

2:15 PM V12.4

NANOWIRES AS BUILDING BLOCKS FOR BOTTOM UP ASSEMBLY NANOSCALE ELECTRONICS AND OPTOELECTRONICS. Xiangfeng Duan, Charles M. Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

The semiconductor industry has been dominated by top-down manufacturing technologies, in which bulk materials are carved into small features by lithography processing to form functional devices. Driven by many scientific and technological innovations, the semiconductor industry has experienced a remarkable miniaturization trend, providing even faster, smaller and cheaper computers. However, this joyride will soon end within the next 10-20 years because of the fundamental limitations associated with the top-down manufacturing technologies. Nevertheless, the push for ever more powerful and miniaturized computing system will still continue if not increase. To enable the future of electronics, a new generation of devices will have to be built using fundamentally new approaches. Bottom-up approach, in which functional electronic structures are assembled from chemically synthesized nanoscale building blocks, has the potential to go far beyond of the limits of top-down technology with molecular precision, large area control and low cost. Here we present a new paradigm for bottom-up assembly of electronics and optoelectronics using nanowires as the building blocks. First, a laser-assisted catalytic growth approach will be described for the synthesis of semiconductor nanowire building blocks with controlled electronic properties; second, a variety of nanoscale electronic and optoelectronic devices, including field effect transistors (FET), p-n junction, light emitting diodes (LED) and non-volatile memory (NVM) devices, have been constructed using these chemically synthesized nanowires as building blocks. In addition, rational approaches for assembling of these nanowires into integrated device arrays will also be described. The demonstrated ability to assemble active devices in the absence of multi-billion-dollar fabrication line opens up a new paradigm for future device fabrication and electronics manufacturing.

2:30 PM V12.5

OXIDE NANOPARTICLES/POLYMER/HETEROPOLYACIDS COMPOSITES AS PROTON CONDUCTING MEMBRANES.

D. Carrière, P. Barboux, K. Lahilil, F. Chaput, J.-P. Boilot, Ecole Polytechnique, Laboratoire de Physique de la Matière Condensée, Palaiseau, FRANCE.

Oxide nanoparticles exhibit large range of acidobasic properties due to their surface groups. These properties can be modified through ionic adsorption or organic grafting. We have used such particles for the synthesis of proton conducting membranes by dispersion into an organic polymer (PVDF-co-HFP) and optional impregnation with an electrolyte such as H_3PO_4 . Stable sols of SiO_2 and ZrO_2 with controlled sizes and close morphologies were synthesized through sol-gel and hydrothermal processes. This allows comparison between non grafted SiO_2 that shows poor interaction with the electrolyte and non grafted ZrO_2 that strongly adsorbs H_3PO_4 . Further grafting of various carboxy- and amino-phosphonates onto zirconia surface changes interaction with H_3PO_4 . Proton diffusion mechanisms were studied both in the microscopic scale (liquid-state, MAS NMR, $1/T_1$ and gradient field spectroscopy) and in the macroscopic scale (ionic conductivity as a function of temperature and relative humidity). For low oxide contents, proton diffusion occurs through liquid electrolyte trapped in the organic polymer. Subsequently, optimization of the proton conductivity requires control of the pore size, content and connectivity. For higher nanoparticles contents, proton diffusion occurs at the surface of the nanoparticles. Optimization of the conductivity requires a control of the nanoparticle size, connectivity and surface properties through grafting of acid and/or basic functions. The resulting membranes can find application in systems such as fuel cells, supercapacitors or electrochromic devices.

2:45 PM V12.6

NANOPHASE SILICON SOL-GEL COATINGS FOR CORROSION PROTECTION OF Al ALLOYS. M.S. Donley, V.N. Balbyshvay, and A.J. Vreugdenhil, Air Force Research Laboratory, Materials and Manufacturing Directorate, Nonmetallic Materials Division, Coatings Research Group, Wright-Patterson AFB, OH.

This paper describes a nanophase silicon sol-gel coating that forms a defect free barrier to corrosive species using a pre-formed Self-assembled Nanophase Particle (SNAP) sol-gel system on metal substrates. SNAP coatings provide functionality for bonding to the substrate and tailorable chemistry for interaction with polymer layers. Aqueous solution processes generate nanophase particles with a predominantly inorganic interior and a more organic exterior. Upon application, these particles are cross-linked to produce a dense,

protective thin film on metal substrates. The particles have been characterized by IR and GPC, and chemical models have been generated. The SNAP coatings have been characterized by variety of surface analytical techniques and coating adhesion tests. The electrochemical behavior of the SNAP films with variable organic/inorganic ratios on aluminum 2024-T3 has been evaluated by potentiodynamic scan and electrochemical impedance spectroscopy. Cross-link density and coupling agent application have been studied in detail. Film durability is directly related to the coupling agent. This is consistent with strong bond formation between the substrate and the SNAP film. The chemistry and morphology of the films have been investigated by TEM, XPS and TOF-SIMS and a model film structure will be presented.

3:30 PM V12.7

EFFECTS OF PHYSICAL CONFINEMENT (< 125 nm) ON THE CURING BEHAVIOR OF POLYMERS. Samuel Amanuel and Vivak M. Malhotra, Southern Illinois University, Dept. of Physics, Carbondale, IL.

The mechanical properties of nanocomposites are strongly influenced by dispersion of nano-sized inorganic phase in the polymer matrix and the interaction between the organic and inorganic phases. Efforts are underway to explore whether self-healing ability could be induced in these materials. We are exploring the fabrication of nanocomposites in which porous (< 125 nm) but spherical silica particles are dispersed in phenolic, polyester, and acrylic polymers. Our previous studies have indicated that the physically confined (< 125 nm) fluid's thermodynamic properties are substantially modified with respect to the bulk fluid. Therefore, we subjected polymer-impregnated porous silica to differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM) measurements to explore whether confinement would affect the curing behavior. Our results indicate that unlike bulk resin, the polymer impregnated silica showed a two-step curing, i.e., the physically confined polymer cured at a temperature which was 26 K lower than the bulk phenolic resin. However, no such effects were observed when non-porous but spherical fly ash particles were dispersed in the polymer.

3:45 PM V12.8

MONO-SIZED AND SINGLE-WALLED 4-ANGSTROM CARBON NANOTUBE ARRAYS. N. Wang and Z.K. Tang, Department of Physics, the Hong Kong University of Science and Technology, Hong Kong, CHINA.

Mono-sized and single-walled carbon nanotubes (SWNTs), synthesized by pyrolyzing tripropylamine molecules in the channels of porous zeolite crystals, have been evidenced by high-resolution transmission electron microscopy. As confirmed by imaging simulations, SWNTs measure just 4 angstrom in diameter. Different imaging conditions for the ultra small carbon nanotubes have been simulated. SWNTs formed in the nanochannels of zeolite crystals were highly aligned and packed in hexagonal arrays. Some interesting electrical transport characteristics especially at low temperatures have been measured. For example, the temperature dependence of the SWNT conductivity can be well described by variable-range hopping in a disordered one-dimensional conducting system.

4:00 PM V12.9

NONLINEAR OPTICAL PROPERTIES OF METALLIC NANOWIRES. Michael Kröll, Stéphane Laurent, Werner J. Blau, Physics Department, Trinity College Dublin, IRELAND.

Metallic nanowires are prepared within the pores of anodic alumina membranes. The membranes represent a mesoporous template material with adjustable properties like a pore diameter in the range between 5 and 250 nm and a pore length from 100 nm to 200 microns. Metal is plated inside the pores using an AC plating procedure. The composite materials produced by this method are investigated regarding their nonlinear optical properties. The linear optical properties are dominated by plasmon resonances in the visible region of the electromagnetic spectrum in the case of gold, silver, and copper nanowires. Iron, cobalt, nickel, tin and other nanowires on the other hand do not show a strong plasmon resonance in visible region. Apart from these intraband excitations interband transition are observed for all metals. Due to the centrosymmetric shape of the wires they are not supposed to show any second-order nonlinear optical behavior. Third-order nonlinear properties of nanowires are investigated using the Z-Scan technique. Here the sample is moved through the focal plane of a short-pulsed Nd-YAG laser leading first of all to an increase in laser intensity inside the sample when the sample approaches the focal plane. After having passed the focal plane the 200 intensity of the laser beam decreases again. The Z-Scan technique thus offers the possibility to study intensity dependent optical behaviors without actually changing the intensity of the laser beam. Since nonlinear effects can only be observed at high intensities an inset of nonlinear

behavior can be observed near the focal plane. Nonlinear effects like saturated absorption, self-(de)focusing and nonlinear scattering are investigated by this approach. Current results on nonlinear optical properties of gold, silver, copper and other metal wires are presented. The wire diameter is varied to analyse its possible influence on the optical properties.

4:15 PM V12.10

THERMOELECTRIC POWER AND MAGNETO THERMOELECTRIC POWER MEASUREMENTS OF DOPED MULTIWALL CARBON NANOTUBES. Richard Czerw, David L. Carroll, Dept. of Physics, Clemson Univ., Clemson, SC; Young-Moon Choi, Dong-Soo Lee, Yung-Woo Park, Dept. of Physics and Cond. Matter Research Inst., Seoul National Univ., Seoul, KOREA; Nicole Grobert, Fullerene Science Center, CPES, Univ. of Sussex, Brighton, UNITED KINGDOM; Mauricio Terrones, School of Chemistry, Physics and Environmental Science, Univ. of Sussex, Brighton, UNITED KINGDOM; Sigmar Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.

The temperature dependent thermoelectric power (TEP) and magneto-TEP of undoped multiwalled carbon nanotube (mwnt), boron doped mwnt, and nitrogen doped mwnt mats has been measured. At high temperatures the TEP of the pure and boron doped samples is large and hole-like with the pure MWNTs having a larger TEP than the B-doped materials. The larger TEP in the pure vs. B-doped case is attributed to carrier scatter within the B-doped materials. In comparison, the nitrogen doped material in the same temperature range shows a large negative TEP, suggesting electron-like conduction. As $T \rightarrow 0$, all materials tend toward a 0 TEP. The magneto TEP was measured by applying a magnetic field of up to 6 Tesla, and the temperature dependence and field dependence at fixed temperatures is discussed and compared for the three samples.

4:30 PM V12.11

LYOTROPIC LIQUID CRYSTALS CADMIUM SULFIDE TEMPLATED BY LYOTROPIC LIQUID CRYSTALS. Bryan M. Rabatic¹ and Samuel I. Stupp^{1,2,3}. ¹Department of Chemistry, ²Department of Materials Science and Engineering and ³Medical School, Northwestern University, Evanston, IL.

Controlling size and morphology of inorganic materials on the nanometer size scale remains a challenge and it is motivated by the potential for novel physics and chemistry in nanomaterials. We report here on the use of lyotropic liquid crystals based on the amphiphile cholesteryl oligo(ethylene oxide) to template the II-VI semiconductor cadmium sulfide (CdS). Mineralization of CdS occurs at ambient temperature and pressure and results in a copy of the self-assembling mesophase. This is explained by the fact that CdS growth is excluded from the hydrophobic compartments of the template. The mineral reproduces the liquid crystalline symmetry and the dimensions of the internal nanostructure of the surfactant phase used. By varying the length of the hydrophilic coil length of the amphiphile, molecular packing in the template can be controlled to produce both lamellar and hexagonal mineralized phases. We have been able to precipitate lamellar and hexagonally ordered CdS from the corresponding phase of cholesteryl oligo(ethylene oxide). We have also been able to synthesize nanoscale hybrid composite materials that contain both CdS and TiO₂ compartments. This is accomplished through a 2-step templating procedure using precursors to TiO₂. These materials are potentially interesting in environmental photocatalysis and because of the chemical structure of the template may also be useful in biological applications.

4:45 PM V12.12

CONTACTS AND SELF-ASSEMBLY OF SHAPE-CONTROLLED MAGNETIC NANOCRYSTALS. Z.L. Wang and Z.R. Dai, Center for Nanoscience and Nanotechnology, School of MS&E, Georgia Institute of Technology, Atlanta, GA; Shouheng Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Controlled assembly of monodisperse nanocrystals (NCs) has been a key issue in fabricating functional nanodevices. Extensive investigations in NC assemblies have revealed that the symmetry of the observed superlattices is influenced by the NC size, NC shape and relative dimensions of the NC core and the organic capping. Our study has been focused on investigating the roles played by NC shape in self-assembly and the mechanism by which defects are created [1]. This presentation will focus on the structure characterization of three-dimensional (3-D) packing of Co [2] nanocrystal superstructures. It has been found that the self-assembly of nanocrystals with faceted shape is dominated by surface-to-surface contact. This simple geometrical matching is the root for creating defects in the self-assembly. The structural transformation of shape-controlled nanocrystals has been studied by transmission electron microscopy. [1] Z.L. Wang (ed.) Characterization of Nanophase Materials (Wiley-VCH, 2000); Z.L. Wang, Adv. Mater. 10 (1998) 13; Z.L. Wang,

J. Phys. Chem. B, 104 (2000) 1153; J.S. Yin and Z.L. Wang, Phys. Rev. Lett., 79 (1997) 2570. [2] Z.L. Wang, Z.R. Dai and S. Sun, Adv. Mater., 12 (2000) 1944.

SESSION V13: POSTER SESSION NANOPHASE AND NANOCOMPOSITE MATERIALS IV

Thursday Evening, November 29, 2001

8:00 PM

Exhibition Hall D (Hynes)

V13.1

SYNTHESIS AND CHARACTERIZATION OF TAPERED NANOWIRES OF SINGLE CRYSTALLINE MgO. Yadong Yin, Guangtao Zhang, Younan Xia, Dept. of Chemistry, University of Washington, Seattle, WA.

A vapor-solid approach has been demonstrated to produce tapered nanowires of single crystalline MgO. In this process, the evaporation rate of MgO decreased with time, and thus led to the formation of uniform, tapered nanowires whose diameters continuously changed from ~1 μm to ~20 nm over a distance of hundreds of micrometers. In this presentation, we will discuss the detailed procedure and growth mechanism as indicated by our SEM and TEM studies. Some unique applications for these tapered nanowires will also be described.

V13.2

SYNTHESIS AND CHARACTERIZATION OF NANOSIZED PURE AND DOPED TITANIA WITH FINE HIERARCHY PORES.

Yuhong Zhang^{a,b}, Jan Hanss^a, Olav S. Becker^a, Anke Weidenkaff^a, Bernd Renner^a, Armin Reller^a. ^aSolid State Chemistry, Institute of Physics, Augsburg University, Augsburg, GERMANY; ^bDepartment of Chemistry, Zhejiang University, Hanzhou, CHINA.

Pure and doped TiO₂ catalysts with both micrometer-sized macropores and nanometer-sized mesopores have excellent advantages in industrial heterogeneous catalysis reactions because the macropores provide pathways for rapid molecular transportation and the mesopores serve as large active surface. However, by using the conventional methods, it is difficult to concurrently control the size of macropores and mesopores for ceramic materials, and the fabrication of such structures that can be directly used without any binder or substrate has remained an experimental challenge. Numerous investigations are in progress for designing and synthesizing of structure-directing materials. In this paper, we report a novel sol-gel technique for preparation of hierarchical macroporous and mesoporous nanocrystalline TiO₂ by using cotton as template. Centimeter-scale nanocrystalline mesoporous pure and doped TiO₂ with macroporous structure were produced. The samples were characterized by XRD, nitrogen adsorption and desorption isotherm, scanning electron microscopy and transmission electron microscopy. The studies of using scanning electron microscopy (SEM) revealed that the fine internal structure of "titania cotton" is fully templated from the natural cotton. The macroscale structure of the prepared materials is controlled by cotton and the nanometer-scale assembly is achieved by the sol-gel process. The dimension and the macrostructure of the prepared materials can be tailored by the choice of cotton-texture's quantity, size and pattern.

V13.3

Cu₂₀ NANOWIRES BY A NOVEL REDUCTION METHOD. Wenzhong Wang, Guanghou Wang, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing, Jiangsu, PR CHINA.

Cu/Cu₂₀ layered nanostructured materials with interesting opto-electronic properties have been prepared by electric-codeposition. Cu₂₀ is a p-type semiconductor with a direct band gap of 2eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy. Recently Cu₂₀ submicrospheres have been found to be used as negative-electrode materials for lithium-ion batteries. Here, we report a novel reduction route to prepare Cu₂₀ nanowires with high quality in the presence of a suitable surfactant polyethylene glycol (PEG) (Mw 20000) at room temperature. Most of nanowires have the diameters of about 8nm and the lengths ranging from 10 to 20 μm . They are single crystal with interplanar spacing of 0.2465nm for {111} plane. XPS proves that the surface of Cu₂₀ nanowires absorbs O. This method requires no complex apparatus and techniques. The synthesis is very fast and may be used in industrial application.

V13.4

SOFT REVERSE CURRENT-VOLTAGE CHARACTERISTICS IN V₂O₅ NANOFIBER JUNCTIONS. Gyu-Tae Kim, Jörg Muster, Marko Burghard, Siegmund Roth, Max-Planck Institut für Festkörperforschung, Stuttgart, GERMANY.

V₂O₅ nanofiber showed the rectifying current-voltage characteristics under asymmetric electric contact configuration at room temperature, indicating the formation of a Schottky junction. The ideality factors of the rectifying curves were estimated to be 6.1 at forward bias and 1.4 at reverse bias. Apparently the reversal of the forward bias was observed, which was attributed to the occurrence of the field emission because of its ultimate narrow size of each nanofiber. The soft reverse characteristics in V₂O₅ nanofiber junction indicates the importance of the consideration of the ultra-thin geometries for the usage as electronic components.

V13.5

GROWTH OF SOLID AND HOLLOW NANOWHISKERS FROM NANOSCALE POWDERS. Robert Karakhanyan, Razmik Malkhasyan, Mary Nazaryan, Scientific-Production Enterprise "ATOM", Yerevan, ARMENIA.

The fast mass growth of solid and hollow nanowhiskers of MoO₃ and WO₃ is obtained owing to heating of nanoscale powders of these materials by means of electron beam. It is found that nanowhiskers can grow separately with arbitrary orientation as well as with formation of blocks from closely packed nanowhiskers with same crystallographic orientation. The width of MoO₃ and WO₃ nanowhiskers is about 8nm, and the length is about 1 micrometer. It is disclosed that the MoO₃ and WO₃ nanowhiskers are growing in a direction [001] which correspond to the maximal rate of growth. Such coincidence of MoO₃ and WO₃ nanowhiskers growth directions is caused by the well-known proximity of their crystalline structure. It is showed that the length and the number of these nanowhiskers depend on the density of nanoparticles we start from. There are some stages of emerging and decomposition of nanowhiskers depending on their size and time of heating with the electron beam. At the first stage right after the formation of noticeable amount of separate nanoparticles a momental growth of nanowhiskers is observed. During further heating the first stage of their slow destruction with their transition into polycrystalline nanowhiskers is observed. During further heating by the means of more intense electron beam nanowhiskers of MoO₃ and WO₃ are completely destroyed and folded into clew. Based on our TEM observations the growth mechanism of MoO₃ and WO₃ nanowhiskers is proposed.

V13.6

MÖSSBAUER STUDY OF Fe-Co NANOWIRES IN SELF-ASSEMBLED ARRAYS. Ziyu Chen, Qingfeng Zhan, Jianbo Wang, Desheng Xue and Fashen Li, Department of Physics, Lanzhou University, Lanzhou, CHINA.

Arrays of Fe_{1-x}Co_x (0.0 ≤ x ≤ 0.92) nanowires have been prepared by co-depositing Fe and Co atoms into the pores of anodic aluminum, the compositions of which were determined by atomic absorption spectroscopy. Transmission electron microscope results show that the nanowires are regularly spaced and uniform in shape with length of about 7.5 μm and diameter of 20 nm. X-ray diffraction indicates a texture in the deposited nanowires. For the composition below 82 at.% cobalt, the nanowires had a body-centered-cubic (bcc) structure with a [110] preferred orientation. For the 92 at.% cobalt sample, the alloy exhibited a mixture of bcc and face-centered-cubic (fcc) structure. The room temperature 57% Fe Mössbauer spectra of the arrays of Fe_{1-x}Co_x nanowires have second and fifth absorption lines of the six-line pattern with almost zero intensity, indicating that the internal magnetic field in the nanowires lies along the long axis of the nanowire. The maximum values of the hyperfine field ($H_{hf} = 365.6 \pm 0.5 kOe$) and isomer shift ($IS = 0.06 \pm 0.01 mm/s$) occurs for 44 at.% cobalt. The variations of the isomer shift and the line-widths with composition indicates that the Fe-Co nanowires have atomic disorder.

V13.7

A NEW METHOD FOR BULK SYNTHESIS OF HIGHLY ORDERED SILICON OXIDE NANOWIRES. Bo Zheng, Jie Liu, Duke University, Department of Chemistry, Durham, NC.

Ultra-long (up to 5 mm) and highly ordered silicon oxide nanowires have been synthesized from molten silicon-gallium balls at elevated-temperature. Scanning electron microscopy, transmission electron microscopy, and x-ray photoelectron spectroscopy were used to characterize the product. These wires were found to be very uniform, with a diameter around 15nm. X-ray and electron diffraction indicated that the SiO₂ nanowires were amorphous. Blue light emission was observed from the nanowires with two peaks at 393nm and 440nm. Details of our experiment will be presented along with a discussion of the growth mechanism.

V13.8

THE GENERATION OF A CARBON NANOTUBE CYCLODEXTRIN INCLUSION COMPLEX. Gordon Chambers,

Marc in het Panhuis, Media Lab Europe, Nanostructures Group, Dublin, IRELAND; Alan B. Dalton, Honeywell Technology Center, NJ; Garrett Farrell, Mary McNamara, Emeair Cummins, Hugh J. Byrne, Facility for Optical Characterisation And Spectroscopy, DIT, Dublin, IRELAND.

The insoluble nature of carbon Nanotubes has for a long time hampered the basic chemical characterisation of these novel materials. A number of studies have been reported on the use of micelles for the solubilisation of carbon nanotubes. In this study however the inclusion of small diameter carbon nanotubes (diameter 0.7nm) into the cavity of γ -cyclodextrin is examined as an alternative approach to achieving aqueous carbon nanotubes. γ -Cyclodextrin is the largest of the three cyclodextrins α , β , and γ , with a cavity size of the order of 0.7nm. It was seen that by refluxing an aqueous solution of γ -cyclodextrin (0.02 mol/l) with approximately 25% mass fraction of carbon nanotubes for ~100 hours a number of new features emerged in the absorption spectrum of the γ -cyclodextrin solution. These emerging features have been associated with features that are consistent with the absorption spectra of carbon nanotubes and indicate the formation of a nanotube inclusion complex with the cyclodextrin. This notion was further supported by a loss of approx. 20% by weight of the original nanotube mass. Raman spectroscopy, IR spectroscopy and microscopy have also been used to analyse both the solution and the remaining dried nanotubes to help elucidate the nature of the complex formed. While this work is still in its infancy the possibility of including carbon nanotubes into the cavity of a γ -cyclodextrin may point the way to achieving self-assembly in carbon nanotubes for molecular electronics.

V13.9

SYNTHESIS OF MAGNETIC NANOWIRES INCORPORATED INTO MESOPOROUS SILICA. Andrey A. Eliseev, Alexey V. Lukashin, Alexey A. Vertegel, Moscow State University, Dept of Materials Science, Moscow, RUSSIA; W.H. Kraan, Interfacultair Reactor Instituut, Delft, THE NETHERLANDS; Natalya A. Grigorieva, St. Petersburg State Univ, St. Petersburg, RUSSIA.

Mesoporous silica is a promising potential matrix for the preparation of nanocomposites. One could expect that size and shape of nanoparticles incorporated into mesoporous silica would be consisted with the dimensions of the porous framework. However, in most earlier studies this was not the case [1]. Recently, Cheon et al. [2] succeeded in the preparation of Pd nanowires in MCM-41 matrix using impregnation of the mesoporous silica by a gaseous precursor. Our approach was introduction of a hydrophobic metal complex (e.g., Fe(acac)₃ or Fe(CO)₅) into the hydrophobic part of the as-prepared meso-SiO₂/surfactant composite. Iron nanoparticles in SiO₂ matrix were then synthesized using two methods: 1) reduction by hydrogen at T=550°C and 2) reduction in an aqueous solution of NaBH₄. Thus prepared nanocomposites were characterized by TEM, ED, SAXS, SANS and magnetic measurements. The suggested method results in the formation of iron nanowires inside the silica framework. The diameter of the nanowires is consistent with that of the pores. This work is supported by RFBR (grant 00-03-32579).

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V13.10

SYNTHESIS AND CHARACTERIZATION OF INDIUM NITRIDE NANOWIRES. C.H. Liang and L.C. Chen, National Taiwan Univ, Center for Condensed Matter Sciences, Taipei, TAIWAN; J.S. Huang and K.H. Chen, Academia Sinica, Inst of Atomic and Molecular Sciences, Taipei, TAIWAN; Y.T. Hung and Y.F. Chen, National Taiwan Univ, Dept of Physics, Taipei, TAIWAN.

Indium nitride (InN) nanowires have been formed in high purity by gold catalyzed via a vapor-liquid-solid mechanism. Scanning electron microscopy and transmission electron microscopy investigations showed that the InN nanowires are single crystals with diameters varying from 30nm to 60nm, and lengths up to 3 micro-meters. Energy dispersive x-ray spectrometry showed that the ends of the nanowires are composed primarily of Au, and the rest of the nanowires are InN with no detectable Au incorporations. The Raman spectra showed peaks at 447, 490, and 578 cm⁻¹, which can be assigned to the A1(TO), E2, and A1(LO) phonon modes of the wurtzite InN structure, respectively. Comparison of the photoluminescence spectra of the InN nanowires and their thin films counterparts is also reported in this paper.

V13.11

MAGNESIUM DIBORIDE NANOWIRES: SYNTHESIS AND SUPERCONDUCTING PROPERTIES. Yiying Wu, Matte Law, Peidong Yang, University of California at Berkeley, Dept. of Chemistry, Berkeley, CA.

MgB₂ nanowires are synthesized in two different methods. In one method, boron nanowires are first synthesized and then transformed into MgB₂ nanowires. The obtained nanowires have diameter of hundreds of nanometers and length up to tens of microns. In another method, laser ablation is used to directly grow MgB₂ nanowires with pure MgB₂ as target. The obtained nanowires have diameter of 2-20nm and length up to several microns. Electron diffraction, HRTEM, EDX and EELS are used to characterize their structure and elemental compositions. Magnetization and electronic transport measurement are conducted on these nanowires to characterize their superconducting property. Magnetization measurement shows a transition of 30-39 Kelvin.

V13.12

SUPERHARD CARBON NANOTUBE MATERIALS: MECHANISM OF FORMATION, STRUCTURES AND PROPERTIES.

Leonid A. Chernozatonskii, Inst of Biochemical Physics, Moscow, RUSSIAN FEDERATION; Madhu Menon, Department of Physics and Astronomy, University of Kentucky, Lexington, KY; Boris Mavrin, Institute of Spectroscopy, Troitsk, MOSCOW REGION.

Synthesis of new materials with hardness comparable to or even greater than diamond is essential to many high performance engineering applications. Recently [1] a new superhard material of polymerized single wall carbon nanotubes (P-SWNT) was synthesized by applying a shear deformation. Here we report about a) mechanisms of forming covalent bonds between SWNT, b) modeling different crystal and electronic structure (cross-ply and roping P-SWNT) using a generalized tight-binding molecular-dynamic (GTBMD) scheme [2], c) modeling elastic properties of such structures using Keating scheme [3]. We have considered the following structures of (10,10) nanotubes usually prepared by different methods: a) cross-ply two-dimensional polymerized SWNT, b) 3D cross-ply P-SWNT structures, c) two phases of (10,10) P-SWNT ropes. Our estimations have shown for discussed P-SWNT materials high values of their bulk modulus (400-600 GPa) compared with experimental results [1]. We suppose that considered P-SWNT structures may be synthesized by high-pressure-high-temperature treatment as in the superhard C₆₀ the phases [3].

This work was supported by 'Atomic Clusters and Fullerenes' Russian Government Program and Russian Fundamental Fund of Investigation and NSF. M. Popov, M. Kyotani, Y. Koga et al. Phys. Rev. B (2001, in press) M. Menon, E. Richter, K.R. Subbaswamy, Phys. Rev. B 57 (1998) 4063, L.A. Chernozatonskii, N.R. Serebrynaya, B.N. Mavrin, Chem. Phys. Lett. 316 (2000) 199.

V13.13

FORMATION CONDITION AND MORPHOLOGICAL SERIES OF BN NANOFILAMENTS AND NANOTUBES. Tadao Sato, Renzhi Ma and Yoshio Bando, National Institute for Materials Science, Advanced Materials Laboratory, Tsukuba, JAPAN.

A series of BN nanofilaments like such as rosary, horsetail (bamboo), jellyfish, backbone and whisker, have been synthesized and analyzed by TEM¹). In the present study the formation conditions for each type of filaments and also for nanotubes were investigated. A boron nitride precursor containing oxygen e.g. 10% was charged into the bottom of a closed graphite tube, put at the center of graphite tube resistance furnace. After it was heated at e.g. 1700C for 1 hr in a nitrogen stream white felt-like material was deposited on the outside of the graphite tube at 1200C downstream of the nitrogen. The felt was composed of BN filaments having rBN type layer stacking and occasionally with iron alloy particle on the tip. From the observation it was suggested that they were formed via CVD, and a monovalent anion should have a part in the formation of rBN²). It was concluded that the B₂O₂ produced from C and B₂O₃ was the gaseous boron source. HCN produced by the reaction among C, N and H₂O, which was an impurity absorbed by the carbon black used as heat-shielding material, acted as the reducing and nitridation reagent. These fact was confirmed by using an RF furnace system, and nanotubes were obtained in the RF system without metallic impurities. A correlation was found between the concentration of B₂O₂ and H₂O and the morphology of the filament. As a result, each type of filaments could be obtained preferentially.

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V13.14

CATALYTIC GROWTH AND CHARACTERIZATION OF GaN and GaP NANOWIRES. Chia-Chun Chen, M.-Y. Yu, C.-H. Chen, S.-H. Chung, H.-M. Lin Department of Chemistry, National Taiwan Normal University, Taipei, TAIWAN.

High-purity and quality GaN and GaP nanowires have been prepared by a catalytic vapor-liquid-solid growth. A series of catalysts, different reaction parameters and substrates were applied to control the growth

of the nanowires. The resulting nanowires were up to several micrometers in length, typically with diameters of 10-50 nm. Temperature dependencies of photoluminescence and Raman spectra were performed to understand the optical properties of the nanowires. High-resolution transmission electron microscopy was used to reveal the detailed structural information of the nanowires. The field emission study showing notable emission current with low turn-on field suggests potential of the nanowires in field emission applications. The applications of the nanowires in other optoelectronic devices will be also discussed.

V13.15

FABRICATION AND MECHANICAL PROPERTIES OF Al₂O₃-SiC NANOCOMPOSITES BY SPARK PLASMA SINTERING.

Jae Hong Chae, Korea Institute of Ceramic Engineering and Technology, Seoul, KOREA; Kwang Bo Shim, Hanyang Univ, Dept of Ceramic Engineering, Seoul, KOREA.

Almost ceramic researchers are having an endless anxiety for enhancement of material properties. And many researchers attempted to improve the properties of Al₂O₃-SiC nanocomposites using hot pressing. Recently Niihara and his co-workers had been fabricated by pressureless sintering process and post hot-isostatic pressing (HIP). In this work, the spark plasma sintering method was applied to fabricate Al₂O₃-SiC nanocomposites various conditions in SiC 1~10vol% and 1300, 1400 and 1500°C at heating rate of 200°C/min with holding on 5 minutes and pressing on 7kN. High purity α-Al₂O₃ (Daimei Co., Japan) and β-SiC (Ibiden Co., Japan) were used as starting powders. The mixed powder was ball-milled in methanol using Y-PSZ balls of 5mm diameter in polyethylene pot. The dried cake were crushed by mortar and screened by 100mesh sieve. Relative densities of all compositions were more than 98% at 1300°C and relative densities increased with increasing temperature. Maximum flexure strength appeared at the 10vol% of SiC and flexure strength increased with increasing temperature. In spite of grain growth with increasing temperature, the increase in flexure strength was probably cause by SiC nano-particles existed in intra-grain as observed with TEM.

V13.16

Abstract Withdrawn.

V13.17

SYNTHESIS AND CHARACTERIZATION OF MgO REINFORCED Mg-Ti-Al NANOCOMPOSITE USING REACTION MILLING

APPROACH. V. Shankar, Lu Li, Lai M.O., Materials Science Division, Department of Mechanical Engineering, National University of Singapore, SINGAPORE.

Mg, TiO₂ and Al powders have been milled using a planetary ball mill under inert atmosphere. Weakening of Mg and TiO₂ peaks alongwith broadening suggests refinement in grain size. Progress of reaction is monitored using XRD, DSC, SEM and TEM. Weakening of Mg and TiO₂ peaks alongwith broadening suggests refinement in grain size. Milled powder shows completion of reaction on subsequent heat treatment as is evident with disappearance of TiO₂ peaks and emergence of MgO peaks while unmilled powder does not. Analysis suggests that milled powder undergoes self propagation unlike unmilled powder. Effect of temperature on grain size of matrix is studied. Mechanical properties are enhanced due to nanophase structure.

V13.18

SYNTHESIS AND PROPERTIES OF NANOPHASE TUNGSTEN AND MOLYBDENUM CARBIDES. Minasyan Varya, Levon

Vartikyan, Tamara Gharibyan, Institute of Chemical Physics, NAS, REPUBLIC OF ARMENIA; Susanna Grigoryan, Razmik Malkhasyan, Scientific Production Enterprise "ATOM", Ministry of Industry and Trade, REPUBLIC OF ARMENIA.

Tungsten and molybdenum carbides are applied as heterogeneous catalysts because exhibit similarity with metals of Pt-group on activity. For catalysts it is very important to have a large surface area, this may be achieved by the use of ultra fine powders. The preparation of highly dispersive nanophases powders of W and Mo carbides is the actual task. Nanosize amorphous metals-(W, Mo) are obtained by reducing corresponding metal oxides with nonequilibrium highly vibrationally excited hydrogen molecules[1], have high activity[2]. In this report amorphous metals were used as a component of synthesis of carbides by the thermal carburization in flowing hydrocarbon-hydrogen mixture. It has been shown that as-synthesized powders - Mo₂C and W₂C with an average grain size of 17-20nm. Details on the synthesis and characterization of powders will be presented. Nanosize carbides of W and Mo exhibit significant activity and 100% selectivity similar to Pt for dehydrogenation of cyclohexane into benzene. The samples are stable in air at room temperature and the activity does not change when carry out catalytic investigations for many days.

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V13.19

TRANSFORMATION LENGTHS AND METASTABLE PHASES IN BINARY NANO-ALUMINUM ALLOYS. Vijay Vasudevan, J.A. Sekhar, University of Cincinnati, Department of MS&E, Cincinnati, OH.

Aluminum alloys may be hardened by precipitation from super-saturated solid solutions or by spinodal transformations. A study is conducted to determine the transformation kinetics and interacting length scales in nano size powders of Al-Cu and Al-Zn binary alloys. Such alloys, when studied in bulk form, normally display precipitation behavior and spinodal transformation respectively. When the transformations are studied in nano size particles, competing morphologies of the precipitates and new metastable phases are observed. The present study seeks to address how transition phases like GP zones and early stage spinodal decomposition, which manifest in nanometer dimensions, evolve when the particle size approaches the same magnitude.

V13.20

OPTICAL NON-LINEARITY OF SPUTTERED $\text{Co}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ THIN FILMS. H. Yamamoto, T. Naito^a, T. Hirano^a and K. Hirao^b Nanotechnology Glass Project, New Glass Forum, Tsukuba Research Laboratory, Ibaraki, JAPAN. ^aHitachi Ltd., Hitachi Research Laboratory, Ibaraki, JAPAN. ^bDivision of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, JAPAN.

Recently, we have discovered that thin films consisting of Co_3O_4 and glass composite have great optical non-linearity, that is, refractive index changes drastically during laser irradiation. Therefore these films can be applied as super resolution films for optical disks such as DVDs (digital versatile disks). Refractive index (n) and extinction coefficient (k) in ground and excited states were measured by ellipsometry using a pulse laser with wavelength of 650nm. Laser powers (I) for measuring n and k in ground and excited states were $1.3 \times 10^7 \text{ W/m}^2$ and $4.6 \times 10^9 \text{ W/m}^2$, respectively. The thin films were prepared using an rf magnetron sputtering device. Composition of the films and O_2 volume percentage in the sputtering gas were chosen for parameters of thin film formation. Thickness of the films was about 50nm. Refractive index varied largely in the thin film whose composition was 84.6 $\text{Co}_3\text{O}_4\text{-}7.7\text{SiO}_2\text{-}7.7\text{TiO}_2$ (CST-1; mol%). Argon gas including 10vol% O_2 was most effective to obtain thin films with a large n change. Refractive indexes of ground state (n_0) and excited state (n) of CST-1 were 3.16 and 2.91, respectively, and k values of each state were 0.42 and 0.41. We saw that n decreased about 8% during laser irradiation, although k did not change so remarkably. Optical absorption spectra indicated that the band structure of Co_3O_4 was changed by oxygen percentage in the sputtering gas. TEM observation revealed that this film was consisted of Co_3O_4 crystalline particles that had an average grain size of 10nm, and it depended on composition of the films and oxygen percentage in the sputtering gas. We also looked at the relation between optical non-linearity and nano structure including band structure.

This work carried out in Nanotechnology Glass Project as part of Nanotechnology Materials Program supported by New Energy and Industrial Technology Development Organization (NEDO).

V13.21

GENESIS OF THE STRUCTURE OF ZIRCONIA NANO-PARTICLES AS CLAYS PILLARING SPECIES. Vladislav A. Sadykov, T.G. Kuznetsova, V.P. Doronin, T.P. Sorokina, D.I. Kochubei, B.N. Novgorodov, V.N. Kolomiichuk, E.M. Moroz, D.A. Zyuzin, E.A. Paukshtis, V.B. Felonov, S.A. Beloshapkin, Borekov Inst Catalysis RAS, Novosibirsk, RUSSIA; V.A. Matyshak, G.A. Konin, Semenov Inst Chemical Physics RAS, Moscow, RUSSIA; Julian R.H. Ross, Limerick Univ, Limerick, IRELAND.

Zirconia pillared clays are known to be promising as microporous supports and catalysts of a number of important petrochemical processes and NO_x abatement. Their performance strongly depends upon the size, shape and structure of nanosized zirconia props determined by genesis of zirconium hydroxy polycations in pillaring solutions. Present studies aim at clarifying those relations using in situ X-ray small angle scattering, EXAFS, X-ray structural analysis, UV-Vis and FTIRS, while the microporous structure of zirconia pillared montmorillonite was characterized by analysis of the nitrogen adsorption isotherms. Though in all cases zirconium tetramer Zr_4 was found to be a building unit which is preserved even in calcined pillared clays, the predominant species in aged zirconyl chloride solutions appear to be nanorods formed by stacking of several tetramers due to a rather weak bonding without participation of bridging hydroxyls. In general, addition of alkaline earth cations helps to suppress the formation of large colloidal particles, while increasing

the mean size of nanorods comprised of several tetramers. In solutions aged at enhanced temperatures, their local structure depends upon the nature of added alkaline-earth cation indicating its incorporation into the Zr coordination sphere. The interpillar spacing $\sim 7 \text{ \AA}$ in calcined pillared clays corresponds to the normal orientation of tetramer units in nanorods with respect to the host layers. As a result, thermal stability of pillared clays increases with the length of intercalated nanorods, though steric hindrances for diffusion within galleries increase as well. Pronounced interaction between pillars and host is reflected in the variation of the distances within the aluminosilicate layer and a much lower density of terminal hydroxyls and coordinatively unsaturated Zr cations as compared with bulk zirconia samples of a comparable particle sizes. This work is in part supported by the INTAS 97-11720 project.

V13.22

STUDY OF SUPERCONDUCTIVITY OF NANOEMBEDDED LEAD IN METALLIC & AMORPHOUS MATRICES.

K. Chattopadhyay, V. Bhattacharya, Indian Institute of Science, Bangalore, INDIA; A.P. Tsai, National Research Institute for Metals, Tsukuba, JAPAN.

Nanodispersed lead in metallic and amorphous matrices was synthesized by rapid solidification processing. The optimum microstructure was tailored to avoid superconducting percolation due to coupling of the neighboring particles by the proximity effect. With these embedded particles it is possible to study quantitatively the effect of size on the superconducting transition temperatures by carrying out magnetic measurements. For studies conducted on both amorphous and crystalline matrices, we observe a size dependence of superconductivity. Our result suggests role of the matrix in enhancement of superconducting transition temperature of lead. The origin of such matrix dependent behaviour and size correlation will be discussed at present.

V13.23

QUANTITATIVE EFFECTS OF AMINO ACID SALT REDUCING AGENTS ON THE SYNTHESIS OF Ni AND NiO PARTICLES USING AN OPTIMIZED COMBUSTION SYNTHESIS PROCESS. C.H. Jung, H.G. Lee and G.W. Hong, Functional Materials Group, Korea Atomic Energy Research Institute, Taejeon, KOREA.

A new chemical method for the synthesis of Ni and NiO powders are described. Ionic salt precursors are used which are intimately mixed an aqueous solution of these salts. The exothermic redox reaction and the heat evolved from the reaction completely convert the precursors into their corresponding products at temperatures below 400°C in an oxidizing atmosphere. The characteristics of synthesized powders were investigated with amounts of glycine fuel. Submicron sized Ni phase particles were directly obtained through combustion synthesis process in air atmosphere without further calcinations process, when the fuel content was controlled on the $\Phi_e = 0.61$. In the fuel-lean composition range ($\Phi_e > 1$) and stoichiometric composition ($\Phi_e = 1$), the only NiO phase crystallized from the precursor mixture without forming any intermediate phases. Primary particle size of synthesized Ni and NiO particles were about 20° .

V13.24

SINTERING AND MECHANICAL BEHAVIOR OF NANO-STRUCTURED COMPOSITES BASED ON TITANIUM AND ALUMINUM NITRIDES. Ostap Zgalat-Lozynskyy, Andrey Ragulya, Frantsevich Institute for Problems in Materials Science NAS of UKRAINE; Sergey Dub, Institute of Superhard Materials, Kiev, UKRAINE.

It has been found that the rate-controlled sintering allows resolving the most contradictive task of consolidation the nanosized powders: achievement near full density and remaining the ultrafinegrained microstructure. Having developed this non-isothermal and non-linear process, the titanium nitride and titanium nitride-aluminum nitride nanocomposites were obtained originating from nanopowders of 10-15 nm in size. Ceramics with fractional density of 98-99% and grain size below 50 nm were achieved at lowered sintering temperatures: 1200 °C for TiN and 1650 °C for TiN-AlN (95/5; 80/20). Such a sintering behavior resulted from preliminary purification of powders in the stream of extra dry hydrogen at elevated temperatures. The mechanical properties of sintered ceramics were studied by nanoindentation and conventional Vickers testing. Hardness, fracture toughness and elastic modulus were in the focus of the present research. It has been found that the mechanical behavior of TiN nanoceramics with nanohardness of 30 GPa is appreciably higher as compared to coarse grained TiN (size of single grain of 30 microns and nanohardness of 24 GPa at the same test conditions). Fracture toughness measured by Evans method varies in the range of 1.9-2.6 MPa m^{0.5} for pure TiN. The elasticity modulus was determined as a function of density and grain size and varied in the range 300-500 GPa.

V13.25

STRUCTURAL EVOLUTION OF Cu-Al₂O₃ NANO-SCALE COMPOSITES SYNTHESIZED BY IN-SITU REDUCTION. Marcelo Motta, P.K. Jena, Eduardo Brocchi, Guillermo Solúrzano, PUC-Rio, Dept. of MS&E, Rio de Janeiro, BRAZIL.

Copper-alumina composites is reported to have an excellent resistance to high temperature annealing as well as high thermal and electrical conductivities. Conventional and high resolution transmission electron microscopy have shown that the microstructure of the Cu-Al₂O₃ nano-scale composites synthesized by in-situ reduction is formed by a copper matrix, with crystals in the sub-micron scale, and a fine dispersion of alumina particles smaller than 10 nm in size. The scale of the alumina particles has also been examined by energy dispersive spectroscopy (EDS), which have also suggested the appearance of a spinel in the system. Even after cold rolling and annealing at 900°C, dislocations and sub-grain boundaries still appear in the microstructure. Further research focusing the thermal stability of the Cu-Al₂O₃ composite microstructure resulting from cold rolling and annealing is currently in progress.

V13.26

FABRICATION OF SILICON TETRABORIDE SINTERED BODY. Takashi Kubota, Noriyuki Fukushima, Samon Tanaka, Jun-ichi Matsushita, Tokai Univ, Dept of Material Science, Hiratsuka, JAPAN.

The fabrication of silicon tetraboride (SiB₄) ceramics was investigated in order to determine the suitability of this material for advanced engineering ceramics applications. The samples were prepared by using commercial SiB₄ powder as starting materials by hot-pressing method at 1273 to 1723 K for 1h in vacuum under 40 MPa pressure. The monolithic SiB₄ samples of the 92 % relative density was got in the sintering at 1623 K. According to the X-ray diffraction analysis, SiB₆ phase was detected besides SiB₄ in the sintered body in more than 1648 K for 1 h. X-ray diffraction analysis showed no crystalline phase other than SiB₆ in the dense sample sintered at 1723 K for 1 h. The density of the sintered body was measured by the Archimedes' method. The sintered body was cut into desired size and surfaces were polished with a diamond disk prior to Vickers hardness, electrical conductivity and oxidation studies. The Vickers hardness of the polycrystalline SiB₄ sintered at 1623 K and 1723 K was 8 and 15 GPa, respectively. The electrical conductivity of the SiB₄ sintered at 1623 K and 1723 K was 1.5×10^3 and 7.1×10^3 S/m, respectively. The oxidation of samples started at 1173 K in air. The weight gain of the sample oxidized below 1173 K for 1 h was approximately 2 %. However, even if the oxidation time was prolonged additional weight change did not occur. For samples heated at 1373 K, the weight gain of the sample increased with increasing oxidation temperature. Based on the result of X-ray diffraction analysis, SiO₂ and B₂O₃ were postulated to be present on the oxidized surface of the sample. The samples showed a good oxidation resistance at high temperature, because the surface film of SiO₂ and B₂O₃ formed by oxidation acted as an oxidation resistant layer.

V13.27

FABRICATION OF METAL NANOSTRUCTURES IN MESOPOROUS SILICAS. Kuei-Jung Chao, Chia-min Yang, National Tsinghua University, Department of Chemistry, Hsinchu, TAIWAN.

Metal nanostructures have attracted growing interests in recent years because of their unique physical and chemical properties related to low dimensionality. They can be synthesized within the confined space of host materials, such as anodic alumina membrane of one-dimensional channels and mesoporous molecular sieves with uniform pore diameters (1.5-30 nm). The advantages of mesoporous silica over other templates are the adjustable pore structures and the feasibility of modification of the pore walls to have desired properties. In this report, we demonstrate that densely packed metal nanostructures can be synthesized in the modified silica hosts of 1D and 3D channel systems. The pore surface of mesoporous silicas is modified with functional silanes to carry positive or negative charges, which can interact strongly with oppositely charged metal complexes by electrostatic force. In comparison with traditional metal incorporation methods including impregnation and ion exchange, we found that the surface modification not only increases the metal loading dramatically, but also gives uniform metal distribution inside the host mesoporous silica. Various metal nanostructures including nanowire bundles and nanowire networks can be fabricated by single-step metal incorporation/reduction process. Different nanostructures of Pt, Au and Pd are demonstrated and characterized by TEM and in-situ PXRD or XAS investigations.

V13.28

CYCLODEXTRIN PSEUDOPOLYROTAXANES AS TEMPLATE FOR POROUS SILICAS: FROM MICROPORES TO MESOPORES.

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It is well-known that cyclodextrins are native host compounds, possessing a hydrophobic cavity, which could accommodate various of organic molecules to give inclusion complexes. Suitable linear polymer chains could penetrate through the cavities, giving pseudopolyrotaxanes, e.g. poly(ethylene glycol) (PEG)-alpha-cyclodextrin and poly(propylene glycol) (PPG)-beta-cyclodextrin systems. Nanocasting procedure can imprint the structure of the soft matter in solution into inorganic solid. Herewith we will present the results on the porous silicas obtained via nanocasting procedure templated by the pseudopolyrotaxanes formed from methylated alpha-cyclodextrin with PEG and oligo/poly(ethylene oxide) (EO) groups containing surfactants, and methylated beta-cyclodextrin with PPG. It is interesting that the pH value of sol gel could regulate the pore size. At pH 2.0, microporous silicas (pore diameter ca. 1.9 nm) are obtained. Upon increase in the pH values (3.0 and 4.0), the resulted silicas show mesoporous characteristics (3-4 nm). The porous silicas are characterized by nitrogen sorption and transmission electron microscopy (TEM), showing high porosity and high Brunauer-Emmett-Teller (BET) surface area. Furthermore, the systems employing block copolymer EOPO and EOPEO give more evidence on the rotaxane formation.

V13.29

SYNTHESIS AND OPTICAL PROPERTIES OF POLY(METHYL SILSESQUIOXANE)-TITANIA HYBRID NANOCOMPOSITES. Wen-Chang Chen and Long-Hua Lee, Dept of Chemical Engineering, Natl Taiwan Univ, Taipei, TAIWAN.

A series of Poly(methyl silsesquioxane)(MSQ)-titania hybrid thin films was prepared by an in-situ sol-gel process combined with spin coating and multi-step baking. The titania content in the hybrid materials can be as high as 41.7 wt%. The FE-SEM result shows a nano-size domain of the titania segment. The optical properties can be controlled by the titania content as well as the cage/network ratio of MSQ. The refractive indices of the prepared hybrid thin films can be adjusted from 1.363 to 1.521 with increasing the titania content from 0 to 41.7 wt%. On the other hand, the refractive index increases by enhancing the cage/network ratio of the MSQ segment. The prepared hybrid thin films show an excellent transparency in the visible region. The abbe numbers of the prepared hybrid thin films are in the range of 40-60, which suggests a very low optical dispersion. The UV-absorption edge of the prepared hybrid thin films can be correlated with the titania content. It indicates the size quantization effect of the titania segment in the hybrid thin films. Optical waveguides were prepared from these hybrid thin films. The optical losses of the prepared optical waveguides are in the range of 0.58-1.02 dB/cm. It can be correlated with the titania content. The prepared hybrid materials show excellent thermal stability up to 400°C. The AFM study suggests that the prepared hybrid thin films have excellent planarization. These results suggest that the prepared hybrid films have potential applications in optical devices.

V13.30

SILICATE MATERIALS SYNTHESIZED BY USING GELATIN AS TEMPLATING AGENT. P. Jaime Retuert, Raul Quijada, Veronica Arias, Univ de Chile, Fac Ciencias Fis y Mat and Centro Para la Investigacion Multidisciplinaria Avanzada en Ciencia de los Materiales, Santiago, CHILE.

Micro and mesoporous silicas are an important type of solids with application as catalysts, supports, ion exchange, etc. Commercially relevant are those synthetic approaches starting from sodium silicate. On the other hand, templating procedures are widely used to prepare inorganic structures, controlling their shape, microstructure and hence their properties. Here we report the synthesis of porous silica microspheres using sodium metasilicate as the silica source and the biopolymer gelatin as the structure-directing agent. Commercial gelatin 240 bloom (GE) and sodium silicate 50/52° Be (NaSi) were used for the preparations. NaSi solution was added slowly under vigorous stirring to aqueous 3% solutions of GE in order to have a weight ratio SiO₂/GE = 5. After 2h the mixed solution was precipitated in HCl 1N at pH 1. After 16 h the solid was separated by filtration, dried for 24 h /60 C and calcined at 550 C/2 h. Thereafter, the product was washed thoroughly and recalcined at 550 C/2h. The resulting silica (0.35% Na) present microspherical morphology (0.2-0.3 microns) and a BET surface area of 485 m²/g. From this area 290m²/g correspond to micropore area, with 0.13cm³/g micropore volume (total pore volume 0.24 cm³/g). The porosity distribution analysis showed a well defined bimodal size distribution with micropores (< 20 Å) and mesopores (35 Å). These results can be compared with those obtained from a blank prepared without GE. In this case the silica have BET area of 530 m²/g and showed only the presence of mesopores (51 Å) with a total pore volume of 0.67 cm³/g. This suggests that the GE macromolecules are well dispersed in

nanoscopically confined domains in the silicate hydrogel. Furthermore important results have been obtained showing the dependence of washing procedures on the BET area and microporosity of silica samples obtained from GE/NaSi hybrids.

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V13.31

LANTHANIDE(III) OXIDE-POLYIMIDE NANOCOMPOSITE MATERIALS WITH TUNABLE LINEAR COEFFICIENTS OF THERMAL EXPANSION AND COMPARISONS WITH MONTMORILLONITE-POLYIMIDE COMPOSITES. D. Scott Thompson, D.W. Thompson, Dept. of Chemistry, College of William and Mary, Williamsburg, VA; R.E. Southward, Structures and Materials Competency, NASA Langley Research Center, Hampton, VA.

The work reports investigations on alternatives to silica and titania-based polymeric hybrid films. The synthesis and characterization of nanocomposite inorganic-polyimide films is described. The composite films were prepared by adding tris(beta-diketonato)lanthanide(III) polyhydrate complexes, as sol-gel precursors, to dimethylacetamide and 2-methoxyethyl ether (diglyme) soluble polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/1,3-bis(3-aminophenoxy)benzene, (6F-DA/3,3-APB), and 6FDA/2,2-bis[4-(4-aminophenoxy)]hexafluoropropane, 6FDA/4,4-BDAF. The beta-diketonate-metal complex-containing polyimide films were thermally treated to final temperatures ranging from 220 to 340°C. A combination of thermally promoted hydrolysis and ligand decomposition resulted in a lowering of the linear coefficients of thermal expansion by as much as 40% at low metal(III) oxide concentrations (ca. 5%). Essential thermal and mechanical properties of the parent polyimide were preserved. In selected cases there was an enhancement in the tensile modulus and a decrease in the solvent sensitivity of the composite films. Transmission electron microscopy data are consistent with particle sizes for the lanthanide ion-containing species which are in the nanometer range. Glass transition temperatures and 10% weight loss temperatures in nitrogen were close to those of the undoped polymers. X-ray photoelectron spectroscopy suggests that there are two different lanthanum(III) environments in the nanocomposite films. Films were characterized by thermal, mechanical, X-ray, XPS, and transmission electron microscopy.

V13.32

SYNTHESIS OF EPOXY AND BLOCK OLIGOMER MODIFIED CLAY NANOCOMPOSITE. K.H. Chen, S.M. Yang, Dept of Chemical and Material Engineering, National Central Univ, Chung-Li, TAIWAN.

Acrylic triblock ($A_mM_nB_o$) and diblock (B_oM_n) oligomers containing methyl methacrylate (M), methacrylic acid (A) and dimethyl-aminoethyl methacrylate (B) groups are intercalated into the layers of montmorillonite. The pH of the aqueous solution and number of units in the oligomer can adjust the charges and hydrophobicity of the oligomers. The effect of charge and hydrophobicity of the block oligomer on the d spacing of montmorillonite layers are studied. Regardless of the number of positive charges and hydrophobicity of the block oligomer, d-spacing of montmorillonite layer enlarge from 12.5 Å of Na form to 19-20 Å. Block oligomer carrying negative charges can not intercalate into the clay layer and show a d-spacing of 14.5 Å which is close to 15 Å of H form montmorillonite. Chain length of the block oligomer has no effect on the d spacing of intercalated montmorillonite. The results indicate that the block oligomer lay in a single layer between the clay layers. ICP analyses of Na indicate no unexchanged sodium ions are left in the intercalated clay. Nanocomposite of epoxy and clay modified with block oligomer were synthesized. Glass transition temperature (T_g) of the nanocomposite is 129.6°C ($B_{24}M_{18}^{24}$ modified clay) compared to 84.1°C for the physical mixture of epoxy and unmodified clay. T_g increases with decreasing amount of modified clay. Below 2 phr modified clay content, T_g of higher than 131.7°C can be obtained. Water resistance of the nanocomposite is also improved over epoxy without modified clay.

V13.33

METHYL METHACRYLATE-COPPER NANOCOMPOSITES: MECHANICAL AND ELECTRICAL CHARACTERIZATION. Mauricio E. Pilleux, Mariela Alvarez, Universidad de Chile, IDIEM, Santiago, CHILE; Victor H. Poblete, Comision Chilena de Energia Nuclear, Santiago, CHILE.

Conducting copper-methyl methacrylate (MMA) matrix nanocomposites have been successfully prepared. The composites were made using spherical copper nanoparticles (80-120 nm) suspended in an MMA matrix with different volume concentrations and thermally polymerized. The morphology of the composite was studied using

scanning electron microscopy. The electrical conductivity was analyzed as a function of the amount of infiltrated copper in the polymeric matrix. The critical volume concentration of copper in the matrix (percolation limit) was derived. Mechanical evaluation of the composites was performed.

V13.34

STRUCTURAL CHARACTERIZATION OF NOVEL ALKYL SULFONIC ACID-DOPED POLYANILINE/LAYERED SILICATE NANOCOMPOSITES. Dongkyu Lee, Jooheon Park and Kookheon Char, School of Chemical Engineering, Seoul National University, Seoul, KOREA.

Organic/inorganic nanocomposites involving conducting polymers confined in suitable inorganic host materials such as metal oxides and mica-type silicates have been the subject of considerable recent interest because of their unique properties such as mechanical and electrical properties. A great deal of research on the conducting polymer/inorganic nanocomposites, particularly composed of polyaniline (PANI) and inorganic materials, has been carried out. However, in the case of the PANI/inorganic nanocomposites prepared so far, most of PANI chains in the nanocomposites are doped with hydrochloric acid (HCl) and few study has been focused on clearly addressing the effect of different types of dopant such as dodecyl benzenesulfonic acid (DBSA) on characteristic properties in the PANI/inorganic nanocomposites. In present study, we investigated the structural variation such as interlayer spacing of the DBSA-doped PANI/organically modified layered silicate (OLS) nanocomposites upon the addition of DBSA into the reaction medium containing aniline. In particular, the deintercalation of the layered silicate intercalated with n-dodecylamine (C12-NH₂) upon the addition of DBSA dopant was elucidated with the XRD analysis. The effect of the structural variation on physical properties such as electrical, mechanical and thermal properties was also studied. Finally, the characteristic properties of DBSA-doped PANI nanocomposites were compared with those for HCl-doped PANI.

V13.35

EFFECTS OF CURING AGENTS ON THE EXFOLIATION OF EPOXY-CLAY NANOCOMPOSITES. Do-Il Kong, Chan Eon Park, Pohang University of Science & Technology, Polymer Research Institute, Dept. of Chemical Engineering, Division of Electrical & Computer Engineering, Pohang, KOREA.

Polymer-clay nanocomposites have been widely investigated for their higher mechanical and thermal properties, and better barrier properties than those of conventional polymer-inorganic filler composites. In this study, polymerization behavior in the confined structures of layered compounds has been studied in epoxy-clay nanocomposites. The intercalation and exfoliation of epoxy-clay nanocomposites have been examined using various curing agents. Interspacing distance of clay layer and degree of exfoliation has been measured depending upon the electronegativity of curing agents by small angle X-ray diffraction in Pohang Accelerator Lab. (PAL). Interspacing distance of clay layer has been increased with decreasing the electronegativity of curing agents or reactivity. More than 200° of exfoliation has been achieved with curing agents of low electronegativity and latent curing agents. Also, it was observed that clay layers are expanded gradually at initial time, but jumped to 90-100° of interlayer distance at about 20% of conversion. Three different exothermic peaks have been observed in DSC thermogram of epoxy-clay nanocomposites. Three different curing regions can be speculated such as interlayer region of clay, surface region of clay, and far away region from clay. Effects of curing agents and clay contents on morphology and mechanical properties of epoxy-clay nanocomposites have been investigated, and effects of the extent of exfoliation on mechanical properties of epoxy-clay nanocomposites. The variation of glass transition temperature and cross-linking density of epoxy-clay nanocomposites has been also examined depending on clay contents.

V13.36

ELECTROCHEMICAL CAPACITANCE OF A NANO-POROUS COMPOSITE OF CARBON NANOTUBES AND POLYPYRROLE. Mark Hughes, George Z. Chen, Milo S.P. Shaffer, Alan H. Windle, Derek J. Fray, University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

Composites of carbon nanotubes and conducting polymers are attractive for their ability to merge the desirable mechanical, physical and electrical properties of their two unique component materials. This work reports the supercapacitive properties of electrochemically grown composite films of multi-walled carbon nanotubes and polypyrrole, a conducting polymer. Scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy revealed that the nano-porous three-dimensional arrangement of polypyrrole coated nanotubes in these films facilitated improved electrical and ionic transfer relative to pure polypyrrole films. In fact,

the rate of charge and discharge of the composite films was about an order of magnitude faster than similarly prepared pure polypyrrole films. The excellent charge transfer observed in the composite films was complimented by exceptional low-frequency capacitance, with specific capacitances per mass and geometric area reaching as high as 190 F/g and 1.0 F/cm², respectively.

V13.37

FABRICATION OF NANOPOROUS MEMBRANES USING BLOCK COPOLYMERS. Toshiro Hiraoka, Advanced Materials and Devices Laboratory, Corporate Research & Development Center, Toshiba Corp., Kawasaki, JAPAN.

Controlled fabrication of nanoporous membranes using block copolymers has been developed. A diblock-copolymer comprising a crosslinkable chain, poly(vinylethylene)(PVE), and a degradable chain was used as a self-assembling material. The degradable chains used were poly(methylmethacrylate)(PMMA) and poly(butylmethacrylate)(PBMA). Microphase-separated bicontinuous structures formed in the diblock-copolymer films. The backbones of PMMA and PBMA were decomposed by X-ray irradiation and selectively removed. The backbones of PVE were crosslinked by radical crosslinker. The porous membrane of crosslinked PVE with three-dimensionally continuous pores was obtained.

V13.38

EFFECT OF ION DAMAGE ON THE SHAPE OF CARBON NANOTUBE. Lim Hyuck, Hunjoon Jung, Byoung-Dong Kim, Wonsick Shin, Choel-Ho Park, Seung-Ki Joo, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

Since the discovery of carbon nanotube (CNT), it has attracted considerable interest because of its unique physical properties and many applications. For CNT to be used in the practical applications, its growth direction and diameter become important factors especially in FED application. In this work, we tried to control the shape of vertically grown CNTs through ion bombardment with various kinds of gases in IMDS (Ion Mass Bombardment System). Argon bombardment induced CNTs to be bent to one direction all alike and the bending extent was proportional to the DC bias voltage. In the case of oxygen bombardment, CNT walls were damaged by the impact and the oxidation. Especially for vertically aligned CNTs, the oxygen bombardment made CNT walls thinned uniformly. But for not vertically aligned ones, it made CNT walls rugged. Oxygen plasma without DC acceleration also thinned CNT walls but less fascinating than the case with DC bias. Conclusively, we found a method to control the diameter of CNT walls and make all CNTs bent to one direction effectively with an ion bombardment.

V13.39

HYBRID-ORGANIC-INORGANIC MATERIALS: BETWEEN MORPHOLOGY CONTROL AND STRUCTURAL PROPERTIES. Jean-louis Bantignies, David Maurin, Philippe Dieudonné, Jean-louis Sauvajol, Groupe de Dynamique des Phases Condensées (UMR CNRS 5581), Université Montpellier II, Montpellier Cedex, FRANCE; Joel Moreau, Michel Wong Chi Man, Luc Vellutini, Hétérochimie Moléculaire, ENSCM, Montpellier Cedex, FRANCE.

Sol-gel chemistry has allowed the emergence of the so-called hybrid materials. The synthesis of organo-polysilsesquioxanes leads to a well defined three-dimensional network owing to the presence of covalent bonds between organic and inorganic fragments. The unique structural properties of these materials consist in the controlled synthesis of organized materials. Interestingly, we point out that self-assembly properties of the organic component (hydrophobic interactions, H-bonds) control the short and long range order organization of the material closely connected to the texture (fiber, tube, lamellar structure). Our study of the structure of the material at different levels : from the molecular level to nanoscopic and microscopic levels, has been carried out by polarized infrared spectroscopy, electron microscopy and X-Ray diffraction. The control of the polymolecular organization may open new ways towards hybrid devices for various applications.

V13.40

SIZE AND TEMPERATURE EFFECTS IN RAMAN SPECTRA OF SINGLE-WALL CARBON NANOTUBES. A.V. Osadchy, E.D.

Obraztsova, S.V. Terekhov, Natural Science Center of General Physics Institute RAS, Moscow, RUSSIA.

The Raman spectra of the single-wall carbon nanotubes (SWNT) at the different temperatures have been registered in the vacuum oven with temperature stabilization. It is shown that the spectrum of SWNT at high temperatures (more than 600°C) contains not only the "breathing" mode at 186 cm⁻¹, but also a new peak at 203 cm⁻¹, which is absent in the spectrum at room temperature. The intensity

of the new peak is practically the same as the peak at 186 cm⁻¹. It indicates that the new peak is excited also in the resonant conditions. To estimate the value of a "mirror" gap for the nanotube corresponding to the new peak, we have estimated the nanotube diameter from the "breathing" mode position: 223.75/w = 1.1 nm (where w is the mode frequency in cm⁻¹) and have calculated the electronic density of states (DOS) for this nanotube using Monte-Carlo numerical integration method. The resulting DOS looks like a mirror spike array. The positions of the spikes depend on the tube geometry (chirality and diameter). The resulting dependence has shown that a thermal energy stored in the SWNT at high temperatures is not enough to excite the new peaks in the Raman spectra. The problem may be solved if to take into account a thermal broadening of the spikes in DOS. The broadening value (according to our data) is about 2-3 kT, where k is a Boltzman constant, T is a temperature (in Kelvins).

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V13.41

HIGH EFFICIENT CARBON NANOTUBE CATHODES.

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The development of reliable and low voltage electron emitters of carbon nanotubes is the objective of this study. We believe that by applying the emission optimization concepts learned during the optimization of carbon/diamond field emitters by our team, we can improve the carbon nanotube cathodes. Optimization strategy involves fabrication of aligned nanotubes of controlled diameter and density on electronically useful substrates. The well-aligned uniform array of multi wall nanotubes MWNTs on catalysts on various substrates has been synthesized using plasma enhanced hot filament CVD. A D.C. discharge plasma is applied for the aligned growth of high concentration MWNTs. In our experimental studies, the diameters of MWNTs can be controlled systematically from about 10 nm to 100 nm by controlling the substrate temperature and the composition of reactive gases. The length of MWNTs can be controlled by varying the growth time. The growth rate of MWNTs in nitrogen/methane system is about 20 μm/hr. Different reactive gases C₂H₂ or C₂H₄ and growth parameters can also alter the growth rate. The electron field emission in a diode structure can be turned on at a field as low as 1.2 V/μm. Scanning electron microscopy, X-ray diffraction, and Raman scattering were used for surface morphology characterization of the synthesized thin films.

V13.42

THE EFFECT OF NICKEL, IRON AND COBALT ON THE MORPHOLOGY AND MICROSTRUCTURE OF ALIGNED CARBON NANOTUBES. Zhongping Huang, Dezhi Wang, Jianguo Wen, Shaoxian Yang, Michael Sennetta, Heidi Gibson, and Zhifeng Ren, Dept. of Physics, Boston College, Chestnut Hill, MA; Material Science Team, US Army Soldier Biological & Chemical Command, Research, Natick Soldier Center, MA.

We investigated the morphology and microstructure of aligned carbon nanotubes catalyzed by nickel, cobalt and iron respectively. It has been found that the carbon nanotubes catalyzed by Ni have the best alignment and the smoothest wall surface, whereas Co produced nanotubes with amorphous carbon and nanoparticles on the surface. Furthermore, the wall thickness of the nanotubes grown by catalysts Ni, Fe and Cobalt are different. Interestingly, some opened areas on Fe side wall were observed by TEM and SEM.

V13.43

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF MESOPOROUS SILICA FILMS CONTAINING FERROELECTRIC AND PHOTOISOMERIC CHIRAL MOLECULES.

Takahiko Kurosawa, JSR Corporation, Tsukuba Research Laboratories, Ibaraki, JAPAN; Bradley F. Chmelka, Univ of California, Dept of Chemical Engineering, Santa Barbara, CA; Galen D. Stucky, Univ of California, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

Ferroelectric liquid crystal arrays that are also photoisomers have been made using an azobenzene unit and an asymmetric carbon in the molecular assembly. If the ferroelectric liquid crystal is used as a template for the synthesis of highly ordered mesoporous silica films, the silica films might be expected to exhibit ferroelectricity because of ordering of the template into the mesopore. The azobenzene unit exhibit trans-cis isomerization induced by photo irradiation. The ferroelectricity of the silica films containing the ferroelectric azobenzene compound as a template should change upon photo irradiation because of the isomerization of the organized azobenzene units. The ferroelectric silica film could be used for new optical switching materials. Mesoporous silica films were prepared using block

copolymers or cationic alkylammonium surfactants and a ferroelectric azobenzene compound as co-templates. The organic ferroelectric showed liquid crystalline behavior, and the mesoporous silica film synthesized with the organic ferroelectric showed thermotropic optical properties. The same isotropic temperature was observed for both the organic ferroelectric and mesoporous silica film. The structures of the mesoporous silica films were studied by X-ray diffraction, optical microscopy and transmission electron microscopy. We will describe the synthesis of the chiral azobenzene molecules and mesoporous silica films, and the optical and ferroelectric properties of the chiral molecules and the corresponding mesoporous silica films.

V13.44

INTERNALIZATION OF INORGANIC-BIOMOLECULAR NANOHYBRID INTO EUKARYOTIC CELL. Jin-Ho Choy, Seo-Young Kwak, Sung-Ho Hwang, Yong-Joo Jeong, Jong-Sang Park, Seoul National Univ, School of Chemistry and Molecular Engineering, Seoul, KOREA.

Generally, the layered double hydroxide(LDH) consisted of magnesium and aluminum has already been used as medicine due to its applicability as an agent for treating peptic ulcers, since it inhibits the action of hydrochloric acid and pepsin in the gastric juice. MgAlCO₃-LDH meets various requirements imposed on an antacid, and its excellence may be attributed to its structural features. The reaction rate of MgAlCO₃-LDH with gastric acid is similar to that of Mg(OH)₂, while the buffering pH is rate-controlled by dissolution of Al(OH)₃ monomer, and reaches a pH value around 4, which is slightly higher than the one at which Al(OH)₃ dissolves. Moreover, since Al(OH)₃ does not polymerize, while the aluminum hydroxide gel does, the LDH dissolves completely in the acid. The high antipeptic activity of LDH can be attributed both to the adsorption of negatively charged pepsin onto positively charged surface of LDH, and to buffering of the pH at about 4 for a long time. Therefore, we believe that the present LDH is quite bio-compatible. In this work, it has been clearly demonstrated that ATP could be intercalated in the inorganic layered double hydroxide, giving rise to biomolecular-inorganic nanohybrids with preserving the physico-chemical and biological integrities of the encapsulated biomolecules. Moreover, the hybridization of ATP with LDH resulted in a remarkable transfer efficiency of ATP into target cells by alleviating the electrical repulsion at the cell walls due to the neutralization of negative charge of phosphates with positive hydroxide layers. From cellular uptake experiment with laser scanning confocal fluorescence microscopy, it is revealed that the FITC-LDH hybrid is effectively transferred into NIH3T3 cells. Such an unique feature of biomolecule-LDH hybrids will open a new opportunity for LDHs to be useful as reservoir and carrier of genes, drugs, and other functional biomolecules.