

# SYMPOSIUM L

## L: Continuous Nanophase and Nanostructured Materials

December 1 - 5, 2003

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\* Invited paper

**8:30 AM \*L1.1**

**Nano-Structured Oxide Ceramic Composites by Solidification of Eutectic Melts.** Masahiro Yoshimura, Shunji Araki and Jose M Calderon-Moreno; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Generally, most of polycrystalline ceramics have been made from fine powders via their shape forming and sintering or their precursors via pyrolyzing, not via melt/casting. It is believed that melt/solidified ceramics would crack during cooling due to (1) brittle nature of ceramics and (2) residual stress accumulation after their solidification. In order to prevent the accumulation of residual stresses, we have tried to make the samples by rapid solidification of the eutectic systems. Since the grain growth of solidified crystals can be minimized in eutectic systems, particularly ternary eutectic ones, thus cracking also can be minimized. In the ternary systems of Zirconia(Hafnia)-Alumina-YAG, we have succeeded to fabricate transparent nano-structured bulk ceramics by just simple solidification of the melt. The samples had no cracking and consisted of 20-100 nm size crystals: c-ZrO<sub>2</sub>(HfO<sub>2</sub>), Al<sub>2</sub>O<sub>3</sub>, and YAG. Other ternary eutectic systems have given similar nano-structured composites. Amorphous transparent bulks have been obtained in several ternary systems like ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-RAIO<sub>3</sub> (R=Rare earth), ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-AMO<sub>3</sub> [perovskites]. Those amorphous could be changed to nano-composites by appropriate annealings. Those ceramic nano-composites can be applied for wide areas; structural, functional, and coating materials.

**9:00 AM L1.2**

**Influence of Multiple Interfaces on Oxygen Ionic Conductivity in Gadolinia-doped Ceria and Zirconia Thin Films.** Samina Azad, Suntharampillai Thevuthasan, vaithiyalingam shutthanandan, McCready Dave, laxmikant saraf, Chongmin Wang, Lyubinetzky Igor and peden chuck; Chemical Sciences, Pacific Northwest National Lab, Richland, Washington.

Ion conductance in solid electrolytes plays an important role in electrochemical devices such as batteries, sensors and fuel cells. Development of electrolyte materials that possess high oxygen ion conductance at relatively lower temperatures is essential to increase the efficiency of these devices. It has been established previously that ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yttria-stabilized zirconia, the major component currently used in fuel cells. In a recent study, a nanoscale lamellar structure of calcium and barium fluoride was found to exhibit considerably higher ion conductance along the interfacial directions at moderate temperatures. In our present study, we investigate a novel approach to increase the ion conductance of gadolinia-doped ceria and zirconia by introducing nanoscale interfaces parallel to ion conduction. Highly oriented multi-layered films of gadolinia-doped ceria and zirconia were epitaxially grown on sapphire substrates and these films were characterized using in situ reflection high-energy electron diffraction (RHEED) and ex situ x-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) along with channeling. The electrical conductivity of these films was measured using a four-probe van der Pauw technique and the oxygen ion conductance, at relatively low temperatures, was found to increase with increasing number of layers in these films. Detailed studies on the influence of multiple interfaces on oxygen ion conductance in these layered oxide films are currently underway.

**9:15 AM L1.3**

**Formation of Nanosized Metal Grains and Oxide Created by Oxidation of Ag Single Crystals with Hyperthermal Atomic Oxygen.** Long Li and Judith C. Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Atomic oxygen (AO) is considered as a more reactive oxidizing species than molecular oxygen (O<sub>2</sub>). Many metals which are stable in O<sub>2</sub> atmosphere can react significantly with AO, and thereby produce new metal-oxide nanostructures. In this work, we chose silver single crystals as a typical system, which does not intensely react with molecular oxygen below 500C, but continually reacts with AO. Single Ag crystals (Ag(100), Ag(111)) were exposed to a 5eV hyperthermal atomic oxygen, created by the laser detonation of molecular oxygen at 220C for 7 hours. The experimental results indicate that Ag reacts intensively with AO at this low temperature. Very thick oxide scales (~10 microns) formed on both Ag (100) and Ag (111) substrates. The microstructural investigation of the oxide films by high resolution transmission electron microscopy (HRTEM), electron energy loss spectrum (EELS), and X-ray diffraction (XRD) revealed that this "oxide scale" is composed of nanosized polycrystalline silver grains (5-100nm) and nanosized silver oxides, which is remarkably different

from the O<sub>2</sub> oxidation. The HREM investigation suggests that the formation of this structure was caused by the rapid diffusion of silver from the substrate to oxide scale and {111} planes are the preferred oxidation frontiers. Our results indicated that AO could be used to create oxide films containing randomly distributed nanosized metal clusters in an oxide scale.

**9:30 AM L1.4**

**Assembly of nano-domain buildings blocs of copper oxalate with a cubic morphology.** Lucica Cristina Soare, Nathalie Jongen, Paul Bowen, Jacques Lemaitre and Heinrich Hofmann; Institute of Materials, Powder Technology Laboratory, Swiss Federal Institute of Technology, EPFL, CH-1015, Lausanne, Swiss, Switzerland.

Granular magnetic systems, consisting of nanometer-sized particles of a magnetic metal (e.g. cobalt) dispersed in a non-magnetic matrix (e.g. copper) are expected to exhibit giant magnetoresistance behaviour. These nanocomposite particles may be prepared by an oxalate co-precipitation followed by the appropriate thermal treatment. The copper oxalate particles are made up of self-assembled nanocrystallites. Cobalt oxalate is expected to exhibit a similar behaviour due to its crystallographic structure similar to the copper oxalate structure. We synthesised this material by precipitation via an oxalate route followed by an adequate heat treatment. Our first aim is to understand and control the precipitation of copper oxalate before combining it with cobalt oxalate to make a composite. Precipitation of copper oxalate has been investigated in an instrumented and well-mixed reactor by following the kinetic parameters to investigate the growth mechanism of the precipitation. The copper oxalate nanoparticles seem to be made up of self-organised building blocks. The precipitated particles have been further characterised using various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD). The second aim is to control the transformation of copper oxalate nanoparticles of cubic shape into copper using an isothermal process under a reducing atmosphere. The nanocrystals size is characterised as a function of time as the main challenge is to maintain the particles morphology during the reduction. Preliminary analysis of the model compared to the experimental data the mechanism seems to involve a nucleation process followed by anisotropic growth of the nuclei. An alternate route to obtain metallic copper is to start from copper oxide particles with a cubic morphology. The kinetics of this two step decomposition (Cu-oxalate, Cu-oxide, Copper) will be also presented. The paper will discuss in detail possible mechanism of the particle formation by self-organization of nanosized building blocs and their influence on the morphology as well as on the kinetics of decomposition.

**10:15 AM \*L1.5**

**Post Forming Nano-izing of Macroscopic, Technologically Useful, Materials: Role for Microwave and Laser-microwave Hybrid Processes.** Rustum Roy, <sup>1</sup>Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

This paper will point to some routes to make nanoscience useful. The commercial utility of nanopowders is limited and cannot justify the research effort being channeled into this field. Of course, materials such as the new zeolites, with nano level refining, and/or imaginative crystal chemistry, do illustrate the success of tailoring further nano materials as powders. On the other hand, the existence of very useful, commercially proven, true nanocomposites (long before the recent nano emphasis) is not fully appreciated. They are common in nature, and also in metallurgical heat treatment, and in ceramics. Very large bodies, which are true nanocomposites, have been designed and made for decades. The glass-ceramic telescope lens discs (10 m. in dia. x 1 m. thick), containing 3 or 4 crystalline phases, 1-5 nm in size, is a classic case. But it is made by forming and shaping the finished product first and then heat treating to introduce the desired nanostructure. This is clearly the most successful route to a true commercial nano-structured, macroscopic product. Based on this perspective, data will be presented on recent remarkable findings on a new approach: utilizing microwave radiation to directly nano-ize materials already shaped (= make them XRD and Raman amorphous). Extensive data will be presented on the de-crystallization (breaking into sub unit cell regions) of pellets of many common phases containing d or f electrons: ferrites, oxides of 3d and 4f elements, including insulators like TiO<sub>2</sub> - in a few seconds, far below the melting point, via a thermodynamically forbidden solid to solid transition. Such transformations are achieved in a 0.5 gauss AC magnetic field at 2.45 GHz. Laser and laser-microwave combinations have also produced similar effects. While the laser decrystallization has been achieved even in single crystals (diamond) and the metals in solid samples, the microwave effects so far have mainly been in compacted powders.

**10:45 AM L1.6**

**Molecule Derived Nanomaterials: Chemical Concepts for**

**Composition, Morphology and Particle Size Control.**  
Sanjay Mathur and Hao Shen; CVD Technologie, Institute of New Materials, Saarbruecken, Germany.

With the advent of nanotechnology, the challenge of achieving chemical homogeneity down to the nanometer scale (lattice engineering) has emerged that renders the conventional material processing methods rather imprecise. In view of the practical implications of nano-matter there is a current need to develop strategies for a controlled growth of nanomaterials. Although it is difficult to envisage a straightforward recipe but the chemical methods based on molecular precursors represent one of the viable alternatives for targeted synthesis of nanomaterials with different compositions and (micro)structures. If the intimate mixing of different elements present in the precursor persists until the desired ceramic or composite crystallizes, the typical problems of materials synthesis such as selective crystallization or segregation of one constituent and preferential hydrolysis or pyrolysis of one component can be avoided. Assembling all the elements, required to form the material, in a single molecular compound, can augment the advantages of chemical processing. The major attributes of the so-called single-source approach are: (i) the possibility to tune the cation ratio in the precursor, (ii) phase formation at low temperatures since the atoms are chemically linked, no diffusion of ions is necessary and (iii) low organic contamination due to neat ligand elimination mechanisms. To this end, we have developed various molecular sources and examined their single-step conversions to obtain nanoparticles and films of complex oxides (Fe<sub>3</sub>O<sub>4</sub>, GdFeO<sub>3</sub>, YFeO<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, CoFe<sub>2</sub>O<sub>4</sub>), biphasic metal/oxide composites (Ge/GeO<sub>2</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>), oxide-oxide composites (ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, NdAlO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>/Al<sub>2</sub>O<sub>3</sub>), intermetallic/oxide composite (Ni<sub>3</sub>Sn<sub>4</sub>/SnO<sub>2</sub>), and semiconductor nanowires (Ge, SnO<sub>2</sub>). The results illustrate that a predefined reaction chemistry of the precursors enforces a remarkable control over morphology, composition and particle size. Owing to the unique structural features and composite geometry, the investigated nanomaterials show interesting properties. A brief account based on the above lines will be presented.

**11:00 AM L1.7**  
**Correlation between magnetic and structural properties of nanostructured Co film.** Sungkyun Park<sup>1</sup>, X Zhang<sup>1</sup>, A Misra<sup>1</sup>, M R Fitzsimmons<sup>1</sup>, J D Thompson<sup>1</sup>, M F Hundley<sup>1</sup>, M A Nastasi<sup>1</sup>, J Shaw<sup>2</sup> and C M Falco<sup>2</sup>; <sup>1</sup>Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>University of Arizona, Tucson, Arizona.

Nanoscale multilayers, consisting of a Au/Co/Au/Cu(111) architecture on Si(111) substrate, were grown by molecular beam epitaxy in order to study the influence of the interfacial strain on the magnetic properties of the Co layer. The magnetization of an 8 ML Co layer changes from out-of-plane to in-plane when the thickness of the Au underlayer is dropped from 6 ML to 2 ML. We will show that this is due to the difference interfacial strain between Co and Au underlayer depending on the Au underlayer thickness. X-ray and high-resolution cross-sectional TEM studies show that the Co layer, normally hcp, adopts the distorted hcp stacking for the sample with a 2 ML Au layer. In additions, we found the temperature induced magnetization direction change (from in-plane to out-of-plane with cooling below ambient temperatures) for the sample with a 2 ML Au layer, and the related mechanism will be discussed.

**11:15 AM L1.8**  
**Anomalous Electronic Transport Properties in Nanoscale Cu-Nb Bilayer Films<sup>†</sup>.** Michael Hundley<sup>1</sup>, Amit Misra<sup>1</sup>, Eric Bauer<sup>1</sup>, Corwin Booth<sup>2</sup>, Artur Malinowski<sup>1</sup>, Xinghang Zhang<sup>1</sup> and Michael Nastasi<sup>1</sup>; <sup>1</sup>Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Lawrence Berkeley National Laboratory, Berkeley, California.

We report the temperature-dependent (4K to 400 K) electronic transport and structural properties of continuous Cu-Nb bilayer films with bilayer repeat lengths that range from 2.4 nm to 80 nm. The films were prepared by dc magnetron sputtering onto Si {100} wafers. The volume fraction of the two elements in each film is 50%, and the total number of bilayers was varied so that the total film thickness was always 0.5  $\mu$ m. For individual layer thicknesses between 2 and 5 nm extremely large, hysteresis-free anomalies are present between 150 K and 250 K in both the resistivity and Hall coefficient. The transport anomaly connects a high-temperature T-independent moderate resistivity regime ( $\rho \approx 10 \mu\Omega$  cm) with a low-T high-resistivity regime ( $\rho \approx 35 \mu\Omega$  cm). This result is in stark contrast to the monotonic, nearly temperature-independent resistivity exhibited by films with layer thickness greater than 5 nm. The anomalous transport effect cannot be explained by conventional electronic interface scattering mechanism. Instead, it may arise from a lattice mismatch-induced nonequilibrium atomic arrangement of both Cu and Nb atoms in the nanoscale bilayer films that is exacerbated upon cooling due differential thermal contraction. These

temperature-dependent nanostructured atomic arrangements are elucidated via cross-sectional transmission electron microscopy and local-structure measurements of individual Nb and Cu layers via x-ray absorption fine-structure spectroscopy. <sup>†</sup> work performed under the auspices of the US Department of Energy

**11:30 AM L1.9**  
**Nanoscale Pd<sub>0.9</sub>Ag<sub>0.1</sub> Alloy Films and their Hydrogen Interaction Characteristics: Annealing Dependence.** Yulia Sevryugina<sup>1</sup>, Zhouying Zhao<sup>2</sup> and Michael A Carpenter<sup>2</sup>; <sup>1</sup>Chemistry, University at Albany, SUNY, Albany, New York; <sup>2</sup>School of NanoSciences and NanoEngineering, University at Albany, SUNY, Albany, New York.

Thin films of 20 nm Pd<sub>0.9</sub>Ag<sub>0.1</sub> were annealed at 50°C, 75°C, 100°C, 125°C, 175°C, 200°C and 300°C, and their hydrogen interaction characteristics were subsequently investigated. Changes in reflectance of the palladium alloy were monitored during exposure to hydrogen concentrations in the range 0.17-50%. Tendencies measured included an increase in reflectance change and response time for films annealed at higher temperatures. This was attributed to an increase in palladium alloy grain size during annealing which was corroborated with X-Ray Diffraction (XRD) data. Each film showed a significant increase in response time at the  $\alpha \rightarrow \beta$  phase transition. Preliminary results at elevated operating temperatures will be discussed.

SESSION L2: Characterization  
Chair: Sridhar Komarneni  
Monday Afternoon, December 1, 2003  
Room 304 (Hynes)

**1:30 PM \*L2.1**  
**Photo-formed Metal Nanoparticle Arrays In Monolithic Silica-Biopolymer Aerogels.** xipeng liu, yu zhu, chunhua yao and William M. Risen; Chemistry Department, Brown University, Providence, Rhode Island.

Transparent monolithic aerogels based on silica, the bioderived polymer Chitosan, and coordinated ions have been employed to serve as a three-dimensional scaffold decorated with Au, Pt and Pd ions. The coordination states of the metal ions and the initial gel characteristics control the diffusion rates of ions in the gels so that concentration gradients in one or several of the ions are established in the thickness of the monolith that is produced by supercritical CO<sub>2</sub> extraction to form the aerogels. Also in this work, it has been found that the resultant aerogels can be imaged photolytically in the two planar dimensions. The spatially controlled photolysis produces nanoparticles, (Au)<sub>n</sub> in the range of from 20 to 40 nm for example, that constitute two dimensionally imaged arrays whose volumetric concentration also varies in the third dimension. These images microarrays of nanoparticles provide a basis for localization and detection of dyes, amino acids and protein molecules. The formation of these arrays, including the dependence of their properties on light intensity, frequency and exposure, and distribution of ions in the initial aerogel also will be presented.

**2:00 PM L2.2**  
**Creation and Characterization of Gold- and Silicon-Nanoparticles inside a Fullerene Lattice.** Helge Kroeger<sup>1</sup>, P Reinke<sup>3,1</sup>, M Buettner<sup>2</sup> and P Oehlhafen<sup>2</sup>; <sup>1</sup>II.

Physik, Universitaet Goettingen, Goettingen, Germany; <sup>2</sup>Institut fuer Physik, Universitaet Basel, Basel, Switzerland; <sup>3</sup>Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Fullerenes have been doped with a variety of elements, mainly alkalis and rare earths, and these materials exhibit quite intriguing properties. In the present study we extend the material combinations to C<sub>60</sub>-Si and C<sub>60</sub>-Au composites in the concentration range between 2 and 30% of the non-fullerene component. In addition the accumulation of Si and Au on the highly corrugated C<sub>60</sub> surface is investigated. The intent is to use the fullerene lattice as a template for the self-assembly of ultra small clusters (<20 atoms) and the synthesis of porous structures beyond the percolation threshold. Photoelectron spectroscopy (PES) was employed to study the electronic properties of the material and interfaces. It supplied information on the barrier heights and fullerene-Si/Au interaction. PES also provides an indirect measure of the cluster size, respectively the extension of the Si or Au regions embedded in the insulating fullerene. The shift of the core levels as a function of cluster size was quantified independently in other experiments. The extension of the Au and Si regions is directly controlled by the element concentration and since both, Si and Au interact strongly with the C<sub>60</sub> no segregation of the composite thin films takes place. The size of the Si and Au regions and electronic barrier heights to the fullerene are sufficient to provide quantum

confinement in the Au and Si regions. The effect of region/cluster size and interaction with the fullerene matrix on the luminescence spectra and electrical characteristics will be discussed in detail. It has also been found that the thermal stability of the composites is quite high: the migration of Au in the fullerene lattice begins around 450°C, the Si-C<sub>60</sub> layers are transformed to SiC at 700°C. To gain information on the spatial arrangement of Au on the highly corrugated fullerene surface the layer growth is observed with low electron energy diffraction (LEED) and photoelectron spectroscopy. The feasibility of producing regular three dimensional cluster arrays will be discussed.

### 2:15 PM L2.3

**Towards nanocrystal-assembled materials: the role of particle - particle interaction.** Christoph Bostedt, Tony van Buuren, Trevor M Willey and Louis J Terminello; CMS - MSTD, Lawrence Livermore National Laboratories, Livermore, California.

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, which is typically not possible in other growth modes. The clusters are condensed out of supersaturated Germanium vapor, which is cooled down in a He atmosphere and are subsequently deposited on a variety of substrates. Their surfaces can be 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. X ray absorption spectroscopy (XAS) and photoemission (PES) were performed to investigate the electronic structure of Germanium nanocrystal films. We find that submonolayer depositions of unpassivated nanocrystals exhibit strong quantum confinement effects but that with increasing coverage the confinement effects attenuate. However, when the nanoparticle surface is passivated the clusters keep their original properties even in multilayer depositions and it is possible to generate nanocluster assembled materials with unique electronic properties. The results will be discussed in terms of particle - particle interactions. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W 7405 Eng 48.

### 2:30 PM L2.4

**Analysis of the Optical Properties of Nanophase Sculptured Thin Films by Spectroscopic Mueller Matrix Ellipsometry.** Chi Chen<sup>1,2</sup>, Nickolas Podraza<sup>1,2</sup>, An Ilisin<sup>1,2</sup>, Gelio M Ferreira<sup>1,2</sup> and Collins W Robert<sup>1,2</sup>; <sup>1</sup>Material Research Institute, The Penn State University, University Park, Pennsylvania; <sup>2</sup>Department of Physics, The Penn State University, University Park, Pennsylvania.

A multichannel ellipsometer in the dual rotating-compensator configuration has been designed and constructed recently for applications in real time Mueller matrix ellipsometry (~2 to 5 eV) of the fabrication and processing of anisotropic surfaces and thin films [1, 2]. In our initial applications of this instrument, high speed measurements of the 4x4 Mueller matrix have been performed in transmission and reflection for nanophase sculptured thin film structures prepared by glancing angle deposition with simultaneous substrate rotation. The Mueller matrix is important because it provides a complete description of how these thin film structures modify the incident polarization state in the transmission or reflection configuration used for the measurements. Such a description provides insights into the efficacy of the structures as thin film optical devices and sensors. From the 15 elements of the 4x4 Mueller matrix, the real and imaginary parts of the complex amplitude ratios  $\tau_{pp}$ ,  $\tau_{ps}$ , and  $\tau_{sp}$  (six parameters in all) obtained in transmission (or  $\rho_{pp}$ ,  $\rho_{ps}$ , and  $\rho_{sp}$  obtained in reflection) can be extracted [3]. Multiple independent methods for computing these ratios yield results in excellent agreement. The methods first described by Berreman [4] have been applied to analyze  $\tau_{pp}$ ,  $\tau_{ps}$ , and  $\tau_{sp}$  (or  $\rho_{pp}$ ,  $\rho_{ps}$ , and  $\rho_{sp}$ ) and extract structural parameters and optical properties of the films. For a nanophase chiral thin film, for example, analysis of the transmission amplitude ratios provide the film thickness  $d$ , the azimuthal Euler angle  $\phi_0$  at the interface to the substrate (measured with respect to the incident beam polarizer angle), the fixed polar Euler angle  $\theta$ , and the chiral pitch  $P$ . In addition, the optical properties can be determined, including the two principal indices of refraction associated with the form birefringence of the local uniaxial structure. Finally, deviations of the film from a perfect chiral nanostructure can be assessed using a multilayer optical model that incorporates a stepwise variation in the azimuthal Euler angle and non-uniformities with depth into the film. References [1] R. W. Collins and J. Koh, *J. Opt. Soc. Am.* 16, 1997 (1999). [2] J. Lee, J. Koh, and R. W. Collins, *Rev. Sci. Instrum.* 72, 1742 (2001). [3] C. Chen, Ilisin An, and R. W. Collins, *Phys. Rev. Lett.* 90, 217402 (2003) [4] D. W. Berreman, *J. Opt. Soc. Am.* 62, 502 (1972). Corresponding author: Robert W. Collins, The Pennsylvania State University, 275 Materials Research Laboratory, University Park, PA 16802, USA. phone:

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### 2:45 PM L2.5

**Self assembled gold and silver nanoparticulates on silicon nanotips as surface enhanced Raman active substrates.** Surojit Chattopadhyay<sup>1</sup>, H C Lo<sup>1</sup>, K H Chen<sup>1,2</sup>, C H Hsu<sup>2</sup> and L C Chen<sup>2</sup>; <sup>1</sup>Institute of Atomic and Molecular Sciences, Academia, Sinica, Taipei, Taiwan; <sup>2</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Surface enhanced Raman spectroscopy (SERS) has evolved as a powerful and sensitive tool for detection and identification of a wide range of adsorbate molecules down to the limit of single molecule detection. In this paper we report a nanostructured Si substrate on which silver or gold nanoparticulates, with less than 10 nm diameter, can be self assembled at an extremely high density that readily exhibit the surface enhancement. More specifically, prior to depositing metal particles Si nanotips arrays were first produced by self-mask dry etching of Si substrate in an ECR- CVD environment with silane, methane, hydrogen, and argon gas. These nanotips have lengths of few microns and tip diameters about 2 nm. The density of these nanotips were extremely high ranging from 10<sup>10</sup>/cm<sup>2</sup> to 10<sup>11</sup>/cm<sup>2</sup>. Gold, silver or platinum when deposited on these nanotips via ion beam sputtering self assemble into nanometer size particulates over the entire surface of these nanotips. This substrate containing the nanoparticulates on the nanotips are SERS active. Molecules such as Rhodamine 6G, BPE and even carbon nanotubes, adsorbed on these substrates show SERS reproducibly. The large surface area of the nanotips and extremely high density of the nanoparticulates distributed on them enable the substrate to behave as reliable and reproducible SERS active substrates even at very low concentrations (10<sup>-12</sup> M) of the molecules under study. The Raman enhancement factors obtained using these substrates are in the range of 10<sup>6</sup> to 10<sup>8</sup>.

### 3:00 PM L2.6

**Raman Spectroscopy of Nanostructured Diamond.** James Birrell, O Auciello, J E Gerbi, J A Johnson, X Xiao and J A Carlisle; Materials Science, Argonne National Laboratory, Argonne, Illinois.

Although visible Raman spectroscopy is commonly used as an efficient and non-destructive way of determining the bonding structure of diamond thin films, interpreting the spectra of nanocrystalline and amorphous diamond is not straightforward. This is due to the resonantly enhanced signal of the non-negligible sp<sup>2</sup>-bonded carbon content of these films, as well as the appearance of peaks that are thought to be unique to nanocrystalline diamond thin films. Although this problem can be ameliorated somewhat by using a higher excitation energy (i.e. UV Raman spectroscopy), the origin of many Raman features remain unclear. In particular, ultrananocrystalline diamond (UNCD) is an ideal material to probe the effect of the nanostructure and sp<sup>2</sup>-carbon content, because the fine grain size (3 - 8 nm), large number of grain boundaries, and ability to produce a microcrystalline (MCD) or UNCD film structure by varying the deposition parameters. Comparisons of the visible and UV Raman analysis with near edge x-ray absorption fine structure (NEXAFS) and transmission electron microscopy (TEM) measurements on a series of UNCD and MCD films provide critical insights toward understanding the Raman spectrum of UNCD. We find that although the sample has ~95% sp<sup>3</sup>-bonded carbon by NEXAFS and TEM, none of the spectral features seen using visible Raman spectroscopy can be attributed to sp<sup>3</sup>-bonded carbon. Our conclusion is that the visible Raman spectra provide information solely on the bonding structure of the disordered carbon at the grain boundaries of UNCD. This allows us to understand the changes in the Raman spectrum of UNCD grown under different conditions, where the Raman signal is found to change drastically with little concurrent change in the nanostructure of the film. \*This work was supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-13-109-ENG-38.

### 3:30 PM L2.7

**Experimental Determinations of Mean Crystallite Size in Polydisperse Nanocrystalline Materials.** Scott Calvin<sup>1</sup>, C. J. Riedel<sup>1</sup>, E. E. Carpenter<sup>1</sup>, R. Goswami<sup>2,3</sup>, R. M. Stroud<sup>4</sup> and S. A. Morrison<sup>5,1</sup>; <sup>1</sup>Materials Physics Branch, Naval Research Lab, Washington, District of Columbia; <sup>2</sup>Geo-Centers, Fort Washington, Maryland; <sup>3</sup>Physical Metallurgy Branch, Naval Research Lab, Washington, District of Columbia; <sup>4</sup>Surface Modification Branch, Naval Research Lab, Washington, District of Columbia; <sup>5</sup>Chemistry, George Washington University, Washington, District of Columbia.

Existing techniques for determining the mean crystallite size in nanocrystalline materials include electron microscopy, Scherrer analysis of x-ray diffractograms, dynamic light scattering, and extended x-ray absorption fine structure (EXAFS). When applied to samples containing a polydisperse distribution of nanocrystallites or

crystalline nanoparticles, these techniques necessarily yield different results. We have compared these techniques for a variety of materials, including nanocrystalline nickel in an iron matrix, palladium nanoparticles, and core/shell nanoparticles, and compared the results to numerical simulations. We have found that Scherrer analysis generally yields a crystallite size near the high end of the actual distribution, while EXAFS yields a crystallite size near the low end. Together the two techniques therefore provide a more complete picture of the size distribution, including a rough measure of polydispersion. It will also be shown that in certainly nanocrystalline samples, transmission electron microscopy may undercount the smallest crystallites, making EXAFS a valuable adjunct in these cases as well.

### 3:45 PM L2.8

#### Atom Probe Tomography of Thin Film Multilayers.

Gregory B Thompson<sup>1</sup>, M K Miller<sup>2</sup> and H L Fraser<sup>3</sup>; <sup>1</sup>Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama; <sup>2</sup>Metal and Ceramic Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>3</sup>Dept. of Materials Science & Engineering, The Ohio State University, Columbus, Ohio.

The functional properties of nanostructured materials are often dependent upon the compositional structure of the interface. Atom Probe Tomography (APT), due to its high spatial resolution, is an ideal technique to investigate the composition at the interface in these materials. A series of Ti/Nb multilayers have been sputtered deposited and prepared as APT specimens using a Focus Ion Beam (FIB) milling procedure. As the thickness of the Ti layer was reduced, x-ray and electron diffraction indicated that the Ti layer underwent a change in phase stability from hcp to bcc. APT results of the bcc Ti layers have shown a substantial interdiffusion of Nb into the Ti layers to a pseudo-equilibrium concentration of approximately Ti-15at%Nb while maintaining a compositionally modulated interface. In contrast, the hcp Ti layers indicated little Nb interdiffusion within the layers. Reasons for the enhanced interdiffusion will be addressed. Thermodynamic volumetric free energy modeling has shown that this unexpected Nb interdiffusion has helped to facilitate the bcc phase stability in this system to a larger critical layer thickness than previous predictions. The coupling of APT results to the pseudomorphic bcc Ti phase demonstrates the capability APT has in quantifying the compositional characteristics in these types of multilayered nanocomposite systems. \*Research at the SHaRE User Center was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

### 4:00 PM L2.9

#### Spin-dependent STM tunnelling study of the polaronic nanostructure pattern on magnetite (111) surface.

Nikolai Berdunov, Shane Murphy, Guido Mariotto and Igor V. Shvets; Physics Dept., Trinity College, Dublin, Ireland.

Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is a material of fundamental importance in a number of scientific and technical fields. It is believed to be a half metallic ferromagnet with a metal-insulator (Verwey) transition at 123K at which its resistivity increases by some two orders. In our recent study [1] we have demonstrated that under certain conditions, hexagonal nanostructure lattice is formed on the (111) surface of magnetite in ultra-high vacuum. The nanostructure pattern is highly regular as seen by LEED and STM. The pattern can be created reproducibly by varying the oxygen pressure during the sample anneal in the vacuum chamber. The onset of the pattern is sensitive to the surface stoichiometry, which was confirmed by the Auger spectroscopy measurements. The hexagonal nanostructure pattern has a 4.2 nm periodicity. By varying the conditions of the STM measurements we could establish that the nanostructure is of electronic origin rather than being a mosaic of various iron oxide phases. We could also establish that the formation of the pattern is triggered by the lateral strain on the surface and therefore must be considered as a pattern of the localized large polarons. We discuss the observed pattern in terms of the electronic structure of the polaronic pattern. Spin-polarized (SP) STM with magnetic tip was employed to study the electronic and magnetic properties of the nanostructure pattern. SP-STM results demonstrate significant spin-contrast effect on the different patches of the pattern. Additionally, applying a magnetic field 60 mT in our SP-STM experiments we were able to see the changes in the local symmetry of the surface atomic arrangement. Density functional calculations have been employed to explain our spin-sensitive STM results. 1. Berdunov, N., Murphy, S., Mariotto, G., Shvets, I. V., Formation of a strain-induced polaronic superlattice on a magnetite (111) surface, 2003, submitted to PRB

### 4:15 PM L2.10

#### Percolation in Multi-Wall Carbon Nanotube-Epoxy Composites - Influence of processing parameters, nanotube aspect ratio and electric fields on the bulk conductivity.

Jan Sandler<sup>1</sup>, Christian A. Martin<sup>1,3</sup>, Milo S.P. Shaffer<sup>2</sup>,

Matthias-Klaus Schwarz<sup>3</sup>, Wolfgang Bauhofer<sup>3</sup>, Karl Schulte<sup>4</sup> and Alan H. Windle<sup>1</sup>; <sup>1</sup>Materials Science and Metallurgy, Cambridge University, Cambridge, United Kingdom; <sup>2</sup>Chemistry, Imperial College London, London, United Kingdom; <sup>3</sup>Materials in Electrical Engineering and Optics, Technical University Hamburg-Harburg, Hamburg, Germany; <sup>4</sup>Polymer Composites, Technical University Hamburg-Harburg, Hamburg, Germany.

In a recent study we have shown that the use of aligned CVD-grown multi-wall carbon nanotubes (MWCNT) leads to electrical percolation thresholds in an epoxy matrix at filler concentrations as low as 0.0025 wt%. The sample production technique employed is based on a shear-intensive stirring process which leads to well-dispersed individual carbon nanotubes in the resin. This stability of the dispersion can be attributed to a charge-stabilisation mechanism. The existence of negative surface charges on the nanotubes was verified by in-situ observations of the agglomeration of nanotubes at the anode during the application of a DC field. The achievement of such fully dispersed nanotubes then allows an investigation of the percolation process of the filler during further processing. Firstly, the influences of composite processing parameters such as stirring rate, stirring temperature and curing temperature on the resulting bulk conductivity of nanocomposites containing 0.01 wt% MWCNT were investigated. Results from AC impedance spectroscopy ranged from purely dielectric behaviour to bulk conductivities of about 10<sup>-3</sup> S/m, depending on the production parameters. Optical micrographs verified the network formation of the filler as a function of processing parameters. Based on the optimised processing conditions samples with increasing weight fractions of nanotubes with varying aspect ratios were produced and analysed with regard to the resulting electrical properties. For aspect ratios of 250 and 2000 percolation thresholds below 0.005 wt% were obtained. These experimental percolation thresholds are more than one order of magnitude lower than predictions based on statistical percolation models. Aspects of colloid theory are applied to interpret the experimental data. Finally, the influences of applied electric fields during curing of the samples were studied. For both AC and DC voltages the network formation was investigated during in-situ curing of the nanocomposites between electrodes sputtered onto optical microscopy slides and bulk samples. Light microscopy was applied to follow the network formation as a function of the applied field. The results are compared to the behaviour of carbon black in the epoxy matrix.

### 4:30 PM L2.11

#### High-resolution Analytical Electron Microscopy Investigation of Metastable Tetragonal Phase Stabilization in Undoped, Sol-gel Derived Zirconia Nanoceramics. Vladimir P. Oleshko<sup>1</sup>, James M Howe<sup>1</sup>, Satyajit Shukla<sup>2</sup> and Sudipta Seal<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; <sup>2</sup>Advanced Materials Processing and Analysis Center & Mechanical Materials Aerospace Engineering Department, University of Central Florida, Orlando, Florida.

The mechanisms underlying stabilization of the metastable tetragonal (t)-phase in undoped, nanocrystalline ZrO<sub>2</sub> ceramics were studied by high-resolution field-emission analytical electron microscopy, utilizing parallel electron-energy loss (PEEL) and energy-dispersive X-ray nanospectroscopies. The ZrO<sub>2</sub> nanoceramics were sol-gel derived by hydrolysis of zirconium (IV) n-propoxide at ratios of the molar concentration of water to zirconium n-propoxide of R=5 and 60, respectively, followed by calcination for 2h at 400°C in air. The as-precipitated ZrO<sub>2</sub> (R=5) contained aggregated clusters and elongated denser particles 200-500 nm in size that appeared amorphous. However, high-resolution transmission electron microscopy (HRTEM) revealed 5-11 nm-sized nanocrystals randomly distributed in the largely amorphous particles that may serve as nuclei for the t-phase during calcination. Using bright-field/dark-field TEM, selected-area diffraction and HRTEM, we found that the calcinated ZrO<sub>2</sub> particles were spherical (400-600 nm in size) and consisted of 10-100 nm-size t-nanocrystallites. The as-precipitated ZrO<sub>2</sub> powder (R=60) contained primary 4-11 nm-sized particles with an amorphous structure that formed aggregates (~50-100 nm in size). Calcination of this sample led to a mixture of t- and monoclinic (m)-ZrO<sub>2</sub> agglomerated nanocrystals 8-100 nm in size. The net PEEL intensity from the nanopowders matched the expected position of a direct band gap for ZrO<sub>2</sub> between 4-5 eV energy losses. For the as-precipitated nanopowder (R=60), the intensity threshold was less pronounced due to a number of defect states in the gap. Fingerprints of the ZrO<sub>2</sub> band structure in the low-loss and inner-shell PEEL spectra allow differentiation between the amorphous-like and nanocrystalline ceramics. Stabilization of nanocrystallites of t-phase in the spherical ZrO<sub>2</sub> particles with sizes 3-10 times larger than previously reported is likely due to strain-induced size confinement from surrounding growing crystals, which suppress the volume expansion associated with the martensitic t-m phase transformation. Loose particle agglomerates of ZrO<sub>2</sub> nanopowders synthesized with a high R-value cannot suppress the t-m transformation. In this case, the

t-phase may be partially stabilized due to a crystallite size effect and/or to the simultaneous presence of m-phase.

SESSION L3: Poster Session I  
Chairs: Sridhar Komarneni, John Parker and James Watkins  
Monday Evening, December 1, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

### L3.1

**The Effects of Cs Intercalation on the Raman Modes of Single-Wall Carbon Nanotubes.** Brahim Akdim<sup>1</sup>, Xiaofeng Duan<sup>2</sup> and Ruth Pachter<sup>1</sup>; <sup>1</sup>Materials and Manufacturing Directorate, AFRL, WPAFB, Ohio; <sup>2</sup>ASC MSRC, AFRL, WPAFB, Ohio.

It was previously shown that alkali metal doping of single-wall carbon nanotubes results in low-frequency peaks assigned to modes involving both radial motions of the tubes and alkali-atoms vibrations (N. Bendiab, et al., Chem. Phys. Lett., 339, 305 (2001)). In this investigation, we present a first-principles density functional theory study on the effects of Cs doping on the Raman modes of crystalline ropes and isolated single-wall carbon nanotubes. A comparison with the results for pristine tubes, previously reported by our group, will be discussed in detail.

### L3.2

**Spectroscopic Study of Pr- and Er-doped Silicon Rich Silicon Oxide Co-Sputtered Films.** Luis F Fonseca, Carlos Rozo, Oscar Resto and S. Zvi Weisz; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Er-doped Si-rich SiO<sub>2</sub>, Pr-doped Si-rich SiO<sub>2</sub> and Er, Pr-doped Si rich SiO<sub>2</sub> thin films are prepared. Photoluminescence (PL) spectra for visible and infrared are obtained for each as-deposited film. The samples are annealed by steps to different temperatures within the range 600°C-1100°C for 30 minutes at each annealing temperature. PL spectra are obtained at each step and their characteristics are studied. The best annealing temperature for the PL of the rare earth (RE) ions is obtained. PL is reported for the <sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub> (1532 nm) and <sup>4</sup>I<sub>11/2</sub>→<sup>4</sup>I<sub>15/2</sub> (980 nm) transitions of Er<sup>3+</sup> in the Er-doped film. PL is reported for the <sup>3</sup>P<sub>0</sub>→<sup>3</sup>F<sub>2</sub> (650 nm) transition of Pr<sup>3+</sup> for the Pr-doped film. The Er-Pr-co-doped film exhibits PL from both rare-earth ions. The PL spectra of the films are compared with one another to determine how the co-doping with both rare earth ions affects the PL of each.

### L3.3

**ALSA (Atomic Level Surface Assembler) : New Software for Design of Ordered Adlayers at the Well-Ordered Substrate.** Alexandre Tkatchenko and Nikola Batina; Dept. of Chemistry, Universidad Autonoma Metropolitana, Mexico D.F., Mexico.

Although many structural models have been developed for use with well-defined surfaces, the booming interest in nanotechnology and needs for design of new advanced materials with specific and defined properties at the atomic and molecular level, require better understanding and more precise structure evaluation tools. In particular, it is required for better interpretation of the STM and AFM images, which show the material surface at the atomic level. A new software, named ALSA (Atomic Level Surface Assembler), developed recently in our laboratory, is a sophisticated tool for design and analysis of structural properties of adatom adlayers at the well-defined substrate. Although, ALSA is based on simple symmetry principles, it has many advantages in terms of adatom positioning and dynamic movements at the substrate surface then previous methodologies. It is equally useful for design of monolayer and multilayer assemblies, and offers a variety of parameters, such as : interatomic distance, dimension of the adsorbate/substrate unit cells, corrugation between atoms within a single or several adlayers and layer thickness, which can be presented in different numerical or graphical forms. In order to simulate changes of adlayer structure during phase transition processes, a set of dynamic analysis tools was developed, which allows characterization of the surface morphology for adlayers with continuous translation or rotation over the substrate surface. ALSA has been tested on simulation of the (3x3)I-Pt(111) system. Results indicate existence of three distinctive structures assembled in symmetric, asymmetric and linear shape. The STM image presentation mode of the simulated structures allows easy comparison with existing experimental data. Using ALSA resources we were able to test stability of each of these configurations. We believe that ALSA offers a new approach in the materials simulation, which will be useful for the STM/AFM image interpretation, as well as a powerful tool for design of new advanced materials with desired properties and structure defined at the atomic level.

### L3.4

**Nanoparticulate NiO in an SiO<sub>2</sub> Matrix for CO Sensing Using Optical and Electrical Conductivity Transduction.** Mike Post<sup>1</sup>, Alex Martucci<sup>2</sup>, Massimo Guglielmi<sup>2</sup> and Carlo Cantalini<sup>3</sup>; <sup>1</sup>ICPET, National Research Council of Canada, Ottawa, Ontario, Canada; <sup>2</sup>Dipartimento di Ingegneria Meccanica S. Materiali, Universita di Padova, Padova, Italy; <sup>3</sup>Dipartimento di Chimica e dei Materiali, Universita dell'Aquila, Aquila, Italy.

The enhanced physical and chemical properties of some materials when they are prepared at low dimension has provided a means of improving gas sensor functionality for some interesting sensor systems. In the present work, nanoparticulate NiO imbedded in a porous SiO<sub>2</sub> matrix has been studied for the application of carbon monoxide sensing. Thin films of the NiO/SiO<sub>2</sub> composite have been prepared using sol-gel techniques and a dip coating method. A range of NiO compositions (10% to 40%NiO) in the matrix have been prepared, and these have been subjected to a series of controlled post treatments at selected temperatures in the range 500°C to 900°C. TEM imaging reveals NiO nanoparticles of size 2.5nm with a narrow size distribution and which are homogeneously dispersed in the SiO<sub>2</sub> matrix. When the films are at temperatures above 230°C and exposed to CO, a fast and reversible increase in optical transmittance takes place. This effect has been studied in the wavelength range 400nm to 900nm and for CO concentrations from 100ppm to 1%. Reported here will be a description of the apparatus used for the in-situ CO exposure experiments and the results of the optical transmittance study. The relationship which exists between the sensor response characteristics and the degree of densification in the SiO<sub>2</sub> matrix, which is produced by the various thermal post-treatments, will also be highlighted. Additionally, it has been shown that accompanying the optical transmittance changes upon CO exposure are variations in the electrical conductivity of the films. Some preliminary data demonstrating this feature of the composite films will also be reported.

### L3.5

**Helical Silica Nanosprings.** Hai-Feng Zhang<sup>1,2</sup>, Chong-Min Wang<sup>2</sup> and Lai-Sheng Wang<sup>1,2</sup>; <sup>1</sup>Department of Physics, Washington State University, Richland, Washington; <sup>2</sup>Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

Amorphous helical SiO<sub>2</sub> nanosprings (80 to 140 nm in diameter and up to 8 microns long) were synthesized with a chemical vapor deposition technique, characterized by scanning (SEM) and transmission (TEM) electron microscopy. Demonstration of the storage of mechanical energy and flexibility of the nanosprings was performed. A growth model was proposed for the formation of these novel nanostructures based on the detailed structural characterization. Present study suggested that these nanosprings may have great potential for applications related to nanomechanical and nanoelectronic devices.

### L3.6

**Photoregulation Of Mass Transport Using Photoresponsive Mesoporous Nanocomposite Films.** Nanguo Liu<sup>1</sup>, Darren R. Dunphy<sup>2</sup>, Zhu Chen<sup>1</sup>, Plamen Atanassov<sup>1</sup> and C. Jeffrey Brinker<sup>1,2</sup>; <sup>1</sup>Chemical and Nuclear Engineering, The University of New Mexico, Albuquerque, New Mexico; <sup>2</sup>Dept.1841, Sandia National Laboratories, Albuquerque, New Mexico.

Stimuli-responsive nanocomposite materials have potential applications in nanofluidic channels or devices, molecular gates, or valves due to their ability to undergo volumetric or dimensional changes in response to environmental stimuli, such as pH, temperature, or light. In an effort to make such responsive materials, we synthesized a photoresponsive organosilane, 4-(3-triethoxysilyl-propylureido)azobenzene (TSUA). Trans-cis isomerization induced by light or heat of azobenzene ligands contained in TSUA cause a dimensional change of ca. 3Å. Evaporation induced self-assembly (EISA) was adopted to incorporate TSUA molecules into an ordered, periodic silica framework to make photo-responsive, self-assembled nanocomposite films. In this synergistic nanocomposite, the 3-dimensional organization of the responsive ligands allows transduction of photo energy into a useful mechanical response of interest for molecular valves or gates. We modified the working electrode of a photochemical cell with our photoresponsive film and, using ferrocene dimethanol as a molecular probe, performed chronoamperometry experiments with alternate UV and visible light exposure. We observed reversible optically-mediated responses indicating the reversible photoregulation of mass transport of the molecular probe.

### L3.7

**Electrical Response to Different Gases of Nanostructured**

**YCoO<sub>3-y</sub> and Y<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-y</sub> Prepared by a Solution Method.** Carlos R. Michel<sup>1</sup>, Aldo Saul Gago<sup>1</sup>, Claudia Catalina Luhrs<sup>2</sup> and Arturo Chavez-Chavez<sup>1</sup>; <sup>1</sup>Physics, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico; <sup>2</sup>Chemistry, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

In recent years, cobaltites with perovskite-type structure have received a lot of attention for their applications in fields like ceramic membranes for oxygen separation and cathodes for nitric oxide reduction<sup>1-2</sup>. Among these cobaltites, the members of the solid solution: La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-y</sub> have been the most studied compounds in those fields, due to their superior physical and chemical properties. These oxides are characterized to be non-stoichiometric, with cobalt in a mixed-valence state +2 and +3. For those applications, their properties are usually enhanced when the mean particle size of the powder is in the order of nanometers. In this work, samples of nanostructured YCoO<sub>3-y</sub> and Y<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-y</sub> were prepared by a solution method, which employed the dissolution of stoichiometric amounts of Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Sr(NO<sub>3</sub>)<sub>2</sub> in an aqueous media containing urea. The precursor resins obtained from the solutions after heating to dryness, were analyzed by DTA and TGA, and they were also thermally decomposed in a tubular furnace in a temperature range from 300°C to 900°C in air. X-ray powder diffraction was performed in samples calcined every 100°C in order to identify the formation mechanism from an amorphous phase to the perovskite. Pure samples of YCoO<sub>3-y</sub> and Y<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-y</sub> were obtained at 900°C for 24 hr; their TEM analysis gave as a result a mean particle size of 15 nm. The electrical properties were measured on pellets and thick films using the Van der Pauw four-point probe method. Nanostructured thick films were made by the screen printing method and deposited on alumina substrates. These results show a semiconductor behavior from room temperature to 700°C. The electrical response of these perovskites to different gases was also measured in the same temperature range, and the results were compared with those obtained from LaCoO<sub>3-y</sub> and La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3-y</sub>. References : 1.Huang K., Goodenough J.B. J. Electrochem. Soc. 148, (5) E203 (2001). 2.Kamer Hansen K., Skou E.M., Christensen H. J. Electrochem. Soc. 147, (5) 2007 (2000).

**L3.8 Gas-sensing properties of SnO<sub>2</sub> nanohole array.** Masayoshi Uno<sup>1</sup>, Tsuyoshi Hamaguchi<sup>1</sup>, Nobuaki Yabuki<sup>1</sup>, Akihiro Ieda<sup>1</sup>, Tomoaki Nakata<sup>1</sup>, Makoto Egashira<sup>2</sup>, Yasuhiro Shimizu<sup>2</sup> and Takeo Hyodo<sup>2</sup>; <sup>1</sup>Department of Nuclear Engineering, Osaka University, Suita, Osaka, Japan; <sup>2</sup>Department of Materials Science and Engineering, Nagasaki University, Bunkyo-machi, Nagasaki, Japan.

The SnO<sub>2</sub> nanohole arrays have been prepared by anodic alumina in ammonium hexafluorostannate solution at room temperature for a few hours. Pt, Au and Pd electrodes were sputtered on the tin oxide nanohole arrays. H<sub>2</sub> and NO<sub>2</sub> gas sensing properties of SnO<sub>2</sub> nanohole array sensors have been evaluated in dry air at 250-500 °C. In the case of H<sub>2</sub>, every sensor showed quick response to H<sub>2</sub> but fairly low sensitivity. Pt-SnO<sub>2</sub> and Au-SnO<sub>2</sub> sensors exhibited highest sensitivity at 500 °C, and the sensitivity decreased as temperature decreased. On the other hand, Pd-SnO<sub>2</sub> sensor exhibited resistance increase upon exposure to H<sub>2</sub> at 300-400 °C. This is probably due to resistance increase by the hydrogen solid solution in Pd electrode.

**L3.9 A New Emulsion Method to Synthesize Adjustable and Robust Mesoporous Materials.** Guangsheng Luo,<sup>1</sup>Chemical Engineering, Tsinghua University, Beijing, China; <sup>2</sup>Chemical Engineering, Tsinghua University, Beijing, China.

A new emulsion method to prepare adjustable, robust mesoporous materials with PEGs as swelling agents has been developed in the present work. The synthesis conditions including emulsion types, PEG chain lengths, PEG concentrations, duration of aging, and the time when the swelling agents were added to the crystallization system were discussed. It was found that the concentration and the chain length of PEGs were the most influential factors to the particle morphology. With the increases of PEG concentrations, the pore sizes increased from 2 nm to 100 nm all with very narrow distributions. When larger MW PEGs were added, the particle remained finely spheric shape with decreased size and less agglomeration. The results showed that the interior and exterior structures of the particles were both controlled very well with an emulsion as the preparation condition. The particles prepared with the new method were spheric and uniform compared to those with the hydrothermal method and not prone to agglomerate. Compared the results of o/w emulsion with those of w/o emulsion, it could be seen that the former was superior for both the pore and the particle morphology although the latter should be theoretically more suitable for the optimization of the particle size for its average water droplet enwrapped in the oil phase.

The explanation was given in our work. By controlling the time of addition of the swelling agents, a 'core-shell' mesoporous material could be prepared. In this process the pore size moved to the upper edge of mesopores, that is, 20-80 nm. The emulsion method is particularly useful for those applications that strictly require particle uniformity and structure rigidity such as chromatography separation.

**L3.10 Controlled Hierarchical Pore Structures in Ethylene-Bridged Polysilsesquioxane Gels.** Kazuki Nakanishi<sup>1,2</sup>, Yuki Kobayashi<sup>1</sup> and Kazuyuki Hirao<sup>1</sup>; <sup>1</sup>Material Chemistry, Kyoto University, Kyoto, Japan; <sup>2</sup>PRESTO, JST, Kawaguchi, Saitama, Japan.

Beautiful examples of supramolecularly templated bridged polysilsesquioxanes have been recently demonstrated by Inagaki et al. In the present study, an introduction of supramolecularly templated mesopores into the well-defined macroporous gel skeletons which can be formed via spinodal decomposition of gelling bis(trimethylsilyl)ethane, BTME, system has been attempted. The incorporation of cationic surfactant such as CTAB unexpectedly turned out to be ineffective to induce the phase separation which leads to the formation of micrometer-range co-continuous morphologies, as far as the starting composition is chosen to form homogeneous monolithic gels. Triblock copolymer, EOPEO, is also known to induce phase separation in tetramethoxysilane, TMOS, system because of its strong hydrogen-bonding interaction between silanol groups. It was found that triblock copolymers, L121, P123, F127 induce phase separation in BTME systems to result in co-continuous macroporous structure in limited composition ranges. The pore size distribution in the nanometer range, however, depended strongly upon the length of terminal PEO chains sandwiching the core PPO chain. That is, cylindrical pores of ca. 4nm in diameter formed only when P123 was used as a template, while possibly lamella-shaped mesopores in addition to major micropores were formed in the cases of L121 and F127, in the BTME-based systems. In the BTME-P123 system, the resultant mesopores exhibited narrow distributions after the heat-treatment at 350C, and the pore volume was well correlated with the incorporated amount of the triblock copolymer. The three triblock copolymer have identical lengths of PPO, 70 units, and different length of PEO, 5, 20 and 106 units for L121, P123 and F127, respectively. It is therefore presumed that the mesoporous templating in macroporous BTME-derived gels is effective only with surfactants having strong enough hydrogen bonding to silanols as well as ability to form undisturbed supramolecular assembly in the gel network.

**L3.11 Surface Plasmon Resonance From Pulsed Laser Deposited Thin Film With Self-Assembled Ag Nanodots.** Takehiro Yamamoto<sup>1</sup>, Sanhiro Nagare<sup>2</sup> and Mamoru Senna<sup>1</sup>; <sup>1</sup>Faculty of Science and Technology, Keio University, Yokohama, Japan; <sup>2</sup>Nara Machinery Co., Ltd., Tokyo, Japan.

Nanocomposite films comprising self-assembled Ag nanodots and boron-based glass matrix were prepared by one-step pulsed laser deposition on glass substrates. Microstructure of the thin film was evaluated in terms of size distribution, volume fraction and degree of assemblage of Ag nanodots. Characteristics of the nanocomposite films were monitored quantitatively by measuring the changes in the Ag surface plasmon resonance (SPR) absorption, by using transmission UV/Vis spectroscopy. Properties of SPR at around 400nm were examined in terms of the structure and distribution of the dots, as well as the dielectric properties of the matrix. Control of these properties was elucidated by systematically varying the operation parameters of PLD, e.g. gas species (N<sub>2</sub>, Ar, He) and pressure (between 6mPa and 1kPa) in the chamber. Optimization of operational conditions given above, and target preparation for controlled dot assembly, and hence sharp and strong plasmon resonance was explored.

**L3.12 Approaches to Building Networks of Tungsten Sulfide Clusters.** Catherine M Oertel, Craig M Downie and F J DiSalvo; Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Octahedral tungsten sulfide clusters of the form W<sub>6</sub>S<sub>8</sub>L<sub>6</sub> (L = N- or P- based ligand) can be viewed as building blocks for inorganic-organic networks. Such architectures have the potential for interesting electronic and magnetic properties stemming from ligand-mediated cluster-cluster interactions. Two new approaches to network formation use ligand-ligand interactions and varying ligand binding strengths to direct linkage of clusters. Use of ligands such as isonicotinic acid and isonicotinic acid that are capable of hydrogen bonding can increase intermolecular forces among clusters and provide a means of non-covalently linking clusters. Linkage may also be directed by use of both labile and relatively inert ligands. The inert cluster compounds W<sub>6</sub>S<sub>8</sub>[bis(diphenylphosphino)ethane]<sub>6</sub> and

W<sub>6</sub>S<sub>8</sub>[bis(diethylphosphino)ethane]<sub>6</sub> have been synthesized and can serve as starting points for construction of dendrimeric structures. Our progress in these efforts will be presented and discussed.

### L3.13

**Magnetic Properties of Nanocrystalline Fe<sub>50</sub>Co<sub>50</sub> Materials.**  
Basavaraju Shashishekar and Ian Baker; Thayer school of Engineering, Dartmouth College, Hanover, New Hampshire.

Nanocrystalline powders of stoichiometric FeCo were prepared by mechanically alloying elemental Fe and Co powders using a high energy ball mill. The microstructural evolution was studied as a function of milling time and subsequent annealing using X-ray diffractometry, scanning electron microscopy and differential scanning calorimetry. The magnetic behavior of these specimens were characterized using a vibrating sample magnetometer and a magnetic force microscope. A reduction in grain size coupled with increase in coercivity was observed as a function of milling time. Smallest grain size of 6 nm, which exhibited a coercivity of 102 Oe and saturation magnetization of 1.8 T was obtained after 240 hours of milling. Interestingly, a decrease in coercivity was not observed, below a grain size of 50-100 nm, as noted in number of other soft magnetic alloys by Herzer (G. Herzer, J. Magn. Magn. Mat., 112, 258-262, (1992)). The above work is sponsored by NIST grant 60NANB2D0120.

### L3.14

**Bone-shaped Nanomaterials for Nanocomposites Application.**  
Terry T Xu, Frank T Fisher, Cate L Brinson and Rodney S Ruoff; Department of Mechanical Engineering, Northwestern University, Evanston, Illinois.

A novel template synthesis of bone-shaped (dumbbell-shaped, dogbone-shaped) nanomaterials is demonstrated. Porous anodic alumina (PAA) templates with uniform nanochannels were fabricated using a four-step anodization process and used to form bone-shaped carbon nanostructures with stem and end diameters and lengths of 40nm, 70nm, and 5 μm, respectively. These nanomaterials, which we refer to as bone-shaped T-CNTs (templated carbon nanotubes), have potential application in nanocomposites, where improved strength and toughness through mechanical interlocking is anticipated. Support is appreciated from the Office of Naval Research on Mechanics of Nanostructures, the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat), and from the NASA Langley Research Center on Computational Materials: Nanotechnology Modeling and Simulation Program.

### L3.15

**Preparation and Oxidation Activity of Gold Cluster/Aerogel Nanocomposites.** Yutaka Tai<sup>1</sup>, Koji Tajiri<sup>2</sup>, Junichi Murakami<sup>1</sup>, Masakazu Date<sup>3</sup>, Susumu Tsubota<sup>3</sup> and Masatake Haruta<sup>3</sup>; <sup>1</sup>Institute for Structural and Engineering Materials, AIST Chubu, Nagoya, Aichi, Japan; <sup>2</sup>Ceramics Research Institute, AIST Chubu, Nagoya, Aichi, Japan; <sup>3</sup>Research Institute for Green Technology, AIST Tsukuba, Tsukuba, Ibaraki, Japan.

Chemical and physical properties of small metal particles have been the subjects of intensive research because of their scientific and technological importance. It is now well recognized from the studies that the properties differ depending on the particles size. For example, chemical reactivity of some metals is enhanced when they take a form of fine particles. Even gold, the least reactive metal, can catalyze chemical reactions when the diameter of a gold particle is less than 10 nm [1]. When the sizes of metal particles become even smaller and the number of constituent atoms are less than ≈100, their chemical reactivities significantly differ depending on the number of atoms or nuclearity [2]: sometimes reactivity differs by an order of magnitude when the nuclearity differs by one. This is due to the fact that the electronic structures of such small particles are functions of the number of atoms. Such a strong nuclearity dependence of nanoparticle reactivity is well known for free nanoparticles in vacuum but not for supported nanoparticles in ambient conditions. However, it is imagined that if one can fabricate an ensemble of monodispersed nanoparticles consisting of several tens of atoms and support them on a substrate, it can work as a very efficient catalyst. We have recently reported that thiol-passivated Au nanoparticles are efficiently adsorbed on a silica wet-gel in organic solvents like toluene [3]. The Au particles were immobilized on the silica structure to such an extent that they are not flushed out even upon supercritical CO<sub>2</sub> drying. By recent progresses in the surfactant-passivation methods, isolated nanoparticles of various elements like noble metals, transition metals, and metal oxides etc. with a minimum core size as small as 1nm have been synthesized. The silica or titania aerogel would be a good support for these nanoparticles. In this presentation, we will report on the preparation and oxidation activities of aerogels incorporating gold nanoparticles and discuss the size dependent reactivity of the Au cores. Reference [1] M. Haruta, Catal. Today 36, 153 (1997). [2] See for example L. Holmgren et al., J. Chem. Phys.

109, 3232 (1998). [3] Y Tai et al, Adv. Mater. 13, 1611 (2001).

### L3.16

**Multi-wall Carbon Nanotubes Combined with DNA.**  
Weiwei Chen<sup>1,2</sup>, Lawrence Tzang<sup>3</sup>, Jian xin Tang<sup>1,2</sup>, Michael Yang<sup>3</sup> and S. T. Lee<sup>1,2</sup>; <sup>1</sup>Centre of Super Diamond and Advanced Films, Hong Kong, Hong Kong; <sup>2</sup>Department of Physics and Material Science, Faculty of Science and Engineering, Hong Kong, Hong Kong; <sup>3</sup>Department of Biology and Chemistry, Faculty of Science and Engineering, HONG KONG, Hong Kong.

We have developed a multistep method to the combination of covalently linked adducts of multi-wall carbon nanotubes (MWNT) and deoxyribonucleic acid (DNA) oligonucleotides. X-ray photoelectron spectroscopy (XPS) was used to characterize the initial chemical modification to form amine-terminated MWNTs, which were then covalently combined with DNA. The morphology of the resulting DNA-MWNT adducts was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical functionalization occurs at the ends as well as the defect site of the sidewalls of the MWNTs. The combination is an important first step in realizing a DNA-guided self-assembly process for carbon nanotubes.

### L3.17

**Template-Assisted Synthesis of Fe<sub>3</sub>O<sub>4</sub> Ultrafine Particles with Narrow Size Distribution from Polymer-Metal Complex Gels.**  
Cheng Huang<sup>1</sup>, C.Z. Yang<sup>2</sup> and L. Chen<sup>3</sup>; <sup>1</sup>Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Department of Polymer Science and Engineering, Nanjing University, Nanjing, Jiangsu, China; <sup>3</sup>NanoStructure Laboratory and Electrical Engineering Department, Princeton University, Princeton, New Jersey.

Although studies on the Fe<sub>3</sub>O<sub>4</sub> magnetic particle formation have been markedly advanced by the strenuous efforts of numerous researchers, the preparation and formation of ultrafine Fe<sub>3</sub>O<sub>4</sub> particles with narrow size distribution still remain as an open area due to their broad applications. A new method for the titled template-mediated synthesis of Fe<sub>3</sub>O<sub>4</sub> ultrafine magnetite particles (several tens of nanometers) with narrow size distribution from a polymer matrix has been investigated. Hydrazine hydrate was used as a reducing agent to prepare the poly(itaconic acid-co-acrylic acid) gel-supported iron metallic nanoclusters, which served as nuclei, and were later transferred into ultrafine iron oxide powders in NaOH base solution. The morphology, particle size, structure and magnetic properties, as well as the formation of the particles with narrow size distribution, were investigated by means of transmission electron microscopy, selected area electron diffraction, laser light scattering, wide-angle X-ray diffraction, Fourier-transform infrared spectroscopy, and electron spectroscopy for chemical analysis, as well as magnetic measurements, respectively. It was revealed that the Fe<sub>3</sub>O<sub>4</sub> ultrafine particles prepared from the Fe<sup>3+</sup>-poly(itaconic acid-co-acrylic acid) complex gel system kept narrow size distribution, which originated from the oxidation and aggregation growth of the primary particles, and the metallic iron nanoclusters would act as "templates" in the later magnetite particles growth stage. This new attempt of template-mineralization of Fe<sub>3</sub>O<sub>4</sub> ultrafine particles in our preparation was proved to be effective for preparing template-mediated ultrafine magnetite particles with narrow size distribution quickly, which could also be used to prepare other kinds of inorganic particles.

### L3.18

**Synthesis and Characterization of GaN nanowires by Chemical Vapor Deposition using Co catalyst.**  
Young Heon Kim<sup>1</sup>, Jeong Yong Lee<sup>1</sup>, Seung Chul Lyu<sup>2</sup>, Moon Youn Jung<sup>2</sup> and Cheol Jin Lee<sup>2</sup>; <sup>1</sup>Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; <sup>2</sup>Department of Nanotechnology, Hanyang University, Seoul, South Korea.

Gallium nitride (GaN) nanowire is one of the most potential candidates for various nano-scale devices and ideal system for understanding dimensionally confined transparent phenomena and quantum effects. In this study, GaN nanowires have been successfully synthesized by thermal chemical vapor deposition (CVD) which is the promising method for the large-scale synthesis of high-purity one-dimensional nanostructures. The mixture of Ga/GaN powders was used as a source and cobalt (Co) particles were used as a catalyst for the synthesis of GaN nanowires. The GaN nanowires were synthesized at 950–1050 °C in ammonia (NH<sub>3</sub>) ambient. We investigated the morphology of Co nanoparticles distributed on alumina substrate. The morphology and microstructure of the GaN nanowires have been investigated using scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM), and Raman spectroscopy. The optical property has been studied by photoluminescence (PL) analysis. Transition metal as catalyst plays a key role in the growth of one-dimensional nanostructures by thermal

chemical vapor deposition. In this experiment, Co nanoparticles play a crucial role for the growth of the crystalline GaN nanowires. On the case of the absence of catalyst, amorphous materials were deposited on the alumina substrate. The diameters of the GaN nanowires increased with growth temperature. **Acknowledgements** This work was supported by the Ministry of Education and Human Resources Development of Korea through Brain Korea 21 (BK21) program and by the Ministry of Science and Technology of Korea through the National Research Laboratory Program.

### L3.19

**Growth of Carbon Nanotubes Using Uniformly Distributed Cobalt Nanoparticles as Catalyst: Controlled Growth and Structural Characterization.** Yoon Huh<sup>1</sup>, Jeong Yong Lee<sup>1</sup>, Tae Jae Lee<sup>2</sup>, Sang Kyu Choi<sup>2</sup> and Cheol Jin Lee<sup>2</sup>; <sup>1</sup>Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea; <sup>2</sup>Dept. of Nanotechnology, Hanyang University, Seoul, South Korea.

One of key factors for growth of carbon nanotubes (CNTs) using thermal chemical vapor deposition (CVD) is transition metal as catalyst. Catalytic nanoparticles, which serve as catalyst for CNT growth, should be formed from metal layer with a shape of thin film, by pre-treatment processes such as thermal annealing or ammonia (NH<sub>3</sub>) etching. Even though the size of catalytic nanoparticles is varied with the thickness of metal film and the conditions of pre-treatment, the nanoparticles are distributed with a wide range of size, resulting in the growth of CNTs with a non-uniform diameter. For various applications of CNTs, the controlled growth of CNTs with a uniform diameter should be attained. In our work, CNTs were controllably grown using uniformly distributed cobalt (Co) nanoparticles as catalyst. Co nanoparticles with a uniform size of 8 nm were synthesized by thermal decomposition process and colloidal solutions were prepared by dispersing the Co nanoparticles in toluene. We employed a spin-coating method for uniform distribution of the Co nanoparticles on silicon (Si) substrates. The density of Co nanoparticles was controlled by adjusting the molar concentration of the colloidal solutions. CNTs with a uniform diameter were synthesized on the Co nanoparticles by thermal CVD of acetylene (C<sub>2</sub>H<sub>2</sub>) gas. We demonstrated that the density, diameter, vertical alignment, growth rate, and crystallinity of CNTs could be controlled by adjusting the density of Co nanoparticles and growth temperature of CNTs. We investigated the morphology of the Co nanoparticles distributed on Si substrates. The structure and distribution of the CNTs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. **Acknowledgements** This work was supported by the Ministry of Education and Human Resources Development of Korea through Brain Korea 21 (BK21) program, by the Ministry of Science and Technology of Korea through the National Research Laboratory Program and by the National R&D project for Nano Science and Technology of MOST.

### L3.20

**Orientation-Controlled Assembly and Solvothermal Ion-exchange of Layered Double Hydroxide Nanocrystals.** Jong Hyeon Lee<sup>1</sup>, HyeJin Nam<sup>1</sup>, JungSeong Lee<sup>1</sup>, SeogWoo Rhee<sup>2</sup> and Duk Young Jung<sup>1</sup>; <sup>1</sup>chemistry, sungkyunkwan university, suwon, South Korea; <sup>2</sup>Bio-medical Engineering, University of California at Irvine, irvine, California.

A novel method to immobilize nanocrystals of layered double hydroxide (LDH) on the Si substrates and to intercalate dicarboxylate ions into interlayer space of fixed LDH nanocrystals by solvothermal treatment is described. The orientation-controlled LDH crystal assembly on solid substrates is considered as nano-sized 'chemical actuator', chemically controllable by altering anion species utilized. The AFM and XRD studies for the immobilized LDH crystals provide us with snapshots of the intercalation reaction followed by the anisotropic layer expansion. The basal spacing after the anion exchange reaction remarkably changed in comparison with that for MgAl-LDH. The AFM results present the as-adsorbed MgAl-LDH crystals on Si and the same samples after anion-exchange. Most of the LDH crystals kept their lateral positions on Si after the anion-exchange and their measured diameters of LDH crystals remain constant. The heights of anion exchanged MgAl-LDH crystals dramatically expanded, corresponding to the ratio of basal spacing values based on the X-ray diffraction data. The results gave several examples of the direct measurement for the selected inorganic layered crystals during the intercalation reaction, which opens a new method for reaction mechanism and a wide range of applications.

### L3.21

**Synthesis Of Hydroxyapatite - Glycosaminoglycan Nano Composite Sol Under Well Controlled Condition.** Yuko Ishikawa and Mamoru Senna; Faculty of Science and Technology, Keio University, Yokohama, Japan.

Hydroxyapatite (HAp) - glycosaminoglycan (GAG) nano composite sol was prepared at room temperature, at pH 8, by a coprecipitation method from CaCl<sub>2</sub> or (CH<sub>3</sub>COO)<sub>2</sub>Ca and H<sub>3</sub>PO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SHPO<sub>4</sub>. These soluble Ca sources were used in order to increase the number of nucleation sites for HAp on GAGs. Hyaluronic acid, chondroitin sulfate and its desulfated product were used as GAGs. Starting materials were supplied by two kinds of processes to give solution(s) of (a) only PO<sub>4</sub><sup>3-</sup> or, (b) PO<sub>4</sub><sup>3-</sup> and Ca<sup>2+</sup> dropwise into GAG solution containing Ca<sup>2+</sup> to elucidate the details of nucleation mechanism of HAp. Morphology of the aggregates and crystallite size as well as lattice parameters of the HAp were examined by TEM and XRD data with Rietveld refinement. We observed needle like aggregates of crystallites of HAp. The aspect ratio of the aggregates and HAp crystallite was controlled by supplying processes of Ca sources. Lattice parameters of the samples prepared from CaCl<sub>2</sub> shifted towards those of chloroapatite. Those from (CH<sub>3</sub>COO)<sub>2</sub>Ca, however, corresponds to theoretical values of HAp. The results of FT-IR spectra and the changes of rheological property indicate the electrostatic interactions between negatively charged functional groups of GAGs and HAp.

### L3.22

**Preparation And Control Of The Microstructures Of Protein Thin Film Deposited Via Laser Ablation And Colloid Chemical Routes.** Sayuri Nakayama<sup>1</sup>, Ichiro Taketani<sup>1</sup>, Sanshiro Nagare<sup>2</sup> and Mamoru Senna<sup>1</sup>; <sup>1</sup>Faculty of Science and Technology, Keio University, Yokohama, Japan; <sup>2</sup>Nara Machinery Co., Ltd., Tokyo, Japan.

Protein thin film (mainly silk fibroin) was prepared by pulsed laser deposition (PLD) and dip or spin coating. Microstructures of the deposited film, i.e. film thickness, surface roughness, crystallinity, were studied by TEM, AFM, and thin film XRD. Hot pressing conditions for target preparation (pressure and temperature), laser wavelength (266 - 1064 nm), and laser power density were varied systematically for PLD. Secondary structure (beta sheet, alpha helix, or random coil) of the target and film was examined by FT-IR. The PLD film properties were compared with those deposited via colloid chemical routes in terms of their microstructures, interactions with the substrate, and the surface chemical states.

### L3.23

**Fast Deposition of Structured Coatings from Microspheres and Nanoparticles.** Brian Prevo, Ruben G. Carbonell and Orlin D. Velev; Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

In view of the future technological applications of micro- and nanoparticle coatings, it is important to develop assembly procedures that are rapid, inexpensive and easily controlled. We report here a technique for controlled deposition of structured micro- and nanoparticle particle coatings by dragging a meniscus with constant velocity. The advantages afforded by this technique are improved process efficiency and reduced material consumption relative to standard dip coating techniques. Structured coatings larger than few cm<sup>2</sup> are deposited in minutes from aqueous suspension volumes of approximately 10 microliters. Three different systems were studied: latex colloidal crystals, thin metallic nanoparticle coatings, and structured porous nanoparticle coatings obtained via microsphere templating. The governing mechanism of particle deposition is convective assembly at high volume fractions. The most accessible and easily controlled process parameters are the deposition speed and particle volume fraction. Varying these parameters provided the means to control and tune coating, thickness, structure and properties. A volumetric flux balance incorporating the evaporating solvent and assembling particle fluxes was used to relate the deposition process parameters to coating structure and properties. Operational diagrams were constructed that demonstrate good correspondence of data over a wide range of parameters to the coating structure predicted at these parameters. These operational diagrams will be instrumental in turning the colloidal deposition from bench-top science into usable and scaleable technology.

### L3.24

**Self-Assembly of Polymer-Coated Nanoparticles in a Block Copolymer.** Grigori Sigalov and Anna C. Balazs; Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Self-assembly in a nanocomposite material that consists of an AB block copolymer filled with coated spherical nanoparticles is studied with the help of a combined Self-Consistent Field Theory (SCFT) / Density Functional Theory (DFT). The filler particles are coated with a layer of end-grafted chains of polymer C. The equilibrium material

structure is the result of a complex interplay of the inherent length scales (A, B, and C radii of gyration, particle size), entropic factors, and enthalpic contributions (AB, AC, and BC interactions). The effective pair interaction of coated particles immersed in block copolymer is calculated using the SCFT technique. A Pickard-type iterative procedure is improved by using variable iteration steps and some elements of the conjugated gradient minimization method. This yields a considerable decrease in the number of iterations to convergence. After the filler particle pair interaction potential is calculated, the behavior of an ensemble of such particles in a block copolymer melt is analyzed using DFT approach. It is shown that, by varying the chemical nature and architecture of the copolymer blocks and chains grafted on the particles, it is possible to control the morphology and properties of the nanoparticle/diblock copolymer composite material. The above approach may be instrumental in design and synthesis of 'smart' nanostructured materials for various applications.

### L3.25

**Magnetic Nanoparticle as A Solid Support in Various Reactions.** Dongwoo Yoo, Tae-Jong Yoon, In-Jung Han and Jin-Kyu Lee; School of Chemistry and Molecular Engineering, Seoul National University, Seoul, South Korea.

The surface of Co ferrite magnetic nanoparticles was modified with deliberately prepared cationic organic molecules, quaternary ammonium salts from nitrilotriacetic acid (NTA), to give long term stability in many organic solvents without an excess amount of capping molecules. By introducing specific organic functional groups into NTA, controlled reactions can happen on the magnetic nanoparticle surface. Unlike the micron size organic and inorganic polymer support materials, compounds immobilized on nanometer size support show the high reactivity comparable to the homogeneous reaction and they can be easily separated from the reaction mixture by applying external magnetic field. Various reaction results on the magnetic nanoparticle surface such as catalytic reaction, polymerization reaction, and other coupling reactions will be discussed to show broad application area of magnetic nanoparticle support.

### L3.26

**Hydrothermal synthesis of ZnO on Silicon, alumina and sapphire substrates (1Jan2003-1Dec2003).** Yee Wee Koh, Jing Hui Zeng, Edward R.T. Tiekink and Kian Ping Loh; Chemistry, National University of Singapore, Singapore, Singapore.

Hydrothermal synthesis of ZnO on silicon, A-plane sapphire, C-plane sapphire as well as alumina template was investigated with a view in understanding the mechanism for direct nucleation on these substrates, as well as the possible role of the substrate in controlling high density growth of aligned ZnO nanorods. It is difficult to produce pure ZnO crystals on untreated silicon in aqueous-based solvents due to the growth of hemimorphite ( $Zn_4Si_2O_7(OH)_2(H_2O)$ ) crystal. A thin layer of petal-like nanocrystallites with walls aligned perpendicularly to the substrate was found to act as a buffer layer for the growth of a secondary layer of hemimorphite crystals. On alumina or sapphire substrate however, pure ZnO nanorods which exhibit sharp exciton-derived emission peaks in the photoluminescence spectra could be grown.

### L3.27

**Ce 1-x Zr x O2 Solid solutions made by liquid-feed flame spray pyrolysis.** Min Kim, Julien Marchal and Laine M Richard; Materials science and engineering, Univ. of Michigan, Ann Arbor, Michigan.

We describe here the synthesis of nanopowders in the Ce 1-x Zr x O2 system by liquid-feed flame spray pyrolysis (LF-FSP) for applications in three-way auto exhaust catalysts (TWCs) and diesel emission control. Through the choice of the correct precursor chemistry, we are able to produce Ce 1-x Zr x O2 materials of any composition in the phase space. The resulting powders have typical particle sizes of < 100nm, and surface areas of up to 50m<sup>2</sup>/g without nanoporosity. The materials were characterized by SEM, DTA-TGA, FT-IR and XRD and their catalytic activities evaluated.

### L3.28

**Beyond Imaging: Detailed Simulation of NSOM images.** Sungwon Kim<sup>1</sup> and Venkatraman Gopalan<sup>2</sup>; <sup>1</sup>Materials, Penn State Univ, university park, Pennsylvania; <sup>2</sup>Material science and engineering, Penn State University, University park, Pennsylvania.

Near Field Optical Microscopy (NSOM) is widely used now for imaging on 40nm length scales using light. To quantitatively understand NSOM images, numerous numerical methods are adapted. We present experimental NSOM images that show unexpected optical contrast at antiparallel ferroelectric domain walls in a lithium niobate (LiNbO3) single crystal. To simulate these images, Finite Difference

Time Domain (FDTD) method is applied near the NSOM tip area in the near-field light propagation region, and the Beam Propagation Method (BPM) method is to simulate wave propagation along the crystal thickness direction. We introduce a new FDTD numerical simulation method to calculate the Optical Transfer Function (OTF) at the NSOM tip. By decomposing the incident field underneath the sample, we can regenerate the incident wave as an individual plane wave. This plane wave is easily activated by using standard FDTD total/scattering field algorithm. We have developed a dual source Total/Scattering field algorithm to conserve the propagating and evanescent field till the end of the NSOM tip. By simulating each individual plane wave, we can successfully calculate the NSOM OTF. We mathematically prove that this FDTD simulation and OTF are equivalent under the linearity condition. Therefore, if we know the field distribution under the sample surface, we can extract final image by using OTF. The agreement between theory and experiments is excellent. The local refractive index profile across the wall is extracted also.

### L3.29

**Genesis and Growth of Nanoparticles during Sol-Gel Synthesis.** Nan Yao<sup>1</sup>, King Lun Yeung<sup>1</sup> and Guo xing Xiong<sup>2</sup>; <sup>1</sup>Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China; <sup>2</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

Sol-gel synthesis is an established method for preparation of advanced materials including ceramics, catalysts and functional nanomaterials. The genesis and growth of the nanoparticles during sol-gel synthesis are influential factors that determines the final properties of the material. This phenomenon had been investigated at different length and time scales using various spectroscopic techniques[1]. However, vital information on the local structural environment (i.e., 1-100 nm) are often deduced from indirect measurements rather than from direct observation. This paper demonstrates the use of atomic force microscopy (AFM) for in situ observation of the nanoscale morphological transformations that occur during the sol-gel process. Recently, it had been reported that mesoporous metal oxide catalysts with narrow pore size distribution at mesopore region could be prepared using a new templateless method based on a modification of traditional sol-gel technique. The structural evolution during the sol-gel synthesis of mesoporous silica, alumina and silica-alumina catalysts were observed using AFM. The formation of fractal structure is strongly correlated to the silicon-content of the sample. Both silica and silica-alumina samples displayed fractal growth forming intricate branched structures. The branches consisted of nanometer-sized clusters that exhibit complex structural transformations that include coarsening, ostwald ripening and sintering at room temperature. Analysis indicated that these transient processes play an important role in the final structure of the mesoporous catalyst. Pure alumina sample does not form fractal network but instead deposits as individual or aggregated nanoparticles. Ageing at room temperature transforms the original spherical alumina into polygon-shaped nanoparticles. The final metal oxide catalysts were analyzed by electron microscopy, X-ray diffraction, N2 physisorption and NMR to determine its structure and chemistry.

### L3.30

**Incorporation of Functional Metal Oxide Materials in Chemical Microsystems.** Nan Yao and King Lun Yeung; Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Recent advances in the design and fabrication of micromixers, microseparators and microreactors bring closer the realization of desktop miniature factories and micro-pharmacies. They represent a cheap alternative way for the production of specialty chemicals and pharmaceuticals by a continuous process, allowing simpler process optimization, rapid design implementation, better safety and easier scale-up through replication. This enables rapid product deployment to the marketplace and thus ensuring a significant competitive edge. One of the important issues in chemical microsystem is the proper incorporation of functional materials (e.g., catalysts, adsorbents and membranes) within the microchannel architecture. Metal and metal oxide thin films can be deposited using traditional microfabrication methods of thermal deposition, chemical vapor deposition and sputter coating. However, the incorporation of structurally complex metal oxides such as ordered mesoporous materials and molecular sieves, requires a different strategy. This study discusses several methods for the precise incorporation of mesoporous TiO2 catalyst in silicon microchannel. Using a modified sol-gel method, TiO2 aerogel was deposited into the microchannel from a TiO2 alcogel. Precise control over the sol-gel process within the confined environment of the microchannel is a must. Synthesis conditions were adjusted to obtain better aerogel adhesion to the microchannel wall and control the shrinkage of the wet gel during drying. After temperature treatment,

a complex aerogel network filled the microchannel. The structure and density of the aerogel network was dictated by the composition of the original alcogel. The strength of the aerogel was tested under flow conditions and the activity of the TiO<sub>2</sub> was evaluated for photocatalytic destruction of methyl orange dye in aqueous solution. Monolithic TiO<sub>2</sub> with ordered and disordered macropore channels were also prepared using a template method. Polymer microbead were used as template material to create the macroporous materials. Comparison indicated that monolithic TiO<sub>2</sub> provides lower pressure drop, while maximising the contact area between catalyst and reaction mixture.

### L3.31

**Construction of Nano-Stepped Surfaces Using High-Temperature Viscous Flow of Ultra-Thin Film Silicate Glass.** [Shusaku Akiba](#), Shuhei Sato, Akifumi Matsuda and Mamoru Yoshimoto; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Very few attempts have been made to investigate nano-scale behavior of glass at high temperatures, but glass materials controlled at the nano-scale have possibility to develop new functionalities of nano-electronics. Softening behavior and viscous flow resulting from the supercooling state, which is characteristics to glass materials, are expected to be utilized for construction of novel nano-structures as well as for soldering the nano-elements. Here we report the fabrication of the nano-structured oxide glass surfaces using softening and viscous flow of ultra-thin film glass at high temperatures. The ultra-thin films (about 5nm thick) of soda lime silicate glass were deposited by pulsed laser deposition (PLD) method using the glass target onto the ultrasmooth sapphire substrates, which have atomic steps of 0.2 nm in height and ultrasmooth terraces of 50~100 nm in width. These sapphire substrates were obtained by annealing in air at 1000°C (Appl. Phys. Lett. Vol. 67 (1995) 2615). The specimens were annealed around the glass transition temperatures of 550°C. It was observed with AFM that the surface morphologies were drastically changed on an atomic scale by viscous flow of ultra-thin film glass. It was found that the surface flattening of ultra-thin film glass became remarkable just over the glass transition temperature. Furthermore, the surface morphology of the annealed glass film reflected the nano-stepped structure of the sapphire substrate. The nano-stepped surface was verified to be amorphous state (glass) from the halo pattern of reflection high energy electron diffraction (RHEED). Control of viscous flow in the nano-scale was also performed using nano-scale patterning by AFM tip scanning. Further investigations on viscous flow of ultra-thin film oxide glass in combination with the micro-scale heating by optical fibers may provide us with a novel nano-tools such as nano-adhesive for micromachines or a nano-scale insulator for biological devices.

### L3.32

**Sintered Tantalum and Niobium Sub-micron Powders of Solid Electrolyte Capacitors.** [Yuri Pozdeev-Freeman](#)<sup>1</sup>, Alexander Gladkikh<sup>2</sup> and Yuri Rosenberg<sup>2</sup>; <sup>1</sup>Vishay-Sprague, Sanford, Maine; <sup>2</sup>Wolfson Applied Materials Research Centre, Tel Aviv University, Tel Aviv, Israel.

Sintered tantalum and niobium sub-micron powders are widely used in modern electronics as porous anodes of Ta and Nb solid electrolyte capacitors. Due to high surface area of the anode, these capacitors demonstrate excellent specific charge per unit of their volume. At the same time, some of these capacitors degrade their DC and AC characteristics during life test or in the field. In the Ta capacitors degradation usually shows as an abrupt catastrophic increase of the DC leakage of the dielectric, anodic oxide film of Ta. In the Nb capacitors, the DC leakage of the dielectric, anodic oxide film of Nb, increases gradually. Simultaneously, activation energy of conductivity gets lower and bias dependence of the capacitance becomes larger. The results of x-ray study and electrical measurements are brought together in order to understand a difference in the capacitors performance and failures. It is shown that a different ability of Ta and Nb metal powder to formation and decomposition of oxygen solid solution during high temperature processing may be critical for stability of the interface between metal anode and oxide dielectric. Both Ta and Nb original powders are very clean in terms of oxygen content in a bulk according to their lattice parameter, and contain oxygen mainly in the form of a thin native oxide of 2-5 nm on their surface. Sintering of the powder into pellet at temperature about 1200 °C dissolves oxygen from the amorphous surface oxide into the powder metal, and this effect is strong due to a high surface to volume ratio. After sintering, in the case of Ta, oxygen exists mainly in the form of solid solution in Ta lattice, according to a quite large Ta lattice parameter. In the case of Nb, oxygen is mainly in the form of NbO phase, which precipitates due to cool down from sintering temperature, leaving Nb lattice rather clean, with lattice parameter close to its original value. The effects of dissolving of oxygen and phase transformations in the sintered Ta and Nb powders on

structure, current-voltage, current-temperature, and capacitance-voltage characteristics of the dielectric oxide film formed of their surface are under the discussion.

### L3.33

**Pb on Ge(111) 2D growth mode.** [Fulvio Ratto](#)<sup>1,2</sup>, Alberto Morgante<sup>2,3</sup>, Luca Floreano<sup>2</sup>, Dean Cvetko<sup>2,4</sup> and Gregor Bavdek<sup>2,4</sup>; <sup>1</sup>EMT, INRS, Varennes, Quebec, Canada; <sup>2</sup>TASC, INFN, Trieste, Italy; <sup>3</sup>Dipartimento di Fisica, Università di Trieste, Trieste, Italy; <sup>4</sup>Jozef Stefan Institute, University of Ljubljana, Ljubljana, Slovenia.

The study of the 2D Frank-van der Merwe growth mode of thin metallic films on insulating substrates has been receiving a thoroughly increasing interest, both for technological applications and for purely scientific motivations. In particular, the Pb/Ge interfaces have always been considered as a model system for the singling out and characterization of the elements determining the Schottky barrier height. Nevertheless, due to the anomalous properties of thin layers [1], the merely basic scientific studies have recently been attracting most of the attention. According to different theoretical simulations [2, 3], variations in the electronic and morphological properties of the growing metallic film are to be expected, as a function of the film thickness itself. These modulations are usually called quantum size effects (QSEs), and have effectively been observed in other similar systems [4]. We propose a characterization of the geometrical structure of growing metastable Pb 2D films on Ge(111) at very low temperatures, performed by helium atom scattering (HAS), and based on the theoretical analysis developed by Lent and Cohen [5]. We show that the HAS technique can lead to a complete morphological description of the evolving surface structure and of the statistics of the steps distribution, during the very first stages of the growth process. As an example, the physical model we adopted allows to obtain a convincing determination of the most interesting geometrical features of the topmost exposed layers in the deposited Pb on Ge(111) films. The interpretation of the experimental data and of the subsequent analysis clearly points to the appearance of structural QSEs, likely driven by the occurrence of electronic QSEs. [1] F. Ratto, MSc Thesis in Physics (2002); [2] F. K. Schulte, Surf. Sci. 55, 427 (1976); [3] P. J. Feibelman, D. R. Hamann, Phys. Rev. B 29, 6463 (1984); [4] A. Crottini, D. Cvetko, L. Floreano, R. Gotter, A. Morgante, F. Tommasini, Phys. Rev. Lett. 79, 1527 (1997); [5] C. S. Lent, P. I. Cohen, Surf. Sci. 139, 121 (1984).

### L3.34

**Structuring Of Silicon Wafer Surfaces On The Sub-100 nm Scale By Hydrogen Plasma Treatments.** [Reinhart Job](#) and Alexander G. Ulyashin; Department of Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany.

Plasma hydrogenation applied on standard Czochralski silicon (Cz Si) wafers causes the structuring of the treated surface regions on the sub-100 nm scale, i.e. a thin silicon nano-phase layer is created. In addition, in the subsurface regions up to about 1 μm depth, quasi two dimensional extended defects, so called platelets, which are oriented in the (111)- and (100)-crystallographic directions, are also formed by such treatments. The formation of those nano-structural defects at the surface and subsurface regions of the hydrogenated wafers was investigated after hydrogen plasma treatments under various process conditions and substrate temperatures up to about 250 C. Plasma hydrogenation was applied either at a 13.56 MHz or 110 MHz frequency. Also the impact of post-hydrogenation annealing on the morphology and evolution of the structural defects was studied up to 1200 C. In dependence on the plasma power, the duration of the plasma exposure and the substrate temperature the properties of the treated wafer surfaces and sub-surface regions were analyzed by atomic force microscopy (AFM), high resolution scanning electron microscopy (SEM), and Raman spectroscopy. In addition the properties of the optical reflection of the treated samples were also studied. The effects of the doping concentrations in the wafers and their crystallographic orientation will be discussed. The impact of the nano-structural defects and the silicon nano-phase formation at the wafer surface and in the subsurface regions will be finally discussed with regard to several technological processes applied for the formation of various semiconductor device structures.

### L3.35

**Study of the nucleation and crystallization behavior of optically active Cr doped nanocrystallites in glasses.** [Leslie L. Isaacs](#), Baoping Wang, A B Bykov, V Petricevic and R R Alfano; Chemical Engineering and Physics, CCNY, New York, New York.

Cr(IV) doped olivines (forsterite, cunyite etc) emit in the 1100 to 1600 nm spectral range. Controlled ceramization procedure of an appropriate glass may produce transparent glass-ceramics with embedded nano-crystallites of Cr(IV) doped olivines. Glass-forming ability and devitrification behavior of Ca-Ge-B-O composites is

studied using Differential thermal analysis and X-ray diffraction. Surface crystallization of Cr(IV):Ca<sub>2</sub>GeO<sub>4</sub> was observed for a number of Ca-Ge-B-O glass compositions. We are studying the kinetics of the nucleation and growth process of Cr(IV) doped laser crystallites, in GeO<sub>2</sub> based glass media. Optical characterization studies include spectroscopic and gain measurements to evaluate the feasibility of the materials for optical amplification applications. The major feature of laser active glass ceramic media is that different sites are available for the luminescent ion sites in the glass phase, sites inside the nano-crystals and sites at the crystal-glass interface. Detailed study of the optical and laser properties of the Cr(IV) centers in glass ceramic host will be the basis for identify general criteria to produce highly efficient materials suitable for applications in optical communications.

### L3.36

**Long-range order and Verwey transition on the Fe<sub>3</sub>O<sub>4</sub>(001) surface.** Igor V Shvets, Guido Mariotto, Shane Murphy, Nikolay Berdunov, Sergio F Ceballos and Ken Jordan; Physics, Trinity College, Dublin, Ireland.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been the subject of intensive studies during the last decades. The efforts to understand its magnetic and electrical properties have intensified in the past few years due to its half-metallic nature, which makes magnetite an interesting material for applications in spin electronics. However, the nature of the electronic transport and the metal-insulator (Verwey) transition at  $T_V=123$  K has not yet been clarified. We have studied the (001) surface of synthetic single crystals of Fe<sub>3</sub>O<sub>4</sub>. The crystals have been characterized *ex-situ* by x-ray diffraction, resistivity versus temperature measurements, Raman spectroscopy and magnetisation measurements. The *in-situ* surface preparation procedure consisted of a combination of Ar<sup>+</sup> ion sputtering, annealing in ultra high vacuum (UHV) and in an oxygen partial pressure. The crystals were characterized by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), which showed a sharp ( $\sqrt{2} \times \sqrt{2}$ )R45° mesh. Scanning Tunneling Microscopy (STM) measurements were performed at room temperature using a tip of antiferromagnetic MnNi alloy. Atomically resolved STM images provide evidence of a surface terminated at the octahedral plane (*B* plane), with rows of Fe cations aligned along the [110] and [1-10] crystallographic axes. Two different kinds of Fe cations with a separation of 6 Å are imaged; the periodicity between Fe cations of the same kind is about 12 Å. A highly regular structure remained uninterrupted throughout the terrace length, suggesting that long-range order had set on the surface at a temperature that is at least 170 K above the bulk Verwey temperature. The data provides evidence of a Fe<sup>2+</sup>-Fe<sup>2+</sup> and Fe<sup>3+</sup>-Fe<sup>3+</sup> coupling at the *B* sites. We propose two mechanisms that may be responsible for the coupling and the set-in of long range order at the Fe<sub>3</sub>O<sub>4</sub>(001) surface. The first model is based on the interaction between the conduction electrons of the Fe 3*d* levels and the lattice, leading to the formation of bipolaronic ordering at the surface. The formation of bipolarons induces a deformation of the crystal lattice that lowers the symmetry of the crystal, splitting the energy levels and lowering the energy of the system. The second model explains the observed results in terms of orbital ordering (OO) at the surface. The strong electronic correlation at the *B* sites creates an OO state with a one-dimensional electronic structure. Such a system has a Peierls instability with two times the interatomic distance, in agreement with the interpretation of our STM images of a bond dimerization state. Furthermore, we provide an explanation to account for the massive increase of  $T_V$  induced by electron localization at the Fe<sub>3</sub>O<sub>4</sub>(001) surface.

### L3.37

Abstract Withdrawn

### L3.38

**Microstructural Characterisation of Aluminosilicate Inorganic Polymers by Scanning Electron Microscopy.**

Matthew Ryan Rowles and Brian O'Connor; Applied Physics, Curtin University of Technology, Perth, Western Australia, Australia.

The Materials Research Group at Curtin University is investigating structure-property relationships for aluminosilicate inorganic polymers, also known as geopolymers. These polymers consist of an amorphous three-dimensional structure resulting from the polymerisation of aluminosilicate monomers in an alkaline solution. One of the prospective uses of these materials is as Portland cement replacement. The study to be reported forms part of a broader structure-property investigation of inorganic polymers produced by sodium silicate activation of mixtures of metakaolinite and silica fume. This work follows an optimisation study of compressive strength with respect to the Al, Si and Na concentrations [1]. SEM imaging and associated EDS measurements have been used to characterise the processing chemistry at a microstructural level by examining the microchemistry of features in the images. The polymers were formed by mixing metakaolinite with a sodium silicate solution

and curing at 75 °C for 24 hours. The sodium silicate solution was made by mixing the different amounts of silica fume and sodium hydroxide to produce a polymer with the required chemical composition. SEM analysis shows that there are two distinct phases present, which are the fully reacted polymer and residual metakaolinite. The relative amounts of these two phases vary systematically with chemical composition. EDS measurements confirm the conclusion of a dual phase system, with the elemental composition of the phases being significantly different in terms of the relative amounts of Si and Na present. EDS also shows partitioning of the impurity phases that are present in the original starting material. Impurity elements such as Ca and Mg are found in the polymer phase, whilst impurities such as Fe and Ti are found in the residual metakaolinite. Reference [1] Rowles, M. and O'Connor, B. 2003, 'Chemical optimisation of the compressive strength of aluminosilicates geopolymers synthesised by sodium silicate activation of metakaolinite', Journal of Materials Chemistry, vol. 13, pp. 1161-1165.

### L3.39

**Pulsed Laser Deposition Parameters Optimization for Growth of Alumina Thin Films on Silicon(100).** xinyu wang<sup>1,2</sup>, Zhigang Xu<sup>1,2</sup>, Dhananjay Kumar<sup>1,2</sup>, Sergey Yarmolenko<sup>1,2</sup> and Jagannathan Sankar<sup>1,2</sup>; <sup>1</sup>Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina; <sup>2</sup>NSF Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, North Carolina.

We have grown alumina thin films on silicon(100) substrate using KrF excimer pulsed laser. The thickness, nanohardness and Young's modulus of the films were analysed using a profilometer and a nanoindenter. The relation between mechanical properties and nanostructures was studied using a SEM and an AFM. The optimum values of pulsed laser deposition (PLD) parameters, laser fluence and substrate temperature were evaluated.

### L3.40

**A Thermodynamic Approach in Tuning Phase Stability in Nanocomposite Multilayers.** Gregory B Thompson<sup>1,2</sup>, Arda

Genc<sup>2</sup>, Rajarshi Banerjee<sup>2</sup> and Hamish L Fraser<sup>2</sup>; <sup>1</sup>Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama; <sup>2</sup>Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

Changes in the crystallographic phase stability of individual layers in a multilayered thin film are expected to have a significant influence upon the functional properties of the nanocomposite structure. The ability to predict and tune these phase stability states is of relevant importance in order to maximize the functional properties of the multilayer. A classical thermodynamic methodology, based upon competitive volumetric and interfacial free energies, has been used in the prediction and subsequent confirmation of the hcp to bcc phase stability in a Ti/Nb multilayer. An outcome of this approach is a new type of phase stability diagram that can be used to predict the hcp Ti and bcc Ti phase stability as a function of length scale and composition. The Ti layers were subsequently alloyed with the bcc-stabilizing element, V. The selective alloying of Ti resulted in a corresponding free energy change that helped to stabilize the bcc Ti phase to a larger layer thickness as compared to the unalloyed Ti/Nb multilayers. The percentage of alloying element added to the Ti layer in controlling the critical transition thickness between the phase states had good agreement with the predictions proposed by the free energies. The successful use of tuning the phase stability suggests that is now possible to engineer a specific phase to a desired nanometer thickness for the enhancement of the nanocomposite properties.

### L3.41

**Sol-Gel Synthesis And Magnetic Studies of Titanium Dioxide Doped With 10% M (M= Mn, Fe, Co, Ni).**

Ayyakkannu Manivannan, Garry P Glaspell and Mohindar S Seehra; Department of Physics, West Virginia University, Morgantown, West Virginia.

Nanoparticles of titanium dioxide doped individually with 10% of cobalt, manganese, iron, and nickel were successfully prepared by the sol-gel route. Synthesis was achieved using appropriate amounts of respective metal nitrate into ethanol and adding titanium isopropoxide. The resulting solution was placed in oven to remove the ethanol. The dry powder was then calcinated below 500 °C to produce the doped titanium dioxide. The dominate phase of titanium dioxide was anatase which was confirmed by X-ray diffraction. The particle sizes for cobalt, manganese, iron and nickel doped titanium dioxide were determined via peak analysis to be approximately 10 nm from the widths of the XRD patterns. Magnetic properties of these doped oxides are being analyzed following the procedures reported in our recent paper [1]. [1]. A. Manivannan, M.S. Seehra, S.B. Majumder, and R.S. Katiyar, Appl. Phys. Lett., **83** (July 7, 2003 issue).

### L3.42

**Synthesis and characterization of polymer composite materials with uniformly dispersed magnetic nanoparticles.** H Srikanth<sup>1</sup>, J L Wilson<sup>1</sup>, P Poddar<sup>1</sup>, K Mohomed<sup>2</sup> and J P Harmon<sup>2</sup>; <sup>1</sup>Department of Physics, University of South Florida, Tampa, Florida; <sup>2</sup>Department of Chemistry, University of South Florida, Tampa, Florida.

Magnetic nanoparticles embedded in polymer matrices have excellent potential for electromagnetic device applications like EMI noise reduction etc. We have synthesized polymer composites [polystyrene(PS), and poly (methyl methacrylate) (PMMA)] doped with varying concentrations of iron nanoparticles (diameter ranging from 20 to 50 nm). These nanocomposites were processed as spin-coated thin films as well as in bulk form using various synthetic techniques including in situ ultrasonic polymerization and melt blending. The polymer processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix. Iron nanoparticles were produced using a microwave plasma technique and the concentration and dispersion of nanoparticles were varied in a controlled way. These composites were characterized by high resolution scanning electron microscopy to monitor the particle distribution in the polymer matrix. Surface characterization with SEM and AFM indicates that, to a large extent, the Fe nanoparticles are embedded in the bulk; the surface mainly showed ridges associated with the polymer surface. Static magnetic properties such as susceptibility and M-H loops were studied using a Physical Property Measurement System (PPMS). The variation of the ferromagnetic response was consistent with the varying volume concentration of the nanoparticle, the polymer itself contributing a diamagnetic response. At room temperature, hysteresis loops exhibited a somewhat large coercivity (270 Oe) presumably associated with a surface oxide layer on the particles. Overall, the excellent dispersion coupled with reasonable control over magnetic properties achieved in our experiments is promising for electromagnetic applications of these materials. H.S. acknowledges support from NSF grant # ECS-0140047.

### L3.43

**Mullite rectangular single-crystal microtubes.** Xiang yang Kong<sup>1,2</sup>, Zhong Lin Wang<sup>1</sup> and Jiansheng Wu<sup>2</sup>; <sup>1</sup>School of materials science and Engineering, Georgia Institute of Technology, Atlanta, GA, Georgia; <sup>2</sup>School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, China.

Tubular structures in micro- and nano-scale have attracted extensive interest over the past decade due to their great potential for studying space-confined transport phenomena and applications in nanotechnology. Most of the tubes have a cylindrical symmetry, and some of them are amorphous, polycrystalline or textured nanocrystal films. Due to the strong drive towards applications in nanoelectronics and nano-optoelectronics as well as catalysis, research has been mainly devoted to synthesizing nanotubes of smaller sizes in a few to a few tens nanometers. The nanotubes usually have a uniform exterior wall structure, but the interior is small and sometime partially or completely blocked by growth product; hence, the inner walls and the cavity channels are less useful than the exterior walls. For applications in biomedical drug delivery, biochips, and microfluidics in the micro-electromechanical systems (MEMS), it is desirable to have microtubes of sizes in a few micrometers with high mechanical strength and chemically robustness, which will be effective for penetrating bio-tissues and transporting fluid. In this paper, using a simple solid-vapor process, a novel single-crystalline microtubular structure of allumium-rich mullite has been synthesized for the first time. The microtube has a perfect rectangular-framed cross-section as defined by the (110) and (1-10) facets. The microtubes has the [001] growth axis, dislocation-free volume, a large through hollow interior channel of 0.5-3 micrometers in width, and a thin wall of 50~100 nanometers. The ceramic microtubes are mechanically hard with potential applications as hollow needles for drug delivery, microchannels for micro-electromechanical systems and biochips, and as optical resonance cavities and waveguide

### L3.44

**The SrTiO<sub>3</sub> (001) Surface: TiO<sub>2</sub>-rich Reconstructions with (2x1), c(4x2) and c(6x2) Unit Cells.** Natasha Erdman<sup>3</sup>, Oliver Warschkow<sup>1</sup>, Courtney H Lanier<sup>3</sup>, Kenneth R Poepelmeier<sup>2</sup>, Mark Asta<sup>3</sup>, Donald E Ellis<sup>1</sup> and Laurence D Marks<sup>3</sup>; <sup>1</sup>Physics and Astronomy, Northwestern University, Evanston, Illinois; <sup>2</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>3</sup>Materials Science and Engineering, Northwestern University, Evanston, Illinois.

We have recently reported solutions for the (2x1) and c(4x2) surface reconstructions of SrTiO<sub>3</sub> (001) obtained through high-resolution transmission electron microscopy, direct methods analysis and density functional theory. Common to both reconstructions are the formation of TiO<sub>2</sub> overlayers in which truncated TiO<sub>5</sub> polyhedra are arranged

into edge-shared structures in contrast to the corner-shared TiO<sub>6</sub> octahedra in bulk. We present preliminary results of a third reconstruction with a c(6x2) unit cell.

### L3.45

**Microstructure of Precipitated Au Nanoclusters in TiO<sub>2</sub>.** chongmin wang<sup>1,2,3</sup>, V Shutthanandan<sup>1,2,3</sup>, Y. Zhang<sup>1,2,3</sup>, S. Thevuthasan<sup>1,2,3</sup> and D. R. Baer<sup>1,2,3</sup>; <sup>1</sup>Pacific Northwest National Laboratory, Richland, Washington; <sup>2</sup>pacific Northwest National Laboratory, Richland, Washington; <sup>3</sup>pacific Northwest National Laboratory, Richland, Washington.

Gold nanoclusters dispersed in single crystal TiO<sub>2</sub> (110) have been formed by 2MeV Au<sup>2+</sup> implantation at 300 K and 973 K followed by annealing at 1273 K for 10 hours. The morphological features, size and crystallographic orientation of the Au nanoclusters with respect to the TiO<sub>2</sub> matrix have been investigated using conventional transmission electron microscopy and electron diffractions. In particular, the interface structure between the Au nanoclusters and TiO<sub>2</sub> was investigated. Atomic structural model of interface between Au and TiO<sub>2</sub> was established based on high-resolution transmission electron microscopy (HRTEM) imaging and HRTEM image simulations. Two types of orientation relationship can be identified, Au<110>//TiO<sub>2</sub>[001] and Au{111}//TiO<sub>2</sub>(200), and Au<110>//TiO<sub>2</sub>[001] and Au{111}//TiO<sub>2</sub>(110). Au clusters are faceted along Au{112} and Au{111} or Au{220} and Au{002} planes. The precipitated Au clusters show extensive (111) twins. These orientation relationships are the same for Au clusters grown on stoichiometric TiO<sub>2</sub>(110) surface, indicating that lowering interfacial energy to be a governing factor for setting the orientation relationship.

### L3.46

**The stability and reproducibility of carbon nanotube modified electrodes for glucose biosensor.** Sigeng Wang<sup>1</sup>, Qing Zhang<sup>1</sup>, Ruiling Wang<sup>2</sup>, S.F Yoon<sup>1</sup> and J. Ahn<sup>1</sup>; <sup>1</sup>School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore; <sup>2</sup>Department of Community Occupational & Family Medicine, National University of Singapore, Singapore, Singapore.

Two of the major problems that concern the research of biosensors today are stability and reproducibility. These two problems are of great important for the success of these devices as analytical instruments. In this paper, a novel amperometric biosensor with electrode modified using carbon nanotubes for detecting glucose, has been developed. The initial results showed that the carbon nanotubes provide suitable electrode matrices for glucose oxidase immobilization, they also increase the glucose oxidase stabilization. The biosensor stability and reproducibility therefore were greatly improved, and superior to those with electrodes modified using other carbon materials.

### L3.47

**LPE Growth of Atomically Flat Ge Layer on a mesa pattern.** Takahiro Maruyama<sup>1,2</sup>, Keiji Matsuda<sup>1</sup>, Norikazu Saikawa<sup>1</sup> and Shigeo Naritsuka<sup>1,2</sup>; <sup>1</sup>Science and Engineering, Meijo University, Nagoya, Japan; <sup>2</sup>21st CENTURY COE program NANO FACTORY, Meijo University, Nagoya, Japan.

We successfully obtained atomically flat Ge surfaces on mesa structure with an area of 10×10μm<sup>2</sup> by liquid phase epitaxy (LPE). These atomically flat areas will be useful for the hetero-epitaxy related to Ge, because monolayer step on Ge surface induces anti-phase domains of GaAs epitaxial layer grown on it. The control of the step formation will play central role in the nano-hetero epitaxy. By standard photolithographic technique, mesa patterns were prepared on Ge(001) and Ge(111) substrate. They have square-shaped mesa areas with an edge length of 2-15μm separated by grooves with 8μm wide and 1μm deep. After wet-etching for removal of surface oxide, the LPE growth was carried out by the super-cooling technique. Aiming at the growth of step free surface on mesas, we tried to suppress the formation of 2D nuclei on grown surface by decreasing the supersaturation. When the supersaturation was enough small at the growth temperature below 340 °C, flat facets were formed on some mesas after the LPE growth for 30 min. We considered that these facets are formed on mesas with dislocation-free surface, considering the dislocation density of Ge substrate. AFM observation indicated that some triangle hollows with monolayer step in depth were present on these facets, but that other regions were atomically flat within the surface of the facets. It was also found that the amount and the size of the hollows were related to the supersaturation during the LPE growth. Our results show the possibility that atomically flat Ge area beyond 100μm<sup>2</sup> will be obtained by the control of the growth condition.

### L3.48

**Metal Nanotubes.** Yugang Sun and Younan Xia; Department of Chemistry, Univ. of Washington, Seattle, Washington.

Metal nanotubes have been prepared through a galvanic displacement reaction between silver nanowires and appropriate salts. The morphology and void space of these nanotubes were determined by the silver nanowires. For example, gold/silver alloyed nanotubes with pentagonal cross sections have been successfully prepared by reacting aqueous chloroauric acid solutions and silver nanowires. The wall of these nanotubes could be easily decorated through varying the reaction conditions and/or post-treatments. For instance, some holes could be formed on the walls when the concentration of chloroauric acid was high enough. These nanotubes exhibited strong surface plasmon resonance peaks in the red and near infrared spectral regimes. It is believed that these Au/Ag alloyed nanotubes are good substrate for surface-enhanced Raman spectroscopic studies. Nanotubes made of different compositions could be generated by replacing chloroauric acid with other salts, such as palladium nitrate and platinum acetate.

### L3.49

**Direct Observation of Nanostructured Monolayer Photoswitching for Control of Surface Energies.** J Taraci<sup>1</sup>, R Rosario<sup>1</sup>, A A Garcia<sup>1</sup>, D Gust<sup>1</sup>, M Hayes<sup>1</sup>, S. T. Picraux<sup>1</sup>, B C Bunker<sup>2</sup>, B I Kim<sup>2</sup> and J E Houston<sup>2</sup>, <sup>1</sup>Arizona State University, Tempe, Arizona; <sup>2</sup>Sandia National Laboratories, Albuquerque, New Mexico.

We report the first direct nanoscale observation of photoswitchable chemical interactions with nanostructured surface monolayers. These force microscopy measurements of reversible electrostatic interactions are to be distinguished from earlier reports of optomechanical switching of molecules on surfaces. Previously we designed and demonstrated that the reversible light-induced opening and closing of the rings of tethered spiropyran monolayers on glass surfaces leads to the switching of the hydrophobicity of the surface, with wetting angle changes of up to 13 degrees. Irradiating the photoactive surface with UV light causes the spiropyran rings to open and creates a more polar surface, while irradiation with visible light causes the rings to close and reversibly returns the surface to its original state. We have now used an interfacial force microscope (IFM) to observe the changes in surface chemistry that accompany the light activated switching of tailored monolayers of photoactive molecules such as spiropyrans. Contact potential difference measurements with the IFM in air are used to measure the change in surface polarity upon photoswitching and show a reversible shift of  $-0.27$  V from closed to open spiropyran rings. Normal force measurements in liquids with different functionalized tips allow the chemical interactions between the tip and surface to be monitored. For example, a bare glass tip undergoes an attractive interaction with the surface, whereas an amine coated tip exhibits a repulsive interaction when the spiropyrans are in the open state. From these results we conclude that open ring structures are protonated in electrolyte solutions, forming a positively charged surface and amplifying the switching of electrical double-layer forces. Potential applications of these photoswitchable surfaces include micro and nanofluidic valves, pumps, preconcentrators, and separation, as well as drug delivery, sensing, and environmental monitoring.

### L3.50

**Fabrication of Silver Nanowires from Silver Oxide Solution.** Yasuhiko Iwanabe<sup>1</sup> and Junji Tominaga<sup>2,1</sup>, <sup>1</sup>Tokyo Denki University, Tokyo, Japan; <sup>2</sup>Center for Applied Near-Field Optics Research, National Institute for Advanced Industrial Science and Technology, Tsukuba, Japan.

The optical response of silver nanoparticles and structures is very attractive from a viewpoint of physics and optics for a long time. In this paper, we describe a method to generate silver nanowires (hereafter we use nano-noodles) using a laser beam and silver oxide (AgOx) film. The method is very useful for the study of surface plasmon polaritons (SPP). Recently, using a AgOx film deposited by sputtering, a strong surface enhanced Raman spectrum (SERS) of benzoic acid (BA) molecules which diluted in 2-propanol (IPA) was reported, in addition, Ag nanoparticles and nano-noodles were found in and around the SERS active spot. However, the outbreak of the formation has not been well identified. In order to clarify the mechanism, we in-situ observed the nanowire generation by a laser microscope (NEOARK Ltd. LSM-220F with a wavelength of 405 nm and lens numerical aperture (NA) of 0.50. First we prepared benzoic acid solution ( $1 \times 10^{-3}$  M) diluted by IPA in a small glass container and a AgOx film which was deposited on a glass wafer by RF reactive sputtering with a Ag target and Ar-O<sub>2</sub> gas mixture and 100 nm thick. The AgOx sample was placed on the bottom of the BA-IPA container. When the laser power was increased by 0.8 mW, a small gas bubble was generated on the sample surface, and the size of the bubble was increased with the laser power. At more than a threshold power, the bubble was exploded and rapidly disappeared. During the process, it was found that several small black materials slowly moved towards the bubble from the outside. After the experiment, the active point was observed by a scanning electron microscope. It was found that the

black materials are Ag nano-noodles (diameter $\sim$  20-50 nm) and the nanoparticles are only generated in the active spot. As a result, it was suggested that the solubility of the AgOx in the BA-IPA solution and super-cooling due to the micro-convection be the source of the nano-noodle formation. Following the experiment, saturated-AgOx-BA-IPA solution was prepared and the same experiment was carried out with a Si wafer surface. Even in this condition, Ag nano-noodles were indeed generated around the bubble point without Ag nanoparticles.

### L3.51

**Magnetron Sputtering of Nanocomposite (Ti,Al)CN Coatings.** Michael Stueber<sup>1</sup>, Y. Huang<sup>2</sup>, Andras Kovacs<sup>3</sup>, Peter Barna<sup>3</sup>, Ulrich Albers<sup>1</sup>, Michael Charles Simmonds<sup>2</sup>, John Rodenburg<sup>2</sup> and Hans Holleck<sup>1</sup>, <sup>1</sup>IMF, Forschungszentrum Karlsruhe, Karlsruhe, Germany; <sup>2</sup>MRI, Sheffield Hallam University, Sheffield, United Kingdom; <sup>3</sup>Research Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences, Budapest, Hungary.

The use of lubricant particles such as MoS<sub>2</sub> or graphite incorporated into coatings is of interest in developing self-lubricant hard coatings. In this study, a series of TiAlCN coatings with differing carbon contents (0-27 at.%) have been deposited by the reactive sputtering of TiAl in a mixture of N<sub>2</sub> and CH<sub>4</sub> gases. The microstructure and chemistry of these coatings have been investigated using EPMA, AFM, XPS, HRTEM, Raman spectroscopy and X-ray diffraction and pole figures. The pure TiAlN grows with the expected cubic structure. As carbon is added to the film there is a commensurate increase in the interplanar lattice parameters which may be due to carbon lattice substitution. The pure TiAlN displays a columnar structure with a strong preferred (111) texture. The coatings become more randomly orientated as carbon is added to the films. The grain size changes from microcrystalline to nanocrystalline to nearly amorphous with increasing carbon content. A fairly small internal stress is measured for the samples which is compressive in the TiAlN film and tensile in carbon containing films. At carbon contents above 8 at.% there is unambiguous evidence for the presence of a free carbon species, which is a significant step towards accomplishing a self-lubricant hard coating.

### L3.52

**Monitoring Polymer/Clay Nanocomposites Compounding Using On-Line Dielectric and Fluorescence Measurements.** Anthony J. Bur<sup>1</sup>, Steven C. Roth<sup>1</sup>, Yu-Hsin Lee<sup>1</sup> and Michael McBrea<sup>2</sup>, <sup>1</sup>NIST, Gaithersburg, Maryland; <sup>2</sup>Chemical Electro Physics, Hockessin, Delaware.

A new multipurpose instrument has been used to obtain real-time dielectric and fluorescence spectroscopy from polymer/clay nanocomposites compounding. The instrument, which is mounted at the exit of a twin screw extruder, contains a flow-through slit channel that provides a constant geometry platform for dielectric and fluorescence sensors. The results of real-time monitoring of nylon 6 and ethyl vinyl acetate copolymer (EVA) compounded with organo modified montmorillonite clays will be presented. The on-line data are correlated with off-line dielectric measurements, and analysis of these data yielded a wealth of dielectric relaxation phenomena. Significant differences in the dielectric relaxation parameters were observed for clay nanocomposites in the aggregate, intercalated and exfoliated states. Maxwell-Wagner interfacial polarizations were observed in the nanocomposites reflecting polarization associated with the polymer/clay interfaces. Microstructure characterizations using TEM, X-ray and SANS observations were also carried out. Fluorescent dyes, doped into EVA copolymer, are being used as molecular probes to study the effects of microstructure conformation on their spectra. Real-time monitoring of both fluorescence and dielectric properties offers the potential for deducing microstructural character during processing without the need for off-line, post processing experiments.

SESSION L4: Applications

Chair: John Parker

Tuesday Morning, December 2, 2003

Room 304 (Hynes)

### 8:30 AM \*L4.1

**Industrial Applications of Transparent Conductive Nanoparticles.** Changwoo Park<sup>1,2</sup> and Honglyoul Ju<sup>3</sup>, <sup>1</sup>Dept. of Chemical Technology, Hanbat National University, Taejeon, South Korea; <sup>2</sup>ANP Research Center, Advanced Nano Products Co., Ltd., Chungwon, South Korea; <sup>3</sup>Department of Physics, Yonsei University, Seoul, South Korea.

Due to the unique natures from small particle size, the importance of industrial applications of nanoparticles is gradually increasing. Some of these properties of nanoparticles include high transparency, quantum effects, high surface area and high surface energy. Bulk

production of the nanoparticles has been successful via various novel processes, and physicochemical milling technique using surface modifying agents and high energy milling tools enables the segregation of the aggregated nanoparticles into the nanosized entities in many solvent media to form sol. While nanoparticles have the promising future to substitute most of traditional powders in wide industrial areas, transparent conducting nanoparticles show the most successful model in current industrial applications. These particles are being massively used for electronic and display industries. High performance transparent IR blocking films are being produced using conductive nanoparticles with much lower cost and much higher production capability compared to the traditional methods. The fabrication of ultrahigh density sintered bodies is one of the natural applications of the conductive nanoparticles. In this presentation, general procedure for producing transparent conductive nanoparticles and their industrial applications will be discussed.

**9:00 AM L4.2**

**HSA-CERCANAM: A New Material with a Continuous Nanopore Network.** Balakrishnan Nair, Merrill Wilson and Akash Akash; Ceramtec, Inc., Salt lake City, Utah.

A new ceramic material called HSA-CERCANAM (a trademarked abbreviation for High Surface Area CERamatec CAsable NAno Materials), having an engineered microstructure with continuous nanoporosity has been developed. The ceramic solids can be tailored for specific applications by compositional variations to have flexural strengths as high as 60-70 MPa and component surface areas as high as 100 sq.m/gram have been developed. The very high surface area is due to a network structure of continuous nanoporosity with pore-dimensions ranging from 10-100 nm. The material has been shown to be thermally stable to temperatures as high as 1000 C with no loss in surface area. The ceramic is being used for fabrication of microchannel devices and microreactors for applications such as hydrogen/syngas generation.

**9:15 AM L4.3**

**Iron Oxide / Silica Nanocomposites.** Michael Kroll, Markus Pridohl and Guido Zimmermann; Creavis Technologies and Innovation - Advanced Nanomaterials, Degussa AG, Hanau, Germany.

Iron oxide / silica nanocomposites are produced in a pyrogenic process. The iron oxide domains have adjustable diameters of 5 to 20 nm and are coated with an amorphous silica layer which can be varied in size. They consist of magnetic phases (determined by XRD) and are isolated and well distributed in the silica matrix. Due to their size the magnetic phases are superparamagnetic rather than ferro- or ferrimagnetic. The magnetisation curves therefore do not show any or depending on the mean domain size just a small hysteresis. The saturation magnetisation can be varied from 5 to 35 Am<sup>2</sup>/kg depending on the size of the magnetic domains and the iron oxide content in the composite material. The specific surface area of the nanocomposites can be varied between 40 and 215 m<sup>2</sup>/g by controlling the thickness of the silica layer or the magnetic domains by adjusting the flame temperature. The superparamagnetic behaviour can be utilised in different applications. If the nanocomposites are exposed to an external magnetic AC field they get heated up. This behaviour is useful in applications like hyperthermia (cancer therapy) or adhesives (bonding/debonding on demand). Due to their magnetisation they can be used for ferrofluids, shielding layers, receptor particles for microwaves or magnetic sinter agents or as pigments or lubricant additives. This paper presents methods for the synthesis of iron oxide / silica nanocomposites, the physical characterisation with special emphasis on the magnetic properties and an outlook for future applications.

**9:30 AM L4.4**

**Single-Walled Carbon Nanotube Rope for Gas Sensor Application.** Jinwoo Lee, Youngmin Choi, Kijeong Kong, Hyunju Chang and Byunghwan Ryu; Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, Chungcheong Namdo, South Korea.

Single-walled carbon nanotube(SWNT) ropes were placed on the oxidized Si wafer surface by alignment of nanotubes across neighboring two gold electrodes. SWNTs were dispersed in conventional organic solvent, and dropped on the pre-deposited electrode patterns. The shape and location of SWNT ropes were observed with FE-SEM(Field Emission Scanning Electron Microscopy). We have found that nearly all neighboring two electrodes were connected via SWNT ropes. We have measured I-V characteristics across the fabricated SWNT ropes, and they showed the characteristic of semiconductor which can be applied to gas sensors. The change of conductivity of these SWNT ropes in the presence of NO<sub>2</sub> and NH<sub>3</sub> will be discussed in the point of view of chemical gas sensor applications. We will also discuss how the conductivity of SWNT depends on the gas molecule from our previous

electronic structure calculations on gas adsorption of SWNT[1]. [1] H. Chang, J. D. Lee, S. M. Lee, and Y. H. Lee, App. Phys. Lett., Vol.79, p.3863 (2001)

**9:45 AM L4.5**

**Polymer-Silicate Nanocomposites: Morphological Studies and Their Application as Electrolytes in Lithium Polymer Batteries.** Mary Kurian<sup>1</sup>, Arnab Dasgupta<sup>1</sup>, Mary Galvin<sup>1</sup>, Frederick Beyer<sup>2</sup>, Patrick Trapa<sup>3</sup> and Anne Mayes<sup>3</sup>; <sup>1</sup>Materials Science & Engineering, University of Delaware, Newark, Delaware; <sup>2</sup>Polymers Research Branch, Army Research Laboratory, Aberdeen, Maryland; <sup>3</sup>Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Polymer-layered silicate nanocomposites (PSNs) have both scientific and commercial significance. Scientifically, they are ideal for studying polymers in confined geometries and the influence of surface/polymer interactions on polymer dynamics. Commercial interest arises from the fact that they exhibit dramatic enhancements in tensile strength and heat and solvent resistance, as well as a decrease in gas permeability when compared to the polymer matrix. However, nanocomposite properties are intricately linked to their morphology. In our work, the morphological behavior of nanocomposite materials has been investigated by the fabrication and extensive characterization of model systems. Due to their unique properties, PSNs are also promising materials for use as electrolytes in lithium polymer batteries (LPBs). Though LPBs garner the advantages of substantially diminished flammability and explosive tendency compared with lithium ion batteries containing liquid electrolytes, emphasis has to be placed on the mechanical integrity of the electrolyte, while keeping the battery substantially light for portable power needs. Our work focuses on the development of a new class of nanocomposite electrolytes. The incorporation of Li<sup>+</sup> exchanged nanoscale clay sheets into a suitable polymer matrix is expected to impart the inherent favorable characteristics of PSNs to the electrolyte. This modification is also expected to substantially eliminate the need for lithium salt dopants currently used to achieve significant conductivities. Nanocomposite electrolytes have been fabricated and characterized using small angle X-ray scattering, transmission electron microscopy, dynamic rheological and impedance spectroscopic methods. Preliminary results provide us with the basis to develop electrolytes of enhanced conductivities combined with optimal mechanical properties.

**10:00 AM L4.6**

**Nanobelts as nanocantilevers.** William L. Hughes and Zhong L. Wang; Materials Science and Engineering, Georgia Tech, Atlanta, Georgia.

Semiconducting oxide nanobelts of ZnO have been sectioned and manipulated for micro-electromechanical systems [1,2]. Fracturing nanobelts is possible because the bond character is primarily ionic in nature, and thus an atomic displacement of half the lattice constant generates a cleavage due to coulomb repulsion. ZnO nanobelts have been sectioned via transmission electron microscopy (TEM) and atomic force microscopy (AFM). Utilizing the capillary forces, responsible for the adhesion strength between AFM probes and sample surfaces, ZnO nanobelts have been individually lifted from silicon substrates. Combining the aforementioned techniques with micromanipulation has lead to the horizontal alignment of individual ZnO nanobelts onto silicon chips. The aligned ZnO cantilevers were manipulated to have a range of lengths, exemplifying our ability to tune the resonance frequency. Structurally modified nanobelts demonstrate potential for nano-cantilever based-technologies [2]. With dimensions ~35 - 1,800 times smaller than conventional cantilevers, the nano-cantilevers are expected to have improved physical, chemical, and biological sensitivity for scanning probe microscopy and sensor-based applications. The ability to dimensionally control and manipulate nanobelts for cantilever devices and applications establishes a framework from which ultra sensitive cantilevers will be developed. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 291 (2001) 1947-1949. [2] W.L. Hughes, Z.L. Wang, Appl. Phys. Letts., 82 (2003) 2886-2888.

**10:30 AM \*L4.7**

**Properties and Applications of Pulsed Plasma Produced Nanopowders.** Dennis Wilson and Denny Hamill; Nanotechnologies, Inc., Austin, Texas.

Nanotechnologies, Inc. was founded in October 1999 to commercialize a proprietary process for synthesizing custom-engineered nanoparticles with unique size and composition. The company's technology is based on a high-power, pulsed plasma device that creates a homogeneous gas phase suspension of nanoparticles. Our process uses commodity feed stock, e.g. aluminum at room temperature and pressure. We convert this material into a high-temperature (50,000 K), high-pressure (100 atm) plasma. By controlling the plasma quench

rate (which is in excess of 1 million K per second) we are able to control the mean particle size from sub-10nm to 100nm and produce largely unagglomerated nanoparticles. The combination of unique process features allows us to reach parts of the materials synthesis parameter space that conventional plasma processes cannot reach. An overview of chemical and physical synthesis processes will be given with special attention to the homogeneous gas phase nucleation route for producing unagglomerated nanoparticles. These nanoparticles produced by our pulsed power process have immediate application in a number of rapidly growing, high-performance markets such as electronic materials, life sciences, energy and energetics. Applications include: electrically and/or thermally conducting fillers; direct write electronics; transparent optical coatings; photovoltaics; fuel cells and advanced energetics for explosives, propellants and primers. The talk will discuss recent developments in which our nanoparticles have demonstrated performance advantages in existing and emerging markets. Selected results from independent commercial and government laboratories that have tested our product in a variety of applications will be presented.

#### 11:00 AM L4.8

**Nanocrystalline Mixed Metal Oxides - Novel Oxygen Storage Materials.** R. W. Brotzman, Harry Sarkas, Patrick G. Murray and Aaron Fay; Nanophase Technologies Corporation, Romeoville, Illinois.

Nanophase Technologies Corporation employs a new physical vapor synthesis technique to manufacture ceria-based mixed rare earth oxide nanomaterials. The mixed rare earth oxide nanoparticles are nonporous, dense, discrete crystals. The compositions are solid solutions that remain thermally stable to above 1050 degrees C. Ceria is an active oxygen storage material. Doping ceria with other rare earth metals enhances the thermal stability of nanocrystalline particle size and increases the oxygen storage capacity (OSC). The mean particle size, and static and dynamic OSC of the mixed rare earth oxides will be presented as a function of particle composition, morphology, and thermal history. These materials are being engineered for several applications including oxygen storage catalysts and polishing materials.

#### 11:15 AM L4.9

**Surface modification of ceramic particles using a newly developed thermal DC plasma spray system.** Bong Geun Choi<sup>1</sup>,

Kyoung Hun Kim<sup>1</sup>, Oh Seong Kwon<sup>1</sup>, Se Hoon Kim<sup>1</sup>, Kyung Joo<sup>2</sup>, Ihn Kee Hwang<sup>2</sup> and Kwang Bo Shim<sup>1</sup>; <sup>1</sup>Ceramic Engineering, Hanyang Univ, Seoul, South Korea; <sup>2</sup>Kovaco Ltd, Incheon, South Korea.

A new thermal DC plasma spray system has been developed for not only the production of the nanoparticles with a uniform size distribution and without agglomeration but also the surface modification of nanoparticles for the improved powder functionality. The 2-step cyclone chamber, operating at the low pressure, was adapted for dividing the particle size and disagglomeration the plasma-treated particles. The enlarged plasma length up, to 60cm, in the reaction tube was also very effective to disagglomerate the plasma-treated particles during cooling and to lead them to 2-step cyclone chambers with a stable temperature distribution. The new thermal plasma system was applied for various ceramic powders such as Al<sub>2</sub>O<sub>3</sub>, ZrB<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The experimental results showed that the irregular shaped ceramic powder changed typically to spherical shape depending on the various process condition (powder, feeding rate of powder, pressure, etc.). The particle size tends to reduce gradually with a narrow size distribution from reaction tube to 2<sup>nd</sup> chamber.

#### 11:30 AM L4.10

**Proton Conducting Nano Hybrid Membranes Synthesized From Temperature Tolerant Polydimethylsiloxane Polymers.** Je-Deok Kim and Itaru Homma; National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

Flexible and temperature tolerant nano-hybrid membranes consisting of zirconium (titanium) oxides and polydimethylsiloxane (PDMS) with the different molecular mass of 4500 and 600 have been synthesized by sol-gel processes. The polymeric membranes showed enhanced thermal stability and flexibility up to 300°C due to the presence of cross-linkable inorganic nano-phase in the hybrid macromolecular matrix. The membrane becomes proton conducting polymer electrolyte when doped with 12-phosphotungstic acid (PWA). The proton conducting properties of the hybrid membranes with various PWA concentration were measured in the temperature range from room temperature to 150°C under saturated humidity conditions. A maximum conductivity of 2x10<sup>-2</sup> S/cm was obtained at 150°C when the PDMS/zirconium oxides hybrid matrix was changed to gel state due to the higher water activity at elevated temperatures.

#### 11:45 AM L4.11

**A Plasma Enhanced CVD Low-k Film For the 65nm**

**Technology Node.** Yi Zheng, Wen Zhu, Tzufang Huang, Srinivas Nemani, Kang Sub Yim, Li-Qun Xia and Hichem M'saad; Dielectric System & Module, Applied Materials, Santa Clara, California.

A second-generation organosilicon glass (OSG) low-k film for the 65nm technology node was developed with a k value of 2.5-2.6, corresponding to a 15% capacitance reduction from the first-generation Black Diamond<sup>®</sup> film. The k value was achieved by introducing nanometer-sized pores into the film, which was prepared with a plasma enhanced CVD (PECVD) method using organosilicon molecule and small organic molecule precursors. Post deposition, the OSG film was treated by electron beam to enhance its electrical and mechanical properties. An organic molecule was used as the porogen. This molecule forms very small pores that are preferable to meso-pores (tens of nanometers). The organic molecules were embedded, along with silicon-containing precursors, into the film through the plasma gas phase reaction and substrate surface reaction. The precursors were activated in plasma; the surface reaction is simply an adsorption-desorption limited process, as indicated by negative activation energy from an Arrhenius plot. Subsequent e-beam treatment removed volatile species and generated pores. While conventional thermal annealing can produce porous low k films, it is slow and incompatible with thermal budget requirements. E-beam is more effective in removing porogen and more importantly, it can treat selected layers by controlled treatment depth. The energetic electrons also promote molecular cross-linking, giving enhanced film modulus and hardness, thus making it compatible with CMP and packaging. The e-beam energy and dose can be adjusted for various types of films with different thickness to achieve optimal properties. Compared to the 90nm Black Diamond film, the new OSG film has a lower density with similar chemical composition (see Table 1). The pores have a narrow size distribution that peak at 1nm, as measured by ellipsometric porosimetry. Modulus of up to 11 GPa can be achieved through e-beam treatment. The film remained stable with little change in k, RI and FTIR signal after 10 days in atmosphere and 36 hours in a humidity chamber at 85% humidity / 85°C. Extendibility from 90nm to 65nm is simplified due to the similarity between the first and second-generation film properties. A single damascene structure was fabricated using 50nm of BLOkTM as an etch stop layer and 500nm of the new OSG film. Interline capacitance measurement and TMA Raphael simulation indicated an integrated k value of 2.6. A similar effective k value was also achieved with a dual damascene structure. Plate capacitance measurements indicated a breakdown strength of >6.7MV/cm, and >95% yield was measured on a 9 million via chain.

SESSION L5: Properties

Chair: John Parker

Tuesday Afternoon, December 2, 2003

Room 304 (Hynes)

#### 1:30 PM \*L5.1

**Organization of Nanocrystals on a Mesoscopic Scale:**

**Collective Properties.** Marie-Paule Pileni, LM2N, Universite Pierre et Marie Curie, Paris, France.

Nanocrystal are organized in 2D superlattices forming either in a compact hexagonal network, rings or chain like. In 3D superlattices a large variety of organizations are obtained with formations of stripes, dots, labyrinths and hexagons. In this presentation we will describe the various parameters involved in controlling the nanocrystal organizations. The physical properties of this nanocrystal assembly differ from either those of isolated particles or the bulk material. Collective properties are observed with magnetic nanocrystals. They are organized either linearly or form a monolayer. Magnetic properties governed by dipolar interactions markedly differ with the structural order.

#### 2:00 PM L5.2

**Improved Tribological Properties of Diamondlike**

**Carbon/Metal Nanocomposites.** Roger Jagdish Narayan and Mike Weatherspoon; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

One of the many forms of carbon, diamondlike carbon (DLC) consists mainly of sp<sup>3</sup>-bonded carbon atoms. DLC coatings possess properties close to diamond in terms of hardness, atomic smoothness, and chemical inertness. Unfortunately, DLC exhibits poor adhesion to metals and polymers. The adhesion of the DLC film is determined by internal stresses in the film and by interfacial bonding. This research involves processing, characterization and modeling of diamondlike composite films on metal and polymer substrates specifically to improve adhesion and wear properties. A novel target design was adopted to incorporate metal (e.g., silver or titanium) atoms into the DLC films during pulsed laser deposition. Atomic structure with a resolution of 1.6 Angstroms was performed using STEM-Z contrast at

ORNL. Since scattering power or contrast depends upon atomic number squared ( $Z^2$ ), heavy noncarbon atoms in the DLC matrix can be studied in detail. STEM of the DLC/metal nanocomposites has shown that metals that do not form carbides (including silver) form 2-10 nm inclusions within the DLC matrix. Wear resistance measurements made on these samples have demonstrated that DLC/metal nanocomposites possess the highest wear resistance. On the other hand, pure DLC possesses the lowest wear resistance. Diamond-like carbon nanocomposites also exhibit significantly enhanced adhesion. Careful analysis of the Raman data also indicated a significant shift to shorter wavelength in DLC nanocomposite films, indicating a reduction in compressive stress within these films. Raman spectroscopy studies also demonstrate a high fraction of  $sp^3$ -bonded carbon in both DLC/metal nanocomposite films and pure DLC films. The chemical properties of these films were studied using electron energy loss spectroscopy (EELS) and x-ray photoelectron spectroscopy (XPS). By varying the metal concentration as a function of distance from the interface, it is possible to create a functionally gradient DLC nanocomposite. These DLC/metal nanocomposite coatings have multiple biomedical applications. For example, we have shown that DLC/silver coatings possess antimicrobial properties against *Staphylococcus aureus*. DLC/metal nanocomposites are wear-resistant and infection-resistant coatings that can be applied to polymers and metals used in products ranging from medical prostheses to cooking surfaces.

### 2:15 PM L5.3

#### Correlation of Oxygen Diffusivity with Grain-Boundary Dynamics and its Impact on Ionic Migration in Doped Nano-Crystalline CeO<sub>2</sub> Films. Laxmikant V. Saraf<sup>1</sup>, V

Shutthanandan<sup>1</sup>, C M Wang<sup>1</sup>, K T Koch<sup>1</sup>, O Marina<sup>2</sup> and S Thevuthasan<sup>1</sup>; <sup>1</sup>Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, Washington; <sup>2</sup>Energy Science and Technology Directorate, Pacific Northwest National Laboratory, Richland, Washington.

Oxygen storage and related vacancy/interstitial migration in doped electrolytes like CeO<sub>2</sub> has been center of focus for the recent years in the areas of catalyst and solid oxide fuel cells (SOFC). The high efficiency intermediate temperature energy conversion from chemical to electric state reducing the pollutants makes materials like doped-CeO<sub>2</sub> an attractive candidate for SOFC electrolyte. The nature and impact of ionic conduction in doped-CeO<sub>2</sub> relies heavily upon grain boundary dynamics. Study of doped nanocrystalline CeO<sub>2</sub> gives the perfect opportunity to study an enhanced grain boundary effect and its impact on diffusivity and ionic transport. In this study nanocrystalline Y, Gd and Sm doped CeO<sub>2</sub> films in the size range 3 to 80 nm are deposited by DC magnetron sputtering as well as sol-gel method. Oxygen diffusion measurements were carried out by nuclear reaction analysis (NRA) and the diffusivity correlation is established with ionic transport by measuring the a.c. conductivity by impedance spectroscopy. The grain boundary analysis is carried out using high-resolution transmission electron microscopy (HRTEM). Initial 18O diffusion results indicate increased diffusion in nanocrystalline ceria compared to polycrystalline films treated at elevated temperatures. A detailed discussion will also be presented correlating the 18O diffusivity profile tailoring effect with the 'brick model', especially considering the case of nano-crystalline materials. Finally, a comparison will be presented between sol-gel and DC sputter growth process from the point of view of connectivity and improved density and its effect on the long-range interstitial/vacancy migration.

### 2:30 PM L5.4

#### Thermal Equilibrium and Transport Properties of Nanocrystalline FCC Metals. Peter M Derlet and Helena Van Swygenhoven; Paul Scherrer Institute, PSI-Villigen, Switzerland.

The equilibrium thermal properties of nanocrystalline (nc) materials using molecular dynamics have recently been investigated via the Fourier transform of the velocity-auto-correlation-function (Phys. Rev. Lett. 87 205501 (2001)). It was found that the vibrational density of states (VDOS) of the grain boundary region is responsible for the enhanced low and high frequency phonon modes, thus elucidating on the anomalous nc-VDOS previously observed by incoherent thermal neutron scattering experiments. In the present work, we investigate in more detail the nc phonon properties, by directly calculating the onsite and inter-site phonon Greens function derived from large-scale computer generated atomic nc configurations. We investigate this as a function of local grain boundary environment and grain size, and consider the effect of the grain boundary structure on general phonon scattering and the thermal conductivity properties of nc materials.

### 2:45 PM L5.5

#### Vanadium Oxide Nanofibers and Vanadium Oxide Polyaniline Nanocomposite: Preparation, Characterization and Electrochemical Behavior. Samuel T Lutta, Dong Hong, Peter Y Zavalij and M Stanley Whittingham; Department of Chemistry and

Institute for Materials Research, SUNY-Binghamton, Binghamton, New York.

Vanadium oxide nanofibers have been prepared using poly (methyl methacrylate) (PMMA) as templating reagent. Sol-gel reaction and subsequent hydrothermal synthesis of V<sub>2</sub>O<sub>5</sub> and PMMA resulted into NH<sub>4</sub>V<sub>2</sub>O<sub>5</sub>· $\delta$ ·nH<sub>2</sub>O rods. Solid state reactions of NH<sub>4</sub>V<sub>2</sub>O<sub>5</sub>· $\delta$ ·nH<sub>2</sub>O in nitrogen and oxygen at 300 °C formed V<sub>3</sub>O<sub>7</sub> and V<sub>2</sub>O<sub>5</sub> nanofibers respectively. Polyaniline-vanadium oxide nanocomposite was prepared by sol-gel reaction of vanadium (V) oxytriisopropoxide and polyaniline fibers. The compounds were characterized by SEM, XRD, TGA, and IR. The vanadium oxides are redox active and can electrochemically insert lithium reversibly. A specific charge of about 150 mAh/g (with respect to the oxides) were measured for lithium insertion and remained fairly constant for at least 10 cycles. The electrochemical behavior of the vanadium oxide polyaniline is also discussed. This work is being supported by NSF grant DMR0313963

### 3:00 PM L5.6

#### Nanoscale Structure and Electronic Characteristics of Highly Conductive N-type Ultrananocrystalline Diamond.

Jennifer E Gerbi<sup>1</sup>, Oliver A Williams<sup>2</sup>, Judith E Baker<sup>3</sup>, James Birrell<sup>3,1</sup>, Stephane P Curat<sup>2</sup>, Haitao Ye<sup>2</sup>, Orlando Auciello<sup>1</sup>, Dieter M Gruen<sup>1</sup>, Richard B Jackman<sup>2</sup> and John A Carlisle<sup>1</sup>; <sup>1</sup>Materials Science, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>University College London, London, United Kingdom; <sup>3</sup>University of Illinois, Urbana-Champaign, Illinois.

Ultrananocrystalline diamond (UNCD) is a very fine-grained (3-5 nm) diamond material with atomically abrupt mixed  $sp^2$  and  $sp^3$  bonded grain boundaries. Synthesized using microwave plasma enhanced chemical vapor deposition (MPCVD) with Ar-rich Ar/CH<sub>4</sub> plasmas, the electronic, structural, and tribological film properties of UNCD films can be tailored by doping with a controlled amount of nitrogen. These changes correspond with transformations in the film structure, whereby both the grain and grain boundary sizes increase, and the grain boundary bonding structure is altered. These effects result in an n-type, highly conductive film that can retain the excellent tribological and structural properties of a small-grained, smooth, and phase-pure diamond film if the nanostructure is properly controlled. Here we discuss the relation between the electronic and structural properties of UNCD films deposited using a novel MPCVD system that enables large-area (100 mm diameter) film deposition. For a range of nitrogen doping concentrations, we discuss the structure (including grain size, preferred orientation, and texture) of nitrogen doped UNCD films as measured by x-ray diffraction, and present measurements of the nitrogen concentrations as determined by high-mass resolution SIMS. We also present new Hall voltage and AC conductivity results performed with a dedicated field switching setup at variable temperatures. These data provide insight into the unique conduction mechanism of nitrogen-doped UNCD, along with confirmation of the carrier concentrations, mobilities, and conductivities of this material as a function of nitrogen doping and film nanostructure. [1] This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38 and the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. DOE under grant DEFG02-91-ER45439.

### 3:30 PM \*L5.7

#### Nanocrystalline Oxides as Fillers in Nanocomposites to Enhance the Performance of Polymeric Electrolytes. Silvia Licoccia and Enrico Traversa; Dept. of Chem. Sci. Technol., University of Rome Tor Vergata, Roma, Italy.

New technologies of energy production and storage are needed for sustainable development, to reduce the pollutant emissions from fossil fuel combustion. Polymeric electrolyte fuel cells (PEFCs) are very promising as electrochemical power sources for application in portable technologies and in electric vehicles. Lithium ion batteries are already commercialized for electronic products, although improvement is needed for other applications (with the use of solid electrolytes). These electrochemical devices are based on polymeric electrolyte membranes, which use has been reported also for biomedical devices such as cardiac pacemakers or neurostimulators. Nafion, a perfluorinated sulfonated proton conductor polymer, is the commercial material used in PEFCs. For vehicles, the use of methanol instead of hydrogen as a fuel has several practical benefits such as easy transport and storage. The slow oxidation kinetics of methanol and its crossover through the membrane are the factors that limit applications of direct methanol fuel cells (DMFCs). Nafion cannot be used at temperatures above 100°C because its conductivity is due to the presence of water within its structure. Membranes made of polymeric gels containing lithium salts for Li batteries couple the high energy, long life characteristics of the lithium process with the reliability and easy processing of the plastic configuration. The reduction in size at the nanometric level have shown the possibility to

derive unique physico-chemical properties of materials. Composite materials have shown the ability to develop new or multifunctional properties when materials with differing properties are integrated together. Thus, the use of nanocomposites (with nano-sized fillers) is now receiving wide attention for many functional applications. We here report that the addition of nanocrystalline ceramic oxides to polymeric membranes improves their electrical and mechanical performances both in DMFCs and lithium batteries. It is worth noting that the beneficial effect of nanocrystalline powders was found both in protonic and Li-ion conductors. Improvement in conductivity was observed in both cases albeit the different nature of the charge carriers. A similar strategy was applied for developing new composite polymeric gel electrolytes based on PMMA to be used as interface between the skin and electrical instrumentation for the recording of EEG (electroencephalograms). This is, to the best of our knowledge, the first report on the use in a biomedical application of a lithium containing system where the membrane must be used at ambient conditions and in direct contact with the skin. Mechanical properties and non toxic characteristics must in fact be deeply modified for biomedical applications.

#### 4:00 PM L5.8

**Achieving electrical percolation in polymer-carbon nanotube composites: effect of processing conditions on conductivity of textile fibers.** Sameer Rahatekar<sup>1</sup>, Marc Hamm<sup>1</sup>, Milo Shaffer<sup>2</sup> and James Elliott<sup>1</sup>; <sup>1</sup>Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom; <sup>2</sup>Department of Chemistry, Imperial College, London, United Kingdom.

The addition of carbon nanotubes (CNTs) to a polymer matrix is expected to yield benefits in both mechanical and electrical properties. The focus of this work is on CNT-filled thermoplastic polymer textile fibers and the enhancement of their electrical properties. The challenge is to determine the type and size of nanotubes that are most effective for a given application, and how they should be dispersed or modified to interact with the polymer. The objective of this work is to develop an understanding of how the processing methods and properties of nanotube polymer composites are related to the geometry of the nanotubes used, their orientation, and their packing fraction. It will then be possible to design desired composite properties by controlling the relevant variables. The research primarily involves mesoscale simulations (dissipative particle dynamics) of packed assemblies of oriented CNTs suspended in a polymer matrix. Computer simulation has been carried out to study the effect of processing conditions, aspect ratio of CNTs and effect of electric field. The percolation threshold required to achieve an electrically conductive polymer-CNT fiber can be predicted for given set of process variables. The model predictions can be compared with experimental data from measurement of bulk resistivity, X-ray diffraction and SEM from CNTs dispersed in thermoplastic polymers. This work will also make a significant contribution to the theoretical understanding of particle packing and percolation.

#### 4:15 PM L5.9

**Magnetic Behavior of Iron and Iron-Oxide Nanoparticle/Polymer Composites.** Colin Baker<sup>1</sup>, S. Ismat Shah<sup>1,2</sup> and Khurshid Hasanain<sup>3</sup>; <sup>1</sup>Materials Science and Engineering, University of Delaware, Newark, Delaware; <sup>2</sup>Physics and Astronomy, University of Delaware, Newark, Delaware; <sup>3</sup>Physics, Quaid-i-Azam University, Islamabad, Pakistan.

An inert gas condensation (IGC) technique was used to prepare nanometer-sized particles of metallic iron and iron oxide by the evaporation of metallic iron into a flowing inert gas stream. The particles were passivated by the controlled oxidation of the particle surface leading to a Fe-oxide shell, Fe core structure. X-ray diffraction and transmission electron microscopy measurements indicated that, depending on the deposition conditions, mean particle diameters between 10 and 20 nm could be obtained. The particles were spin cast into Polymethylmethacrylate (PMMA) films forming a uniform dispersion of particles in the polymer matrix. This allowed the magnetic properties of the particles to be investigated as a function of the particle loading. Magnetization hysteresis loops, magnetic moment vs. temperature in field cooling and zero field cooling, and magnetization relaxation measurements were all performed on the same 10.8 nm particles compressed into pellets and dispersed into the polymer composites. All experiments were performed at temperatures from 300K to 5K. The particles were observed to exhibit an exchange bias as indicated by a shift in the hysteresis loops for samples cooled in a field. This exchange bias was examined as a function of the particle concentration in the polymer samples. The magnetic relaxation results indicate that the particles dispersed in the PMMA exhibit significantly reduced relaxations through the entire temperature range as compared to the non-dispersed compressed powder, suggestive of heightened anisotropy barriers.

#### 4:30 PM L5.10

**Luminescence Properties of Europium Doped Yttrium-Silicate Phase Separation Glasses and Glass-Ceramics Prepared via Stable Immiscibility.**

Atsuo Yasumori and Naruhiro Kiso; Dept. of Materials Science and engineering, Tokyo University of Science, Noda-shi, Chiba, Japan.

Luminescent materials with high emission efficiency and with thermal and physical stability are very important for recent flat panel displays; further, in order to have much higher picture resolution, fine fluorescent particles with high luminous intensity will be also necessary. On the other hand, emission enhancement owing to light scattering accompanied with the microstructure of organic-inorganic composite materials has been investigated recently in order to fabricate novel laser materials. Thus, the luminescence from the glassy materials as host materials, which have inner microstructure due to phase separation, was examined in this study. As a candidate for such materials, in this study, yttrium-silicate phase separated glasses and glass ceramics containing europium (II) and (III) ions, which are typical luminescence center of blue and red color, were prepared by melt-quenching process via stable immiscibility region with some third component. The size of phase separation texture of the obtained materials was controllable by adding alumina as the third component. As the size of phase separation texture changed into fine grains, the luminescence intensity increased. This enhancement of luminescence is considered to be caused by the multiple scattering effect of excitation light at the interface of phase separation textures. The addition of alumina, titania and/or metal silicon also affected on the valence alternation of europium ions in the materials.

#### 4:45 PM L5.11

**Thermal and Electrical Transport Measurements of**

**Single-walled Carbon Nanotube Strands.** Claire Nanot<sup>3</sup>, Theodorian Borca-Tasciuc<sup>1</sup>, Bingqing Wei<sup>2</sup>, Robert Vajtai<sup>2</sup> and Pulickel M. Ajayan<sup>2</sup>; <sup>1</sup>MANE Dept., Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>3</sup>E.N.S.M.A., Futuroscope, France.

Thermal and electrical properties of carbon nanotubes are of high interest for a variety of applications ranging from nanoelectronics and nanoelectromechanical systems to nanocomposites for thermal management. This work reports temperature dependent thermal and electrical properties characterization of long (few centimeters) single walled carbon nanotube strands grown by catalytic pyrolysis. Thermal conductivity and heat capacity of the bundle is determined using an AC driven self-heating method. Electrical conductivity is measured using a 4-point method. Mechanisms responsible for reduction of electrical and thermal carriers mean free path will be discussed.

### SESSION L6: Templated and Self-Assembled Materials

I

Chair: Kazuki Nakanishi

Wednesday Morning, December 3, 2003  
Room 304 (Hynes)

#### 8:30 AM \*L6.1

**The Use of Mesoporous Systems for Preparation of One-Dimensional Ordered Magnetic Metal Nanowires.**

Yuri Dmitrievich Tretyakov, Andrei Eliseev, Alexei Lukashin, Kirill Napolskii, Alexei Vertegel and Maxim Pavlovich Nikiforov; Department of Materials Science, Moscow State University, Moscow, Russian Federation.

Creation of the functional nanomaterials with the controlled properties is emerging as a new area of great technological and scientific interest, in particular, it is a key technology for developing novel high-density data storage devices. Today, no other technology can compete with magnetic information carriers in storage density and access rate. However, usually very small (10-1000 nm<sup>3</sup>) magnetic nanoparticles shows para- or superparamagnetic properties, with very low blocking temperatures and no coercivity at normal conditions. One possible solution of this problem is preparation of highly anisotropic nanostructures. From the other hand, the use of purely nanocrystalline systems is limited because of their low stability and tendency to form aggregates. These problems could be solved by encapsulation of nanoparticles in a chemically inert matrix. The promising matrices for preparation of highly anisotropic magnetic nanoparticles are mesoporous silica and mesoporous aluminosilicates. Mesoporous silica is an amorphous SiO<sub>2</sub> with a highly ordered uniform pore structure (the pore diameter can be controllably varied from 2 to 50 nm). This pore system is a perfect reactor for synthesis of nanocomposites due to the limitation of reaction zone by the pore walls. Here we suggest a novel variant of synthesis of ordered magnetic nanowires in the mesoporous silica matrix. The method is

based on the introduction of a hydrophobic metal compound, into the hydrophobic part of silica-surfactant composite. Thus prepared nanocomposites were characterized by TEM, ED, SAXS, SANS, BET and magnetic measurements. It was showed that particles shape and size are in good agreement with the shape and size of the pores. Particles are uniform and well ordered in the silica matrix. Thus, mesoporous silica serves as nanoreactor for the formation of nanowires. This approach leads to functional materials, which could find application as high-density data storage devices. However this method also have some disadvantages: the quantity of metal intercalated using this method could not be varied or set and maximal quantity is rather small. Therefore, we suggested another approach based on charging silica matrix by replacing part of silicon atoms by aluminum, which give rise to possibility of controlling loading value by varying silicon to aluminum ratio. Besides that the use of mesoporous aluminosilicates as nanoreactors enables one to load cations by simple ion exchange. In the present study mesoporous aluminosilicates prepared by different methods were compared. Incorporation of silver ions into mesoporous silica matrix was studied by TEM, ED, SAXS and BET as a modeling system. It was showed that particles shape and size are in good agreement with that of the pores. Thus, the suggested method leads to preparation of one-dimensional anisotropic nanostructures. This work is supported by RFBR (03-03-32182) and INTAS (01-204).

#### 9:00 AM L6.2

**Electrochemical Reactions Within Confines of Nanostructured Films.** Dhaval Doshi<sup>1</sup>, Darren Dunphy<sup>2</sup>, Adam Cook<sup>2</sup>, Jarek Majewski<sup>1</sup>, Timothy Stachowiak<sup>2</sup> and C Jeffrey Brinker<sup>2,3</sup>; <sup>1</sup>LANSC-12, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Sandia National Laboratories, Albuquerque, New Mexico; <sup>3</sup>Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico.

Chemical reactions within nanostructured materials provide opportunities for making new functional materials and discovering novel phenomena. Amphiphilic structure directing agents such as surfactants and block-co-polymers have been utilized to self-assemble inorganic precursors on the 1-50 nm length scale. Electrochemical polymerization of conducting polymers within confined environments has resulted in enhanced electrical properties of these materials. Here, we have electrochemically grown polyaniline wires within pores of a nanostructured silica thin-films coated on a electrode. Evaporation induced self-assembly (EISA) approaches are used to form thin-film silica nanostructures with various morphologies and framework chemistry on top of electrodes. The voltamograms for the electrochemical polymerization of aniline carried out on coated electrodes show a marked difference compared to bare electrodes. Results from cyclic voltametry of polyaniline grown in nanoporous films and the electrochromic behavior via UV/Vis experiments are used to understand the growth mechanisms within self-assembled nanostructures. In-situ neutron reflectivity experiments conducted during electropolymerization provides a structural probe to better understand the growth mechanism and determine the length of the polyaniline wires. This work was supported by Los Alamos National Laboratory under DOE contract W7405-ENG-36, and by the DOE Office of Basic Energy Sciences

#### 9:15 AM L6.3

**Mesoporous Polyhedral Cages and Shells formed by Textured Self-assembly of ZnO Nanocrystals.** Puxian Gao and Zhong Lin Wang; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Mesoporous structured polyhedral drum and spherical cages and shells are synthesized using a novel self-assembly process during epitaxial surface oxidation. The cages/shells exhibit unique geometrical shapes and their walls are composed of mesoporous and textured ZnO nanocrystals. The structures of the cages and shells are studied and a growth mechanism is proposed to be a liquid deposition, surface oxidation and sublimation process. Textured feature comes from the growth of wurtzite ZnO into metallic Zn polyhedra, and the epitaxy relationship between original Zn particles and synthesized ZnO cages is preserved. While large lattice mismatch of 23.7% between ZnO and Zn gives rise to the formation of mesoporous structure of ZnO cages and shells. This is a new approach for synthesis of self-assembled nanostructures. The equilibrium shapes for original Zn particles and the subsequent shapes of the nanostructured ZnO shells/cages might be determined by temperature gradient. The textured cage structure reported here could be components for integrating piezoelectric structures with micro-electromechanical systems (MEMS) and for drug delivery. [1] P. X. Gao & Z. L. Wang, J Am. Chem. Soc., Submitted (2003) \* Corresponding author: zhong.wang@mse.gatech.edu

#### 9:30 AM L6.4

**Nanostructured Hybrid Inorganic-Organic Films Formed by**

#### Selective Mineralization in Block Copolymers.

Brian Joseph Melde<sup>1</sup>, Thomas P Russell<sup>2</sup> and Sandra L Burkett<sup>1</sup>; <sup>1</sup>Chemistry, Amherst College, Amherst, Massachusetts; <sup>2</sup>Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts.

Asymmetric diblock copolymer thin films have been used as templates for the mineralization of silica. Films of polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) and polystyrene-block-poly(ethylene oxide) (PS-b-PEO) were prepared in which cylindrical PMMA or PEO domains were oriented perpendicular to the surface. Silicon oxide could be selectively grown in the PEO cylinders by vapor-phase and liquid-phase sol-gel processes using tetraethoxysilane (TEOS). Vapor-phase TEOS treatment of PS-b-PMMA films could also be used to deposit silica in the PMMA cylinders. Liquid sol-gel processing resulted in swelling of the PMMA so that it covered the PS matrix and formed nanopores, followed by silicon oxide mineralization in the PMMA layer. Reaction conditions influenced the extent of silicon oxide growth on the polymer film surfaces. Distinct silica caps could be obtained. The block copolymers may act as templates for other metal oxides to create nanostructured hybrid inorganic-organic thin films.

#### 9:45 AM L6.5

**Biomimetic Mineralization of Type I Collagen with Nano-Hydroxyapatite by a Polymer- Induced Liquid-Precursor (PILP) Process.** Munisamy Sivakumar, Matthew J Olszta and Laurie B Gower; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Bone can be described as a highly ordered composite of type I collagen integrated with an inorganic mineral phase, hydroxyapatite. Synthetic bone replacement materials such as composites comprised of calcium phosphate and collagen are now widely used in bone repair and replacement. In this study, in-situ mineralization of type I reconstituted collagen with nano hydroxyapatite was carried out under simulated physiological conditions using acidic biopolymers, such as poly(aspartic acid) and poly(vinyl phosphonic acid), to induce an amorphous liquid-phase mineral precursor of calcium phosphate. The novelty of our approach is that the polymer-induced liquid-precursor (PILP) phase can be drawn by capillary action into the gaps and grooves of the collagen matrix. The PILP phase then subsequently crystallizes into hydroxyapatite as the waters of hydration are thermodynamically driven off, leaving the collagen embedded with nano-crystals of hydroxyapatite, and generating a highly mineralized composite that mimics the nanostructured architecture of bone. The mineralized nano-structured composite was characterized by various techniques, such as SEM, TEM, XRD, FT-IR, EDS and electron diffraction. It is evident from the XRD and FT-IR data that the crystal structure and characteristic groups present in the mineralized composites are the hydroxyapatite phase of calcium phosphate, which was further confirmed from EDS and electron diffraction data. Etching studies reveal that the mineral phase is generated both on and within the collagen fibrils, leading to an interpenetrating network of mineral and collagen. These preliminary observations indicate that a liquid-phase mineral precursor of calcium phosphate may prove useful for in vitro model systems for the study of intrafibrillar mineralization of collagen, mimicking that of secondary bone formation. In addition, our biomimetic process for the mineralization of collagenous matrices may lead to the development of novel biomaterials for bone repair and replacement.

#### 10:00 AM L6.6

**Macroscopic One Dimensional Photonic Structures based on Electrostatic Layering of Homopolymer Nanoparticles.** Myunghwan Kim<sup>1</sup>, Lynne A. Samuelson<sup>2</sup> and Jayant Kumar<sup>1</sup>;

<sup>1</sup>Chemistry and Physics, Center for Advanced Materials, Lowell, Massachusetts; <sup>2</sup>U.S. Army RDCOM, Natick Soldier Center, Natick, Massachusetts.

Polymeric dielectric Bragg gratings have been fabricated on transparent substrates in the visible optical wavelength region by a combination of electrostatic layering and annealing of sulfated polystyrene latex (PS) and carboxylated poly (methyl methacrylate) latex (PMMA) nanoparticles. This approach allows for the fabrication of relatively uniform PS and PMMA realms over large areas. Negatively charged latex (PMMA) nanoparticles have been deposited by electrostatic layer-by-layer deposition onto positively charged substrates. These layers were then annealed, via a facile chemical treatment, into a transparent thin layer, with uniform coverage of the substrate. The polymeric layer was then modified by the deposition of polyelectrolytes to provide adequate surface charge density to enable subsequent deposition of a second polymeric latex, PS. In this way low refractive polymer (PMMA) and higher refractive polymer (PS) were assembled into multilayer structures. Maximum peak reflectivity of the multilayers at normal incidence occurs at a wavelength of 522 nm (a homogeneous metallic green in reflection color is observed) with

a half bandwidth of less than 55 nm. The reflectivity maximum matches well with theoretical prediction. The period of the Bragg grating is measured to be 153 nm, which is consistent with the reflection data. This is an extremely versatile process in that the composition and thickness of these layers may be easily modified to build in the desired optical properties. Multilayer assembly and the optical properties of these multilayered structures will be presented.

#### 10:30 AM L6.7

**Porous Carbon Nanoturf composites using anodized alumina templating.** Ramakrishnan Rajagopalan, Krishna Dronavajjala and Henry C Foley; Pennsylvania State University, University Park, Pennsylvania.

Nanoporous carbon derived from polyfurfuryl alcohol have very interesting size and shape selective properties that have a pore size of 4-5 Å. In this investigation, we report the development of oriented porous carbon nanoturf. We also report the formation of metal doped porous carbon nanoturf using metals such as iron, cobalt and Silver. The development of these nanostructures could lead to various applications that include sensors, probes and catalysis.

#### 10:45 AM L6.8

**Synthesis of New Nanoporous Carbon Materials Using Various Nanostructured Silica Templates.** Jinwoo Lee, Sangjin Han, Jaeyun Kim and Taeghwan Hyeon; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We have developed new synthetic procedures to synthesize various nanoporous carbons using nanostructured silica materials as templates. Nanoporous carbons with high pore volumes and uniform pore sizes have been produced using silica sol nanoparticles as template. Mesoporous carbons with several different pore structures have been synthesized using mesoporous silicas such as MCM-48, HMS, and MSU as templates. Mesocellular carbon foams have been synthesized using mesocellular aluminosilicate foam as templates. We synthesized carbon capsules with hollow macroporous core and mesoporous shell structures. Macroporous carbon tubes with mesoporous shells were synthesized. Bimodal mesoporous silica material composed of 30 ~ 40 nm sized nanoparticles with 3.5 nm mesopores was synthesized. Using the bimodal mesoporous silica as a template, bimodal mesoporous carbon was synthesized. Ordered mesoporous carbon materials were synthesized through a simple direct synthetic method using as-synthesized silica/surfactant nanocomposites. New mesoporous silica with onion-like pore structure was synthesized and the mesoporous silica was successfully applied as the template for the synthesis of carbon nano-onions. Mesocellular silica and carbon materials with ordered pore structures were synthesized for the first time. These nanoporous carbons have been successfully applied as electrode materials for supercapacitors and adsorbents for water pollutants.

#### 11:00 AM L6.9

**Systematic Molecular Control of Interfacial Structure in Nanoporous Carbons.** Kengqing Jian<sup>1</sup>, Nancy Y.C. Yang<sup>2</sup>, Gregory P. Crawford<sup>1</sup> and Robert H. Hurt<sup>1</sup>; <sup>1</sup>Division of Engineering, Brown University, Providence, Rhode Island; <sup>2</sup>Sandia National Laboratories, Livermore, California; <sup>3</sup>Chemistry Department, Brown University, Providence, Rhode Island.

A host of new carbon materials have been synthesized using nanostructured sacrificial templates to control pore structure. The present paper describes a new concept for synthesizing nanoporous carbons that allows control of not only the pore structure, but also the molecular structure of the internal surfaces. Interfacial molecular control can be achieved through the use of discotic liquid crystalline precursor whose molecular orientation on the substrate material is known or can be determined by simple measurements on flat substrate test samples. Thermal carbonization of the liquid crystal/template composite produces novel porous carbons whose internal adsorption surfaces consist primarily of either graphene edge-sites or basal sites, reflecting the original anchoring state of the discotic (either edge-on or face-on). The contrasting chemistry of these two types of carbon surfaces (p-bonding sites vs. reactive or functionalized sigma-bonding sites) provide another degree of freedom in synthesis to optimize solids for selective adsorption or electrochemistry. Pore structure control is achieved simultaneously by selection of template form, organic precursor, and infiltration solvent if any. This paper reviews the background studies of discotic molecular orientation ("surface anchoring") that provide the basis for systematic template selection. New lithographic techniques will also be presented for manufacturing two-component planar templates used for orientational micropatterning of discotic films. Finally, the most recent work will be presented on porous carbons made from a series of three-dimensional nanometric templates including aerogel, silica gel, and two controlled pore glass templates of 12 nm and 100 nm pore size. The structure and properties of the resulting nanoporous carbons will be described

and compared, and promising applications discussed.

#### 11:15 AM L6.10

**Spherical Mesoporous Carbon Particles from Aerosol-Assisted Mesoporous Silica Templates.** John Eric Hampsey, Zhiwang Wu, Qingyuan Hu, Jiebin Pang, Donghai Wang, Byron McCaughey and Yunfeng Lu; Department of Chemical Engineering, Tulane University, New Orleans, Louisiana.

Spherical mesoporous carbon particles have been synthesized using mesoporous silica particles as a template. The templates were synthesized using an aerosol-assisted self-assembly process. Briefly, starting with a precursor solution prepared by reacting tetraethoxysilane (TEOS), ethanol, water, HCl, and surfactant, the silica particles are prepared by passing the solution through an atomizer followed by evaporation induced self-assembly of the surfactant and silicate species into ordered mesostructures. After condensation of the silica and removal of the surfactant, mesoporous silica particles are formed. A sucrose solution was then infiltrated into the pores of the silica and converted into carbon by heating the samples to 900 degrees C under a nitrogen blanket. Finally, the silica was removed with a NaOH solution. The carbon particles are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS), nitrogen adsorption/desorption, thermal gravimetric analysis (TGA), and other techniques. These mesoporous carbon particles may have future applications as catalyst supports for fuel cells and as a filler in nanocomposite materials.

#### 11:30 AM L6.11

**Synthesis and Characterization of Mesoporous Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.** Shenmin Zhu<sup>1</sup>, M. Hibino<sup>1</sup>, Haoshen Zhou<sup>1</sup>, I. Honma<sup>1</sup> and Masaki Ichihara<sup>2</sup>; <sup>1</sup>Energy Materials Group, Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, Umezono 1-1-1, Tsukuba, Japan; <sup>2</sup>Material Design and Characterization Laboratory Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, Japan.

Alternative cathode materials for lithium batteries have been investigated widely to replace the expensive and oxidatively unstable LiCoO<sub>2</sub> after it was first commercialized by Sony Company. Among them, phosphates of iron are regarded as an ideal candidate for the low cost and environmental benign. Since then Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple-based materials have been investigated extensively. Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was first discovered by Goodenough in 1997 to be able to intercalate lithium ions into its structure, to generate about 2.8 V vs Li/Li<sup>+</sup> while maintaining excellent capacity, which can be used as the cathode material for rechargeable Li-ion batteries. However, two main obstacles have to be solved to improve electrochemical performance in these compounds: low diffusion rate and electronic conductivity. Usually, small particles were fabricated in order to enhance interface diffusion and obtain acceptable energy and power from the lithium cells. The mesoporous structure with relatively high surface area will benefit the cathode performance, for it facilitating the penetration of the liquid electrolyte into mesopores inside of electrodes and hence increase lithium diffusion rate. Here, we reported for the first time the synthesis of ordered hexagonal mesoporous Li<sub>3</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> employing cationic, cetyltrimethylammoniumchloride as the template. The obtained samples exhibit self-ordered mesoporous structure on their XRD spectra. The hexagonally ordered mesopores can be directly observed in the TEM images. The surface area was calculated to be 177 m<sup>2</sup>/g with an average pore size of 3.2 nm according to N<sub>2</sub> adsorption/desorption analysis.

#### 11:45 AM L6.12

**Highly Swollen Liquid Crystals as new reactors for the synthesis of nanomaterials.** Eric Prouzet<sup>2</sup>, Geetarani Surendran<sup>2,3</sup>, Miriam Tokumoto<sup>2</sup>, Eduardo Pena dos Santos<sup>2</sup>, Patricia Kooyman<sup>4</sup>, Hynd Remita<sup>3</sup> and Laurence Ramos<sup>1</sup>; <sup>1</sup>Groupe de dynamique des Phases Condensées (CNRS), Montpellier, France; <sup>2</sup>Institut Européen des Membranes (CNRS), Montpellier Cedex 5, France; <sup>3</sup>Laboratoire de Chimie Physique (CNRS), Orsay, France; <sup>4</sup>Centre for high Resolution TEM, Delft, Netherlands.

We present a general method to synthesize nanostructured materials within the aqueous or organic phase of highly Swollen Liquid Crystals (SLC) that exhibit hexagonal, cubic or lamellar symmetry. Various materials structured at the nanoscale can be prepared by different procedures. Rod-like nanoaggregates of metal nanoparticles are synthesized by chemical reduction in the aqueous part of the hexagonal mesophase, porous microrods of zirconia are obtained by crystallogenesis from hydrated zirconium oxychloride and polymer micro- and nano-fibers are obtained in the organic phase by photopolymerization or radiolysis. Hexagonal SLCs were first observed in the phase diagram of quaternary mixtures combining the anionic surfactant sodium dodecyl sulfate (SDS), an aqueous solution of inorganic salt (NaCl), cyclohexane as a hydrophobic swelling

solvent and pentanol-1 as a co-surfactant. They display at room temperature a direct hexagonal phase constituted of infinite nonpolar cylinders swelled by cyclohexane and stabilized by a monolayer of the SDS surfactant, arranged in a hexagonal array in water, and whose diameter ranges usually between 3 and 30 nm. If one wishes to use these mesophases as actual nanoreactors whose characteristics (nature of solvents, pH...) could be monitored as a function of the physico-chemical properties required for any desired synthesis, the concept of SLC had to be extended to a broader range of compositions than those reported previously. We demonstrated that this concept can be extended to the whole range of surfactants (nonionic, anionic, cationic) and in a wide range of pH (from -0.6 to 11). These SLC constitute a new general concept of nanoreactor that will be illustrated by the preparation of metal (Pt, Pd, Sn), oxide (ZrO<sub>2</sub>) or polymer (PDA) nanostructures whose shape is highly controlled by the geometry of the swollen mesophase.

SESSION L7: Templated and Self-Assembled Materials  
II  
Chair: James Watkins  
Wednesday Afternoon, December 3, 2003  
Room 304 (Hynes)

1:30 PM \*L7.1

#### **MRS MEDAL AWARD TALK PRESENTATION**

**Self-Assembly of Biologically Inspired Complex Functional Materials.** C. Jeffrey Brinker,<sup>1</sup> Department of Materials Chemistry, Sandia National Laboratory, Albuquerque, New Mexico;  
<sup>2</sup>Departments of Chemical and Nuclear Engineering and Chemistry, University of New Mexico, Albuquerque, New Mexico.

Nature combines hard and soft materials often in hierarchical architectures to get synergistic, optimized properties and combinations of properties with proven, complex functionalities. Emulating such natural material designs in robust engineering materials using efficient processing approaches represents a fundamental challenge to materials chemists. We are exploring chemically- and mechanically-based self-assembly strategies to create complex nanocomposites in thin film and particulate forms. This presentation will first review our progress on evaporation-induced silica/surfactant self-assembly to prepare porous thin film nanostructures of interest for membranes and low *K* dielectrics. I will then describe recent work where we use surfactant self-assembly to simultaneously organize hydrophilic and hydrophobic precursors into hybrid (organic/silica or metal/silica) nanocomposites that are optically or chemically polymerizable, patternable, or adjustable. For example, the co-self-assembly of amphiphilic photoacid generators with silica precursors results in photosensitive thin film mesophases in which the pore size, pore volume, surface area, and refractive index may be continuously varied over a range depending on the UV exposure time. Incorporation of switchable hydrogel or azobenzene moieties provides a means to create nanostructures exhibiting chemo-, thermo- or opto-mechanical actuation. Biocompatible self-assembly allows us to immobilize cells in a robust self-contained, self-sustaining environment of interest for stand-alone cell-based sensors. As a new direction, we have exploited mechanically-based self-assembly to create superhydrophobic, fractal silica surfaces mimicking those of the Lotus leaf and desert beetle. These surfaces are self-cleaning and fundamentally affect flow, making them of general interest for fluidic-based microsystems.

2:00 PM L7.2

**Cubic and Cubic Bicontinuous Mesophases From Designer Macromolecules.** Anurag Jain<sup>1</sup>, Byoung-Ki Cho<sup>1</sup>, Calos B.W. Garcia<sup>1</sup>, Gil E. Toombes<sup>2</sup>, Sol M. Gruner<sup>2</sup> and Ulrich B. Wiesner<sup>1</sup>;  
<sup>1</sup>Materials Science & Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Department of Physics, Cornell University, Ithaca, New York.

Block copolymers form a unique class of materials because of their ability to self-assemble into a variety of morphologies at the nanoscale. A particularly fascinating research area that has captivated researchers for quite some time is the synthesis and characterization of co-continuous nanostructures from block copolymers. These materials not only have unique structural and physical properties but the continuous nature of nanoscale channels opens avenues for applications in areas like catalysis, molecular separation, photonics, energy generation and storage or electronics. Extensive theoretical and experimental research has shown, however, that in classical block copolymers, energetics combined with space filling requirements put considerable constraints on the equilibrium mesophases that can be obtained. Indeed, the double gyroid mesophase has been the only bicontinuous phase that has been found to be stable in diblock copolymer systems in a highly restricted parameter space. Here we

demonstrate how novel synthesis concepts can be used to extend the range of accessible cubic and cubic bicontinuous mesophases in polymeric systems. Full characterization of these structures involving small angle x-ray scattering combined with transmission electron microscopy will be shown.

2:15 PM L7.3

**Replication of Ordered Organic Templates in Supercritical Fluids: A Novel Approach to the Preparation of Nanostructured Metal Oxide Films.** Rajaram Achut Pai and James J Watkins; Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Ordered nanostructured materials are of enormous interest for applications in photonics, sensors, catalysis, separations, microfluidics and as low dielectric constant films (low *k*) in microelectronics. The traditional approach to preparation of these materials involves the cooperative self-assembly of organic templates (including surfactants) and precursors in aqueous solution. Cooperative self-assembly has been remarkably successful for controlling the pore structure at the local length scale, but holds more limited promise for controlling long-range structure over the length scales of the device. We have developed a new technique for the preparation of nanostructured metal oxide films that involves phase-selective condensation of metal alkoxides in pre-formed structured organic templates diluted with supercritical carbon dioxide. By separation of the template formation and the metal oxide condensation steps, highly ordered structures realizable in organic materials can be fully replicated in metal oxide without loss of structural detail. For example, the film structure of block copolymer templates at the local and device levels can be achieved using established techniques prior to infusion of the inorganic phase. This approach also offers flexibility with regard to framework chemistry and the nature of the copolymer template, which can now be chosen independently without regard to compatibility in solution or concerns about disrupting the coordinated self-assembly process. The application of the technique to preparation of ordered mesostructured silicate/organosilicate films and their application are discussed.

2:30 PM L7.4

**Pore-Regularity Control in SBA-16 Type Mesoporous Silica Thin Films Synthesized with a Tri-Block Copolymer.**

Sajo P. Naik<sup>1,2</sup>, Shigehiro Yamakita<sup>1</sup>, Yukichi Sasaki<sup>3</sup>, Masaru Ogura<sup>1</sup> and Tatsuya Okubo<sup>1,2</sup>; <sup>1</sup>Department of Chemical Systems Engineering, The University of Tokyo, Tokyo, 7-3-1, Hongo, Bunkyo-Ku, 113-86, Japan; <sup>2</sup>PRESTO, TOKYO, Japan; <sup>3</sup>Material Research and Development Laboratory, Japan Fine Ceramics Center, 2-4-1, Mutsuno, Atsukata-ku, Nagoya, 456-8567, Japan.

Abstract Because of their potential for advanced applications in separation technologies, electronic and optical devices, mesoporous silica thin films have attracted much attention in recent years. Pore accessibility is one of the important factors in industrial applications, and since 3D SBA-16 type mesoporous silica thin films have accessible pores on the top surface, they are candidate materials for many industrial applications. In this work we have synthesized and characterized mesoporous silica thin films of SBA-16 type with F127, a non-ionic block copolymer. We demonstrate, for the first time, the usefulness of FE-SEM (field emission scanning electron microscopy) in direct observation of pore opening in mesoporous silica thin films. The effects of factors such as dip rate, composition of the sol and extent of TEOS hydrolysis on the pore regularity, and the stability of mesostructure were also investigated further. Based on these studies, we propose methods to optimize pore regularity and to produce a stable mesostructure. TEM (transmission electron microscopy) studies revealed that the film had a laminated-layered type of structure, clearly showing about 10 sub-layers, each of thickness ~ 5 nm. The size of the sub-layer observed was in agreement with the x-ray and N<sub>2</sub> adsorption-desorption measurements. The periodic ordered spaces in SBA-16 mesoporous films produced here were exploited for growing high quality single walled carbon nanotubes (SWNTs) 2 References 1. Naik et al., Chem. Mater. (communicated) 2. Murakami et al. (CPL, in press)

3:00 PM \*L7.5

**Macroporous Alkylene-Bridged Polysilsesquioxane Gels with Templated Nanopores.** Kazuki Nakanishi<sup>1,2</sup>, Yuki Kobayashi<sup>1</sup>, Takamitsu Yamato<sup>1</sup> and Kazuyuki Hirao<sup>1</sup>; <sup>1</sup>Material Chemistry, Kyoto University, Kyoto, Japan; <sup>2</sup>PRESTO, JST, Kawaguchi, Saitama, Japan.

Siloxane-based sol-gel systems accompanied by polymerization-induced phase separation are known to give well-defined co-continuous macroporous morphologies. In pure silica systems, when the phase separation is induced by the presence of surfactants that have supramolecular templating abilities, sharply-distributed mesopores are formed within the well-defined co-continuous gel skeletons. Similar types of phase separation are

observed also in organic-inorganic hybrid systems including those derived from alkyltrialkoxysilanes or bis(trialkoxysilyl)alkanes. Depending on the types of templating agents and siloxane networks, however, a wide variety of templating effects are observed. For example, cationic surfactants such as CTAB, which has successfully templated mesopores as well as induced the phase separation in pure silica system, could not induce the phase separation in bis(trimethoxysilyl)ethane-based systems. The EO-PO-EO type polyether block copolymers were able to induce phase separation in most organic-inorganic hybrid systems, while their templating strength were greatly affected by the local configuration of organic-containing parts in the siloxane-based gel networks. Poly(oxyethylene) alkyl ether was effectively used to template slit shaped mesopores in bis(trimethoxysilyl)hexane-based gels. These examples suggest the possibility of simultaneously controlling macro- and mesopores in polysilsesquioxane gels in general.

### 3:30 PM L7.6

**Synthesis of controllable mesostructured heteropoly oxometalate thin films with hierarchical structures by triblock copolymer templating.** Itaru Honma<sup>1</sup>, Hao Shen Zhou<sup>1</sup>, Yun Hui Suk<sup>2</sup> and Makoto Kuwabara<sup>2</sup>; <sup>1</sup>EEL, AIST, Tsukuba, Ibaraki, Japan; <sup>2</sup>Dept. of Materials Science, Univ. of Tokyo, Bunkyo-ku, Tokyo, Japan.

Mesostructured metal oxides, which can be prepared using surfactant-mediated synthesis method<sup>1-3</sup>, have attracted much attention due to their potential applications such as catalyst, sensor devices, and novel electrodes<sup>4-19</sup>, 28. Here we report a simple, reproducible, and versatile procedure for the synthesis mesostructured metal oxides thin films with hierarchical structure. We used 12-phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·#61655; nH<sub>2</sub>O; PWA) and other heteropoly oxometalates as raw materials which might promise applications involving catalyst, solid electrolytes and fuel cell due to their strong Brønsted acidity and special structural properties<sup>23-25</sup>. We also used amphiphilic triblock copolymers as structure-directing agents. Mesostructured metal oxide thin films have hexagonal or cubic structures with d100 spacing of 77-112 Å; The films also have cubic structure with d100 spacing of 23 Å; in the framework. We believe that the former structure are formed as a results of structure directing interactions between triblock copolymer and metal oxide cluster, while the latter structure are formed through crystal-like alternating ethylene oxide and metal oxide cluster as role of cation ion and anion ion, respectively. Calcined thin films remain their mesostructure with large surface area (160~180 m<sup>2</sup>g<sup>-1</sup>) and show interesting electrochemical properties.

### 3:45 PM L7.7

**Multi-Functional Responsive Particles Prepared by Aerosol-Assisted Self Assembly.** Yi Yang<sup>1</sup>, Xingmao Jiang<sup>1</sup>, J David Bullock<sup>1</sup>, Nanguo Liu<sup>1</sup> and C Jeffrey Brinker<sup>1,2</sup>; <sup>1</sup>Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, The University of New Mexico, Albuquerque, New Mexico; <sup>2</sup>Sandia National Laboratories, Albuquerque, New Mexico.

Evaporation-induced self-assembly of aerosol droplets can be used as a route to create mesoporous nanocomposite powders. Using the aerosol assisted self-assembly, different mesostructured cerium-, hydrogel-, or azobenzene-containing silica nanocomposite particles were prepared and their transport properties studied. Ce-containing silica nanocomposites exhibited core/shell structures (dense cerium core and hexagonal ordered silica shell). The special core/shell structure may benefit the controllable release of Ce from the composite particles, a property that is critical in applying CeCl<sub>3</sub> as one of the most promising corrosion inhibitors for protection of metal alloys. Hydrogel-containing silica nanocomposites exhibited hexagonal order or wormlike structure. Dye molecules were incorporated as indicators into the composite particles to monitor the transport property of the particles. Preliminary results showed the particles were capable of controlled release of the dye molecules, facilitated by the sensitivity of the hydrogels (PNIPAM or polymethacrylates) to changes in external stimuli such as temperature or pH. Pendant azobenzene-containing composites exhibited onion-skin like structures. These synthesized materials demonstrate light controllable transport properties due to optically induced *trans*- and *cis*- isomerization of azobenzene ligands.

### 4:00 PM L7.8

**Thin Film Of Silica Nanoparticles With Highly Ordered Pores By Wet Coating.** Hideshi Sasakura<sup>1</sup>, Shigeki Chujo<sup>1</sup>, Masahiro Fujita<sup>2</sup> and Yukio Yamaguchi<sup>2</sup>; <sup>1</sup>Japan Chemical Innovation Institute, Tokyo, Japan; <sup>2</sup>The University of Tokyo, Tokyo, Japan.

We describe simple and fast methods to obtain a thin film of silica nanoparticles with highly ordered pores. The thin film was fabricated in wide area, say 10cm<sup>2</sup> with high speed, say more than 1mm/s by employing both a spin coater and a capillary coater. This silica thin film is applicable to, for example, a scaffold for assembling particles,

an anti-reflection film and a cathode panel for a field emission display. The mixture of polystyrene latex (PSL) and silica nanoparticles was coated on a glass substrate. After that, the PSL particles were completely decomposed at a temperature of approximately 400 degree Celsius, and results in highly ordered pores. The pore size can be controlled by selecting the size of PSL particles in the range of 50-1700nm. The ordering of pores on the silica thin film was evaluated by Voronoi polygon analysis. The ratio of hexagon calculated as the quantity of hexagonal ordering was 98%. The average deviation of hexagon angles from 120 degree calculated as the quality of hexagonal ordering was only 1.5 degree. Therefore it is concluded that the pores are highly hexagonal ordered. We also discuss the effect of silica nanoparticles having the diameter of 5nm. PSL particles without silica particles were fabricated on glass substrate, and the ordering of PSL particles was compared with that of pores fabricated by decomposing PSL particles. The ordered domain size of the pore was much larger than that of the PSL. It is concluded that PLS particles with silica particles are highly ordered. The mechanism of ordering is mainly due to high mobility of PSL particles, which is caused by abundant collisions of silica nanoparticles having high particle energy due to Brownian motion. It is also due to weakening of the interaction between PLS particles and the substrate by silica nanoparticles. The mechanism will be discussed by using our original simulation model based on capillary force and DLVO force among particles with considering particle substrate interaction during drying. This work is supported by the New Energy and Industrial Technology Development Organization (NEDO)'s "Nanotechnology Materials Program - Nanotechnology Particle Project".

### 4:15 PM L7.9

**Optically Activated Mesostructured Titania Composites with Controlled Morphologies.** Michael H. Bartl<sup>1</sup> and Galen D. Stucky<sup>1,2</sup>; <sup>1</sup>Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Materials Department, University of California at Santa Barbara, Santa Barbara, California.

In the last several years mesostructured nanocrystalline titania has become a particularly interesting material for its potential applications in photovoltaics, batteries, photocatalysis, and photonics. With respect to shape control and patterning, however, the morphologies reported so far for mesostructured titania, in contrast to mesostructured silica, are restricted to powders and thin films. Here, we present a sol-gel based block copolymer templating synthesis route utilizing a newly developed, highly stable titania precursor solution, which enables patterning of mesostructured titania composites into a variety of different morphologies, such as optically transparent and crack-free films, coatings, fibers, and micron-scaled structures. Furthermore, we show that our sol-gel self-assembly synthesis and patterning approach allows for activation of these mesostructured titania composites by either incorporation of optically active species (e.g., dyes, ions) into the precursor solution or by in-situ synthesis of semiconductor nanocrystallites within the mesostructure. Examples of different activated mesostructured titania composite materials are demonstrated together with their optical and electro-optical properties.

### 4:30 PM L7.10

**Metathesis Depolymerization for Removable Surfactant Templates in Materials Synthesis.** Timothy M Long<sup>1</sup>, Blake A Simmons<sup>2</sup>, James R McElhanon<sup>2</sup>, David R Wheeler<sup>3</sup>, Kamyar Rahimian<sup>4</sup>, Douglas A Loy<sup>5</sup> and Gregory M Jamison<sup>1</sup>; <sup>1</sup>Chemical Synthesis and Nanomaterials, Sandia National Labs, Albuquerque, New Mexico; <sup>2</sup>Materials Chemistry, Sandia National Labs, Livermore, California; <sup>3</sup>Micro-Total-Analytical Systems, Sandia National Labs, Albuquerque, New Mexico; <sup>4</sup>Microsystems Materials, Tribology and Technologies, Sandia National Labs, Albuquerque, New Mexico; <sup>5</sup>Polymers and Coatings, Los Alamos National Labs, Los Alamos, New Mexico.

Current methodologies for the production of meso- and nanoporous materials include the use of a surfactant to produce a self-assembled template around which the material is formed. However, post-production surfactant removal often requires centrifugation, calcination, and/or solvent washing which can damage the initially formed material architecture(s). Surfactants that can be disassembled into easily removable fragments following material preparation would minimize processing damage to the material structure, facilitating formation of templated hybrid architectures. Herein, we will describe the design and synthesis of a novel class of surfactants with regularly spaced unsaturation in their hydrocarbon tails that allow for their facile decomposition via catalytic metathesis depolymerization, to produce relatively volatile cycloalkenes. Evidence will be presented illustrating surfactant organization in oil/water mixtures as well as surfactant decomposition upon exposure to ruthenium-based catalysts. Further, demonstration of the use of these surfactants for the templating of porous organic and inorganic materials will be illustrated.

4:45 PM L7.11

**Effects of Deep-UV Exposure on Nanocomposite Silica Thin Films: Mechanism and Photochemical Pattern Generation.** Andrew M. Dattelbaum<sup>1</sup>, Gary A. Baker<sup>1</sup>, Meri L. Amweg<sup>2,1</sup>, Chanel E. Yee<sup>2</sup>, James H. Werner<sup>1</sup>, Hsing-Lin Wang<sup>1</sup>, Atul N. Parikh<sup>2</sup> and Andrew P. Shreve<sup>1</sup>; <sup>1</sup>Bioscience Division, Los Alamos National Lab, Los Alamos, New Mexico; <sup>2</sup>Department of Applied Science, University of California, Davis, California.

In recent years, methods have been developed for the generation of complex organic/inorganic nanocomposite materials through organic templating of inorganic structures. One approach involves preparation of composite materials by an evaporation induced self-assembly process involving organization of organic surfactants and formation of inorganic silica from soluble precursors. Recently, we have shown that deep-UV light (185-254nm) is efficient at removing the surfactant microphase for a routine production of well-ordered mesoporous silica thin films. Here we probe the evolution of structural and morphological characteristics of surfactant-templated thin film silica mesophases as a function of deep-UV exposure using a combined application of FTIR, single wavelength ellipsometry, and X-ray diffraction. Further, we show that the use of this UV-induced photochemical process together with a physical mask can lead to patterned mesoporous regions in a mesostructured film. This process is shown to generate patterned, sensing materials when applied to nanocomposite films functionalized by fluorescent species sensitive to changes in the vapor or liquid phase. Chemical treatment of patterned mesostructured/mesoporous films is also shown to selectively remove the mesostructured regions, leading to patterned mesoporous structures. Such tunability in the processing under near room-temperature conditions allows for spatial control and patterning of function related to optical properties, topology, porosity, hydrophobicity, and structural morphology of the mesoscopic thin film material on a wide range of substrates.

SESSION L8: Poster Session II

Chairs: Sridhar Komarneni, John Parker and James Watkins  
Wednesday Evening, December 3, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

#### L8.1

**Carbon-Based Nanocomposite Materials For Cold Cathode Sources.** Alexander V. Karabutov<sup>1</sup>, Viktor G. Raichenko<sup>1</sup> and Sergey K. Gordeev<sup>2</sup>; <sup>1</sup>Natural Science Center, General Physics Institute, Moscow, Russian Federation; <sup>2</sup>Central Research Institute of Materials, St-Petersburg, Russian Federation.

Some diamond and related structures such as CVD diamond thin films, DLC film, diamond nanopowders, carbon nanotubes, etc. can show outstanding low-field electron emission with threshold fields of 1-3 V/mm. Numerous microscopic studies of the emission centers show that the emission is often associated with diamond grain boundaries and diamond/sp<sup>2</sup>-bonded carbon interfaces. However, a role of the diamond phase (e. g., the negative electron affinity (NEA) of diamond) for the emission is still not clear enough. Here we call in question an importance of the diamond for effective carbon emitters and we design novel type of bulk material for effective cold cathode applications. We have produced a set of nanocomposite samples in which different insulating particles were used such as nanopowders of silicon oxide, boron nitride in cubic and hexagonal forms, as well as nanodiamond. The samples of non-diamond/pyrocarbon and diamond/pyrocarbon nanocomposite materials were prepared by the same technique, in which the matrix is pressed from nanoparticles and then saturated with pyrocarbon during a CVD process. Besides, nanopores exist in the samples that also play a role of "dielectric inclusions". The thickness of pyrocarbon shells covering the dielectric particles can be controlled in a wide range during the CVD process (by changing of a mass ratio of the phases). Each kind of the samples was made at a set of different growth conditions to study an influence of the sample structure on the field emission and to find an optimal structure for efficient emission and cold cathode applications. The best samples of the nanocomposites show excellent field emission properties with threshold fields of as low as 0.5-1 V/mm, good surface uniformity and long-term stability. It was found that for the best samples it does not matter, which type of dielectric material is used as a nanopowder. Nevertheless, the emission properties strongly depend on the samples structure, and for non-optimal one, samples showed relatively poor emission. The structure of the composites was studied using micro-Raman spectroscopy and SEM. Special STM study of emission intensity, work function, electrical conductivity, and topography maps of the emission centers was made to understand the nature of the emission in the materials. A mechanism of the emission

is supposed basing on quantum properties of nanostructured carbon forms including reduction of the tunneling barrier on insulator/graphite interfaces due to quantum well effects for thin (two-dimensional) carbon nanolayers covering the dielectric particles. The mechanism does not suggest taking into account specific diamond properties (NEA) and it could be suitable for wide range of nanostructured carbon objects.

#### L8.2

**Size Effect Characterization for Nanostructured Material in Nanoindentation Test.** Yueguang Wei, Ying Du, Siqi Shu and Chen Zhu; LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing, China.

Nanostructured materials, such as the nanocrystalline material, the multi-layer thin film systems at nano-scale, etc., manifest the advantage mechanical behaviors. Comparing with the conventional material, a nanostructured material has the higher Young's modulus, higher yield strength and higher hardness, etc. These advantage properties can be measured by using the nanoindentation test method. On the other hand, the experimental measurements show that the behavior of the nanostructured material strongly depends on the specimen sizes. The difference of the behaviors at the different specimen sizes is referred to as the size effect. In the present research, the several nanostructured cell models are presented and developed to characterize the geometrical and physical behaviors of the nanostructured material. The size effect and the geometrical effect, come from the effect of the small-scale description and the effect of the representative size of the nanostructured cell, are analyzed by adopting a length-scale mechanics theory—strain gradient plasticity theory. Simultaneously, the geometrically necessary dislocation density concept is used in the analysis to obtain the size effect characterization. A correlation between strain gradient and the geometrical necessary dislocation density is obtained. Furthermore, for comparison, the conventional mechanics theory (elastic-plastic theory) is also adopted to analyze the nanostructured cell models and further the size effect, however, the trial is not success. In the present research, the effect of the indenter tip curvature radius on the size effect is also considered and discussed. The above analysis results about the size effect of the nanostructured material will be used to compare with the nanoindentation experimental results for a nanocrystalline Al-alloy material.

#### L8.3

**Synthesis and Field Emission Properties of Novel Carbon Nanoflakes.** Jianjun Wang<sup>1</sup>, Mingyao Zhu<sup>1</sup>, Xin Zhao<sup>1</sup>, Ron Outlaw<sup>1</sup>, Dennis Manos<sup>1</sup>, Brian Holloway<sup>1</sup>, Chinh Park<sup>2</sup>, Tim Anderson<sup>2</sup> and Victor Mammana<sup>3</sup>; <sup>1</sup>Department of Applied Science, The College of William and Mary, Williamsburg, Virginia; <sup>2</sup>Department of Chemical Engineering, University of Florida, Gainesville, Florida; <sup>3</sup>International Technology Center, Raleigh, North Carolina.

Nanometer edged carbon structures, carbon nanoflakes (CNFs), have been synthesized by radio-frequency (RF) plasma enhanced chemical vapor deposition (CVD) system on 50~150 nm diameter nickel arrays. The Ni dot arrays are patterned using a nanosphere lithography technique capable of creating arrays of regularly spaced nanometer diameter structures of Ni. Different gas systems are involved in generating CNFs, such as CH<sub>4</sub>-H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>-H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>-NH<sub>3</sub>. Typical deposition conditions are: substrate temperature of 680°C, overall gas flow rate of 10 sccm, chamber pressure of 25~120 mTorr, and hydrocarbon concentration in the range of 5~80 %. Scanning electron microscopy shows CNFs preferentially growing on the Ni dots with the irregular carbon flakes standing perpendicular to the substrate. The flake edge widths are ~10 nm and inter-flake spacing on a given Ni dot are on the order of 15~100 nm. Experiments show that the density, height and inter-spacing of the flakes are controllable by varying patterning and deposition parameters. Furthermore, the structures show no degradation or vibration under small spot SEM imaging, indicating good thermal stability. Raman spectra of this structure show a typical carbon feature with D and G peaks at 1350 and 1580 cm<sup>-1</sup>, respectively. Intensity ratio of these two peaks, I(D)/I(G), varies with hydrocarbon concentration, indicating a change in crystallinity of the CNFs based on deposition conditions and feedgas composition. The work functions determined by Kelvin probe measurement are about 4.3 eV, which are near that of pure graphite. Preliminary results of field emission testing, including field emission spectroscopy, I-E curves, Fowler-Nordheim plots and stability curves, indicate that this structure could act as a conductive, robust, edge emitter.

#### L8.4

**Preparation Of Fe-Pt Nanowires Through Anodic Oxidation Of Sputtered Aluminum On Glass Surface.** Satoru Inoue, Song-Zhu Chu, Kenji Wada and Yasushi Kanke; Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba,

Ibaraki, Japan.

New process for the preparation of Fe-Pt nanowires has been developed through anodic oxidation and electro deposition technique. Aluminum thin film sputtered on ITO thin film on a glass surface was decomposed into alumina by anodic oxidation technique. The anodic alumina layer possessed nanometer size pore array standing on the glass surface. The barrier layer at the bottom of the nanopores was removed by acid etching to attain DC field smooth electro deposition. Fe-Pt components were introduced into nanopores of the anodic alumina by electro deposition. The magnetization of the Fe-Pt nanowires was investigated. The magnetization perpendicular to the glass surface was very strong and the in-plane magnetization was very small, indicating that the magnetic Fe-Pt nanowires could be potentially applied to ultra high density magnetic recording. The density of the nanowires was estimated to be about 1Tbits /inch<sup>2</sup>.

**L8.5**  
**Nanocomposites Prepared by Laser Ablation of Microparticles (LAM) and Subsequent Thin Film Deposition.** Weijie Wang, Daniel T. O'Brien, Jonghoon Baek, Michael F. Becker, John W. Keto and Desiderio Kovar; Texas Materials Institute, University of Texas at Austin, Austin, Texas.

We have developed a system that allows nanoparticles produced by Laser Ablation of Microparticle aerosols (LAM) to be incorporated into thin films. This system separates nanoparticle (NP) formation from thin film growth using a multi-chamber UHV system, allowing individual control of both processes. In this paper, we introduce the features of the system, including an innovative electrostatic NP collection cell that allows precise control of NP size. The electrostatic cell is essentially an electrostatic aerosol mobility analyzer, where the NP charge is supplied by the LAM process. We report results for GaN NP embedded in AlN films produced by pulsed laser deposition (PLD) using this system. In all of these studies, c-plane-oriented sapphire was used as the substrate. Results indicated that the size of the GaN NP were strongly dependent on the voltage applied to the electrostatic cell. Within the voltage range studied (0 -1000V), the NP mean size was controlled from 5 nm to 60 nm. The structure and optical transmittance of PLD AlN films deposited without NP was strongly dependent on substrate temperature (room temperature to 900 °C) and ambient condition (vacuum or nitrogen gas) during the deposition. Adding nitrogen and increasing the substrate temperature improved the stoichiometric composition of the film and also its optical transmittance. Based on the optimum conditions for GaN nanoparticle collection and AlN thin film deposition, nanocomposites of GaN/AlN were prepared, and their linear and nonlinear optical properties have been characterized. \* This material is based in part upon work supported by the Texas Advanced Technology Program under Grant No. 003658-0239-2001 and an NSF GOALI under Grant No. CTS-9978926.

**L8.6**  
**In-situ Observation of Formation Processes of Anodic Porous Alumina on a Si Substrate Using Infrared Absorption Spectroscopy.** Yasuo Kimura<sup>1,2</sup>, Hirokazu Shiraki<sup>1</sup>, Hisao Ishii<sup>1,2</sup>, Sachiko Ono<sup>3</sup>, Kingo Itaya<sup>2,4</sup> and Michio Niwano<sup>1,2</sup>; <sup>1</sup>Research Institute of Electrical Communication, Tohoku University, Sendai, Japan; <sup>2</sup>CREST, Japan Science and Technology Corporation, Sendai, Japan; <sup>3</sup>Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, Tokyo, Japan; <sup>4</sup>Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, Japan.

Recently, nanodevices utilizing quantum effects are widely studied. It is necessary to form ordered nanostructures on semiconductors for fabricating and integrating nanodevices with uniform properties. In particular, it is important to fabricate nanodevices on a silicon (Si) substrate in terms of hybridization with a traditional silicon technology such as a complementary metal-oxide-semiconductor (CMOS) technology. Electrochemical etching technique is one of methods of forming nanostructures. Porous alumina, which is formed by anodizing aluminum in an acid solution, is the most famous because highly ordered nano-hole arrays are self-organized on an aluminum (Al) substrate. In general, an Al layer of about 50 μm in thickness is wasted for electrochemical polish and growth of deep pores, which are necessary for fabricating highly ordered nano-hole arrays of porous alumina. However, it is difficult to prepare such a thick Al layer on a Si substrate. Thus, it is important to clarify formation processes of porous alumina to fabricate self-organized ordered nano-hole arrays from a thin Al film deposited on a Si substrate. In this study, we investigated formation processes of porous alumina on a Si substrate using infrared absorption spectroscopy in the multiple reflection geometry (MIR-IRAS). In particular, we focused on anodization near the interface between an Al film and a Si substrate. We observed a drastic increase in the peak intensity due to an oxalic acid solution, which was used as an electrolyte,

simultaneously with a decrease in anodic current density. The decrease of anodic current density indicates that pores in the anodic alumina membrane reached the surface of Si substrate and that Al was expended, which is consistent with the spectral changes. This result suggests that MIR-IRAS is useful to clarification of anodization processes of Al.

**L8.7**  
**Synthesis of Porous Ceramics Through Directional Solidification and Freeze-Drying.** Predrag Kisa, Patrick J Fisher, Al M Olszewski, Nicholas G Eror and Ian Nettleship; University Of Pittsburgh, Pittsburgh, Pennsylvania.

This study investigates microstructural characteristics of the directionally solidified freeze-dried silica sol. The porous structures were formed by depositing silica sol on Silicon (100) single crystals, afterwards deposited sol was solidified on the copper block immersed in liquid nitrogen and subsequently freeze-dried. Freeze-drying removal of ice crystals created three-dimensional pore channels ranging 3-10 micrometers in diameter aggregated in grain like colonies 50-100 micrometers in diameter. Pore size, spacing, colonies size and microstructure is investigated using Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) while the structure of amorphous SiO<sub>2</sub> is characterized by X-ray Diffraction (XRD). The microstructure results are compared and contrasted with silica aerogel obtained through conventional processing using supercritical CO<sub>2</sub>.

**L8.8**  
**The Synthesis of Fe<sub>2</sub>O<sub>3</sub> Nanoparticles in MgO - Al<sub>2</sub>O<sub>3</sub> Matrix from Layered Double Hydroxides.** Maxim Pavlovich Nikiforov<sup>2,1</sup>, Yury D Tretyakov<sup>1</sup>, Alexey V Lukashin<sup>1</sup>, Marina V Chernisheva<sup>1</sup>, Andre A Eliseev<sup>1</sup>, Yury V Maksimov<sup>3</sup> and Igor Petrovich Suzdalev<sup>3</sup>; <sup>1</sup>Materials Science, Moscow State University, Moscow, Russian Federation; <sup>2</sup>Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>3</sup>n/a, Semenov Institute of Chemical Physics, Moscow, Russian Federation.

In the present work, the chemical modification of anion-substituted layered double hydroxides (LDH) was used for the preparation of oxide nanostructured materials. The method is based on chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and the possibility to prepare nanostructures directly in the matrix. Chemical modification of LDHs intercalated with metal complex is a promising way for synthesis of iron oxide nanoparticles fixated in the matrix. During chemical reactions of anions in the interlayer space of LDHs, reaction zone is spatially constrained by the hydroxide layers, giving rise to the conditions similar to those in 2D nanoreactors, such as Langmuir-Blodgett films and self-assembling monolayers. Mg-Al LDH were prepared in carbonate form by co-precipitation technique. Intercalation of FeEDTA was performed using the ability of annealed Mg-Al LDH to trap anions from water solution. It was found that reduction of intercalated LDH in hydrogen (at 1000°C) followed by oxidation in air results in the formation of iron oxide nanoparticles. The role of oxidation temperature on the phase composition of nanocomposites was investigated. It was found that annealing at 350°C gives nanocomposite of α-Fe<sub>2</sub>O<sub>3</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> in MgO-Al<sub>2</sub>O<sub>3</sub> matrix and increase of the annealing temperature to 600°C leads to the formation of MgFe<sub>2</sub>O<sub>4</sub> particles for samples with overall iron content 13 mol. %. Since gamma iron oxide is promising magnetic material, the phase composition of nanocomposites annealed at 350°C versus iron loading value was investigated. The content of γ-Fe<sub>2</sub>O<sub>3</sub> decrease with the increase of iron loading achieving the maximum value of 56% for sample with overall iron content 25 mol. %. Quenching in air of the samples reduced at 1000°C was performed to increase γ-Fe<sub>2</sub>O<sub>3</sub> content, but no significant increase was observed (the maximum γ-Fe<sub>2</sub>O<sub>3</sub> content was 60% for the sample with overall iron content 25 mol. %). In order to study the influence of LDH preparation technique on phase composition of nanocomposites direct co-precipitation of Mg-Al LDH in FeEDTA form was used. It was observed that reduction in H<sub>2</sub> flow followed by oxidation in air at 350°C leads to the formation of the mixture of α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles in oxide matrix. The maximum content of Fe<sub>3</sub>O<sub>4</sub> is 44 % for sample with overall iron content 25 %. All nanocomposites were characterized by XRD, TEM and Mossbauer spectroscopy. This work is supported by INTAS (01-204).

**L8.9**  
**Controlling Hierarchical Nanostructures and Optical Properties of Cadmium Chalcogenide Semiconductor Thin Films.** Donghai Wang, Aziz Albassam, Jiebin Pang, John Eric Hampsey, Bryron Francis McCaughey and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanostructured thin films consist of cadmium chalcogenide (CdS, CdSe, CdTe) nanowires or nanomeshes have been synthesized through electrodeposition using mesoporous silica as template. The

nanostructured cadmium chalcogenide thin films have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-Vis spectroscopy, and other techniques. Our results indicate that it is possible to tune the hierarchical structures and optical properties of cadmium chalcogenide thin films using templates with controlled pore structure. For example, diameter of the nanowires can be controlled by the pore diameter of the templates; while mesostructure of the nanowires or nanomeshes can be controlled by the template mesostructure. Optical and band-gap properties of these nanostructured semiconductor thin films can be efficiently tuned by controlling the pore structure of templates. This provides a new fabricating technique to synthesize nanostructured semiconductor thin films for optical host, photovoltaics, sensor and other applications.

### **L8.10**

#### **Effects of DC and AC Magnetic Fields on Grain Growth in Electrodeposited Nanocrystalline Nickel.** Takashi Matsuzaki<sup>1</sup>,

Takehisa Yamada<sup>1</sup>, Kotaro Juami<sup>1</sup>, Sadahiro Tsurekawa<sup>1</sup>, Tadao Watanabe<sup>1</sup> and Gino Palumbo<sup>2</sup>; <sup>1</sup>Nanomechanics, Tohoku University, Sendai, Japan; <sup>2</sup>Integran Technologies, Toront, Ontario, Canada.

Nanocrystalline materials are expected to use for micromachines in recent years. The smaller the size of machines, the more important microstructural homogeneity becomes. In particular, grain boundary microstructure like grain boundary character distribution may govern bulk properties in nanocrystalline materials because of a higher density of grain boundaries. Nanocrystalline materials are often prone to severe heterogeneity in microstructure owing to the abnormal grain growth, which may limit their attractive properties. Recently it has been found that a magnetic field can affect some metallurgical phenomena. One of the authors (T.W.) reported that abnormal grain growth in Fe-Co alloy could be suppressed by application of a magnetic field. The purpose of this work is therefore to study the effects of DC and AC magnetic fields on grain growth in nanocrystalline materials. Nano-Ni sheets of 99.9% purity was produced by the electrodeposition technique. The initial average grain size was 40nm. The annealing were conducted at 573K(0.33Tm, ferromagnetic temp.) and 693K(0.4Tm, paramagnetic temp.) in a vacuum of 5x10<sup>-3</sup> Pa for 2min -50h with a direct current (DC) magnetic field up to 6T or an alternating current (AC) magnetic field of 0.5T with 50Hz. The direction of applied magnetic fields were perpendicular and parallel to the surface of specimens. The evolution of grain boundary microstructure was examined using a HITACHI S-4200 FE-SEM equipped with TSL OIM system. It was found that rapid grain growth occurred at 573K for 2 min and that a DC magnetic field enhanced the rate of grain growth at the early stage of annealing. After the rapid grain growth, further grain growth scarcely occurred in a DC magnetic field, whereas the grain growth successively occurred during non-magnetic annealing. After 10h of annealing at 693K, the late stage of abnormal grain growth happened, where a DC magnetic field also increased the rate of grain growth in spite that the annealing was carried out at a paramagnetic temperature. Of particular importance is the observation that a magnetic field enhanced grain growth could produce a very uniform grain boundary microstructure after the rapid grain growth irrespective of whether DC or AC magnetic field was applied.

### **L8.11**

#### **Synthesys and Characterization of Nanocrystalline Silicon Films Prepared By PECVD.** Katerina Vydata and Viktor

Vikulov; radiophysics, Kiev national university, Kiev, Ukraine.

Nanocrystalline silicon films (nc-Si) with different thicknesses are deposited by plasma-enhanced chemical vapor deposition (PECVD). The nanocrystals formation is confirmed using X-ray diffraction method (XRD). The average size of nanocrystals is estimated to be 4.8 nm. XRD analysis on nc-Si/Silicon substrate showed growth oriented along (004) plane nanocrystals system. The structural-chemical properties are observed by Fourier Transform Infrared spectroscopy (FTIR). Atomic force microscopy (AFM) imaging demonstrates the developed surface of deposited films, which is column-like. The observed photoluminescence at room temperature depends of film thickness.

### **L8.12**

#### **Synthesis of ultrafine oxide powders by**

**hydrothermal-ultrasonic method.** Pavel Meskin<sup>1</sup>, Alexander Burukhin<sup>1</sup>, Yury Kolenko<sup>1</sup>, Alexander Baranchikov<sup>2</sup>, Bulat Churagulov<sup>1</sup> and Nikolai Oleynikov<sup>1,2</sup>; <sup>1</sup>Department of Chemistry, Moscow State University, Moscow, Russian Federation; <sup>2</sup>Institute of General and Inorganic Chemistry, Moscow, Russian Federation.

At the present work the development of a new method of highly dispersed oxide powders preparation has been carried out. This technique allows to combine the hydrothermal treatment and the acoustic cavitation appearing in the liquid medium under action of

powerful ultrasound. Hydrothermal-ultrasonic treatment was carried out under the following conditions: T= 423 - 523 K, t = 10 min - 3 h and frequency of ultrasound waves 21.5 kHz. The control experiments without ultrasound were performed simultaneously with synthesis in an ultrasonic field. The products were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM). The specific surface area was determined by the BET method. The use of ultrasound for the high-temperature hydrolysis of aqueous solution of cobalt (II) nitrate, followed by the formation of Co<sub>3</sub>O<sub>4</sub>, has allowed to considerably increase the conversion degree and to achieve the smaller particle size: 60-70 nm (with ultrasound) contrary to 600-650 nm (without ultrasound). It is important that the Co<sub>3</sub>O<sub>4</sub> samples obtained by hydrothermal-ultrasonic synthesis are characterized by mesoporous structure. Ultrasonic treatment for the hydrothermal processing of amorphous gels of zirconil and titanil hydroxides promotes the substantial growth of the rate of crystallization process. In results powders of zirconia and titania with the particle size 4-17 nm were obtained. The use of ultrasonic treatment for the hydrothermal processing of amorphous gel of zirconil and 0.3M aqueous solution H<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> leads to the increase in the fraction of thermodynamic stable phases in the products of synthesis. In the case of hydrothermal synthesis of ferrites with spinel structure (NiFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, Ni<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>) the ultrasonic treatment results in increasing the size of crystallites of the synthesis product and more narrow particle size distribution.

### **L8.13**

#### **Separation of Copper and Lead using Selective Ordered**

**Mesoporous Silica Adsorbents.** Louis Koon Fung Lam, King Lun Yeung and Gordon McKay; Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Ordered mesoporous silica (OMS) belongs to an important class of inorganic materials. The ordered mesoporous silica with its enormous surface area, uniform pore system and tunable pore chemistry, is an excellent material for adsorbents. The cylindrical pore structure and high degrees of pore symmetry found in ordered mesoporous silica make it an ideal system for testing new and existing adsorption and diffusion models. The simple pore geometry allows for easier mathematical description and the amorphous pore wall is a good approximation of an ideal Langmuir surface. The width of the pore channel restricts the size and shape of the molecules that can enter and leave the pores. This gives rise to molecular sieving effects that have many beneficial applications in separation. The chemical environment within the pore channel can be manipulated to influence the adsorption and transport properties of the diffusing species resulting in many unique separation properties. The ability to introduce well-defined surface chemical groups onto the pore wall is invaluable for developing an accurate model for surfaces with multiple adsorption sites. This provides an excellent opportunity for studying site interaction and synergism. The separation of Cu<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solution by selective adsorption using chemically modified MCM-41 was investigated. Unmodified MCM-41 was a poor adsorbent for copper and lead, but grafting chemical moieties such as amino, carboxyl and thiol imparted the MCM-41 with different adsorption affinities for copper and lead. OMS-NH<sub>2</sub> displayed large adsorption capacity for both metal ions and had higher affinity for copper. Copper was selectively removed from a copper-lead mixture using OMS-NH<sub>2</sub> adsorbents. Single component adsorption isotherms for different copper salts were also obtained. The results suggested that copper adsorption on OMS-NH<sub>2</sub> is strongly affected by the nature of the counterion. OMS-COOH displayed low adsorption capacity for the metals, despite its reported role in metal adsorption in carbon-based adsorbents. OMS-SH displayed high selectivity for Pb over copper and can selectively adsorb lead from the Pb-Cu mixtures. However, the presence of copper can inhibit the adsorption of lead resulting in lower adsorption capacity for mixture compared to the single component experiments.

### **L8.14**

**Strongly Photonic Macroporous TiO<sub>2</sub> Network.** Junko Konishi, Koji Fujita, Kazuki Nakanishi and Kazuyuki Hirao; Material Chemistry, Kyoto University, Kyoto, Japan.

Complex dielectrics systems interact strongly with light when the dielectric constant varies on a length scale of the order of the wavelength of light. Such materials have an index of refraction that can be either periodic or random in space, showing fascinating fundamental phenomena, such as light localization. Recently, the field of such photonic materials has undergone a spectacular growth due to wide applications that they have: efficient light emitting diodes, low-threshold lasers, microcavities, waveguides, and fast optical switches. To attain light localization, i.e., inhibition of light propagation due to interference, in random photonic materials, light should be elastically scattered, meaning that light absorption must be

negligible. Also, the material should be extremely strongly scattering. The scattering strength, or photonic strength, is largest for large relative variations in refractive index on the length scale of wavelength. So far, most studies on random photonic materials have focused on fine particles such as powders and colloidal suspensions, and the scattering properties have been controlled by changing the density and size of particles. However, monolithic structures are favored rather than fine particles for strict structural control. In this context, pore formation derived via a sol-gel method has emerged as a very promising technique for tailoring the photonic strength. The macroporous morphologies can be obtained by inducing the phase separation parallel to the sol-gel transition. Based on this concept, Nakanishi *et al.* found that monolithic macroporous silica gels with controlled pore structure have been successfully prepared from systems containing silicon alkoxide. Rutile-type titania has a large refractive index of  $\sim 2.8$  and very low absorption in the visible region. Hence, strongly scattering and weakly absorbing media are realized for the visible light, and localization effects are anticipated. In spite of this advantage, few works have been performed on porous titania because the kinetics of hydrolysis and polycondensation in the system containing titanium alkoxide is too fast to control the reaction, compared to that in the system started with silicon alkoxide. Here, we present successful preparation of titania gels with three-dimensionally interconnected macroporous pore structures using colloidal titania as the starting material, instead of using titanium alkoxide. After the heat treatment of titania gels at 1000°C, the crystal structure of skeleton is transformed from anatase into rutile. In addition, the macroporous network is maintained even after the heat treatment. We show that the macroporous rutile-type titania is very strongly scattering medium for visible light. Besides photonic applications, the macroporous titania with large surface area due to the interconnected pore structure are widely applicable to electrode materials, gas sensors, and chromatography.

#### **L8.15**

**Field Emission Properties of Vertically-Aligned Carbon Nanotube Films and Zinc Oxide Nanowire Films.** Sung-Ho Jo<sup>1</sup>, Y Tu<sup>2</sup>, J Y Lao<sup>1</sup>, Z P Huang<sup>3</sup>, D L Carnahan<sup>3</sup>, D Z Wang<sup>1</sup>, Z F Ren<sup>1</sup>, R A Farrer<sup>2</sup>, T Baldacchini<sup>2</sup> and J T Fourkas<sup>2</sup>; <sup>1</sup>Department of Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Department of Chemistry, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>NanoLab, Inc., Brighton, Massachusetts.

The length and the spacing of carbon nanotubes are varied independently to investigate their effect on the field emission characteristics of the vertically-aligned carbon nanotube films grown by plasma-enhanced hot filament chemical vapor deposition. It is shown that the operating electric field can be reduced by increasing the length and the spacing of carbon nanotubes. It is also shown that the same screening effect also affects the field emission from zinc oxide nanowire films grown by the thermal evaporation/condensation method. By decreasing the areal density of zinc oxide nanowires, field emission characteristics comparable to vertically-aligned carbon nanotube films can be obtained. In addition, the aging properties of field emission current from the vertically-aligned carbon nanotube films and the zinc oxide nanowire films are investigated. Two types of distinctive aging properties of field emission current are observed from the vertically-aligned carbon nanotube films.

#### **L8.16**

**Hydrothermal Synthesis of Sodium Manganese Oxide Octahedral Molecular Sieve (OMS) Nanomaterials with a 2 x 3 Tunnel Structure.** Xiongfei Shen<sup>1</sup>, Yunshuang Ding<sup>1</sup>, Jia Liu<sup>1</sup>, Jun Cai<sup>2</sup>, Francis S. Galasso<sup>2</sup> and Steven L. Suib<sup>2,1</sup>; <sup>1</sup>Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Sodium manganese oxide OMS nanomaterials with a 2x3 tunnel structure have been synthesized using Na<sup>+</sup> as a cation template. Na-Birnessite precursors were first prepared from a redox reaction of MnCl<sub>2</sub> and KMnO<sub>4</sub>, followed by a hydrothermal treatment at 175-240 °C for 2 days. HRSEM showed the nanofibrous morphology of the synthesized 2x3 manganese oxide OMS materials. The 2x3 manganese oxide has thermo-stability up to 500 °C. At temperatures higher than 500 °C, the 2x3 tunnel collapses because of a loss of lattice oxygen. The materials have a BET surface area of about 25 cm<sup>2</sup>/g. Pore size distribution measurements by the BJH method showed that the 2x3 manganese oxide is a mesoporous material. The average pore size is about 23 nm and the pore volume is about 0.1 cm<sup>3</sup>/g. XRD and HRTEM were also used to characterize the synthesized 2x3 manganese oxide.

#### **L8.17**

**Synthesis and characterization of nanostructured magnetic particles.** Dhananjay Kumar, Mechanical and Chemical Engineering, North Carolina A & T State University, Greensboro, North Carolina.

A novel thin film processing method is reported based on pulsed laser deposition to process nanocrystalline materials with accurate size and interface control with improved magnetic properties. Using this method, single domain nanocrystalline Fe and Ni particles in the 5-10 nm size range embedded in amorphous alumina as well as in crystalline TiN have been produced. By controlling the size distribution in confined layers, it was possible to tune the magnetic properties from superparamagnetic to ferromagnetic behavior. Magnetic hysteresis characteristics below the blocking temperature are consistent with single-domain behavior. The paper also presents our results from investigations in which scanning transmission electron microscopy with atomic number contrast (STEM-Z) and electron energy loss spectroscopy (EELS) were used to understand the atomic structure of Ni nanoparticles and interface between the nanoparticles and the surrounding matrices. It was interesting to learn from EELS measurements at interfaces of individual grains that Ni in alumina matrix does not form an ionic bond indicating the absence of metal-oxygen bond at the interface. The absence of metal-oxygen bond, in turn, suggests the absence of any dead layer on Ni nanoparticles even in an oxide matrix.

#### **L8.18**

**Bramble-like Mesostructured Nickel Oxide Fiber Clusters.** Jieming Cao, Jun Wang, Jinsong Liu, Shuquan Chang, Baoqing Fang, Xianjia Ma, Xin Chang, Guoyue Xu and Jie Tao; Institute of Nanomaterials, College of Material Science & Technology, Nanjing University of Aeronautics and Astronautics, Nanjing, Jiangsu, China.

Discovery of the mesostructured metal oxides with different morphologies formed by the self-cooperative assembly of inorganic metal species and organic surfactants is considered a great achievement for the past decade. Mesostructured nickel oxide/surfactant fibers were synthesized by using anionic surfactants (sodium dodecylsulfonate or sodium dodecylsulfate: SDS) as templates, and nickel salts as inorganic precursors, via the "S-I+" route in alkaline condition. The as-prepared samples were characterized by means of XRD, FT-IR, SEM, TEM and TG/DTA techniques. XRD pattern of NiO/SDS shows a hexagonally packed mesostructure, corresponding to the d-spacing is 28Å. FT-IR spectra indicate that the presence of the surfactants in as-synthesized samples. The several influential factors (pH, surfactant concentration and different nickel sources) of the mesophase formation were studied. The SEM image of mesostructured NiO/SDS composite shows there were some bramble like fiber clusters on the surface of the samples. These bramble clusters were composed of ellipse or flat pipe fibers. The diameter of fibers pipe varies from 200nm to 600nm, and the length of those varies from 1um to 10um. We believed that mesostructure could be synthesized followed by "cooperative templating mechanism" during the interaction between SDS and nickel species, and the mesostructure grow along some orientations in the size of micron. Such form of mesostructured nickel oxide is found for the first time and is believed to have potential applications in catalysis, host-guest chemistry, and electrochemical devices. Reference 1. a) C.T. Kresge, *et al.*, *Nature*, 359(1992)710; b) Q. Huo, *et al.*, *Nature*, 368(1994)317. 2. a) P.D. Yang, *et al.*, *Nature*, 396(1998)152; b) Y. Xia, *et al.*, *Adv. Mater.*, 5(2003)353.

#### **L8.19**

**Morphology and size of nano pores in porous silicate thin films characterized by variable-energy positron annihilation spectroscopy.** Kenji Ito, Yoshinori Kobayashi, Kouichi Hirata, Hisashi Togashi, Kiminori Sato, Runsheng Yu, Toshiyuki Ohdaira and Ryoichi Suzuki; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Low-*k* dielectrics for future ULSI can be engineered by incorporation of nano porosity into an insulating silicate matrix. One promising class of low-*k* dielectrics is spin-on-glass films with nano porosity introduced by decomposition of a thermally degradable pore generating material (sacrificial porogen). A critical issue is a proper control of pore morphology in the films, that is, whether it is an open or closed cell. Closed pores in the films are desirable because pore interconnectivity could lead to low mechanical strength and breakdown voltage. Positron annihilation is a powerful tool for characterizing nano pores in porous thin films; pore size and open pore connectivity can be determined by the positron lifetime and 3γ annihilation probability, respectively. In this work, nano pore formation after curing was investigated for hydrogen-silsesquioxane films by means of variable-energy positron annihilation γ-ray and lifetime measurements. Variations of the morphology and size of formed pores with preparing condition will be discussed.

#### **L8.20**

**Development and characterization of the nanostructured diamond-like carbon films.** Won Jae Yang<sup>1</sup>, Tohru Sekino<sup>2</sup>, Koichi Niihara<sup>2</sup> and Keun Ho Auh<sup>1</sup>; <sup>1</sup>Ceramic Processing Research Center,

Hanyang University, Seoul, South Korea; <sup>2</sup>Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan.

Hard coating materials are widely required for many structural applications and also electronic devices. They offer protection of materials from wear, friction and corrosion and therefore enhance their lifetime. Diamond-like carbon (DLC) films have a potential as protective coatings because they have excellent mechanical and tribological properties. Furthermore, they provide interesting features such as deposition at room temperature and superior surface roughness. However, they have a limitation for the industrial applications due to their low thermal stability, high internal residual stress and environmental dependence of the wear properties. The development of nanostructured films is required for the progressive improvement of hard coating materials. The nano-scale design of coating materials is usually achieved by means of nanocomposite and nano-multilayer films. We modified the microstructure of DLC films in such a way that the second phases of carbide or silica were embedded in DLC matrix for the nanostructured DLC films. The relationship between the microstructure and physical properties will be investigated.

#### **L8.21**

##### **Mean Inner Potential of Nanostructured Noble Metal**

**Catalysts.** Satoshi Ichikawa<sup>1</sup>, Tomoki Akita<sup>1</sup>, Kazuyuki Okazaki<sup>1</sup>, Mitsutaka Okumura<sup>2</sup>, Koji Tanaka<sup>1</sup> and Masanori Kohyama<sup>1</sup>; <sup>1</sup>Special Division of Green Life Technology, National Institute of Advanced Industrial Science and Technology, Ikeda, OSAKA, Japan; <sup>2</sup>School of Science, Osaka University, Toyonaka, 560-0043, Japan.

Catalytic properties of noble metal catalysts are often caused by their nanostructures. Gold catalysts are typical cases. It is especially interesting that the catalytic property of gold suddenly changes to resemble that of platinum when the mean size of gold dispersed on certain oxides is <2nm. This phenomenon should be owing to the change of the local electronic structure of the gold particle or the interface between the gold and the oxides, however its detail has not been cleared yet. We measured the mean inner potential of gold particles supported on TiO<sub>2</sub> using electron holography and HREM, and found that the mean inner potential of gold depend largely on the size of the gold particles. When the size is >5nm, the mean inner potential is the same as the reported values of bulk gold (experimental: 21-23V, calculated: 25-30V). When the size is <5nm, it begins to increase >30V, and it begins to increase suddenly >40V at the size <2nm. It indicates that the electronic structure of the gold particle varies from that of the bulk state as the size of the gold reduces due to the nano-size effect or the interaction at the interface, since the mean inner potential is sensitive to the electronic state of the outer valence electron. On the other hand, the behavior of the platinum catalysts is different from that of gold catalysts. When the size of the platinum particle on the TiO<sub>2</sub> support is >1.5nm, the mean inner potential of platinum is the same as that of the bulk (~25V). In case of the particle with the size <1.5nm, it begins to increase and the increase rate is lower than that of the gold particles with the size <2nm. It is suggested to be due to the difference of the interaction with TiO<sub>2</sub>.

#### **L8.22**

##### **Novel Allotropic Fullerene-Like and Nanotubular BN**

**Structures.** V. Vladimir Pokropivny<sup>1</sup>, Richard Partch<sup>2</sup> and Alex Pokropivny<sup>1</sup>; <sup>1</sup>Theor.mat.sci., Inst.Problems of Materials Science of NASU, Kiev, Ukraine; <sup>2</sup>Clarkson University, Potsdam, New York.

Abundance of allotropic forms of boron nitride (E-phase, etc.) are known to exist many years ago, the densities of which are intermediate between a graphite-like BN and a diamond-like zinc-blende borazon. However their complicated structures remain to be unresolved until now, the interpretation of which has become possible only after discovering of fullerenes and nanotubes. In a first time the possibility of the cubic crystals built from fullerene molecules B12N12, C24, B24N24 have been suggested in ref. [1]. In particular, a "hyperdiamond" with C24 molecules in a superdiamond lattice, and a body-centered cubic fullerite Me2-B12N12 (doped with the small donor metal impurities Me=Li, Be, etc.) with the density  $\rho = 4.11-5.28 \text{ g/sm}^3$  higher than for diamond have been predicted [1]. Crystal-chemistry analysis in couple with quantum-chemistry MNDO calculation of the B12N12, B24N24, B36N36 fulborenes and (6,0) and (6,6) BN-nanotubes have permitted us to establish the structures of above unconventional novel cubic and hexagonal phases of boron nitride, the analogs of "cubic graphite", a-carbyn, b-carbyn, chaoite and other unconventional hexagonal forms of carbon are suggested, that still wite their discovering. Like a zeolites all such phases contain two-dimensional lattices of cylindrical nanochannels in their structure, that may be utilized as special molecular sieves. In result of size effects, appearing at  $\rho = 4.11-5.28 \text{ g/sm}^3$ ;  $\sim d$ , the unusual optic and other properties are expected to be arose in novel materials on base of such fullerene-like forms of boron nitride

that will find novel perspective applications. [1].V.V.Pokropivny, et.al., J.Solid St.Chem. 154, 214 (2000).

#### **L8.23**

##### **A Model of New VUV NLO Materials Based on Borate. A Novel Noncentrosymmetric Borophosphate Compound**

**Be<sub>3</sub>BPO<sub>7</sub>.** Zhangzhen He<sup>1</sup> and Hiroshi Moriyama<sup>2</sup>; <sup>1</sup>Materials & Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; <sup>2</sup>Department of Chemistry, Toho University, Funabashi, Japan.

The model compounds formulated as  $M_xA_{1,2}(BO_3)_{1,2}O_y$  may be a prospective candidate for the new VUV NLO material, considering the SHG coefficients, UV absorption edge, and moderate birefringence. The model suggests that the investigation for a new VUV NLO material would be fairly conducted by focusing on boroberylate, borooaluminate, and borophosphate on the basis of the anionic group theory. For example, a novel nonsymmetric beryllium borophosphate compound Be<sub>3</sub>BPO<sub>7</sub> has been synthesized by solid-state reaction. Microcrystalline compound Be<sub>3</sub>BPO<sub>7</sub> is a hexagonal system and contains the BO<sub>3</sub> anionic group as its basic structural unit, which should play an important role for SHG coefficients. In fact, Be<sub>3</sub>BPO<sub>7</sub> powder was found to have the significant SHG effect.

#### **L8.24**

##### **Fabrication of carbon nanofiber films for electrochemical**

**capacitors.** Chien-Te Hsieh, Jin-Ming Chen, Rong-Rong Kuo and Yue-Hou Huang; Industrial Technology Research Institute, Chungung, Taiwan.

Highly-density carbon nanofibers (CNFs) film synthesized by a thermal chemical vapor deposition was employed to explore the electrochemical characteristics of supercapacitors fabricated with the CNFs. Open-end CNFs having a mean diameter of 80-100 nm were grown at 900°C, using decomposition of toluene as carbon precursor, and Ni-electrodeposited substrate as catalyst. Nitrogen adsorption experiments showed that the CNFs had a BET surface area of 120 m<sup>2</sup>/g, and mainly mesoporosity, i.e., pore size ranged from 2 to 11 nm determined from DFT model. The performance of the capacitors was tested in 3 M KOH, using potential sweep cyclic voltammetry (CV) and constant current charge-discharge cycling. CV test showed that no obvious Faradaic current and distributed capacitance effect at potential reversal were found, indicating that the CNFs exhibited a purely double-layer capacitance character. The double-layer capacitance of the capacitor almost maintained a constant value of ~15 μF/cm<sup>2</sup> at different current densities, 1, 2, 10, 30, 50 mA/cm<sup>2</sup>. It confirmed that the distributed capacitance effect in the CNFs can be negligible, which was agreement with CV results. Finally, charge-discharge cycling showed that the capacitor fabricated with the CNFs exhibited a stable cycleability (~15 μF/cm<sup>2</sup>) and excellent Coulombic efficiency (~99.5 %) during 200 cycles.

#### **L8.25**

##### **Mesoporous Silica Film Preparation By Novel Supercritical Fluid Extraction Of Organic Templates.**

**Nobuyuki Kawakami<sup>1</sup>, Takayuki Hirano<sup>1</sup>, Yoshito Fukumoto<sup>1</sup> and Yoshiyuki Nagase<sup>2</sup>;** <sup>1</sup>Electronics Research Lab., Kobe Steel, Ltd., Kobe, Hyogo, Japan; <sup>2</sup>Chemical & Environmental Technology Lab., Kobe Steel, Ltd., Kobe, Hyogo, Japan.

Novel technology to fabricate surfactant-templated mesoporous film is proposed. Mesoporous materials are expected as the promising candidates for electronics applications with their low dielectric constants and low dielectric losses. Although the surfactant templates have been removed by calcination or solvent extraction, when using such techniques, the meso-structures are collapsed resulting in less porosity and higher dielectric constant, due to the high temperature or interfacial tension during the process. In this study, supercritical fluid extraction (SFE) technique by using supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>), which enables low temperature and no interfacial tension in the process, has been developed in order to remove organic templates from the film without structure collapse. Surfactant-templated silica films were coated on substrates by using precursor solution prepared from tetramethoxysilane as the silica source and cetyltrimethylammonium bromide (CTAB) as the surfactant. The films were then processed to the SFE by using sc-CO<sub>2</sub> added with hydrogen peroxide solution at the pressure of 19.6 MPa and the temperature of 80 °C. FTIR spectra were measured on the films processed to the SFE with and without hydrogen peroxide solution. In the case that hydrogen peroxide solution is introduced into sc-CO<sub>2</sub>, absorption intensities of CH<sub>3</sub> or CH<sub>2</sub> bonds, which originate from CTAB molecule, are reduced, i.e., CTAB can be extracted from the film, while no extraction of CTAB from the film is observed in the case that SFE is performed only by pure sc-CO<sub>2</sub>. XRD and TEM measurements were also carried out with the specimen after CTAB extraction by the SFE with hydrogen peroxide solution. The results show the film has highly ordered porous structure with a lattice parameter of 2.8 nm, which suggests that the surfactant can be extracted without meso-structure collapse. In order

to analyze the chemical changes in the film during the SFE with hydrogen peroxide solution, XPS were measured on the films. Before the SFE, only two peaks in the C1s XPS spectra, which is assigned to C-H and C-N bonds in CTAB molecule, are observed. After the films are processed to the SFE, the intensity of C1s is decreased, which result from CTAB extraction, however, the increase of the C1s peak shoulder, which is assigned to C=O bonds, is observed. This result explains that CTAB molecules are oxidized by the SFE, which corresponds that hydrogen peroxide solution acts as an effective oxidant agent in sc-CO<sub>2</sub>. It is also suggested that CTAB is decomposed to low molecular weight compounds by the oxidation, thus, the organic templates can be extracted by sc-CO<sub>2</sub>. This research was supported by grants from NEDO of Japan.

#### L8.26

**Anisotropic Luminescence of Individual CdS Quantum Dot Ensembles.** Jifa Qi<sup>1,2</sup>, Chuanbin Mao<sup>2</sup>, John M White<sup>2</sup> and Angela M Belcher<sup>1,2</sup>; <sup>1</sup>Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Chemistry and Biochemistry, University of Texas, Austin, Texas.

Like the shapes and sizes of the individual quantum dot (QD) components are important to the physical properties of the QD ensemble, the crystallographic orientation of the individual QDs is important to the optical anisotropy. The optical anisotropy of individual QDs can be due to either their noncubic crystalline structure or to their non-spherical shape, since the polarization depends on the symmetry of the wave function. The polarized emission from a QD ensemble is a three dimensional problem, due to the orientation of the optical transition dipole of a QD regarding to the excitation light and observation. In this work, we report photoluminescence (PL) observations for individual QD ensembles comprised of about 2.5 nm diameter spherical wurtzite structured CdS quantum dots. The QD ensembles were prepared by a cold treatment process that provided control over the shapes of the ensembles. The ensembles are themselves either spherical (100 to 300 nm diameter) or rod-shaped. PL measurements were performed on the QD ensembles transferred onto a silicon (100) wafer and measured at low temperature around 6 K. A conventional far-field micro-PL system was used to collect the PL signal. For a given spherical ensemble the PL is anisotropic and the anisotropy is independent of the polarization of the optical excitation. The directions of the maximum linearly polarized PL were different for different spherical QD ensembles. Rod-shaped ensembles exhibit a maximum PL intensity in the direction perpendicular to the long axis of the ensemble, independent of the incident polarization. The results are consistent with preferential crystallographic orientation of individual QDs within a given ensemble.

#### L8.27

**Controlled Assembly of Carbon Nanotubes Fibrils by Dielectrophoresis.** Jie Tang<sup>1,2</sup>, Bo Gao<sup>1</sup>, Huaizhi Geng<sup>1</sup>, Orlin D Velev<sup>3</sup>, Lu-Chang Qin<sup>1</sup> and Otto Zhou<sup>1</sup>; <sup>1</sup>University of North Carolina, Chapel Hill, North Carolina; <sup>2</sup>National Institute for Materials Science, Tsukuba, Ibaraki, Japan; <sup>3</sup>North Carolina State Uni., Raleigh, North Carolina.

Carbon nanotubes (CNTs) have unique material properties that are promising for a wide range of technological applications. Although advance has been made in the synthesis of raw CNT materials, the lack of efficient processes for assembly and integration of the CNTs into functional forms has hindered the development of CNT-based devices. Here we report a dielectrophoresis method to manipulate, align and assemble 1D nanostructures using alternating-current electric field. Pre-formed CNTs dispersed in water are assembled into micro-electrodes and sub-micron diameter fibrils with variable lengths from micrometer to over 1cm. The CNTs within the fibril are bonded by van der Waals force and are aligned along the fibril axis. The method affords fine control of the fibril length and is capable of parallel fabrication of many fibrils using the same source. The short CNTs fibrils can potentially be used as the probes for scanning probe microscopes and the longs as electrodes and conducting wires. [1] J. Tang, B. Gao, H.Z.Geng, O.D. Velev, L.C. Qin, and O. Zhou, Adv. Mater. in press

#### L8.28

**Meso-Structure and Micro-Structure of A Silica Thin Film with Spherical Voids.** Kui Yu<sup>1</sup>, X. Wu<sup>1</sup>, J.A. Ripmeester<sup>1</sup>, B. Smarsly<sup>2</sup>, G. Xomeritakis<sup>2</sup> and C.J. Brinker<sup>2</sup>; <sup>1</sup>Steele Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada; <sup>2</sup>University of New Mexico., Albuquerque, New Mexico.

Silica thin films with nanometre-scaled voids organized in an ordered array and with controllable hydrophobicity may be highly desirable for future semiconductor devices. We present here a thorough

characterization of the meso-structured porous silica thin film formed on a (001) Si substrate. In addition to the meso-structure, we also present a comprehensive investigation on the micro-structure. The film presented was fabricated by solvent evaporation-induced sol-gel and self-assembly processes (EISGSA), with methyl triethoxysilane (MTES, Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>CH<sub>3</sub>) as the silica precursor and a polystyrene-block-poly(ethylene oxide) (PS-b-PEO) diblock as the structure-directing agent; pyrolysis was performed carefully to remove the template. Regarding the meso-structure determination, a novel transmission electron microscopy (TEM) approach was used, which involved sample tilting to get different zone axes, simulation, as well as the calculation of plane spacings and angles for comparison of the experimental values with corresponding theoretical ones. The TEM exploration concluded that the meso-structure was exclusively body-centered cubic (bcc) rather than face-centered cubic (fcc); the bcc meso-structure with a slight distortion was further assigned to be body-centered tetragonal (bct) with the preferred cell parameters of a = 13.5 nm and c = 13.0 nm. The pore was ca. 4 nm in diameter. The meso-structure was also confirmed by 2D-grazing incidence small-angle X-ray scattering (GISAXS). Furthermore, two types of dislocations were observed by TEM. One was an edge dislocation, with the Burgers vector b = a[010] and the dislocation line direction x = [100]. The other was a dislocation dipole with the Burgers vectors b = (a/2)[-1,1,1] on a (0,1,-1) plane. The origin of the edge dislocation was argued to be the tensile strain developed during the formation of the meso-structured thin film via the EISGSA processes. The formation of the edge dislocation partially relieved the strain developed in the film; the critical thickness for the formation of this dislocation was estimated using an elastic strain energy argument. Regarding the micro-structure, N<sub>2</sub> sorption by surface acoustic wave (SAW) measurements showed the absence of micro-porosity interconnecting the meso-pores; furthermore, 2D GISAXS indicated the absence of additional porosity due to the PEO removal. However, gas permeation (GP) found there was a small number (less than 4% vol.) of PEO-induced micro-pores of ~1 nm in diameter. Thus, the power of GP experiments on the determination of the interconnection of the meso-structured porous materials is worthy of notice. The present comprehensive characterization of the novel silica thin film with nano-scaled voids arranged in a cubic array should provide a general methodology for both the meso- and micro-structure characterization of other related porous films prepared by similar processes.

#### L8.29

**Size Dependent Ionic Conductivity Observed for Ordered-Mesoporous Alumina-Ionic Conductor Composites.** Hideki Maekawa<sup>1,2,3</sup>, Ryo Tanaka<sup>1</sup>, Yutaka Fujimaki<sup>1</sup> and Tsutomu Yamamura<sup>1</sup>; <sup>1</sup>Department of Metallurgy, Tohoku University, Sendai, Japan; <sup>2</sup>PRESTO, Japan Science and Technology Corporation, Kawaguchi, Japan; <sup>3</sup>Center for Interdisciplinary Research, Tohoku University, Sendai, Japan.

Ordered-mesoporous Al<sub>2</sub>O<sub>3</sub> was synthesized by the sol-gel method using neutral surfactants as templates. The pore size can be controlled over the range of 2.8~12.5 nm by using different surfactant copolymers and by different synthetic conditions. Composites composed of the synthesized mesoporous Al<sub>2</sub>O<sub>3</sub> and the lithium ion conductor (LiI) was prepared. The dc electrical conductivity of 50LiI-50(mesoporous Al<sub>2</sub>O<sub>3</sub>) with 4 nm pores was more than 100 times higher than that of pure LiI. The pore size dependence of the conductivity of LiI-mesoporous Al<sub>2</sub>O<sub>3</sub> composite was examined. A systematic dependence of conductivity upon pore size was observed, in which the conductivity increased with decreasing the pore size.

#### L8.30

**Solvent interaction with carbon nanotube bundles under hydrostatic pressure.** Kristin Rule, James Elliott, Jan Sandler and Alan Windle; Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom.

The high theoretical modulus and strength of single-wall carbon nanotubes (SWNTs) makes them an ideal candidate for use as a filler material in polymer composites. More recently, the response of carbon nanotubes to molecular pressure produced by the cohesive energy density (CED) of a solvent has opened up the possibility of using carbon nanotubes as molecular sensors. Aspects of both of these potential applications of carbon nanotubes are explored by computer simulation via the application of hydrostatic pressure. In this paper, we apply constant stress (NST) Molecular Dynamics simulations, using a classical macromolecular force field, to two-dimensional hexagonal bundles of SWNTs surrounded by a solvent bath. The aim of these simulations was (i) to elucidate the effect of bundle size on SWNT collapse pressure, and its relation to the collapse mechanism we have postulated for tubes in infinitely periodic bundles, and (ii) to gain a better understanding of solvent-nanotube interactions under hydrostatic pressure, specifically with relation to solvent polarity and

CED of the solvent. In particular, the effect of solvent CED on the pressure at which the nanotubes inside the bundle collapse is investigated. The effects of solvent crystallisation both inside and outside the nanotube under pressure were also considered.

#### L8.31

##### **Soft magnetic vapor phase co-deposited polymer-metal nanocomposites for GHz applications.** Abhijit Biswas<sup>1</sup>, Usman

Saeed<sup>1</sup>, Joern Kanzow<sup>1</sup>, Oral Cenk Aktas<sup>1</sup>, Vladimir Zaporozhchenko<sup>1</sup>, Franz Faupel<sup>1</sup>, Michael Frommberger<sup>2</sup> and Eckhard Quandt<sup>2</sup>; <sup>1</sup>Nanocomposite Research Laboratory, Lehrstuhl fuer Materialverbunde, Technische Fakultaeet der CAU, Kaiserstr. 2, D-24143, Kiel, Germany; <sup>2</sup>Smart Materials Group, CAESAR, Ludwig-Erhard-Allee 2, D-53175, Bonn, Germany.

Future GHz driven mobile communication handsets and portable information tools demand new requirements for further miniaturization and lower insertion loss for inductive components installed in Monolithic Microwave Integrated Circuits (MMIC). The possible carrier frequency range is from 800 MHz to 3 GHz including audio and intermediate frequencies. Magnetic thin-film inductors will be advantageous over currently used air-core spirals if loss generation in the magnetic film is low at the frequency of interest. Besides parasitic effects due to the design of the magnetic device, two main loss mechanisms limit the applicability of soft magnetic films at very high frequencies (1 GHz and above). Eddy current losses occur due to the conductivity of the materials (magnetic film and spacer), shape and especially thickness of the films. Another prominent loss occurs in the form of ferromagnetic resonance when the frequency of the applied rf field matches the characteristic precession frequency of the spins. Two component nanocomposites of fine mixtures of magnetic nanoparticles protected in insulating polymer matrices are promising candidates and could play important roles particularly in such magnetic high frequency applications with higher cut-off frequencies in the GHz regions. Appropriately volume filled isolated magnetic nanoparticles dispersed three dimensionally (3 D) in an insulating polymer matrix possess good potential to generate quite high saturation magnetization required to shift ferromagnetic resonance in the GHz range alongwith significantly minimised eddy current loss due to the surrounding highly insulating zones. Polymer like Teflon AF having the property of high degree of resistance to any chemical attack is naturally an effective choice to protect the magnetic nanoparticles in organic host. However, there is no easy synthesis route existing to prepare such nanocomposites. Moreover, generating appropriately high magnetic volume of such non-interacting nanoparticles in organic matrix while keeping narrow size distribution is a conflicting process and a technological challenge from the preparation point of view. We introduce a simple one step and solvent free technique of elevated target temperature vapor phase co-deposition to produce nanocomposites (100 nm - 200 nm) of Teflon AF containing 3 D dispersed Fe-Ni-Co nanoparticles capable of functioning in the GHz range. Besides a homogeneous nanoparticles distribution in the polymer host, an extremely narrow particle size distribution of 6 - 8 nm were achieved. Preliminary magnetic results of such nanocomposites are presented which show a saturation magnetization of the nanoparticles of nearly 2 Tesla matching with the corresponding bulk and ferromagnetic resonance appears to occur at around 6 GHz based on the complex permeability measurements.

#### L8.32

##### **Polymer Nanocomposites with Surface Modified Magnetic Nanoparticle.** tae-jong yoon and Jin-Kyu Lee; Chemistry, Seoul National Univ., Seoul, South Korea.

The surface of Co ferrite magnetic nanoparticles prepared by a known co-precipitation method was modified with deliberately prepared cationic organic molecule, quaternary ammonium salts from nitrilotriacetic acid (NTA). The modified Co ferrite nanoparticles are very stable in various organic solvents without an excess amount of capping molecules, and can be homogeneously mixed with polymer to give magnetic nanocomposites. When a block copolymer is mixed with magnetic nanoparticle having a selective solubility, the modified Co ferrite is preferably located in a specific block. These polymer/Co ferrite magnetic nanocomposites could also be fabricated in thin films by spin-coating method. Synthesis and characterization results of these nanocomposites will be discussed.

#### L8.33

##### **Nonlinear magneto-optical Kerr effect in optical third harmonic generation from magnetic granular films exhibiting giant magnetoresistance.** Evgenia Mikhailovna Kim, Tatyana Vladimirovna Murzina and Oleg Andreevich Aktsipetrov; Physics Department, Moscow State University, Moscow, Russian Federation.

Magnetic nanomaterials such as multilayered structures and granular films have received considerable attention because of a number of new magnetic phenomena observed in these systems: the oscillatory

coupling through the nonmagnetic spacers, spin-dependent electron scattering and tunneling, giant magnetoresistance (GMR), etc. Apart from these phenomena magnetic structures reveal significant magnetization induced nonlinear-optical effects as nonlinear magneto-optical Kerr effect (NOMOKE) in second harmonic generation (SHG)[1]. In this work nonlinear magneto-optical Kerr effect in optical third harmonic generation (THG) is experimentally studied in  $\text{Co}_x\text{Ag}_{1-x}$ ,  $\text{Co}_x(\text{Al}_2\text{O}_3)_{1-x}$  and  $\text{Co}_x\text{Cu}_{1-x}$  for the first, to our knowledge, time. Nonmonotonous dependencies of the magnetoresistance and NOMOKE magnetic contrast on the volume fraction of the magnetic component x are found. The nonlinear-optical studies were performed using the unfocused output of a Q-switched  $\text{YAG:Nd}^{3+}$  laser at the wavelength of 1064nm with a pulse width of about 15ns, repetition rate of 24Hz. An angle of incidence was  $45^\circ$ . The third harmonic (TH) signal was detected by a PMT and gated electronics. Three sets of magnetic granular films of  $\text{Co}_x\text{Ag}_{1-x}$ ,  $\text{Co}_x(\text{Al}_2\text{O}_3)_{1-x}$  and  $\text{Co}_x\text{Cu}_{1-x}$  composition were prepared by co-deposition of Co and Ag or  $\text{Al}_2\text{O}_3$  or Cu, respectively, in a dual electron-beam evaporator at room temperature and residual pressure of  $10^{-4}$  Pa on ceramic substrates. The thickness of the films was about 400nm. The crystalline structure was studied by X-ray diffraction and transmission electron microscopy which allowed us to estimate the mean size of Co granules in the annealed films. All types of magnetic granular films exhibit the GMR effect. The room temperature magnetoresistance was measured in the magnetic field up to 8.2 kOe for the in-plane current configuration and three configurations of the external magnetic field application. To study the crystallographic symmetry of the samples the azimuthal anisotropy of the SHG and THG intensity were measured, which showed the existence of a mirror plane in the film structure. Magnetoinduced THG is studied in the geometry of transversal magneto-optical Kerr effect. The maximum of the NOMOKE magnetic contrast is attained at the value of x close to that providing the maximum of the magnetoresistance similar to the dependence of the SHG magnetic contrast observed recently. The THG interferometry did not reveal magnetoinduced changes in the third harmonic phase. [1] T.V. Murzina, T.V. Misuryeva, A.F. Kravets, J. Gudde, D. Schuhmacher, G. Marowsky, A.A. Nikulin, O.A. Aktsipetrov, Surface Science, 482-485 (2001).

#### L8.34

##### **Nylon grafting onto carbon nanotubes.** Krzysztof KK Koziol<sup>1</sup>, Milo SP Shaffer<sup>2</sup> and Alan H Windle<sup>1</sup>; <sup>1</sup>Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Department of Chemistry, Imperial College, London, United Kingdom.

There is a range of possible applications for carbon nanotubes (CNT) in which the CNT form a close association with other types of material particularly polymers. Applications include gas processing and structural composites. Direct grafting of surface polymer chains is an effective way to improve the processability of carbon nanotubes in composites or controlled networks with tailored properties. There have been a number of attempts to alter the surface of carbon nanotubes, but only a few have succeeded in covalently grafting macromolecules. Perhaps surprisingly, the majority of this work has focussed on single-walled material. Here, we report the successful synthesis of grafted multi-walled nanotubes using an in situ polymerisation technique. The resulting product consists of resilient networks of CNT with large accessible surface areas. The multi-walled carbon nanotubes used were grown by a chemical vapour deposition (CVD) technique, which permits control of length and diameter. After a simple purification step, the grafted nanotubes are free of monomer residues. The grafting can be controlled to produce a stable dispersion in different organic or inorganic solvents. The grafting ratio (mass polymer/tube) can be selected by adjusting process parameters and scaffolds of different nanotube densities can be formed. We have analysed the grafted material with electron microscopy, Fourier transform-infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and thermogravimetry (TGA).

#### L8.35

##### **The determination and removal of metal impurities in carbon nanotubes.** Krzysztof KK Koziol<sup>1</sup>, Francis Tailoka<sup>1</sup>, Milo SP Shaffer<sup>2</sup> and Alan H Windle<sup>1</sup>; <sup>1</sup>Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Department of Chemistry, Imperial College, London, United Kingdom.

The determination of the metal catalyst content in carbon nanotubes (CNT) is of importance in many aspects of CNT characterization and applications. The metal impurities can surround nanotubes or, in most cases, be encapsulated within their central core. Depending on the process parameters, multi-walled carbon nanotubes synthesized by a chemical vapour deposition (CVD) technique can contain significant

quantities of metal impurities, typically 3-10 wt%. We were able to decrease this metal content to 0.005 wt% by using a high temperature purification step (1900 °C in an argon atmosphere). High temperature treatment not only yields high purity carbon nanotubes but also improves their structural quality. In order to measure precisely the metal content, inductively coupled plasma atomic emission spectrometry (ICP-AES) was applied. This technique offers low detection limit, high accuracy and relative freedom from matrix but solid samples must be first converted into water solutions. In our case carbon nanotubes samples for ICP-AES measurements were completely digested with a mixture of acids or surfactant was used. One type of surfactant was found to be extremely successful in preparing stable and good quality multi-walled and single-walled carbon nanotubes water dispersions. We have also analysed samples of carbon nanotubes with electron microscopy, thermogravimetry (TGA) and energy dispersive X-ray spectrometry (EDS).

#### L8.36

**TEM and DOE Optimization Studies of Electrospun Polycarbonate Nanofibers.** Nirupama Kattamuri and Changmo Sung; Chemical and Nuclear Engineering, University of Massachusetts, Lowell, Massachusetts.

Electrospinning is the process of generating fibers by applying electrostatic voltage to a polymer solution. The advantage of the process is that the fibers obtained have a larger surface area and porosity in comparison to conventional spinning methods. In the present work, electrospinning of polycarbonate with solvent mixtures of THF (tetrahydrofuran) and DMF (dimethylformamide) has been performed. Polycarbonate is selected because it is a promising thermoplastic and widely used injection molded material. The effect of various process parameters like voltage, concentration, flow rate and distance has been investigated. Morphology changes of polycarbonate fibers with different spinning voltages (25 to 30kV), different polymer concentrations (14% to 18%), different flow rates (0.01 to 0.1 ml/min) and different distances between target and syringe (4 to 10inches) have been studied. The temperature and humidity have also been carefully monitored for all the runs. The bead density and fiber thickness are measured using image processing softwares like GAIA Blue and Scion imaging. The surface morphology of the electrospun fibers has been examined with the help of scanning electron microscopy and transmission electron microscopy. The Design of experiment (DOE) has been conducted with the help of Minitab software to find the most important parameter for uniform nanofibers. The optimum conditions of distance, viscosity and voltage result in nanometer scale (<200nm) polycarbonate fibers. It is found that 16% PC solution with solvent ratios THF and DMF at 60:40 ratios at a voltage of 30kV, flow rate of 0.01ml/min and distance of 9-10inches produced uniform PC nanofibers without beads. From the DOE charts it is found that concentration is the most important factor and flow rate is the least prominent. A theoretical model is also developed from the DOE results.

#### L8.37

**Fabrication of nanostructured components with high porosity using plasma spray.** Shiqiang Rob Hui, Jinxiang Dai, Jeff Roth, Huimin Chen and Danny Xiao; US Nanocorp, Inc., Willington, Connecticut.

Nanostructured components have shown promising results for improving the electrode performance in many electrochemical systems. Fuel cells, membranes for gas separation, batteries, solid-state chemical sensors, and electrochromic devices are just some of the applications for this technology. Such nanostructured components can be obtained through a plasma thermal spray technique. Normally, the porosity of the components is not suitable for electrode applications due to their close pores and low porosity. This work aims to demonstrate the feasibility of fabricating nanostructured components with high porosity as well as high bond strength (adhesion to the substrate). Sacrificial materials were employed in the feedstock to obtain high porosity and uniformly distributed open pores. Several sacrificial materials along with varied spray parameters were utilized and studied for porosity and bond strength attributes within the coating microstructure. The sprayed components were examined using XRD and SEM techniques. Nanostructured components with high porosity have been experimentally realized via plasma thermal spray processing techniques and show much promise in the future.

#### L8.38

**Electrophoretic Deposition of High Quality, Multifunctional Films of Mixtures of Nanocrystals.** Mohammad A Islam<sup>1,3</sup>, Yuqi Xia<sup>3</sup>, Ming Yin<sup>1,3</sup>, Zhen Liu<sup>2,3</sup>, Rastislav Levicky<sup>2,3</sup>, Stephen O'Brien<sup>1,3</sup> and Irving P. Herman<sup>1,3</sup>; <sup>1</sup>Applied Physics and Applied Mathematics, Columbia University, New York, New York; <sup>2</sup>Chemical Engineering, Columbia University, New York, New York; <sup>3</sup>Materials Research Science and Engineering Center, Columbia University, New York, New York.

The importance of films composed of different nanocomponents is being increasingly recognized because they can have intriguing multifunctional properties, such as optical, and either electrical or magnetic properties, that can be tailored and tuned. We have shown that high quality films of mixtures of nanocrystals can be fabricated by electrophoretic deposition. Three nanocrystal components were considered: CdSe nanocrystals capped by TOPO,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) nanocrystals capped by oleic acid and Au nanocrystals capped by dodecanethiol. Electrophoretic deposition from mixtures of CdSe and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocrystals in hexane led to the formation of identical films on the positive and negative electrodes composed of both types of nanocrystals. In contrast, electrophoretic deposition from mixtures of CdSe and Au nanocrystals in hexane led to the formation of films of nanocrystals on only the positive electrode when the density of the Au nanocrystals was above some threshold fraction of the CdSe nanocrystal density, and these films were composed of only CdSe nanocrystals. As the density of the Au dots was decreased below this threshold value, film formation on the negative electrode was no longer inhibited, and films composed of CdSe nanocrystals formed on both electrodes. Such high density arrays of the nanocrystals might be useful in making devices like LEDs and high density magnetic memory devices. This work was supported by the MRSEC program of the National Science Foundation, Award No. 0213574.

#### L8.39

**Application of SOFC-typed cell with nanostructured electrode to practical deNO<sub>x</sub> reactor.** Shingo Katayama<sup>1</sup>,

Takuya Hiramatsu<sup>1</sup>, Osamu Shiono<sup>1</sup>, Masanobu Awano<sup>2</sup>, Yoshinobu Fujishiro<sup>2</sup> and Koichi Hamamoto<sup>2</sup>; <sup>1</sup>Synergy Ceramics Lab., FCRA, Nagoya, Japan; <sup>2</sup>Synergy Materials R.C., AIST, Nagoya, Japan.

SOFC-typed cells, which are electrochemical cells using an oxygen ion conductor, can be applied to not only fuel cells but also oxidation or reduction reactors. One of the applications is a deNO<sub>x</sub> cell that can reduce NO<sub>x</sub> to N<sub>2</sub> without any reducing agents. However, conventional cells without selective electrode have decomposed co-existing O<sub>2</sub> in preference to NO<sub>x</sub>, resulting in an extremely low efficiency and an impracticable high electric power. We have investigated a selective electrode that prefers to reduce NO<sub>x</sub> in the presence of O<sub>2</sub>. The electrode consists of two layers, NiO+YSZ—Pt+YSZ—YSZ(electrolyte). By pre-loading, the NiO+YSZ layer is changed to a self-assembled nanostructure, in which nano-grains of Ni metal are formed at the NiO/YSZ grain interface. NO<sub>x</sub> molecules are selectively reduced at the self-assembled interface because NO<sub>x</sub> and O<sub>2</sub> molecules are adsorbed at different sites. We also fabricated large deNO<sub>x</sub> cells with 100x100mm size and evaluated their deNO<sub>x</sub> performance for the practical application to the reduction of NO<sub>x</sub> in emission from stationary and mobile sources. Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

#### L8.40

**Growth Temperature Dependence of Ultrananocrystalline Diamond Films.** Xingcheng Xiao, James Birrell, Jennifer E. Gerbi, Jian Wang, Orlando H. Auciello and John A. Carlisle; Material Science Division, Argonne National Laboratory, Argonne, Illinois.

The high growth temperatures typically needed when growing diamond films using chemical vapor deposition (CVD) with H<sub>2</sub>/CH<sub>4</sub> plasma chemistries has notoriously limited their range of applications, especially in the field of electronics and MEMS. Ultrananocrystalline diamond (UNCD) films are grown using Ar/CH<sub>4</sub> plasma chemistries that give rise to C<sub>2</sub> dimers that are the principal growth species for UNCD, and the activation energy for the growth of UNCD films is much lower compared to the methyl radical/hydrogen abstraction chemistry used to growing microcrystalline diamond. In this work we have examined the temperature dependence of UNCD growth over temperatures ranging from 400-850 °C. Different diamond seeding processes (including mechanical polishing, ultrasonication in nanodiamond powder suspension) as well as bias enhanced nucleation were employed to pretreat the substrate surface for UNCD growth, achieving high initial nucleation densities. The results showed that the growth rate for UNCD films is much less dependent on temperature compared to diamond films grown using conventional hydrogen-rich plasmas. A combination of SEM, UV Raman, HRTEM and NEXAFS analysis indicate that UNCD films grow with relatively high growth rates even at temperatures as low as 400 °C. The initial diamond nucleation density provided by the seeding process, the choice of substrate, and the high secondary nucleation density resulting from the C<sub>2</sub> growth chemistry all play an important role in determining the overall growth rate and nanostructural development. The grain size of UNCD increases from 3-5 nm to 8-10 nm with decreasing temperature, due to the lowering of diamond grain re-nucleation during growth. The mechanism for the less temperature dependence of UNCD deposition was discussed. The relatively high growth rate of UNCD films at low

temperatures, together with the ability to surface micromachine UNCD films, provides a suitable platform material for diamond-based stand-alone microelectronic and integrated microelectronic/MEMS devices. This work was supported by the DOE-Office of science-Materials Science under Contract No. W-31-109-ENG-38

#### **L8.41**

**Preparation and Mechanical Properties of Nanostructured Tungsten Carbide Alloy Strengthened by Carbon Nanotubes.** Guolong Tan<sup>1</sup>, Xijun Wu<sup>2</sup> and Zongquan Li<sup>2</sup>; <sup>1</sup>Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang, China.

A novel approach for the synthesis of carbon nanotubes strengthened nanostructured tungsten carbide hard alloy was investigated, in which nanophase tungsten powders are carburized by C<sub>2</sub>H<sub>2</sub> instead of CO and a fraction of decomposed carbons are in situ converted to carbon nanotubes. In this way, the composite powders of nanocrystalline WC-Co and carbon nanotubes have been in situ prepared. The composite WC-Co powders are then hot pressed into bulk alloy which shows an exceptionally high microhardness up to 3307 kg/mm<sup>2</sup>. It is proposed that carbon nanotubes with extra high Young's Module (1.8 TPa) play both roles on strengthening the composite matrix and prohibiting growth of WC grains, which results in the great improvement of the mechanical properties of the samples. The average grain size of the prepared WC-Co hard alloys was estimated to be less than 100 nm. The effect of metal binder content and VC grain growth inhibitor on the mechanical properties of the nanostructured WC-Co hard alloys was also studied in detail. The synthesis process of nanophase pure WC powders from the reduction of ammonium tungstate by C<sub>2</sub>H<sub>2</sub>-H<sub>2</sub> mixture gas, including the effect of process parameters such as temperature and gas pressure on the final product phases will also be presented, together with XPS studies of the surface characterization of these composite powders.

#### **L8.42**

**Shear-Induced Grain Boundary Motion in Lamellar Phases of Diblock Copolymers.** Zhi-Feng Huang, Francois Drolet and Jorge Vinals; School of Computational Science and Information Technology, Florida State University, Tallahassee, Florida.

Below their order-disorder transition, nanoscale lamellar phases can be found in symmetric diblock copolymers. However, a macroscopic size sample usually exhibits polycrystalline configurations comprised of locally ordered but randomly oriented domains, with the presence of large amounts of defects. We discuss the effect of an externally imposed oscillatory shear on the global alignment of macroscopically disordered structures, with especial focus on the motion of grain boundaries. A mesoscopic model is developed and a direct numerical solution found for the case of a transverse/parallel grain boundary in the limits of weak segregation and low shear frequency. We find that the boundary exhibits simultaneously two types of motions: a rigid and oscillatory motion following the shear flow, and a break-up and recombination process of the lamellae near the boundary. There is net motion of the grain boundary toward the transverse region, even though both parallel and transverse orientations are linearly stable. This behavior can be understood by a multi-scale expansion of the mesoscopic model equation and the resulting amplitude or envelope equations for the boundary. We find that there are two contributions to the boundary velocity: The first one arises from the free energy difference between the two bulk lamellar regions, while the second comes from local diffusion around the boundary. This second contribution, often neglected in the absence of shear, plays an important role for the shear-induced boundary behavior, causing backward motion of grain boundary and a phase shift of the boundary velocity. The effect of viscosity contrast between the nanophases will also be discussed, in particular for the three-dimensional case that involves a perpendicular/parallel grain boundary.

#### **L8.43**

**Synthesis and Characterization of Novel Organic-Inorganic Nanocomposite Coatings.** Brian P. Mosher and Taofang Zeng; Mechanical & Aerospace Engr., North Carolina State University, Raleigh, North Carolina.

In recent years, federal regulations have become stricter on Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs), creating a demand for cleaner, safer synthesis of coatings. Inorganic solvent-based coatings create minimum VOCs and virtually no HAPs, making them ideal materials in industry. They are, however, not as well developed as those of organic solvent-based coatings. The addition of nanosized particles allows the material's properties to be fine-tuned to specific applications. In this paper, we report the synthesis and characterization of three novel inorganic solvent-based nanocomposite coatings. The nanocomposites were prepared in aqueous solution, dip coated, dried, and then cured. Curing causes

cross-link polymerization, locking in the nanocomposite structure. All of the coatings contain 3-Glycidioxypropyltrimethoxysilane (GLYMO), metal compound and fluorosurfactant. The mechanical properties of the coatings were characterized by microhardness, abrasion and adhesion tests. FTIR was performed before and after curing to determine the degree of polymerization.

#### **L8.44**

**Nano-structured polymer coatings for enhanced ultraviolet protection.** Phaneshwar Katangur, Steven B Warner, Prabir K Patra, Yong K Kim, Autumn Dhanote and Mhetre Shamal; Textile Science, University of Massachusetts, Dartmouth, N. Dartmouth, Massachusetts.

Polymer materials, such as Kevlar and nylon 66 that are susceptible to UV degradation are protected by appropriate design of nanocoatings. Zinc oxide and titanium dioxide nanoparticles of average particle diameter ranging from 50 to 100 nm are used for nanocoating formulation. Layers of nanoparticles alone and in combination with nanocoatings are applied on the fabric substrate. Nanocoatings are prepared by dispersing zinc oxide and titanium dioxide in acrylic solutions. The nanostructured coatings were analyzed by scanning electron micrographs and UV/Visible spectroscopy to understand the topography of the coatings and improvement in UV absorption. SEM images of the nanoparticle embedded acrylic membranes show significant dispersion of nanoparticles. Another representative SEM image of coated fabric shows good dispersion of nanoparticles on the fabric surface. UV/Visible spectra show the substantial improvement in UV absorption of nanoparticle embedded coatings than that of neat polymer. Molecular understanding of UV protection mechanism as effected by nanoparticles will be explained and compared with the efficiency of micro particles. Experimental verification of the mechanism is under way using QUV analysis, TEM, AFM, FTIR and SEM study.

#### **L8.45**

**Solution electrospinning of nylon/ferrite nanofibers.** Autumn Dhanote, Samuel C Ugbohue, Steven B Warner, Prabir K Patra, Phaneshwar Katangur and Shamal K Mhetre; Textile Science, University of Massachusetts, Dartmouth, N. Dartmouth, Massachusetts.

Recent studies on polymer nano-fiber and polymer-host nanocomposites have attracted considerable interest because of their ability to provide materials with significantly enhanced mechanical properties, thermal stability and barrier properties. In our research, we have employed electric field to embed ferrite nano-particles into nylon nano-fibers for improved magnetic properties. The nickel-iron oxide particles used were in the diameter range of 20-30 nm. The nanoparticles were surface treated with 0.05% w/w dodecyl benzene sulfonic acid (DBSA) prior to incorporating them into the polymer solutions. Surfactant coatings on the particles improved their miscibility with the organic polymer thus preventing agglomeration. Ultrasonication was carried out for 30-60 min to dissolve the nylon-6 into the formic acid/nanoparticle dispersion. The 15 % w/v solution of nylon-ferrite system was then electrospun using a point to plate geometry, with field strength of 1.5 kV/cm and a solution flow rate of 3 ml/hr. Using similar spinning conditions, virgin nylon-polymer solution was also electrospun. SEM analyses were carried out on both electrospun samples. The diameter of the virgin nylon nanofibers was found to range from 35-100 nm, and that of nylon-ferrite system was in the range of 80-200 nm. The observed higher diameter of nylon-ferrite composite fibers might be attributed to the increase in the viscosity of solution due to the ferrite particles. The SEM micrographs of the electrospun ferrite-nylon system indicated the absence of nanoparticles on the fiber surface, leaving us to infer that the particles might have been introduced within the polymer fibers. In order to better understand the morphology and nature of dispersion of the nanoparticles within the polymer fibers, XRD and TEM studies are in progress.

#### **L8.46**

**Morphological Influence of Layered Silicates on Nylon 6 Nanocomposites and Chars.** Gunes Inan, Prabir Patra, Yong K. Kim and Steve Warner; Textile Science Department, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts.

Nylon 6/clay nanocomposites are synthesized using a synthetic hectorite (Laponite<sup>®</sup> Na<sup>+</sup>) and a natural montmorillonite (Cloisite<sup>®</sup> Na<sup>+</sup>) clay by in-situ intercalative polymerization method. In the course of the insitu polymerization process, pre-intercalation of clay platelets is employed by the insertion of  $\epsilon$ -caprolactam monomer, and hence, siloxane surface of the platelets remained unmodified. X-ray diffraction studies on montmorillonite powders, pre-intercalates, and nanocomposites show that pre-intercalation process increases the basal space from 10Å to 16Å and polymerization process delaminates the lattices resulting no distinguished basal reflection. In contrast to

montmorillonite, laponite platelets do not exhibit well-defined basal reflection both in powder and nanocomposite forms. It is suggested that the disappearance of the d(001) plane of nylon 6 nanocomposites is controlled by; (1) the extent of delamination, (2) the surface charge and aspect ratio of the platelets, and (3) the clay loading. TEM and electron diffraction studies of powder and char forms of laponite samples show that it has lower crystalline order than that of montmorillonite. Because in-situ intercalative polymerization is a powerful method to achieve highly dispersed clays, it is not appropriate to compare the dispersion of the two platelets in their nanocomposite form. However, preferred re-aggregation of montmorillonite platelets after polymer decomposition indicates that montmorillonite platelets have stronger electrostatic interactions than that of laponite. It is also observed that char residues of laponite, montmorillonite and laponite/montmorillonite containing nanocomposites have different morphologies. The difference in continuity and brittleness of laponite and montmorillonite chars is attributed to different aspect ratios and surface charges, which may influence continuous network formation of clay aggregates. The present research is directed to better understand the influence of clay morphology on flame resistance of laponite and montmorillonite nanocomposites, especially in terms of their reduced heat release and mass loss rates as observed from cone calorimeter.

#### L8.47

**Continuous Nanocrystalline Ionic Silver Halides Optical Fibers with Reduced Optical Scattering.** Leonid N. Butvina<sup>1</sup>, Evgenii Dianov<sup>1</sup>, Andrei Okhrimchuk<sup>1</sup>, Ninel Lichkova<sup>2</sup>, Vladimir Savgorodnev<sup>2</sup> and Olesja Sereda<sup>1</sup>; <sup>1</sup>Fiber Optics Research Center, General Physics Institute of RAS, Moscow, Russian Federation; <sup>2</sup>General Physics Institute of RAS, Moscow, Russian Federation.

The single crystals of silver halides of solid solutions AgCl-AgBr with high purity and homogeneity were grown by Bridgeman technique. Severe deformed and dynamic recrystallized volume optical materials were produced by equal channel multideformation. Nanostructured volume optical materials were obtained with a narrow distribution of the grain sizes in the range 100-300 nm. For the first time, nanocrystalline optical fibers from nanograin ionic materials were produced by extrusion process. The nanocrystalline fibers and fibers extruded from single crystals were studied by an electron transmission microscopy and infrared spectroscopy. Optical losses and scattering were measured. The optical losses in the fibers, extruded from nanograin and single crystal, were compared at visible and middle infrared wavelength regions. The obtained nanocrystalline optical fibers have volume scattering 5-times less than microcrystalline optical fibers made with extrusion of single crystals. The nanocrystalline silver halide optical fibers with losses lower than 1 dB/m in the region from 2 to 20  $\mu\text{m}$  are demonstrated. Influence of vacancy pores with nanodimensions on boundaries and birefringence in nanograin on optical losses, measured in nanostructured ionic materials, will be discussed. Mechanical properties of nanocrystalline and microcrystalline fibers will be compared. Applications of nanocrystalline continuous optical fiber in remote spectroscopic chemical sensing and laser medicine will be presented.

#### L8.48

**Ibs Synthesis of CoPt-SiO<sub>2</sub> and FePt-SiO<sub>2</sub> Nanocomposite Films.** K.W. Lo<sup>1,2</sup>, Y. Gao<sup>1,2</sup>, K.H. Cheng<sup>1,2</sup>, N. Ke<sup>1,2</sup>, W.Y. Cheung<sup>1,2</sup> and S.P. Wong<sup>1,2</sup>; <sup>1</sup>Electronic Engineering, Chinese University of Hong Kong, Shatin, Hong Kong; <sup>2</sup>Materials Science & Technology Research Center, Chinese University of Hong Kong, Shatin, Hong Kong.

In this study, Co or Fe ions were implanted at an extraction voltage of 35 kV into thermally grown SiO<sub>2</sub> on Si substrates at a dose of  $4 \times 10^{16}$  ions/cm<sup>2</sup> using a metal vapor vacuum arc (MEVVA) ion source. Subsequent irradiation of Pt ions to doses ranging from  $1.5 \times 10^{16}$  to  $3 \times 10^{16}$  ions/cm<sup>2</sup> were performed at an extraction voltage of 50 kV. Characterization of these films was performed using Rutherford backscattering spectrometry, x-ray diffraction, transmission electron microscopy, and vibrating sample magnetometry. Under such implant conditions, it was found that Fe<sub>1-x</sub>Pt<sub>x</sub>-SiO<sub>2</sub> and Co<sub>1-y</sub>Pt<sub>y</sub>-SiO<sub>2</sub> nanocomposite films with  $0.40 < x < 0.54$  and  $0.34 < y < 0.51$  were obtained. The Co and Fe as-implanted films showed soft magnetic properties. After Pt irradiation, the coercivity of both the cobalt-implanted and iron-implanted samples increased. This is believed to be an indication of CoPt and FePt nanoparticle formation in these samples. After thermal treatment, the coercivity of most of the samples increased further. The dependence of the structures and magnetic properties of these films on the processing conditions will be presented and discussed. This work is supported in part by the Research Grants Council of Hong Kong SAR (Ref. Number: CUHK4216/00E).

#### L8.49

**Carbon/Nafion<sup>®</sup> Nanocomposite Thin Films as Potential**

**Matrix-free Laser Desorption-Ionization Mass Spectroscopy Targets.** A. Kaan Kalkan<sup>1</sup> and Stephen J. Fonash<sup>2</sup>; <sup>1</sup>Nanofabrication Facility, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>NanoHorizons Inc., State College, Pennsylvania.

Carbon/Nafion<sup>®</sup> nanocomposite thin films developed through a low-cost procedure were shown to function as low-noise, high-sensitivity, high-throughput laser desorption-ionization (LDI) mass spectroscopy targets for small molecule detection. The nanocomposite films were spin casted onto glass or steel substrates from a solution mixture of Nafion<sup>®</sup> polymer and amorphous carbon nanoparticles (average size of 40 nm). The spin-on coating was followed by a soft-bake step (e.g., 120 °C, 5 min). Only a weak mass signal was detectable when Nafion<sup>®</sup> was replaced with another polymer. Hence the role of Nafion<sup>®</sup> is understood to be more than gluing the carbon particles together; it also serves as an efficient ionization enhancer. In fact Nafion<sup>®</sup> (perfluorosulfonic acid/tetrafluoroethylene copolymer in the acid (H<sup>+</sup>) form) is well known for its efficient proton storage, transport and exchange properties. In this composite the amorphous carbon nanoparticles account for efficient light absorption in the visible and UV range such that a Carbon/Nafion<sup>®</sup> nanocomposite with equal weights of polymer and carbon absorbs more than 95% of the impinging light (less than 5% reflectance and undetectable transmission). As a result, analytes can be directly spotted on our nanocomposite targets without the need for an absorption/ionization enhancing matrix, which limits throughput and accounts for the low mass (500 amu and below) background noise in conventional matrix-assisted LDI (MALDI) mass spectroscopy. Our nanocomposite targets do not produce any background unless fragmentation of Nafion<sup>®</sup> occurs. This fragmentation was found to occur for laser power levels well above the ionization threshold of the analyte drug molecules tested. Hence, noise-free detection of low amounts of analyte can be carried out in a broad laser power range. Reserpine (609 amu), for example, was detectable down to femtograms. The signal intensity was found to increase with carbon content in the nanocomposite. On the other hand, only a weak dependence of ionization power threshold on carbon content was observed, whereas ionization threshold power increased with soft-bake temperature and duration. It is likely that the residual water in Nafion<sup>®</sup> enhances ionization. Furthermore, we did not observe any hydrocarbon or other contaminant collection on our target surfaces when they were left in laboratory ambient for weeks. We correlate this long-term cleanliness of our targets with their being superhydrophobic. Furthermore, electrical conductivity of our LDI target films (e.g.,  $\sim 2$  S/cm for the film with equal polymer and carbon weight content) also enables electrical biasing of the analyte during LDI.

#### L8.50

**Spherulitic Morphology and Thermal Stability of PP/ZnO Nanocomposites.** Sandeep Razdan, Prabir K Patra, Yong K Kim and Steven B Warner; Textile Sciences, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts.

The present work emphasizes on the morphological and thermal effects induced by the addition of nano-ZnO in polypropylene. We prepared polypropylene nanocomposites with nano sized ZnO particles as the filler. The composites were prepared using the solution technique, where a solvent is used to form a polymer-particle dispersion and is then evaporated to give the resulting nanocomposite. These synthesized nanocomposites were used for microscopic analysis, in comparison with control samples prepared by the same process. Scanning electron microscopy images of the nanocomposites revealed the formation of an extensive network of spherulites, which were not predominant in the native polymer. Cross-polarized optical micrographs of the composite samples confirmed the presence of this spherulitic network. Differential scanning calorimetric results showed enhanced crystallinity of the nanocomposites as well as crystallization peak shift toward a higher temperature. Also the heat of fusion of the composite samples was found to be 12% higher than the native polymer. It is evident from the results that the nano-ZnO particles were acting as nucleating agents for polypropylene crystallization, leading to the formation of spherulites. The results also showed that the presence of nano-ZnO affected the thermal properties of the polymer, as seen from the change in heat of fusion and crystallization temperature. Investigation regarding changes if any, in other thermal properties such as thermal conductivity, heat release rate and mass loss rate is currently under investigation using a cone calorimeter. Filler induced morphology changes in the PP/ZnO polymer nanocomposites are also being examined using X-ray diffraction and transmission electron microscopy techniques.

#### L8.51

**Contact Compression of Self-assembled Nano- and**

**Micro-scale Pyramid Structures on Au (100) Surface.**  
Junlan Wang, Donald Ward, William A Curtin and Kyung-Suk Kim;  
Division of Engineering, Brown University, Providence, Rhode Island.

An electro-chemical etching induced self-assembly is used to produce nano and micrometer scale pyramid-structures on single crystal gold (100) surfaces. The pyramids grow in a self-similar fashion with the facets aligned in (114) plane. Experimental studies are performed to optimize the etching conditions for the pyramid growth. Using the unique characteristics of the self-similar pyramid structure, contact compression experiments are performed on the single crystal gold surface to study the length scale effect in the plastic deformation of the pyramids. A continuum limit analysis and a finite element simulation as well as molecular dynamics simulations are used to predict the deformation and load-displacement curve of the pyramid compression. The limit analysis predicts the load of compression is proportional to the square of the deflection. The continuum analysis provides estimation on the asymptotic behavior of the elastic-plastic load-deflection response of the pyramid under compression for a large value of deflection. The three dimensional molecular dynamics simulation is utilized to study the dislocation activities during the early stage of the pyramid compression. Experiments are also carried out by pressing the pyramids with an atomically flat mica surface. The deformation of the compressed pyramid is measured using an Atomic Force Microscope (AFM). The continuum analyses predict size independent values of the slope change of the pyramid facets near the contact edge, caused by plastic deformation. However, atomistic simulation predicts opposite value of the slope change to the prediction of the continuum analyses. The AFM measurements of the slope change show size dependent transition from the prediction of the continuum analyses to that of the atomistic simulations. The transition data provide an apparent characteristic length of the size dependence of plastic deformation in a small volume.

**L8.52**  
**Synthesis of Nanostructured Thin Films of Yttria Stabilized Zirconia by Liquid Phase Electrolytic Deposition.** Zhigang Xu, Samuel Tamenu and Jag Sankar; Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina.

Yttria stabilized zirconia (YSZ), a fast ion-conductive material, is widely used as an electrolyte for solid oxide fuel cells (SOFCs) and other electrochemical devices. To prepare thin film electrolyte for solid oxide fuel cells, low-cost and efficient processing is highly desired. Electrolytic deposition has been used for different metal oxides. Compared with sol-gel processing, starting materials used for electrolytic deposition are less expensive, and deposition can be performed from aqueous solutions with relatively low concentrations. Nanostructured YSZ thin film coatings have been deposited on different substrates, such as nickel, porous strontium doped lanthanum manganite (LSM, a cathode material for SOFCs) by electrolytic deposition. The films were processed by cathodic deposition in the solution of the inorganic salts of yttrium and zirconium. Mixture of methanol and water was used as the solvent. The continuous coatings were realized by iterations of very thin film deposition, room temperature drying, intermediate temperature calcining. The coatings were finally sintered at high temperature. The desired thickness and the continuity of the coating were obtained by controlling the metal concentration in the solution, deposition current density, deposition time and sintering temperature. The cubic phase of YSZ in the coatings with 8 mol.% of yttria was confirmed with X-ray diffraction. The microstructures of YSZ coatings were characterized using scanning electron microscope and atomic force microscope.

**L8.53**  
**Synthesis and Processing of Multimetallic Oxide Nanoparticles Produced by Flame Spray Pyrolysis..**  
Julien Claudius Marchal<sup>1</sup>, Richard M Laine<sup>1</sup>, Jose Azurdia<sup>1</sup> and Tom Hinklin<sup>2</sup>; <sup>1</sup>MSE, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Tal Materials Inc., Ann Arbor.

Liquid-feed flame spray pyrolysis (LF-FSP) of ethanol solutions of low-cost metalloorganic complexes provides access to diverse types of mixed-metal, nanosize oxide powders with excellent control of chemical and phase purity. This scaleable synthesis route provides reproducible, high purity, frequently self-dispersing nanopowders at rates up to kg/h. Typical average particle sizes (APS) range from 10 to 150 nm with corresponding surface areas of 100+ to 20 m<sup>2</sup>/g. We will discuss processing nanopowders for photonic applications. For example, nanoYAG powders sinter to full density at 1400 degree Celsius.

**L8.54**  
**Nanostructured Cationic Inorganic Materials for Anion-Exchange.** Dat Tien Tran, Daniel P Brennan and Scott R J Oliver; Chemistry, SUNY at Binghamton, Binghamton, New York.

Many practical applications of nanoporous materials, most notably in the areas of catalysis, separation, ion exchange, fuel cells and sensor technology, have been exploited in recent years using anionic and neutral inorganic (zeolite) materials. Much less work, however, has focused on anions as structure directing agents in the construction of cationic inorganic hosts. Our research involves the solvothermal synthesis and solid-state characterization of new nanoporous and low dimensionality inorganic materials, where the charge on the host is positive. We are currently focusing on lower group 14 elements, as well as selected transition metals, as building blocks for these nanostructured hosts. We have successfully synthesized a variety of new compounds, one member being a cationic, two-dimensional layered material (Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub> as BING-5: State University of New York at Binghamton, structure type 5). We have quantitatively exchanged the interlayer nitrate groups of Pb<sub>3</sub>F<sub>5</sub>NO<sub>3</sub> for dichromate, chromate, permanganate, benzoate and terephthalate under ambient aqueous conditions. The material maintains or slightly expands its nanoscopic layer-to-layer distance. BING-5 is stable to 450°C, which is vastly superior to inorganic and organic resins that are still the standard for anion-exchange. Physical and chemical properties, as well as synthesis and characterization of these new materials, will be discussed.

**L8.55**  
**Baroplastic Core-shell Nanoparticles.** Sang-Woog Ryu, Juan Antonio Gonzalez, Metin H. Acar and Anne M. Mayes; Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Baroplastic core-shell nanoparticles systems were obtained by microemulsion polymerization. Nanoparticle baroplastics can be process and recycled at reduced temperatures. Several parameters determine the bulk properties of these baroplastic nanoparticles, such as composition, size and processing conditions. Composition has a dramatic effect on the mechanical properties, since within a small window of weight percent rubbery to glassy behavior can be achieved. The particle size plays an important role in the properties and processing of these materials, since the processability advantage of baroplastics resides on the size scale of the phases present; different sizes of particles have been studied, finding changes in mechanical behavior and an important change in optical clarity; nevertheless, their baroplastic property was maintained even in particles as large as 200 nm. Different morphologies, such as three-layer particles, were also obtained, in order to improve the properties of these core-shell nanoparticles. Characterization of the obtained particles and comparison of the resulting mechanical and optical properties with changes in composition, size and morphology are presented. Also, the incorporation of inorganic components, such as silica or gold, into the particles core is explored as a mean to obtain baroplastic nanocomposites.

**L8.56**  
**Nanoengineering of Extended ZnO Film Structures.** Z. Ryan Tian, Louise J. Criscenti, Jun Liu, Randall T. Cygan, Timothy J. Boyle, Paul G. Clem, Matthew J. McDermott, Diana L. Moore and James A. Voigt; Chemical Syntheses and Nanomaterials, Sandia National Lab, Albuquerque, New Mexico.

The ability to nanoengineer extended film structures of crystalline materials in solution has been investigated using the nucleation and growth of ZnO as the model system. Through use of growth modifiers, multiple nucleation and growth steps, and dissolution, we have produced a wide range of 3-dimensional ZnO architectures. Molecular simulations of the energetics and structure of various molecular and anionic sorbates and their interactions with the primary growth surfaces of zinc oxide were performed in support of the experimental work. Using batch and constant composition continuous reactor systems, the impact of aqueous and nonaqueous solvent systems and the zinc precursor on film microstructure was investigated. For example, the aqueous system used was an extension of the approach developed by Vayssieres and coworkers [L. Vayssieres, et al., J. Phys. Chem B 2001, 105 (3350-3352)]. The process utilizes a temperature driven thermal decomposition of a Zn-hexamethylenetetraamine complex that produces a pH change. The pH shift, in turn, causes the hydrolysis and precipitation of ZnO. Under the appropriate conditions, ZnO films with an amazing variety of structures can be prepared. These include arrays of simple hexagonal columns, columns capped with plates, columns composed of crystallographically aligned plates, and multi-legged columns. Structural control comes from the growth conditions used and the type and concentration of growth modifier. The growth of these structures will be explained using the results of the molecular modeling. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

**L8.57**  
**Polydiacetylenic Microcrystals with Highly Ordered**

**Mesostructures and Polydiacetylene/Silica Nanocomposites Thereof.** Jiebin Pang, Byron F. McCaughey, Xuan Li, Xiangling Ji and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanostructured materials have attracted a great deal of attention due to the novel material properties and applications. Polydiacetylene (PDA) has been the subject of extensive work because of its ability to form stable, ordered crystals that change color due to thermal, mechanical, or chemical stimuli. In this research, highly ordered mesostructured polydiacetylene sodium (PDA-Na) salt microcrystals have been prepared by the reaction of 10,12-pentacosadiynoic acid (PCDA) with NaOH in an aqueous medium followed by self-assembly, crystallization and UV polymerization. The microcrystals were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD), which indicated that the microcrystals exhibit highly ordered mesoscopic structures with a monoclinic symmetry. Upon thermal treatment, the microcrystals showed interesting thermochromic transition behaviors, such as irreversible red to blue, reversible blue to red, and irreversible red to orange changes at different temperature ranges. The thermochromatism of the microcrystals was investigated by differential scanning calorimetry (DSC) and other techniques. Using the PDA-Na and tetraethyl orthosilicate (TEOS) as precursors and upon the top-chemical polymerization of the monomers, the chromatically yellow or pink PDA/silica nanocomposites with disordered mesostructures have been easily prepared. The nanocomposites were characterized in detail by fourier transform infrared (FT-IR) spectroscopy, <sup>13</sup>C solid-state nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), thermogravimetric analyses (TGA), and differential scanning calorimetry (DSC) techniques. After removal of the PDA organic component by calcination, mesoporous silica was obtained from the results of nitrogen adsorption-desorption isotherms

SESSION L9: Polymer Systems  
Chair: James Watkins  
Thursday Morning, December 4, 2003  
Room 304 (Hynes)

**8:30 AM \*L9.1**

**Hierarchically ordered multi-component block copolymer/particle nanoparticle composites.**

Michael Rainer Bockstaller and Edwin Lorimer Thomas; MIT, Cambridge, Massachusetts.

The effective control of the spatial organization and connectivity of nanosized matter is an important prerequisite for the technological utilization of nanocrystal research. The simultaneous self-organization of block copolymers in the presence of ex-situ synthesized nanoparticles provides an approach to engineer 2D and 3D nanostructures that facilitates control of the structural characteristics of the sequestered component which becomes important when applications rely on size- and shape related properties of nano-objects. In this contribution we demonstrate that chemical compatibilization of the nanoparticles and geometrical characteristics of the block copolymer matrix allow to effective control the particle topology within the composite. Different composite morphologies can be distinguished, that is homogeneous distribution, interfacial segregation or center alignment of the particles within a polymer domain. The different microstructural environments of the sequestered component that are implied by the respective particle distribution result in distinctively different physical properties of the composite and render these materials interesting for a variety of applications.

**9:00 AM L9.2**

**Extending Nanoscale Block Copolymer Self-Assembly Approaches to High Temperature Ceramics.**

Carlos B. W. Garcia, Conrad Lovell, Chris Curry, Marybeth Faught, Yuanming Zhang and Ulrich Wiesner; Materials Science and Engineering, Cornell University, Ithaca, New York.

Nanostructuring of ceramic materials with block copolymers is a fascinating research field holding tremendous scientific as well as technological promise. Non-oxide systems like SiC or SiCN are particularly challenging since their polymeric precursors are often difficult to obtain and ill defined. Nanostructuring of such materials is expected to open up completely novel property profiles adding to those obtained from bulk materials like high temperature stability or mechanical properties. Here, to the best of our knowledge, we demonstrate for the first time the ability to nanostructure SiCN-type ceramics by blending a pre-ceramic polymer with the amphiphilic block copolymer poly(isoprene-block-ethylene oxide). The PI-b-PEO is used as a structure directing agent for a polysilazane, commercially known as Ceraset. Selective swelling of the PEO microdomains of the

block copolymer with the silazane oligomer results in a cooperative self-assembly of block copolymer and Ceraset into nanostructured morphologies. Different mesophases similar to those in pure block copolymer systems are observed by systematically increasing the polysilazane to block copolymer weight fraction. The structure is permanently set by crosslinking the silazane oligomer with a radical initiator. The nanocomposites are cast into films and characterized by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The results suggest that the use of block copolymer mesophases may provide a simple, easily controlled pathway for the preparation of various nanostructured high temperature SiCN-type ceramic materials.

**9:15 AM L9.3**

**Micromechanics of PS/PB/PS Triblock-Copolymer Films with Lamellar Morphology.** theodora tzianetopoulou and Mary C Boyce; Mechanical Engineering, MIT, Cambridge, Massachusetts.

Thermoplastic elastomers (TPEs) are a relatively new class of materials that exhibit behavior consistent with both plastics and rubbers. One class of TPEs is triblock copolymers which microphase separate into rubbery and glassy domains. Highly oriented, near single-crystal lamellar triblock copolymer films with an alternating rubbery-glassy layer morphology possess an interesting anisotropy in their mechanical behavior, which can prove to be attractive for various applications. This research aims in understanding the governing micromechanics in the deformation behavior of single-crystal TPEs. The competing roles of the glassy (PS) and rubbery (PB) phases of the layered configuration are investigated in several numerical simulations with numerous micromechanical finite element unit cell models of a polystyrene-polybutadiene triblock copolymer with oriented lamellar morphology subjected to tensile loading at different directions to the lamellae plane. Various morphological imperfections, common for this family of dual-phase polymeric materials, are studied, including interface perturbations, layer misalignment, and paired-edge dislocations. These structural imperfections provide initiation sites for potential deformation instabilities, such as layer buckling, micronecking and localized plastic deformation. The calculated micro- and macroscopic response to various types of loading is compared to x-ray and microscopy data, which already exist in the literature for these block copolymers, and proved to be successful in linking their macroscopic response to the underlying physics that govern the evolution of the periodic microstructure. Our representative unit cell models are also successful in reproducing the deformation behavior of highly oriented clay-particle lamellar block copolymers. Representative unit cell models of layered-silicate nanocomposites are deformed under the same type of loading conditions, and their response is compared both to experimental data as well as to the behavior of the respective neat block copolymer. The ultimate objective is to facilitate these finite element models to design hierarchically ordered materials with properties, which will be optimally tailored for different classes of applications.

**9:30 AM L9.4**

**Gold Nanoparticle Filtration Through a Nano-structured Polymer Membrane.** Allon Hochbaum, Ariya Akthakul, Francesco Stellacci and Anne M. Mayes; Materials Science and Engineering, MIT, Boston, Massachusetts.

The filtration properties of novel graft copolymer composite membranes were investigated by the filtration of gold nanoparticles. The membrane selective layer consists of microphase separated, hydrophilic PEO channels and a surrounding semicrystalline, hydrophobic PVDF matrix for structural support. Such membranes have significant applications in water purification, recycling, and desalination. The channel structure and selectivity, however, are difficult to characterize in a dynamic filtration environment. Consequently, solutions of ligand-protected gold nanoparticles, which are variable in both size and surface functionality independently, were employed as analytical probes of the membrane filtration performance. Changes in the size distribution of nanoparticle solutions before and after filtration were quantified using TEM and UV-visible spectroscopy. Results show that the nanoparticle size distribution could be cut off at specific and tunable diameters by varying the graft copolymer side chain length, nanoparticle ligand length, filtration solvent, or filtration time. Therefore, just as the size of the filtered nanoparticles provides information about the membrane filtration dynamics, the membranes can also be used to select specific nanoparticle distributions. This work demonstrates that the graft copolymer membranes could produce nanoparticles of low size dispersity in a convenient and inexpensive manner relative to current separation techniques, such as chromatography. Nanoparticles of such narrow size distributions are necessary for many applications in nano-scale electronic and optical devices as well as investigations of the frontier of multi-body particle physics.

#### 9:45 AM L9.5

##### **Sequential, Orthogonal Fields: A Path to Long-Range, 3-D Order in Block Copolymer Thin Films.** Ting Xu, James T.

Goldbach and Thomas P. Russell; Department of polymer science and engineering, University of Mass., Amherst, Amherst, Massachusetts.

The use of two orthogonal, external fields is shown to control the orientation of lamellar microdomains in three dimensions in diblock copolymer thin films. An elongational flow field was applied to obtain an in-plane orientation of the microdomains of the copolymer melt and an electric field, applied normal to the surface, was then used to further align the microdomains. Thin films of symmetric diblock copolymers of poly(styrene-*b*-methyl methacrylate) with long-range order and orientation of the lamellar microdomains were obtained as evidenced by small angle x-ray scattering and transmission electron microscopy.

#### 10:15 AM L9.6

##### **New Advances in Molding and Printing Processes for Organic/Plastic Electronics, using Chemically Modified Stiff, Photocured Poly(dimethylsiloxane) (PDMS) Elastomers Designed for Nano-Resolution Soft Lithography.**

Kyung M. Choi<sup>1</sup> and John A. Rogers<sup>2</sup>; <sup>1</sup>Bell Labs, Lucent

Technologies, Murray Hill, New Jersey; <sup>2</sup>Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

The development of new materials, useful for organic/plastic electronics are currently leading the latest research and allow us to achieve cutting edge devices through unconventional approaches. In nano-fabrication, the 'soft lithography technique' has been widely used in replicating and fabricating small features. It is a low cost alternative to photolithography by generating structures from masters to substrates which employ 'elastomeric materials', such as highly stretchable silicon elastomer, to replicate or transfer the original features to a variety of substrates by molding and printing processes. This technique significantly relies on the performance of polydimethylsiloxane (PDMS) stamp materials. However, commercial PDMS stamp materials have shown limitations due to their low physical toughness and high thermal expansion coefficients and thus are unable to satisfy our set of diverse demands, especially in the area of nano-scale replication. To achieve high performance in molding and printing, we designed and synthesized a new version of stiffer, photocured PDMS silicon elastomer that is developed specifically for nanoscale resolution soft lithography. We demonstrated its unique capabilities, a new advance in molding and printing, for the case of nano-features (300nm wide) with narrow and tall heights (600 nm height) of photoresistor, which is one of the most challenging 'nano-patterning' tasks in submicron scale soft lithography which is often limited in its use at the submicron scale with other commercially available elastomers. We also describe new materials, which result in significant improvements in the performance of optoelectronic devices, including digitally tunable microfluidic optical fiber device systems.

#### 10:30 AM L9.7

##### **Crystalline Structure and Crystallization Kinetics of Single Walled Carbon Nanotube Based Poly(epsilon-caprolactone) Nanocomposites.** Cynthia Ann Mitchell<sup>1</sup>, Ramanan

Krishnamoorti<sup>1</sup>, Jeffrey L. Bahr<sup>3</sup> and James M. Tour<sup>2</sup>; <sup>1</sup>Chemical Engineering, University of Houston, Houston, Texas; <sup>2</sup>Department of Chemistry, Department of Mechanical Engineering and Material Science, and the Center for Nanoscale Science and Technology, Rice University, Houston, Texas; <sup>3</sup>CNI Inc., Houston, Texas.

Nanocomposites of poly(epsilon-caprolactone) (PCL) and single walled carbon nanotubes (SWNTs) were examined in order to understand the influence of the organic-inorganic interactions on the dispersion of the nanotubes, the crystalline habits of PCL and the nucleation capabilities of the nanotubes. The interaction between the polymer and the nanotubes was controlled by either covalently linking the polymer to the nanotube or by the use of surfactants to mediate the interactions. End-tethered PCL nanocomposites were prepared by in-situ polymerization with functionalized SWNTs and a tin octoate based catalyst. The dispersion of the nanotubes was indirectly inferred from their melt state rheology and on the basis of these measurements the strongest interaction between the polymer and the nanotube was shown to lead to the best dispersion and characterized by hydrodynamic percolation at a loading of ~ 0.35 wt % of SWNTs. The crystallization kinetics of the nanocomposites were probed using differential scanning calorimetry and isothermal and non-isothermal studies demonstrated dramatically increased kinetics of crystallization indicative of the nucleating characteristic of the SWNTs. The morphology of the nanocomposites was probed using atomic force microscopy in tapping mode and the dimensions of the spherulites were found to decrease upon addition of the SWNTs providing further evidence of their nucleating ability.

#### 10:45 AM L9.8

##### **Facile Production of Well-Exfoliated Polypropylene-Clay Nanocomposites via a Novel, Solid-State Shear Pulverization Method.** Kosmas Kasimatis<sup>1</sup>, Laura M. Dykes<sup>1</sup>, Wesley R.

Burghardt<sup>1,2</sup> and John M. Torkelson<sup>1,2</sup>; <sup>1</sup>Dept. of Chemical Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Dept. of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

There is great scientific and technological interest in developing polymeric materials that are "lighter, stronger, and harder" by nanocomposite processing. Polymer-clay nanocomposites may achieve such enhancements via substantial clay exfoliation, i.e., homogeneous dispersion of a high fraction of the individual silicate layers in the polymer. The most successful method of producing well-exfoliated polymer-clay nanocomposites is by in situ polymerization, considered undesirable by those interested in solventless and monomerless processing. Another approach that has been studied for producing polymer-clay nanocomposites is twin-screw extrusion (TSE). This method has yielded well-exfoliated nylon-clay nanocomposites but has been unsuccessful in producing well-exfoliated polypropylene (PP)-clay nanocomposites unless all of the PP has been modified with maleic anhydride. We have previously demonstrated that a novel processing method called solid-state shear pulverization (SSSP) can yield well-dispersed and compatibilized polymer blends, overcoming many problems associated with melt mixing of blends. Here we have demonstrated that SSSP can also be applied to PP-clay systems to yield well-exfoliated nanocomposites. Characterization via transmission electron microscopy and wide-angle x-ray diffraction (WAXD) showed that PP-clay systems are poorly exfoliated after one or two passes through a twin-screw extruder. However, when pulverized, or when the product of a single-pass twin-screw extrusion process is then pulverized, well-exfoliated PP-clay nanocomposites resulted, even when the PP matrix was not modified by maleic anhydride. This represents the first application of SSSP to achieve dispersion in systems that are not totally organic/polymeric, and suggests a broad array of applicability of SSSP. The evolution of the well-exfoliated state during static, high-temperature annealing was studied via WAXD and differential scanning calorimetry, the latter showing that crystallization rates are strongly correlated to exfoliation levels. Additionally, novel in situ synchrotron scattering was used to collect 2-D wide-angle x-ray scattering patterns on samples experiencing flow conditions that provide external manipulation and control of the orientation state. These studies revealed high alignment of the dispersed clay, with the plate-like particles 'laying down' in the flow so that scattering and diffraction are concentrated along the velocity gradient direction. Conventional rheometry was also employed, revealing in well-dispersed systems (made by SSSP) the presence of a solid-like plateau in shear storage modulus at low frequencies. This is signature of significantly dispersed polymer-clay systems.

#### 11:00 AM L9.9

##### **Organoclay-Reinforced Biodegradable Nanofibers.**

Vahik Krikorian<sup>1,2</sup>, Cheryl Casper<sup>1,2</sup>, John Rabolt<sup>1,2</sup> and Darrin Pochan<sup>1,2</sup>; <sup>1</sup>Materials Science and Engineering, University of Delaware, Newark, Delaware; <sup>2</sup>Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

In this investigation we have explored the possibility of making nanofibers of rigid polymer layered silicate nanocomposites via an electrospinning process. The electrospun fibers were made from biocompatible/biodegradable polymer matrices with incorporation of organoclays. Commercially available organophilic clays were employed in order to study the effect of surfactant miscibility with the matrix in overall fiber formation process. The nanocomposites were fabricated by electrospinning a suspension of organoclay/dichloromethane with Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polyester, as the polymeric matrix. We have shown that decreasing the extent of miscibility of the surfactant decreases the tendency of the system to exfoliate and randomly distribute the silicate layers throughout the matrix. Polarized light microscopy shows a high degree of birefringence suggesting that the polymer chains in as-spun fibers are well aligned. Conversely, wide angle x-ray scattering (WAXS) data revealed no crystalline peaks in as-spun fibers whereas annealed samples show extensive amount of crystallinity. While the polymer chains in spun fibers are not in perfect crystalline registry, annealing the samples above glass transition temperature, even for a short period of time, induces a high degree of crystallinity. Transmission electron microscopy (TEM) data shows the ordering of silicate platelets along the fiber axis, consistent with the d-spacings obtained from WAXS. Scanning electron microscopy (SEM) data shows that the fibers are highly porous which may be beneficial in biomedical applications, membranes, reinforcement matrices, etc. In order to show the potential application of these systems in biological environments, results of mammalian cell culturing experiments will also be discussed.

11:15 AM L9.10

**Nanocomposites of Liquid Crystalline Polyhedral Oligomeric Silsesquioxane Particles and Liquid Crystalline Polymers.**

David A. Schiraldi, Alline P. Somlai and Subramanian Iyer; Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio.

New liquid crystalline nanoparticles have been synthesized by reaction of cyanobiphenyl derivatives with polyhedral oligomeric silsesquioxanes (POSS<sup>®</sup>). Several liquid crystalline nanoparticles can be made by varying the aliphatic spacer length of the cyanobiphenyl derivatives. A representative synthesis involves the reaction of allyl bromide with 6-bromohexanol in the presence of sodium hydroxide and tetrahydrofuran. The proceeding product is then reacted with 4'-hydroxy-4-biphenylcarbonitrile in the presence of potassium carbonate and acetone. The cyanobiphenyl terminated alkene is then reacted with octasilane POSS<sup>®</sup> via a hydrosilation reaction employing a Karstedt's catalysis. The LC POSS<sup>®</sup> nanoparticles were then compounded into thermotropic polyester liquid crystalline polymers (LCP)s as well as a "frustrated" LCP based on 4,4'-biphenyl acid and aliphatic diols. These LCP materials are currently being studied for potential use in high performance fibers and high gas barrier packaging materials. A comprehensive study of LCP/LC nanoparticle composites will focus on changes in the thermal and mechanical properties of the LCPs as a function of nanoparticle addition. It will be determined how incorporation of LC nanoparticles affects the liquid crystalline phases of an amorphous and semicrystalline LCP. Of special interest is the incorporation of an LC nanoparticle into a frustrated LCP. It is proposed that the LC nanoparticle will help to "frustrate" the LCP. The thermal stabilities, glass transition temperatures, and the moduli of these LCP/LC nanoparticle composites will be reported.

11:30 AM L9.11

**Nylon-6/Clay Nanocomposites Probed by Dielectric**

**Relaxation Spectroscopy.** Yu-Hsin Lee, Anthony J Bur, Natsuko Noda and Vivek M Prabhu; polymers division, National Institute of Standards & Technology, Gaithersburg, Maryland.

The study of polymer layered silicate nanocomposites has been performed by both time-domain and frequency-domain dielectric relaxation spectroscopy (DRS) in attempt to understand the correlation between the filler dispersion and the relaxation behavior of polymer at molecular level. Two types of microstructure, namely, agglomerated and exfoliated are obtained by extruding Nylon-6 with Cloisite 15A and 30B, respectively. Time-domain spectrometer enables us to probe the low frequency dispersion (0.01 Hz to 100 Hz) and the network analyzer collects data in the high frequency domain (100 Hz to 1 MHz). The evolution of the characteristic frequency, relaxation strength, as well as the width of relaxation time distribution is carried out by fitting raw data with the modified Cole-Cole function in which the electrode polarization effect has been taken into consideration. DRS results reveal the existence of three glass transition related relaxation modes. Above the T<sub>g</sub> of bulk Nylon-6, filled systems exhibit a shorter relaxation time as a result of a depressed crystallinity. On the contrary, a suppressed chain dynamics is detected below the T<sub>g</sub> of bulk Nylon-6 attributed to the reinforcement effect, which is best seen at the glassy state. Maxwell-Wagner (MW) polarization along with three other relaxation modes are observed below the bulk T<sub>g</sub>. Greater relaxation strength obtained in the MW dispersion in the filled systems suggests that the presence of clay creates extra interfaces for ionic polarization.

11:45 AM L9.12

**Glass Transition Temperature Behavior of Alumina/Polymethylmethacrylate (PMMA) Nanocomposites.**

Benjamin J Ash<sup>1</sup>, Linda S. Schadler<sup>2</sup> and Richard W. Siegel<sup>2</sup>;

<sup>1</sup>Sandia National Laboratories, Albuquerque, New York; <sup>2</sup>Materials Science and Engineering Department, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Alumina/ polymethylmethacrylate (PMMA) nanocomposites were synthesized by an in situ free-radical polymerization process using 38 nm and 17 nm diameter alumina nanoparticles. At extremely low filler weight fractions (< 1.0 wt% in 38 nm fillers and < 0.5 wt% in 17 nm fillers) the glass transition temperature (T<sub>g</sub>) of the nanocomposites dropped by 25 C when compared to the neat polymer. Further additions of filler did not lead to additional T<sub>g</sub> reductions. This novel thermal behavior is shown to vary with particle size, but this dependence disappears when normalized by specific surface area. The nanocomposite T<sub>g</sub> phenomenon is thought to be due non-adhering nanoparticles that act as well-dispersed internal void/polymer interfaces that break up the percolating structure of polymer domains recently hypothesized to be responsible for the T<sub>g</sub> reductions in polymer ultrathin films. The results also point to a dramatically

increased scope of the so-called interaction zone (IZ) and its "far-field" effect on the entire matrix.

SESSION L10: Modeling and Theory

Chair: Rina Tannenbaum

Thursday Afternoon, December 4, 2003

Room 304 (Hynes)

1:30 PM \*L10.1

**Kinetics and Mechanism of Nucleation, Growth and Stabilization of Metal Oxide Nanoparticles.** Rina Tannenbaum, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Metallic fragments, or metallomers (similar to the "mer"-based nomenclature used for polymers), formed via the decomposition of organometallic complexes, are highly reactive, generating a nucleation and growth process that culminates in the formation of nanocrystals. In the absence of stabilizing molecules, the aggregation process is self-restricting mainly due to the decreasing mobility of the particles and their declining diffusional rates as a function of their increasing size. On the other hand, in the presence of a polymer in the reaction medium, the growing metallic particles are stabilized by the adsorption of the polymer chains onto their surfaces, thus lowering their surface energy and creating a barrier to further aggregation. Studies of the nucleation and aggregation kinetics of metallic particles formed from the decomposition of organometallic precursors have been used to shed light on the mechanism of their formation. In these studies, the rate of decomposition of the precursor organometallic complexes has been deemed representative of the overall rate of the process. Moreover, it has implicitly been assumed that the formation kinetics of the metal nanoclusters directly mirrors the decomposition kinetics of the precursors. In this present work, we attempt to decouple the kinetic characteristics of the various steps that comprise the overall nucleation and aggregation process of cobalt oxide nanoclusters stabilized by poly(methyl methacrylate)(PMMA). A combination of infrared and x-ray photoelectron spectroscopies, transmission electron microscopy and dynamic light scattering is used to identify the individual contributions of each step to the overall mechanism of metal nanocluster formation. We have shown here that there are several crucial steps in the aggregation process of the nanoparticles, and that the traditional assumptions regarding the dynamics of the process are not correct. The formation of cobalt oxide nanoparticles with an average size above the detection threshold of dynamic light scattering (~3 nm) and TEM (~2-3 nm), does not mirror the decomposition of the precursor during the same time frame. Moreover, the stabilization process, i.e. the adsorption of the polymer chains onto the nanocluster surface, is shown to occur in the later stages of aggregation, as is evidenced by the common and parallel induction period observed in the formation of the cobalt oxide nanoclusters and the transformations that occur in the ester functional groups of PMMA. It is therefore clear that the aggregation and stabilization processes occur only after the reactive metallic fragments, i.e. metallomers, have reached a critical size and a distinct surface structure.

2:00 PM L10.2

**Effect of Grain Growth on Grain-boundary Diffusion Creep in Nanocrystalline Pd by Molecular-dynamics Simulation\*.**

Andrew Haslam<sup>1</sup>, Vesselin Yamakov<sup>1</sup>, Dorel Moldovan<sup>1</sup>, Dieter Wolf<sup>1</sup>, Simon Phillpot<sup>1</sup> and Herbert Gleiter<sup>2</sup>; <sup>1</sup>Materials Science Div., Argonne Natl Lab, Argonne, Illinois; <sup>2</sup>Institute for Nanotechnology, Karlsruhe Research Center, Karlsruhe, Germany.

Molecular-dynamics simulations are used to elucidate the effects of grain growth on grain-boundary diffusion creep and grain-boundary sliding during high-temperature deformation of a nanocrystalline Pd model microstructure. The initial structure consists of a 25-grain polycrystal with an average grain size of about 15 nm and a columnar grain shape. Prior to the onset of significant grain growth, the deformation proceeds via the mechanism of Coble creep accompanied by grain-boundary sliding. Grain growth is generally known to decrease the creep rate due to the increase of the average grain size. However, the results obtained in this study reveal an enhanced creep rate at the onset of the grain growth, when rapid grain-boundary migration occurs. The enhanced creep rate is shown to arise from two distinct causes. First, topological changes during the initial growth phases enhance both the stress-induced grain-boundary diffusive fluxes and grain-boundary sliding. Second, dislocations generated as a result of grain-rotation induced grain coalescence and grain-boundary decomposition in the vicinity of certain triple junctions also contribute to the deformation. ----- \*Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-31-109-Eng-38.

2:15 PM **L10.3**

**On Molecular Dynamics Simulation of Metal Clusters and Their XRD and ELNES Spectra.** Gregorio D'Agostino and Michele Gusso; ENEA, Roma, Italy.

The present paper reports on classical molecular dynamics of close-compact metal nanoclusters. Attention will be focussed to gold and cobalt while most of result do extend to other metals. Owing to present limits in computational power, metal clusters of intermediate size (thousands of atoms) cannot be treated by means of "ab initio" calculations and a classical molecular dynamics approach is compelled. An assessed many-body potential has been adopted which predicts structural and thermodynamic bulk properties of simple metals. Different geometries have been accounted for gold cluster (namely tronco-octahedra, truncated-decahedra and icosahedra) and cobalt (fcc and hcp based) of different sizes. Caloric curves have been evaluated thus showing well known co-existence regions and lowering of melting temperature. All (meta) stable structures were brought to their minimum energy configurations and phonon distributions have been evaluated by direct diagonalization of the dynamic matrix. Low temperature quantum free energies and related Debey-Waller factors have also been derived by simulated phonon spectra via Bose statistics. X rays diffraction patterns and near edge electron energy loss spectra have been simulated and compared. It is worth stressing that broadening of XRD peaks does not allow for direct recognition of the underlying lattice structure while the simulation provides clear interpretation of spectra. At very low temperature, spectra are dominated by finite-size effects and bond contraction at surface whereas at higher temperature Debey-Waller effects become relevant.

2:30 PM **L10.4**

**Nanocomposite Material For Sensing of Halogenated Methanes: A Model Based on Charge Transfer Interaction for Selectivity.** R. Sangoi<sup>1</sup>, L. Fuller<sup>2</sup> and K Santhanam<sup>1</sup>; <sup>1</sup>Center for Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York; <sup>2</sup>Center for Microelectronics Engineering, Rochester Institute of Technology, Rochester, New York.

A nanocomposite of multiwalled functionalized carbon nanotube and poly(3-methylthiophene) has been synthesized for selective sensing of halogenated methanes. TGA analysis of the composite showed two phase transition at about 520 degrees and 750 degrees with a weight percent loss of about 38% at 520 degrees and 100% loss at 750 degrees. The multiwalled functionalized carbon nanotube and poly(3-methylthiophene) showed phase transitions at about 820 degrees and 520 degrees. The IR spectrum of the nanocomposite showed peaks due to both the components. When the nanocomposite is exposed to CHCl<sub>3</sub>, nanocomposite showed a characteristic IR peak due to C-Cl. Similar experiments have been carried out with other halogenated methanes. The sensor has been constructed using two gold or two palladium microelectrodes on Si wafer or polymer substrates. The nanocomposite is cast between the electrodes for measuring either the resistance or voltage. For relevant comparison of the performance of the nanocomposite, sensors have been constructed with functionalized carbon nanotubes or poly(3-methylthiophene) or the blend. The nanocomposite showed high sensitivity for chloroform and very little or none for carbon tetrachloride and methane. Other halogenated methanes have also been investigated to model the mechanism. Based on the results, a mechanism based on non-rigid charge transfer interaction between the nanocomposite and analyte is proposed. The nanocomposite requires analytes with ionization potentials less than 11.50 for the charge transfer interaction. The sensitivity of the nanocomposite appears to be governed by the activation energy of the non-rigid charge transfer complex. The selective sensing of CHCl<sub>3</sub> from a mixture of CHCl<sub>3</sub> and CCl<sub>4</sub> suggests its potentialities for industrial applications.

2:45 PM **L10.5**

**Molecular Modeling Computer Simulations of Organic Polymers: A Novel Computer Simulation Technique to Characterize Nanostructured Materials.** Sarah G. Schulz<sup>1</sup>, Hubert Kuhn<sup>2</sup> and Guenter Schmid<sup>1</sup>; <sup>1</sup>Institute of Inorganic Chemistry, University of Essen, Essen, Germany; <sup>2</sup>AlCove -Molecular Dynamics- GmbH, Gladbeck, Germany.

Complex nanostructured self-assemblies such as colloidal suspensions, micelles, immiscible mixtures, microemulsions, etc., represent a challenge for conventional methods of simulation due to the presence of different time scales in their dynamics. We have recently successfully applied a novel computer simulations technique, Dissipative Particle Dynamics (DPD), to model the behavior of diblockcopolymers at the water/oil interface. With the use of a simple model we have performed simulations of polymer/water/oil systems at different concentrations. In this lecture we present the results of nanoscale "coarse-grained" simulations with DPD. DPD is a mesoscale simulation technique that has been introduced in order to

simulate three-dimensional structures of organic polymer aggregates. In DPD the polymer is modeled using particles which are interacting by conservative, dissipative and random forces. Particles are not regarded as molecules but rather as droplets or nanoclusters of molecules. We have successfully applied this technique to simulate the three-dimensional structures of microemulsions, e.g. the bicontinuous phase of C10E4 in water and n-decane, in domains of less than 100 nm. The different structures of the polymer/water/oil system were effectively characterized with DPD and are in remarkable agreement with the experiment. Even the so called "boosting-effect", a concentration-shift caused by the partially substitution of the polymer, was successfully simulated. The DPD method proved to be a reliable tool to get a better understanding of the nanostructure of self-assemblies and is therefore applicable to support the often complicated experiments or even to obtain experimentally unavailable data. E. Ryjkina, H. Kuhn, H. Rehage, F. Mueller, J. Peggau, *Angew. Chem. Int. Ed.*, (2002), 41(6), 983

3:00 PM **L10.6**

**Predicting the Morphologies of Confined Copolymer/Nanoparticle Mixtures.** Anna C. Balazs, Jae Youn Lee and Zhenyu Shou; Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania.

In order to isolate the factors that control the structure of nanocomposite thin films, we develop a computational model and scaling theory to investigate the behavior of diblock/nanoparticle mixtures that are confined between two hard walls. We find that in such restricted geometries, a polymer-induced depletion attraction drives the particles to these walls. If the particles are chemically distinct from the walls, they will effectively modify the chemical nature of these substrates. This change in chemistry, in turn, affects the polymer-wall interactions and consequently, the structure of the film. We illustrate this point by considering mixtures of particles and symmetric diblocks and show that the confining walls can be exploited to promote the self-assembly of the system into particle nanowires that extend throughout the films and are separated by nanoscale stripes of polymer domains. Such films constitute vital components in the fabrication of nanoscale devices. Furthermore, the results point to a novel technique for modifying the chemical nature of coatings and films entirely through self-assembly. Since this technique relies on entropic effects, it constitutes a fairly robust method that can be applied more generally than approaches that rely primarily on chemistry-specific enthalpic effects.

3:30 PM **L10.7**

**Exploring for 3D photonic band gap structures: the 11 FCC space groups.** Martin Maldovan, Chaitanya Ullal, Craig Carter and Edwin L Thomas; Materials Science, MIT, Cambridge, Massachusetts.

The promise of the photonic crystals and their potential applications, especially in the visible and near infrared wavelength range, has attracted considerable attention towards the establishment of periodic dielectric structures that in addition to possessing robust complete band gaps, can be easily fabricated with current techniques. A number of theoretical structures have been proposed. To date, the best complete photonic band gap structure is that of diamond networks having Fd3m symmetry (2-3 gap). The only other known complete band gap in a FCC lattice structure is that of air spheres in a dielectric having Fm3m symmetry (8-9 gap). Moreover, there is no systematic approach to discovering champion photonic crystals structures. Here we employ a level set approach based on crystallography to systematically examine the photonic band gaps in dielectric composites with symmetries of the eleven FCC space groups. This approach allow us to easily map different structures and gives us an insight into the effects of symmetry and connectivity on photonic band gaps. The eleven FCC space groups are classified into four fundamental geometries on the basis of the connectivity of high symmetry Wyckoff sites. Three of the fundamental geometries studied display complete band gaps - including two: the F-RD with Fm3barm symmetry and a group 216 structure with F4bar3m symmetry that have not been reported previously. By using this systematic approach we were able to open gaps between 2-3, 5-6, 8-9 bands in the FCC systems.

3:45 PM **L10.8**

**Electronic structure calculations on ITQ-4 zeolite with guest alkali atoms.** Hong Li and S. D. Mahanti; Physics and Astronomy, Michigan State University, East Lansing, Michigan.

The geometries and electronic properties of guest alkali atoms in the crystalline zeolites ITQ-4 are calculated within density functional theory (DFT) with GGA approximation using pseudopotential method. The pure ITQ-4 zeolite has a space group symmetry I12/m1 and consists of 32 Si and 64 O atoms in a unit cell. The lattice structures, the density of states (DOS) and the bandstructures of the pure ITQ-4 are first calculated. The optimized volume is 2.44% larger

than the experimental value, the  $c/a$  and  $b/a$  ratios are 0.23% and 0.02% larger than the corresponding experimental ones. The ITQ-4 system doped with alkali atoms is investigated using the same method. Possible positions of the alkali atoms inside the channel are optimized by energy and force minimization process. For 4 Cs atoms/unit cell (2 atoms/channel), it is found that the Cs atoms form a zig-zag chain along the channel, which is in agreement with the previous calculations [1], where a C12/m1 space group symmetry was assumed. Experimentally Petkov et al. [2] find zig-zag chains of Cs atoms along the channel. However, the plane containing the Cs atoms is found to be nearly perpendicular to what is found theoretically. We are reexamining their geometries by looking at other configurations and comparing directly the pdf (pair distribution function [2]) using the theoretical atomic positions with experiment. Results for different atoms (such as Na, K) and for different atomic configurations are being investigated. [1] Z. Li et al., J. Am. Chem. Soc. 2003, 125, 6050. [2] V. Petkov, et al., Phys. Rev. Lett., 2002, 89, 75502.

#### 4:00 PM L10.9

**Atomistic Modeling and Electronic Structure of Molecular Boxes.** Ljubomir Miljacic<sup>1</sup>, Lev Sarkisov<sup>3</sup>, Bin Deng<sup>2</sup>, Donald E Ellis<sup>1,2</sup> and Randall Q Snurr<sup>3</sup>; <sup>1</sup>Physics and Astronomy, Northwestern University, Evanston, Illinois; <sup>2</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>3</sup>Chemical Engineering, Northwestern University, Evanston, Illinois.

Novel classes of nanoscale porous materials assembled from discrete building blocks offer possibilities for size- and shape-selected molecular separation, and control over chemical processes, with applications to catalysis and sensing. We describe "molecular boxes" built from six-coordinate Re complexes forming "corner posts" which are interconnected by various organic links, such as pyrazine, bipyridine, and metal porphyrins. We have performed first-principles density functional, and molecular dynamics analysis of Zn-porphyrin based boxes, in order to characterize their conformation, stacking, electronic, and optical properties. Density functional-calculated torsion forces for a single box, are used to guide improvements in interatomic potentials useful for large-scale atomistic simulations. Analysis of calculated optical absorption profiles in terms of building-block contributions aids interpretation of measured spectra, and reveals electronic response to composition and conformation.

#### 4:15 PM L10.10

**Modeling amorphous systems under high pressure at the nanoscale via molecular dynamics simulations.** Lilian P Davila<sup>1,2</sup>, Maria-Jose Caturla<sup>3,2</sup>, Alison Kubota<sup>2</sup>, Babak Sadigh<sup>2</sup>, Tomas Diaz de la Rubia<sup>2</sup>, James Shackelford<sup>1</sup>, Subhash Risbud<sup>1</sup> and Stephen Garofalini<sup>4</sup>; <sup>1</sup>Dept. of Chemical Engineering & Materials Science, UC Davis, Davis, California; <sup>2</sup>Lawrence Livermore National Laboratory, Livermore, California; <sup>3</sup>Dept. Applied Physics, University of Alicante, Alicante, E-03690, Spain; <sup>4</sup>Dept. of Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Transformations of the medium-range order and the dynamic behavior of silica glass at high pressures is still not well understood despite years of research. Recent papers have shown how this medium-range order can be manipulated experimentally resulting in materials of scientific and technological interest. We have used MD simulations to study the behavior of fused silica under pressure at the nanoscale using empirical interatomic potentials developed by Feuston and Garofalini. In this article we present two different simulation schemes for studying the transformations in fused silica under high pressures, and show their equivalence. Both methods reproduce the equation of state (EOS) obtained from flyer plate experiments. We have centered our studies in the nanostructural changes occurring in the material with increasing pressure and the correlation between the medium-range order (~10 nm), through the structure factor, and the characteristic ring distribution of these amorphous glasses. An analysis of the ring distribution and structure factor reveals the changes occurring in this material in this regime and allows for an interpretation of the equation of state. The transition from elastic and plastic behavior is directly related to variations exhibited in the ring size distribution of this glass. During elastic compression, the ring distribution stays practically unchanged. However, this distribution varies continuously after the transition to the plastic regime takes place. This study can help understand the nanoscale nature of fused silica, influencing applications that depend on its structure under these conditions with implications in geophysics, glass technology and optics. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

#### 4:30 PM L10.11

**Multi-scale modelling of carbon nanotubes.** James Elliott, Huw Smithson, Marc Hamm and Alan Windle; Department of Materials Science and Metallurgy, University of Cambridge, Cambridge,

Cambridgeshire, United Kingdom.

The synthesis, processing and characterisation of carbon nanotubes, along with related fullerene structures, present some interesting challenges in terms of relating structural features on the nanoscale to the bulk mechanical and electrical properties of devices and composite materials. We have been using a number of different computational approaches to tackling these problems, and some selected examples will be described here. These include classical molecular dynamics simulations of single and multi-wall nanotube collapse under high pressures, Monte Carlo simulations of nanotube synthesis by chemical vapour deposition onto a metallic catalyst, and coarse-grained molecular mechanics calculations of nanotube persistence length. The overall aim will be to show that by constructing a modelling hierarchy spanning several orders of length and time scales, it is possible to build up a better understanding of effects at the nanoscale.

#### 4:45 PM L10.12

**Mesoscopic Modeling of Transport through Nanostructured Membranes.** Mark A. Snyder and Dionisios G. Vlachos; Department of Chemical Engineering and Center for Catalytic Science and Technology (CCST), University of Delaware, Newark, Delaware.

The understanding and ability to predict macroscopic transport properties for diffusion of interacting molecular species through nanostructured materials, such as membranes and nanotubes, is key to the development of both traditional applications, such as separations, and novel ones, such as growth of nanowires within nanopores. These systems challenge modeling approaches on several levels, including the strong energetics of the confined diffusion, the energetic anisotropy of the binding sites, the macroscopic gradients driving permeation and separation, and, ultimately, the heterogeneity of the material. Despite their widespread use, molecular simulations (e.g., molecular dynamics and Monte Carlo) are limited to short length and time scales, while inorganic films such as zeolite membranes invoke much larger length scales. The shortcomings of current modeling approaches, therefore, motivate the derivation of a novel mathematical framework for modeling diffusion of interacting species in nanostructured materials over larger length and time scales while retaining molecular scale information. In this work we explore a hierarchical approach, and develop a mesoscopic model for complex three-dimensional single crystal lattices. In particular, we focus on diffusion of aromatics in two practical zeolite systems, Faujasite and MFI. Comparison of gradient continuous time Monte Carlo simulations to the solutions of these new mesoscopic theories will be shown as validation of this approach in the limit of very thin membranes. Furthermore, this new theory allows us, for the first time, to perform quantitative comparisons of predicted macroscopic diffusion properties (e.g., molecular flux) to laboratory permeation experiments (e.g., benzene diffusion in Faujasite). In doing so, we assess the role that polycrystallinity (i.e., grain boundaries) plays in permeation and draw comparisons to the size and distribution of grain boundaries determined quantitatively via confocal imaging of realistic membranes saturated with fluorescent dyes.

SESSION L11: Poster Session III  
Chairs: Sridhar Komarneni, John Parker and James Watkins  
Thursday Evening, December 4, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

#### L11.1

**Solvent Effect on the Morphology of Mesoporous TiO<sub>2</sub>.** hung-jen chen<sup>1</sup>, Leeyih Wang<sup>2,3</sup> and Wen-Yen Chiu<sup>1,3</sup>; <sup>1</sup>Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; <sup>3</sup>Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan.

Mesoporous TiO<sub>2</sub> particles in various shapes were synthesized by a modified sol-gel reaction using amphiphilic block copolymers as organic structure-directing agent. The preparation route involves the adsorption of titanium isopropoxide on the surface of the template formed by the amphiphilic block copolymer in an organic solvent, followed by the growth of TiO<sub>2</sub> via the condensation of the surface-anchored precursor and free titanium isopropoxide monomer. The addition of acetylacetone as inhibitor to slow down the sol-gel reaction rate is essential to prevent the formation of TiO<sub>2</sub> particles in the solvent. The surface morphology of thus-prepared particles was examined by SEM and TEM. The surface area, pore size and its distribution of particles were investigated by BET and XRD techniques. The solvent effect on the shape and porosity of the TiO<sub>2</sub> particles will be presented.

### L11.2

**Carbon nanotube deposition on the surface of metal wire by inductively coupled UHF microplasma CVD.** Yoshiaki Shimizu<sup>1</sup>, Takeshi Sasaki<sup>1</sup>, Naoto Koshizaki<sup>1</sup> and Kazuo Terashima<sup>2</sup>;  
<sup>1</sup>Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan;  
<sup>2</sup>Department of Advanced Materials Science, Graduate School of Frontier Science, The University of Tokyo, Kashiwa, Chiba, Japan.

We have deposited carbon nanotubes (CNTs) on the surface of metal wires such as tungsten, iron, and nickel by inductively coupled UHF microplasma CVD. At atmospheric pressure in ambient air, the microplasma was generated in a quartz capillary of 700 micrometer inner diameter with Ar gas flowing, in which the metal wire of 100 micrometer diameter was inserted, by applying the UHF to coil around the quartz capillary. In case of CNTs deposition on tungsten wire, methane gas and vaporized ferrocene were supplied in the microplasma, while only methane gas was supplied in case of iron and nickel wires. Under the certain conditions of their gas flow rates and UHF power, CNTs were grown perpendicularly on the whole surface of the metal wires.

### L11.3

**HRTEM Characterization of Self-Assembled Manganese Oxide Thin Films.** Kate Laubernds<sup>1</sup>, Jikang Yuan<sup>2</sup>, Josanlet Villegas<sup>2</sup> and Steven L Suib<sup>1,2</sup>, <sup>1</sup>Chemistry, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

The formation of pure inorganic membranes is becoming increasingly important in the field of materials science. This work demonstrates the formation of inorganic free standing thin films without the use of polymeric additives. These inorganic films have applications as selective oxidation catalysts, sensors, and in separation and ion-exchange processes. The free-standing thin films (15-30  $\mu\text{m}$  thick) are composed of manganese oxide octahedral molecular sieves (OMS), which have the advantages of crystalline porous membranes and OMS properties. Oriented crystalline films of manganese oxide nanofibers were prepared in-situ by a gentle thermal treatment of an aqueous manganese solution. The manganese oxide film was characterized by X-ray diffraction, nitrogen adsorption, scanning electron microscopy, transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS). Additionally, conductivity and mechanical testing of the films was performed. TEM was used to gain detailed morphological and structural data of the thin films. Novel approaches were applied for the preparation of TEM samples in order to retain morphological information. The microscopy data showed that the films are composed of OMS-2 (cryptomelane) fiber bundles, arranged in ordered layers. Synthetic OMS-2 consists of mixed valent MnO<sub>6</sub> octahedra, sharing corners and edges to form tunnel structures. OMS-2 is a 2x2 structure with tunnel dimensions of 0.46x0.46 nm. The individual nanofibers aggregate together into bundles, which form the film matrix. The individual fibers and the corresponding bundles have an approximate diameter of 15 and 240 nm, respectively. Cross-sectional samples enabled HRTEM imaging down the long direction of the fibers. Additionally, EELS analysis provided data related to the electronic environment of the manganese species.

### L11.4

**Nanostructured Oxide Films for High Speed Sensors.** John Steele, K. D. Harris and M. J. Brett; Electrical & Comp. Engineering, University of Alberta, Edmonton, Alberta, Canada.

We have engineered nanoscale porosity into oxide thin films using electron beam evaporation and substrate motion control of the Glancing Angle Deposition technique. The films consist of high aspect ratio (~10 to 30) columns separated by longitudinal pores of diameter ~100nm or less, oriented perpendicular to the substrate. This anisotropic architecture comprises high surface area, high porosity films with ready accessibility of the pores to fluids or gases. To demonstrate sensor capability we have sandwiched these nanostructured SiO<sub>2</sub>, SiO, and Al<sub>2</sub>O<sub>3</sub> films between porous metal electrodes to fabricate parallel plate capacitive humidity sensors. The sensors display extremely quick response times of down to 25ms, and a capacitive response to change in humidity of approximately 4 orders of magnitude. The mechanisms responsible for the capacitance response will be discussed, and investigations of the sensors in an interdigitated rather than parallel-plate electrode arrangement will also be reported.

### L11.5

**Nanostructured Ferrite Thin Films Prepared by Atmospheric MOCVD at 360°C.** Yuneng Chang, Chemical Engineering, Lunghwa University of Science and Technology, Taoyuan, Taiwan.

In this presentation, we will report synthesis of ferrite films with nanostructure by MOCVD. We also discovered that magnetic properties of films were closely related to film nanostructure. In this

project, a MOCVD process has been successfully developed to deposit polycrystalline zinc copper ferrite, Cu<sub>x</sub>Zn<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>, films at temperatures from 360 to 440°C, with zinc acetylacetonate, Zn(acac)<sub>2</sub>, copper acetylacetonate, Cu(acac)<sub>2</sub>, iron acetylacetonate, Fe(acac)<sub>3</sub>, and oxygen as reactants, using a horizontal cold wall atmospheric reactor. AES and survey scan XPS results show deposited films have all elements in stoichiometric amount. XRD indicated that these CVD films were polycrystalline spinel ferrite, with grain orientations on (511), (400), (311), and (220) (dspacing=1.61Å, 2.10 Å, 2.52 Å, 2.97 Å), with (311) being the preferential grain orientation for in Cu<sub>x</sub>Zn<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> films. Most films were smooth, composed by clustered grains, as shown by FESEM. The smaller spherical particles, with size of 20-50 nm, clustered together to form dome shaped grain, with height and diameter of 200, 700 nm respectively. The grain size varies with deposition temperature and achieves largest size for film deposited at 400°C. SQUID results showed that CVD films are ferrimagnetic, with low coercive field, (2.5~8 Oe), initial magnetic permeability ( $\mu_i$ ) 3.2x10<sup>-4</sup> emu/Oe, saturation magnetization (Ms), 3x10<sup>-5</sup> - 2.7x10<sup>-3</sup> emu, and remanence magnetization (Mr), 1.6x10<sup>-6</sup> - 2.6x10<sup>-4</sup> emu. SQUID results also show that both  $\mu_i$  and Ms are related to grain size, and deposition temperature.  $\mu_i$  and Ms achieve the largest value at 400°C film. The unit saturation magnetization is 225 emu/cm<sup>3</sup> (41 emu/g), and remanence magnetization is 21.6 emu/cm<sup>3</sup> (4 emu/g).

### L11.6

**Optical Properties of ZnO/Al<sub>2</sub>O<sub>3</sub> Nanostructured Thin Films.** John M Harrison, Masashi Matsumura and Renato P Camata; Dept of Physics, University of Alabama at Birmingham, Birmingham, Alabama.

Zinc Oxide (ZnO) is a wide bandgap semiconductor with promising characteristics for applications in UV sensors and light emitting devices. Significant advances in bulk and epitaxial growth, p-type doping, and production of high quality metal contacts are still needed to enable ZnO as a competitor for large scale UV applications. As a result, most research efforts are currently devoted to these critical issues associated with bulk and continuous ZnO systems. Much less attention has been given to the study of ZnO nanostructures. Nevertheless, ZnO nanoscale systems, such as nanocrystals and nanowires, are already produced with greater purity and better crystal quality than bulk crystals and epilayers, as low defect concentrations are statistically favored in these nanostructures. These low-dimensional systems have a variety of potential applications not only in light emission and detection but also in biosensing devices. In this work we have targeted the creation of well-controlled nanostructured thin films comprising ZnO nanocrystals embedded in Al<sub>2</sub>O<sub>3</sub> matrices and the study of their optical properties. For this purpose we have used a novel technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) to deposit ZnO nanoparticle/Al<sub>2</sub>O<sub>3</sub> films on silicon and sapphire at temperatures ranging from room temperature to 400°C. Contrary to conventional PLD, this approach decouples the deposition of nanoparticles and gas-phase species that often coexist in ablation plumes so that these two processes are manipulated independently. This is achieved by operating two independent PLD-based sources, such that one source exclusively generates nanoparticles while the other employs a gas-phase dominated plume. NBPLD delivers a beam of size-selected nanoparticles of controlled chemical composition while gas-phase species of different materials are deposited using an independent laser source. The NBPLD technique enables the variation of nanoparticle diameter by the simple adjustment of an applied voltage. Using this method we have created layers of Al<sub>2</sub>O<sub>3</sub> containing well-separated, size-selected ZnO nanoparticles with areal densities between 10<sup>10</sup> and 10<sup>12</sup> cm<sup>-2</sup>. ZnO nanoparticles were deposited during the ablation of a ZnO target at 0.3-0.7 Bar in the NBPLD source using a KrF excimer laser (248 nm) at fluences of 1-5 J/cm<sup>2</sup> while deposition of Al<sub>2</sub>O<sub>3</sub> was achieved by ablation of alumina targets at 5-10 J/cm<sup>2</sup> in a 10<sup>-4</sup> Bar O<sub>2</sub> atmosphere. ZnO nanoparticle diameter was tuned in the 5-15 nm range for different samples. We will discuss Atomic Force Microscopy studies comparing samples containing only ZnO nanoparticles and samples in which nanoparticles were encapsulated by Al<sub>2</sub>O<sub>3</sub> deposition. Photoluminescence measurements on these films will also be discussed in relation to the optical properties of continuous ZnO films. Our main focus is on the identification of size effects and interface phenomena in these nanostructured ZnO samples. (Funding: NSF-DMR-0116098).

### L11.7

**The effects of crystallinity on the Er<sup>3+</sup> photoluminescence properties of Er-doped nc-Si/SiO<sub>2</sub> superlattices.** Ji-Hong Jhe<sup>1</sup>, Moonseung Yang<sup>1</sup>, Jung H. Shin<sup>1</sup>, Kyungjoong Kim<sup>2</sup> and Daewon Moon<sup>2</sup>; <sup>1</sup>PHYSICS, KAIST, Taejeon, South Korea; <sup>2</sup>Nano Surface Group, Korea Research Institute of Standards and Science, Taejeon, South Korea.

Er-doping of Si has been studied intensely in hopes of developing

Si-based optoelectronic devices. Despite the large advances, the Er<sup>3+</sup> luminescence efficiency achieved is still rather low to realize the devices operating at room temperature. Recently, silicon rich silicon oxide (SRSO), which consisted of Si nanocrystals (nc-Si) embedded in SiO<sub>2</sub> matrix, appears as one of promising candidate for host material and by using SRSO, it is possible to obtain both the high excitation efficiency of Si and the high luminescence efficiency of SiO<sub>2</sub>. Unfortunately, the size and density of nc-Si and the location of Er atoms, which are key parameters for obtaining efficient Er<sup>3+</sup> luminescence, are difficult to control. However, such parameters can be easily controlled in SiO<sub>x</sub>(x<2)/SiO<sub>2</sub> superlattice. In this work, the effects of crystallinity on the Er<sup>3+</sup> photoluminescence properties of Er-doped nc-Si/SiO<sub>2</sub> superlattices were investigated. The Er-doped SiO<sub>x</sub>/SiO<sub>2</sub> superlattice films were deposited by UHV-ion beam sputtering method and were subsequently annealed at 950 or 1100 °C. After annealing, Er atoms were well confined in SiO<sub>2</sub> layers whose thickness was fixed at 8 nm. The formation of nc-Si was observed in the films annealed at 1100 °C. The size of nc-Si was controlled through the variation of oxygen content (x) and determined by high-resolution transmission electron microscopy (HRTEM). We observed the intense Er<sup>3+</sup> photoluminescence from Er-doped nc-Si/SiO<sub>2</sub> superlattices and more detailed discussion about the Er<sup>3+</sup> photoluminescence properties will be presented.

#### L11.8

**Comparison of conventional and microwave sintering on the barium titanate nanocrystals made by Ambient Condition Sol (ACS) process.** Prerak Badhaka, Jake Jokisaari, Burtrand I Lee and Sarit B Bhaduri; Clemson University, Clemson, South Carolina.

Barium titanate is an important material in the electronics industry. Its high dielectric constant and low dielectric loss factor over a wide range of temperature and frequency make it desirable as a dielectric material for the manufacture of capacitors while its ferroelectric properties are exploited for applications such as piezoelectric transducers. In the present study, nanocrystalline barium titanate powders have been made by ambient condition sol (ACS) process. The powder samples were sintered both in conventional and microwave techniques and the sintering behavior and properties of material processed by each route were compared. The influence of microwave treatment on the phase transition of barium titanate crystals was investigated. Microwave treatment was observed to produce tetragonal phase barium titanate. The crystal structure, crystalline size, phase transition and morphology of the powder samples were analyzed by XRD, Raman, DSL, DSC, TGA and SEM.

#### L11.9

**Aerosol-Assisted Nanocomposite Materials.**

John Eric Hampsey<sup>1</sup>, Jiebin Pang<sup>1</sup>, Qingyuan Hu<sup>1</sup>, Donghai Wang<sup>1</sup>, Byron McCaughey<sup>1</sup>, C. Jeffrey Brinker<sup>2</sup> and Yunfeng Lu<sup>1</sup>; <sup>1</sup>Department of Chemical Engineering, Tulane University, New Orleans, Louisiana; <sup>2</sup>Direct Fabrication Department, Sandia National Laboratories, Albuquerque, New Mexico.

Silica nanocomposite particles have been synthesized by an aerosol-assisted self-assembly process. Constituents such as latex spheres, fluorescent dyes, organic ligands, catalyst particles, and metal oxide nanoparticles were added to the precursor sols prepared by reacting tetraethoxysilane (TEOS), ethanol, surfactant, water, and acid. Using nitrogen as a carrier gas, the solution was sent through an atomizer producing aerosol droplets that pass through a glass tube heated at 400 degrees C. Solvent evaporation from the droplets enriches the non-volatile components and results in the co-assembly of silicate and surfactant into 3-dimensional mesostructures and in the incorporation of the added constituents within the particle. Subsequent removal of the surfactant results in mesoporous silica nanocomposite particles. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), fluorescent imaging, nitrogen adsorption/desorption, and other techniques were used to characterize these nanocomposite materials. This is a novel and convenient technique to prepare various silica nanocomposite particles.

#### L11.10

**Novel Star Architectures of Polystyrene-block-Poly(ethylene oxide) Copolymers as Surface Films at the Air/Water Interface.** Jennifer Lin Logan<sup>1</sup>, Pascal Masse<sup>1</sup>, Brian Dorvel<sup>1</sup>,

Andrew Skolnik<sup>1</sup>, Raju Francis<sup>3,1,2</sup>, Daniel Taton<sup>2</sup>, Yves Gnanou<sup>2</sup> and Randolph Duran<sup>1</sup>; <sup>1</sup>Chemistry, University of Florida, Gainesville, Florida; <sup>2</sup>Chemistry, University of Bordeaux I, Bordeaux, France; <sup>3</sup>Chemistry, University of Calicut, Kerala, India.

The effect of star architecture and composition on the monolayer behavior of polystyrene (PS) and poly(ethylene oxide) (PEO) diblock copolymers at the air-water interface is examined and presented. While numerous studies of linear PS-*b*-PEO systems exist in the literature, our work is the first time that branched structures of these

block copolymers have been examined. Our samples comprise stars containing a PS core and PEO corona (PS<sub>n</sub>-PEO<sub>n</sub> where n=3,4 and is the number of branches of each block polymer) and one dendrimer-like star, PS<sub>3</sub>-PEO<sub>6</sub>. Isotherm experiments demonstrated the surface films to be stable with PS anchoring the PEO to the interface. The presence of a pseudoplateau at a pressure of ca 10 mN/m was found to depend on the amount of PEO present. In addition, pancake and brush regions were also observed in which the former depended on the amount of PEO while the latter reflected PS behavior. By continuously compressing and expanding the monolayer, the ability of the polymer to relax was examined through hysteresis. Greater hysteresis was observed with increasing pressure along with a larger amount of PEO. Canal viscometry experiments showed that the star surface films readily flow at pressures below the pseudoplateau region. Two stars containing the same PS core were chosen to examine the effects of PEO. Using Atomic Force Microscopy (AFM), Langmuir-Blodgett films of these stars transferred at various surface pressures demonstrated a range of morphologies depending on PS:PEO composition.

#### L11.11

**Self-Assembly of Telechelic, Pyrene-labeled Polydimethylsiloxane: Remarkable Melting Point Depression of Pyrenyl Nanocrystals and Novel Oxygen Sensing Capabilities of an Associative Polymer.** Bryce A. Jones<sup>1</sup>, Sung Dug Kim<sup>1</sup> and John M. Torkelson<sup>1,2</sup>; <sup>1</sup>Dept. of Chemical Engineering,

Northwestern University, Evanston, Illinois; <sup>2</sup>Dept. of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Unusually large melting point depressions for organic nanocrystals, up to 100 K relative to bulk, have been observed in an associative polymer, telechelic pyrene-labeled polydimethylsiloxane (Py-PDMS-Py). In contrast to most studies of organic nanocrystals which are done in controlled pore glass formers or similar nanoporous materials, in the case of the Py-PDMS-Py system nanocrystals form in a novel manner within nanoaggregates of pyrenyl units that are strongly immiscible in PDMS. For 5,000 g/mol and 7,000 g/mol Py-PDMS-Py, physical gels (with the pyrenyl nanocrystals serving as junction points in the physical gel) result at room temperature with melting points exceeding 315 K and small-angle x-ray scattering peaks indicating nanoscale order. In contrast, 30,000 g/mol Py-PDMS-Py is not physically gelled and exhibits no SAXS peaks at room temperature; however, after annealing for 12 hours at 268 K, multiple melting peaks are evident at 278-303 K. These Py-PDMS-Py materials also exhibit excellent oxygen sensing capability through a relationship between the pyrene fluorescence excimer-to-monomer intensity ratio and oxygen partial pressure. Notably, by use of a fluorescence intensity ratio as the sensor output, these materials yield "self-referencing" sensors which yield sensitivity to oxygen independent of film thickness, excitation source fluctuations, and monitoring geometry. Additionally, there is little temperature dependence to the relationship between the intensity ratio and oxygen partial pressure. As a result, these materials have excellent prospects to be used in a variety of applications, including pressure sensitive paints.

#### L11.12

**Effect of addition of conducting phase in a dielectric matrix.**

Venkat Anil Kumar Magadala, Jake Jokisaari, Burtrand I Lee and Sarit Bhaduri; Materials Science & Engineering, Clemson University, Clemson, South Carolina.

In recent years, materials with a high dielectric constant have been in demand for insulators in dynamic access memory (DRAMs), capacitors and various other applications. It is known that doping a dielectric ceramic with a conducting material improves sintering, mechanical, and electrical properties. However, limited work has been carried out with larger dopant concentrations, up to the percolation threshold for the conducting phase in a dielectric matrix. In the present study, small amounts of fine silver particles have been intimately mixed with various commercial BaTiO<sub>3</sub> powders for comparative study. Silver was added from 0% silver at 5 wt% intervals up to the percolation threshold. The bulk forms of these composites were sintered both by conventional and microwave techniques to observe the effect of silver addition on sintering behavior and properties. The sintered density and dielectric properties of the composites were investigated. A small amount of silver can improve the sintered densities; but as the level of silver increases the improvement in density levels off. Also, up to a certain limit, silver addition can improve the dielectric constant of BaTiO<sub>3</sub> and influences other dielectric properties such as dielectric strength & dissipation factor. The microwave-sintered samples were found to have higher density and dielectric constant when compared to conventionally sintered samples. Similar experiments were also conducted on ceramic-polymer and metal-ceramic-polymer dielectric composites and systematic studies on effects of doping were conducted. The results of these experiments are presented here.

### **L11.13**

#### **Structure-Selective Synthesis of Mesostructured/Mesoporous Silica Nanofibers.** Jianfang Wang<sup>1</sup> and Galen D. Stucky<sup>1,2</sup>;

<sup>1</sup>Chemistry and Biochemistry, Univ. of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Materials, University of California, Santa Barbara, Santa Barbara, California.

Well-ordered mesostructured/mesoporous silica nanofibers have been synthesized in a quiescent dilute aqueous cationic surfactant/silica precursor reaction mixture under strong acidic conditions. These nanofibers have diameters ranging from 50 to 300 nm and lengths up to millimeters. Transmission electron microscopy (TEM) studies show that the nanofibers exhibit either a circular architecture with the pore channels running in a circular direction around the fiber axis or a longitudinal architecture with the pore channels running parallel to the fiber axis. The pore channels in both arrangements are hexagonally packed. The circular or longitudinal architecture can be selectively obtained during synthesis by varying reaction temperature or using inorganic salts as additives.

### **L11.14**

#### **Dense Silicon Dioxide Thin Films From Packed Silica Nanoparticles.** Xiaobing "Joe" Zhou<sup>1</sup>, Sheng Wang<sup>1</sup>, Kermit S.

Kwan<sup>2</sup>, Zhongtao Li<sup>1</sup>, Ginam Kim<sup>3</sup>, David Q. Ha<sup>1</sup>, David L. Wyman<sup>1</sup> and Eric S. Moyer<sup>1</sup>; <sup>1</sup>Electronics Science & Technology, Dow Corning Corporation, Midland, Michigan; <sup>2</sup>New Ventures: Inorganics R & D, Dow Corning Corporation, Midland, Michigan; <sup>3</sup>Analytical Science, Dow Corning Corporation, Midland, Michigan.

Compared to Chemical Vapor Deposition (CVD), Spin-On Dielectrics (SOD) can provide superior gap-fill capability, but tend to form comparably lower density films in confined spaces (trenches) following thermal anneal. It has been discovered that spin coating a solution of dense hydrophobic silica nanoparticles provided tightly packed films in trenches. The interstitial volume between the particles can be infiltrated with a hydrogen silsesquioxane (HSQ) resin to provide a continuous silica coating. The electronic-grade silica nanoparticles used in this study were prepared by base-catalyzed hydrolysis and condensation of tetraalkyl orthosilicates, and were subsequently surface-modified with trimethylsilyl groups and dispersed in an organic solvent. The resultant silica nanoparticles were spherical with particle densities in the range of 2.00 – 2.16 g/cm<sup>3</sup>, mean particle diameters in the range of 10 - 16 nm and narrow particle size distributions. Following spin coating on patterned silicon wafers and a steam anneal at 700 °C, the silica nanoparticles were found to be tightly packed, even in small trenches with a base width of 80 nm and an aspect ratio of 9 (height/width). The films showed a porous texture. With a solution of silica nanoparticles and HSQ resin dispersed in a solvent, a dense silicon dioxide film could be prepared. A minimal gap-fill limit of 32 nm (2 x mean particle diameter) was observed for silica nanoparticles with a diameter of 16 nm. The film textures of both the nanoparticle coating and the dense silicon dioxide films have been examined by high-resolution scanning TEM using a specimen prepared with a focused ion-beam (FIB).

### **L11.15**

#### **Development of Improved Routes towards Preparation and Surface Modification of Iron Oxide Nanoparticles.**

Lingyan Wang<sup>1</sup>, Jin Luo<sup>1</sup>, Li Han<sup>1</sup>, Masato Tominaga<sup>2</sup> and Chuan-Jian Zhong<sup>1</sup>; <sup>1</sup>Chemistry, SUNY-Binghamton, Binghamton, New York; <sup>2</sup>Kumamoto University College of Medical Science, Kumamoto, Japan.

The ability to control the size and surface composition of iron oxide nanoparticles is important for exploring chemical/biological sensing, catalytic and magnetic applications. This presentation describes recent results of two approaches towards the preparation of iron oxide nanoparticles. In the first approach, iron-storage ferritin was utilized for the preparation of iron oxide nanoparticles. The preparation involves thermal removal of the protein shell from ferritin. In the second approach, iron pentacarbonyl compounds are used for the preparation of iron oxide nanoparticles by thermal decomposition at controlled temperatures and under different capping agents. Iron oxide nanoparticles with a range of core sizes, different surface compositions, and high monodispersity have been prepared. The structure and morphology have been characterized using TEM, AFM, UV-Vis, and FTIR techniques. The implications of the findings to the design of advanced composite sensing materials will also be discussed.

### **L11.16**

**Probing nano scale dynamics in glassy polymers near glass transition temperature.** Koneswaran Sinnathamby and Nathan Israeloff; Dept of Physics, Northeastern University, Boston, Massachusetts.

The cooperativity concept of glassy dynamics has been investigated

by nano scale probing of thermal noise fluctuations in a glassy polymer polyvinyl-acetate (PVAc) near T<sub>g</sub>. Using ultra high vacuum (UHV) capacitance scanning probe microscopy (SPM) techniques, nano scale probing of thermal noise fluctuations in a glassy polymer can be related to second order changes in capacitance. Time series of thermal noise fluctuation and its power spectrum with varying temperature have been analyzed by calculating time dependent changes in local spectral exponent, time series analysis of octave sums, high order spectrum variations and covariance, correlation matrix of the octaves. Statistical analyses of these thermal noise fluctuations have been used to understand the glassy dynamics in nano scale by measuring temperature dependent characteristic lifetimes and length scales of cooperatively rearranging regions [CRR] and energy landscape properties.

### **L11.17**

#### **Nanocomposites with Functionalized Carbon Nanotubes.**

Shamal K Mhetre, Yong K Kim, Steven B Warner, Prabir K Patra, Phaneshwar Katangur and Autumn Dhanote; Textile Science, University of Massachusetts, North Dartmouth, Massachusetts.

Carbon nanotubes are known to have excellent mechanical, electrical and nonlinear optical properties because of their unique atomic geometries. These properties make carbon nanotubes potential candidates for high performance structural and high-response electrical and optical actuator applications. Despite their promises, no significant enhancement in the mechanical strength or modulus has been achieved in nanotube-polymer composites, presumably due to the weak interfacial bond between the CNTs surface and the polymer matrix. Also, most of these nanoparticle/polymer systems are poorly dispersed. One way of improving adhesion is to functionalize carbon nanotubes with chemical moieties that are compatible with the polymer substrate. Functionalization can give stronger adhesion (matrix to carbon nanotube) due to better interaction between the polymeric molecules and the chemical groups that are attached to the carbon nanotubes. Functionalization can also help in nanocomposite preparation giving additional advantages like easy solubility in solvents and better dispersion of nanoparticles in matrix. Our research consists of simultaneous purification, opening, shortening and carboxylic functionalization of carbon nanotubes using acid treatments. Carboxylic functionalized nanotubes will be further treated for methylene benzene group functionalization, which is compatible with polyester substrates. Two approaches for preparation of nanocomposites are under consideration, which consist of sandwiching functionalized carbon nanotubes between two ultra-thin polyester films and other approach is melt-extruding polyester or nylon chips containing uniformly embedded carbon nanotubes. Mechanical, electrical and optical properties of these nanocomposites will be analyzed using different characterization techniques available.

### **L11.18**

#### **Hydrothermal Synthesis of In<sub>2</sub>O<sub>3</sub> Nanocubes.** Bin Cheng<sup>1</sup>, Lei

Zhang<sup>2</sup> and Edward T. Samulski<sup>1,2</sup>; <sup>1</sup>Chemistry, University of North Carolina, Chapel Hill, North Carolina; <sup>2</sup>Curriculum of Applied and Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

Bin Cheng<sup>1</sup>, Lei Zhang<sup>2</sup>, and Edward T. Samulski<sup>1,2</sup> <sup>1</sup>Department of Chemistry, <sup>2</sup>Curriculum in Applied & Materials Sciences University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290 \* To whom correspondence should be addressed, et@unc.edu Forced hydrolysis of In<sup>3+</sup> ions from different precursors was studied in detail. The composition of the final precipitates was identified as In(OH)<sub>3</sub>, InOOH, and In<sub>2</sub>O<sub>3</sub>. Small size (~ 40 nm) and regular shaped In<sub>2</sub>O<sub>3</sub> nanocubes were successfully obtained for the first time by carefully controlled hydrothermal conditions. The composition, crystal structures and morphologies were characterized by XRD, SEM, AFM, TEM, and SAED. The photoluminescence of the as-prepared novel nanostructure of In<sub>2</sub>O<sub>3</sub> was also measured.

### **L11.19**

#### **Spherical Nanoparticle Ordering in Block Copolymers.**

John M Papalia and Mary E. Galvin; Materials Science & Engineering, University of Delaware, Newark, Delaware.

Theoretical work by Balazs suggests that hard spherical nanoparticles included in block copolymers will undergo some form of self ordering. By modifying the particle species, size, and concentration, as well as the composition of the copolymer, ordering of the particles should be obtained. Our investigations have initially centered around utilizing two differently sized particles of the same chemical composition. We have additional ongoing studies of alternative particles. Our work investigates these possible systems, as well as the enthalpic (modified by the inclusion of surfactants) and entropic needs of the system to obtain ordering.

### **L11.20**

## Highly Reproducible Synthesis of Thermally Stable 2D Hexagonal Mesoporous TiO<sub>2</sub>. Sungyeun Choi<sup>1</sup>, Marc

Mamak<sup>1</sup>, Neil Coombs<sup>1</sup>, Naveen Chopra<sup>2</sup> and Geoffrey A. Ozin<sup>1</sup>;  
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Non-siliceous mesoporous materials are of considerable interest, as they usually show special electronic, magnetic and catalytic properties compared with pure siliceous mesoporous materials. In particular, high surface area mesoporous titania (TiO<sub>2</sub>) is a very interesting material, with respect to its potential use in controlled delivery, chemical sensor, optic, catalytic, photocatalytic, or energy conversion applications. Recently, the synthetic approach based on the EISA (Evaporation Induced Self-Assembly) method, which makes use of ethanolic solutions of metal precursors and non-ionic tri-block-copolymers as templates has been shown to be a general route for the preparation of many transition metal mesoporous materials. Additionally, this approach provides significantly more flexibility in processing, allowing for the preparation of mesoporous "bulk" gels, thin films, and fibers. Samples in the form of thin films are most interesting in view of their potential utility as selective electrodes, sensors, photocatalytic, or electrochromic devices. Here we report the use of an alternative solvent for the reproducible synthesis of thermally stable mesoporous titania in the form of either a "bulk" gel (thick film) or thin film (< 1 μm) with a highly ordered hexagonal structure composed of channel walls containing nanocrystalline anatase. This synthetic approach was based upon the well-documented EISA method using the nonionic amphiphilic tri-block-copolymer, Pluronic P123 (PEO<sub>20</sub> PPO<sub>70</sub> PEO<sub>20</sub>) as the templating agent. Titanium ethoxide (Ti(EtO)<sub>4</sub>) was chosen as the inorganic precursor, HCl as a stabilizing agent, and the alternative solvent in the place of commonly used ethanol. The strategy employed here, which is the key to obtaining a robust, well-ordered mesoporous titania product, is based upon increasing the relative ratio of the Ti(IV) precursor to the P123 template concentration in the mother solution. Relatively crack-free transparent thin films were prepared by spin casting followed by controlled aging of the films. The obtained mesoporous titania thick and thin films produced by such modified conditions have a highly ordered 2D hexagonal structure, narrow pore size distribution (H1 type hysteresis), and high specific surface area of over 200 m<sup>2</sup>/g. Moreover, this structure composed of channel walls containing anatase nanocrystallites was stable up to 400°C. Thin film samples are crack-free at the centimeter length scale as determined from optical microscopy. Characterization of mesoporous titania samples were performed by Polarization Optical Microscopy (POM), powder X-ray Diffraction (PXRD), Transition Electron Microscopy (TEM), N<sub>2</sub> sorption analysis, Raman spectroscopy, and Thermogravimetric analysis (TGA).

### L11.21

**Structural characterization of Ni-doped and Co-doped carbon aerogels prepared by ion-exchange method.** Adelina P Santos<sup>1,4</sup>, Nasser S Demir<sup>1</sup>, Gene Dresselhaus<sup>2</sup>, Mildred S Dresselhaus<sup>1</sup>, Ted F Baumann<sup>3</sup> and Joe H Satcher<sup>3</sup>, <sup>1</sup>Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Chemistry and Material Science Department, Lawrence Livermore National Laboratory, Livermore, California; <sup>4</sup>Division of Nuclear Fuel and Materials, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte, MG, Brazil.

Carbon aerogels (CAs) are a class of cluster-assembled porous materials, which have been of interest for both science and applications. Their microstructure consists primarily of a conductive network of covalently interconnected carbon nanoclusters (3-25 nm) (grains), which define an open substructure of mesopores (2-50 nm). A few micropores have also been found to exist inside the grains. This structure leads to very low mass densities (0.1 - 0.6 g/cm<sup>3</sup>), extremely high surface areas (600-800 m<sup>2</sup>/g), and an intrinsic disorder of the system, with a large fraction of dangling bonds and defect states on the surface and inside the grains. Due to their unique microstructure, CAs are expected to have physical properties between those of the molecular and bulk-solid state limits. The introduction of metal species into CAs structure has been recently investigated in order to improve and tailor their electrical, catalytic and adsorption properties. Different approaches have been proposed to achieve metal doping, each one resulting in different effects on both the metal particles and the carbon framework morphologies, and consequently on their CA properties. In the present work, we report on the structural characterization of a series of Ni and Co-doped carbon aerogel systems synthesized by an innovative technique developed by Baumann *et al.* at Lawrence Livermore National Laboratory (LLNL). The method is based on the use of a sol-gel precursor derivative containing an ion-exchange moiety which enables a uniform placement of metal species of ion-exchange sites on the organic skeleton. Different metal-doped aerogel can be prepared using this technique by

replacing the cation sites in the precursor with the desired metal species prior to the carbonization step. The structure and properties of these metal-doped CAs will be discussed. The authors gratefully acknowledge support under LLNL subcontract B 518047 and the Brazilian Agency CNPq Fellowship.

### L11.22

**The Synthesis, Structure and Properties of Periodic Mesoporous Organosilica Thin Films.** Benjamin D Hatton<sup>1</sup>,

Doug D Perovic<sup>1</sup>, Kai Landskron<sup>2</sup> and Geoff A Ozin<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada; <sup>2</sup>Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

Periodic mesoporous organosilicas (PMOs) are polysilsesquioxanes structured using a self-assembled supramolecular surfactant template to create a periodic array of nanoscale channels [1]. Silsesquioxane precursors of the type (EtO)<sub>3</sub>SiRSi(OEt)<sub>3</sub> (where R is an organic group) can be used to introduce functionality into the channel walls of the mesopores. There is a great interest in using these organics to influence the chemical and physical properties, and achieving materials with interesting and novel function (such as catalysis). Generally such materials have been produced as powders, which limits their potential usefulness. Continuous film morphologies have many advantages for applications as sensors, membranes, or displays, and in microelectronics as low-k materials. In addition, films can be patterned using lithography or ink-jet printing. A generalized synthesis for highly-ordered PMO spin-coated thin films is presented here for double-bridged organics such as methylene, ethane, ethylene, 1,4-benzene and triple-bridged organics such as 1,3,5-benzene. Evaporation-induced self-assembly (EISA) [2] has been used with a cationic surfactant to produce hexagonal channel spacings around 40 Angstrom. Interestingly, this spacing varies directly with the organic group and loading. Detailed structural characterization of the films has been achieved using TEM, powder XRD, 2D XRD, SEM, 29Si and 13C NMR, and ellipsometry. The mechanical properties of the films have been measured using nanoindentation. Measurements have been made of the dielectric constant (k) by parallel-plate capacitance, which have been found to decrease with organic content to values as low as 2.0. These PMO films may be attractive as low-k dielectric layers also because they are hydrophobic and demonstrate good mechanical and thermal stability. [1] Asefa *et al.* Nature 402, 867-871(1999). [2] Lu *et al.* Nature 389, 364-368 (1997).

### L11.23

**Photoluminescence from the Silicon Surfaces Treated by Various Ionized Gases and Annealing Processes.** Min-Cherl Jung<sup>2</sup>, Young Ju Park<sup>3</sup>, Changhun Ko<sup>2</sup>, Moon-sup Han<sup>2</sup>, Chulyoung Ham<sup>1</sup>, Sung Ho Jun<sup>1</sup> and Kyoungwan Park<sup>1</sup>; <sup>1</sup>Dept. of Nano Science and Technology, University of Seoul, Seoul, South Korea; <sup>2</sup>Dept. of Physics, University of Seoul, Seoul, South Korea; <sup>3</sup>Nano-device Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Light emission from silicon using standard Si technology is important for applications in field of optical interconnection in future ULSI devices as well as display devices. In this work, we report a detailed structural and optical characterization of nanocluster silicon layer formed by two times of nitridation/oxidation and successive annealing process on silicon surface. Clean Si substrate was firstly exposed to the ionized N<sub>2</sub> gas at room temperature and low pressure. Atomic force microscopy and X-ray photoelectron spectroscopy analyses show that nanometer-scale SiN<sub>x</sub> islands can be formed at the surface. After successive rapid thermal annealing, several ionized gases were exposed on the modified surfaces. Transmission electron micrograph shows that silicon nanoclusters are formed between the SiN<sub>x</sub> islands in the secondarily formed oxide and/or nitride layers. In this experiment we found that two times of the rapid thermal annealing were decisive for the formation of silicon nanoclusters and the emission wavelength could be controlled by using the different matrix formation. The correlation between the luminescence wavelengths in the visible range and the chemical environment of the silicon nanoclusters supports the conjecture that the light emission is associated with both the quantum confinement effect and the surface related states in this nanocluster Si.

### L11.24

**A Processing and Characterization Study of a Biodegradable Nanocomposite.** Christopher Shaffer<sup>1</sup> and Jo Ann Ratto<sup>2</sup>;

<sup>1</sup>Chemical Technology Team, US Army Soldier Systems Center, Natick, Massachusetts; <sup>2</sup>Material Science Team, US Army Soldier Systems Center, Natick, Massachusetts.

A biodegradable polymer, Nodax, is investigated with montmorillonites to produce nanocomposites that may have a potential application for food packaging. The polymer and montmorillonites were extruded at different processing conditions.

X-ray diffraction and transmission electron spectroscopy were used to determine the dispersion and compatibility of the montmorillonite with the polymer. The optimal formulation was used to produce injection molded bars which were evaluated for mechanical properties and thermal analysis. Biodegradation experiments were performed on the pure polymer and the nanocomposites to determine the effect of the montmorillonite on biodegradation rates. Barrier properties (water vapor and oxygen) were also measured for their feasibility for food packaging.

#### **L11.25**

**Thiophene-Terminated Alkanethiol Functionalized Gold Nanoparticles.** Heejoon Ahn<sup>1</sup>, Amol Chandekar<sup>1</sup>, Bongwoo Kang<sup>2</sup>, Changmo Sung<sup>2</sup> and James E. Whitten<sup>1</sup>; <sup>1</sup>Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts; <sup>2</sup>Department of Chemical and Nuclear Engineering and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts.

Organic-covered metal and semiconducting nanoparticles may have future applications for molecular electronics. In the present study, thiophene-terminated alkanethiols, Th-(CH<sub>2</sub>)<sub>n</sub>-SH (Th = 3-thiophene with n = 2, 6, and 12), functionalized gold nanoparticles have been synthesized and characterized by X-ray photoelectron spectroscopy (XPS), FT-IR and UV-vis spectroscopies, and transmission electron microscopy (TEM). XPS demonstrates the formation of gold particles covered with thiophene-terminated alkanethiols. The peak position and peak-to-peak distance of Au 4f spin-orbit-coupled doublet indicate zero-valent gold, and the S 2p XPS spectrum confirms the attachment of the thiols to gold particles via thiolate bonds. FT-IR spectra also confirm that the gold nanoparticles contain thiophene-terminated alkanethiols. TEM images of the functionalized gold nanoparticles show that the size of particles is in the range of 2-7 nm. Optical properties of the gold nanoparticles dispersed in different solvents have been investigated using UV-vis spectroscopy. The 6-(3-thienyl)hexanethiol functionalized gold nanoparticle well disperses in chloroform and toluene, and shows surface plasmon (SP) bands with maximum intensity at 510 and 520 nm, respectively. However, the maximum SP bands shift to 655 and 695 nm in ethanol and hexane, respectively, due to agglomeration of particles. TEM images also show the agglomeration due to the solvent effect.

#### **L11.26**

**Dissipation in Polymer Films and Nanoparticles.** Philip Smith Crider<sup>1,2</sup> and Nathan Israeloff<sup>1,2</sup>; <sup>1</sup>Physics Department, Northeastern University, Boston, Massachusetts; <sup>2</sup>Nanomanufacturing Institute, Northeastern University, Boston, Massachusetts.

Utilizing Ultra High Vacuum (UHV) Scanning Probing Microscopy (SPM) techniques, dissipation in polymer thin films and nanoparticles near the glass transition temperature has been investigated to study cooperativity concepts in glassy dynamics. A Scanning Force Microscope (SFM) has been used to map dissipation across a surface, yielding localized information on the dissipation in glassy polymer polyvinyl-acetate (PVAc) thin films. A combination of scanning probing techniques including phase imaging and local force spectroscopy combined with Herzian dynamics allows local probing of dissipation, yielding insight into ideas of cooperatively rearranging regions (CRR). We also present analysis of methods of probing dissipation and aging in nanoparticles using SPM techniques, continued from previous studies of microparticles.

#### **L11.27**

**Electrostatically Generated SWNT/PEDT Electroactive Nanocomposite.** Afaf K El-Aufy and Frank K Ko; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Recent advances in intrinsically conductive polymers have created new opportunities in a broad range of electrical and electronic applications. Through redox or, in some cases, protonic doping of the conjugated electronic structure, polymers can be prepared with metallic conductivities up to 10<sup>5</sup> S/cm. They have found application in a broad range of technologies from batteries and light emitting diodes to computer electronics. Poly(3,4-ethylene dioxathiophene)/poly(styrene sulfonate)(PEDT/PSS), is widely used in the form of a film in a wide range of applications, (e.g. LED) because of its high conductivity (0.8 to 300S/cm). In this study, PEDT in fiber form was explored. Successfully, PEDT/PAN nanofibrous materials were produced using the electrospinning process. The electrical conductivity of the electrospun fibers was found to increase as the fiber diameter decrease. By using PEDT polymer in fiber form, the application of PEDT is expected to expand in the area of biosensors and wearable electronics. In order to explore the feasibility of producing multifunctional fibrous materials, SWNT was introduced into PEDT matrix to enhance the structural performance and electrical conductivity. The SWNT/PEDT blend was electrospun into nanocomposite yarn to facilitate the formation of higher order

structures. The morphology of the conductive polymer and nanocomposite were examined by ESEM. The structure, electrical properties, and mechanical properties of the SWNT/PEDT yarn were also characterized by Raman spectroscopy, 4-probe electrical conductivity measurement and microtensile testing.

#### **L11.28**

**Nanostructured and nanoporous inorganic host with a cationic charge.** Tolulope Oladipo Salami and Scott S.R.J Oliver; Chemistry, Binghamton University, Binghamton, New York.

Our efforts into the solvothermal (non aqueous synthesis) of new nano-materials will be discussed. Our long-term goal is to synthesize cationic materials for use as sensors, catalysts and sieves with tunable properties. We utilized the largely unexplored methodology of anionic structure directing agents (SDAs), focusing on nanoscopic species that have the potential to act as SDA such as, BF<sub>4</sub>, PF<sub>6</sub>- and CF<sub>3</sub>SO<sub>3</sub>H. These SDAs are able to direct the structure as well as introduced specific charges on the synthesized materials. We also have studied mixed group 14- transition metal systems in an attempt to alter the oxidation state of the building blocks and the charge on the host. Our research has resulted into a series of 0D, 1D, 2D and 3D compounds with interesting materials properties, which will be discussed along with their synthesis and structure.

#### **L11.29**

**Quaternary-matrix, nanocomposite self-lubricating PVD coatings in the system TiAlCN-MoS<sub>2</sub>: structure and tribological properties.** V. Spassov, A. Savan, A. R. Phani and H. Haefke; Micro- and Nanomaterials, CSEM Swiss Center for Electronics and Microtechnology, Inc., Neuchatel, Neuchatel, Switzerland.

Nowadays the demands placed upon the tooling in processes such as cutting, drilling, milling, stamping, bending, etc. are constantly growing and restrictive. On one hand, productivity, cost efficiency and quality all require high-speed processes to be developed. On the other hand, environmental safety requires very little or no lubricant to be used (dry cutting or minimized spray-lubrication). When combined, these two considerations mean: the tool should wear very little, withstand high temperatures and the friction between the tool and the work piece should be minimized. An apparent approach to simultaneously satisfying such requirements is coating the tools with self-lubricating hard coatings. Quaternary TiAlCN is a rapidly developing hard coating suitable for a number of cutting applications. The well-known wear-resistant coating TiN has been demonstrated to have improved high-temperature oxidation resistance when aluminum is included, i.e. TiAlN. Addition of yet a fourth element, carbon, has the primary effect of lowering the high friction coefficient occurring between the ceramic coating and steel. The high hardness, toughness, heat resistance and low friction coefficient of TiAlCN make it the ideal candidate for applications such as milling, hobbing, tapping, stamping and punching. MoS<sub>2</sub> is a well-known solid lubricant widely used as tribological coatings, especially for applications working in vacuum or dry environment. Combining the wear resistance of the quaternary TiAlCN matrix with the lubricating properties of MoS<sub>2</sub> has an extremely beneficial effect in further improving the tribological performance of the resulting composite. The coatings were deposited on hardmetal (WC-Co) and Si (100) substrates using reactive magnetron sputtering. The structure of the coatings is studied by plain-view TEM and XTEM, electron diffraction and EDX. The tribological properties were examined by Pin-on-Disk (PoD) tribometer. The adhesion was estimated by scratch test, and the hardness was measured by nanoindentation. All the coatings examined had a very low friction coefficient (typically below 0.09) and volumetric wear rates against 100Cr6 steel (AISI 52100) in the range of 10<sup>-7</sup> mm<sup>3</sup>/Nm. The relation of deposition parameters to structure to properties is discussed. To the authors' knowledge, this is the first paper describing quaternary TiAlCN matrix with inclusions of MoS<sub>2</sub>.

#### **L11.30**

**Comparative Effects of Nanoparticle Morphology on Properties of Polymer Nanocomposite Films.**

Elizabeth A. Welsh, Michael Sennett, Christopher Thellen, Danielle Froio, Axel Rodriguez, David Ziegler, Jo Ann Ratto and Walter Zukas; US Army RD&E Command (Prov), Natick Soldier Center, Natick, Massachusetts.

Exfoliated graphite nanoparticles (EGN) have the potential to be a low cost, high performance reinforcement for polymers due to their platelet structure and predicted mechanical properties. The effectiveness of EGN as a potential permeation barrier in polymer matrix nanocomposite films has been studied. Barrier and mechanical properties of EGN/polymer nanocomposite films have been compared to similar nanocomposite films having either comparable filler morphology such as smectite clays or similar chemical composition such as conventional carbon black. The relationship between the

properties of the nanocomposites and the nanoparticle composition and morphology were examined. Barrier testing included permeation resistance to water, oxygen, and selected organic permeants.

#### **L11.31**

##### **Structural Analysis of a (CoRe)<sub>27</sub>.**

**Re(5nm)/(Co(2nm)/Re(0.6nm))<sub>19</sub> Superlattice Grown on Al<sub>2</sub>O<sub>3</sub> (110).** Wentao Xu<sup>1</sup>, Timothy Charlton<sup>2,3</sup>, Lance E. DeLong<sup>1</sup> and David Lederman<sup>3</sup>; <sup>1</sup>Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky; <sup>2</sup>Materials Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>3</sup>Department of Physics, West Virginia University, Morgantown, West Virginia.

The structure of a (CoRe)<sub>27</sub>. Re(5nm)/(Co(2nm)/Re(0.6nm))<sub>19</sub> sample grown via magnetron sputtering was thoroughly analyzed via x-ray diffraction (XRD), x-ray reflectivity (XRR) and transmission electron microscopy (TEM). Prior to the superlattice growth, a Re seed layer was grown at 560 °C. The superlattice was grown at 165 °C to maximize crystallinity and minimize interdiffusion. Out-of-plane XRD indicates that the sample is hcp (100) oriented, while in-plane XRD indicates that the sample is epitaxial, with the in-plane c-axis of the superlattice pointing along the c-axis of the substrate. A quantitative analysis of XRR yielded the average thickness of each layer and a ~0.4 nm interface roughness between the Co and Re layers. Cross-sectional TEM confirmed the epitaxial information obtained via XRD. In addition, a careful analysis of the TEM data indicates that the in-plane lattice parameters for Co, Re and Al<sub>2</sub>O<sub>3</sub> are approximately 0.24, 0.43; 0.26, 0.44; and 0.24, 0.44 nm, respectively. The lattice spacings of Al<sub>2</sub>O<sub>3</sub> correspond to a/2 and c/3, respectively. Interestingly, both high resolution and Z-contrast images show a very uniform period thickness. Z-contrast images, however, show that the initial interface roughness between the Re seed layer and the first Co layer is amplified as the layers get farther away from the substrate. A high magnification analysis shows that the bottom Co-Re interface roughness is only about 0.2 nm, whereas the top Re-Co interface roughness is about 0.7 nm. Previous anisotropic giant magnetoresistance measurements will be discussed in light of these new structural data. This work was supported in part by NSF-EPSCoR.

#### **L11.32**

**Development of Electron Beam Cured Low-k Dielectrics by Plasma Enhanced Chemical Vapor Deposition (PECVD) for 65nm Technology.** Kang Sub Yim, Yi Zheng, Li-Qun Xia, Alex Demos, Helen Armer and Hichem M'saad; Blanket Division, Applied Materials, Santa Clara, California.

The demand of high-speed devices with small size requires new low dielectric constant materials with robust mechanical properties. Incorporation of low-polarized methyl groups or porogen molecules for nano-scale porosity has been widely investigated as an approach for lowering the dielectric constant (k). These films typically have poor mechanical properties. Various post-deposition anneals have been used to improve mechanical properties, but these have met with limited success. This paper introduces electron beam (Ebeam) treatment for the production of porous dielectric films. The films are deposited by PECVD using a porogen, and are ebeam treated after deposition. Ebeam removes the porogen and also improves mechanical and electrical properties. Resulting film properties for a k=2.6 film are modulus of 7-10 GPa and breakdown strength of >6.7MV/cm. For a k=2.6 film, e-beam treatment at very low dose causes a drop in k. The k bottoms at 0.05 below the as-deposited k, and further increases in e-beam dose cause k to rise. Hardness increases monotonically with increasing ebeam dose. Hence, the ebeam dose can be tuned to optimize k and hardness. The initial k drop can be explained by removal of labile organic components or dangling bonds, resulting in less-dense film. Higher ebeam dose induces film densification, resulting in higher k and hardness. Mechanical property enhancement is also verified by cracking threshold, which is increased to 5 mm with ebeam treatment. Ebeam-induced film structure changes were studied using FTIR and NMR. The intensity of C-H and Si-CH<sub>3</sub> peaks reduces after ebeam treatment, indicating a loss of methyl components from the film. However, the intensity of Si-O stretching peak about 1030 cm<sup>-1</sup> is slightly increased, indicating that a more cross-linked Si-O network structure is formed at the expense of depletion of C-H components. NMR analysis shows the same change of film structure. Film porosity as measured by ellipsometric porosimetry (EP) showed 7-18% porosity fractions and nano-scale pores <1 nm. Ebeam treatment reduces pore size, and higher ebeam dose compresses the film. A single damascene structure was fabricated using 50nm of nitrogen-doped silicon carbide as an etch stop layer and 500nm of ebeam treated ILD. The k of the ILD layer for this structure was extracted using interline capacitance measurement and TMA Raphael simulation, and the resulting integrated k value was 2.6. Single damascene integration data shows significant reduction of RC delay for this film compared to a k=3.0 film. A 2 level metal dual damascene structure was fabricated. This

structure had a leakage current of 5E-11 A/cm<sup>2</sup> at an electric field of 0.5MV/cm. Long via chains (up to 9 million vias) were tested, and the yield was >95%. No damage to a MOSFET has been observed at ebeam treatment up to 3x10<sup>-3</sup> Amp current.

#### **L11.33**

**Effect of film composition and structure on the diffusion barrier properties of metal alloy layers formed by electroless deposition.** Artur Kolics<sup>1</sup>, Nick Petrov<sup>1</sup>, Nanhai Li<sup>1</sup>, Marina Polyanskaya<sup>1</sup>, Jason Schneur<sup>2</sup> and Igor Ivanov<sup>1</sup>; <sup>1</sup>Blue29, Inc., Sunnyvale, California; <sup>2</sup>KLA-Tencor, San Jose, California.

Despite the numerous advantages of the use of copper as interconnect material in ultra large scale (ULSI) microelectronic devices, the technology faces several problems such as metal corrosion, weak adhesion, high chemical reactivity, and considerable diffusion of copper in silicon. In particular, the poor adhesion of copper to SiN, SiC, SiOC raises significant reliability problems. One of the promising ways to overcome this shortcoming is the application of metal or metal alloy capping layers. The adhesion of these layers to copper is very good, and the capping films are conductive, which decreases the effective k-value of the structure and consequently decreasing the RC delay. In addition, the metal caps can be deposited selectively on copper leaving the dielectric free from metallic residues. Such layers are expected to be thin (50-100 Å) and made up of amorphous alloys of Co(Ni),P and refractory metals, which can be formed using electroless plating method. The corrosion protection and barrier properties of this layer depend largely on their micro and nanostructure as well as their composition. These properties can be altered by the deposition condition and composition of the electroless deposition bath. In the present work we focused on the deposition process and resultant deposit itself. Nucleation, growth mechanism of electroless capping layer together with selectivity and barrier properties of the film under different deposition conditions is scrutinized with the use of scanning electron (JEOL), atomic force microscopic (KLA-Tencor) and Auger-electron spectroscopic (Phi) techniques.

#### **L11.34**

**Oxidative Dehydrogenation of Ethylbenzene to Styrene Over Graphite Nanofibers.** Xuejun Xu and R. Terry K. Baker; Catalytic Materials LLC, Holliston, Massachusetts.

The industrial process is currently carried out at high temperatures (above 650°C) using promoted iron oxide catalysts in the presence of steam. The highly endothermic character imposes a thermodynamic limitation to the conversion of ethylbenzene that can be attained (about 50%), and requires a great deal of energy consumption. The oxidative dehydrogenation of ethylbenzene in the presence of oxygen is one of most promising processes, since the reaction is highly exothermic. Such a reaction can be carried out at lower temperatures and is complete. It was proposed that a carbon layer generated on various solid inorganic catalysts during the reaction enhanced the activity of the system for the oxidative dehydrogenation of ethylbenzene. As catalysts, activated carbons suffer gasification in the presence of oxygen and fast deactivation by the coke formation due to their porous structure. Conventional graphitic materials are more resistant to attack by oxygen and are nonporous. However, their surface areas are extremely low (about 0.5 m<sup>2</sup>/g), limiting their usefulness as practical catalyst materials. Platelet and tubular graphite nanofibers (GNF), developed by Catalytic Materials LLC, have been used as catalysts in this work due to their structural architecture of graphite coupled with a relatively high external surface area of about 250 m<sup>2</sup>/g. The oxidative dehydrogenation experiments were carried out in a packed bed tubular quartz flow reactor. The performances of GNF catalysts are found to be vastly superior to that of a commercial catalyst mainly composed of Fe<sub>2</sub>O<sub>3</sub>. Platelet GNF showed a selectivity of 94% and a conversion of 40% at 547°C. Tubular GNF exhibited a selectivity of 54% and a conversion of 53% at 450°C. No deactivation of GNF was observed during the experimental periods. Used GNF are very safe and easily recyclable.

#### **L11.35**

**Synthesis and Characterization of Thin-film Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst for Preferential Oxidation of CO in Si-based Microreactors.** Haibiao Chen, Xun Ouyang, Lucie Bednarova, Ronald S. Besser and Woo Young Lee; Chemical,Biochemical and Materials Engineering, Stevens Institute of Technology, Hoboken, New Jersey.

There has been a growing interest in the miniaturization of chemical reactors for portable applications such as fuel cells. One of the challenges in the fabrication of microreactors is the incorporation of catalysts in the reaction channel. Thin-film is a preferred catalyst form for microreactors since it causes lower pressure drop in the microchannel in comparison to pack-bed configuration with powder catalyst and reaction kinetics are usually very fast due to the absence

of significant mass transfer and heat transfer limitations in microreactors. In this study, a highly porous alumina thin-film with dispersed metal nanoparticles was deposited on the microchannel wall of silicon-based microreactors. The thin-film catalyst was synthesized by two sol-gel methods. In the first method,  $\text{H}_2\text{PtCl}_6$  was dissolved in 1,3 butanediol to make a Pt solution, then it was mixed with an alumina sol. The liquid mixture was infiltrated into the microreactors, followed by drying, calcination and reduction to form a porous catalyst layer. In the second method, the alumina sol was first infiltrated, deposited, and solidified. Subsequently, Pt was incorporated by impregnation of the Pt solution into the alumina layer. The surface and the fracture-section of the Pt/ $\text{Al}_2\text{O}_3$  layer were observed by scanning electron microscopy. The thickness of the catalyst layer ranged from 0.5  $\mu\text{m}$  to 8  $\mu\text{m}$ , depending on the volume of the injected liquid precursor and the geometry of the microchannel. The BET surface area of the amorphous  $\text{Al}_2\text{O}_3$  support was 480  $\text{m}^2/\text{g}$ , and the diameter of most pores was in the range of 3 to 4 nm. Particle size distribution of the Pt on  $\text{Al}_2\text{O}_3$  was obtained by transmission electron microscopy. Preliminary data showed that most particles have a diameter between 3 to 7 nm. The active metal area and dispersion were measured by CO chemisorption. The microreactors infiltrated with the thin-film Pt/ $\text{Al}_2\text{O}_3$  catalyst were tested for preferential oxidation of CO by  $\text{O}_2$ . This reaction is a critical part of fuel processing for proton exchange membrane fuel cell applications for removing CO from  $\text{H}_2$ -rich reformates. Simulated reformat gas and air were fed into the microreactors at a flow rate which is equivalent to 0.5 W power generation. The microreactors, which typically contained 0.5 mg of the thin-film catalyst showed near 100% conversion of CO at 180~200°C and 1 atm.

#### L11.36

**Effect of Mo Doping and Heat Treatment on Microstructure and Electrochemical Performance of Vanadium Oxide Nanotubes.** Li-Qiang Mai, C. S. Jiang, Wen Chen, Q. Xu, J. F. Peng and Q. Y. Zhu; Institute of Materials and Engineering, Wuhan University of Technology, Wuhan, Hubei, China.

Mo doped vanadium oxides have found a wide range of applications because of their selective oxidation as well as the unique interaction between  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  owing to the similarity of ionic radii and the structures in their highest oxidation state [1-3]. These similarities enable the formation of substitutional solid solutions with different oxidation states of cations. In the present work, Mo doped vanadium oxide nanotubes were prepared by modified sol-gel process from layered oxide precursor and organic molecules as structure-directing templates. The morphologies and structures of the nanotubes are characterized by XRD, SEM, TEM, FTIR, XPS, ESR, etc. Experiments are performed in order to study the effect of Mo doping on the formation and structure of vanadium oxide nanotubes. In contrast to the undoped VONTs, the interlayer distance between oxide layers in the  $(\text{V}_{0.99}\text{Mo}_{0.01})_x\text{ONTs}$  increases owing to replacement of some V in nanotubes by Mo with a larger ionic radius, resulting in an improved electrochemical performance. Moreover, this study reveals that the electrochemical performance of  $(\text{V}_{0.99}\text{Mo}_{0.01})_x\text{ONTs}$  is further enhanced by removing the residual organic template by heating in an inert atmosphere. References: [1] Mai L.O., Chen W., Xu, Q., Zheng J.X., Ke M.Z., Mater Rev 1:6 (2002) 39. [2] Bielanski A., Najbar M., Applied Catalysis A: General 157 (1997) 223. [3] Chen W., Xu Q., Mai L.O., Hu Y.S., Zhu Q.Y., J Mater Chem 12 (2002) 1926. Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 50172036), the Teaching and Research Award Program for Outstanding Young Professors in Higher Education Institute, MOE, P.R. China and the Science Fund for Distinguished Young Scholars of Hubei Province (Grant No. 2002AC008).

#### L11.37

**Self Assembly of Tethered Silsesquioxane "Nanocubes" into Nanostructured Materials: A Molecular Simulation Study.** Charles Xi Zhang<sup>1</sup>, Elaine R Chan<sup>2</sup>, Monica H Lamm<sup>2</sup> and Sharon C Glotzer<sup>2,1</sup>; <sup>1</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Nanostructured assemblies composed of organic/inorganic nanoscopic building blocks hold much promise for providing innovative materials with superior properties. Recent experiments have demonstrated that polymer-mediated self-assembly of polyhedral oligomeric silsesquioxane (POSS) nanocubes is a promising route for creating highly ordered and novel structures. These experiments suggest that control over the final assembled structure, and ultimately the properties of the material, can be attained by manipulating POSS-polymer topology and the conditions under which the assemblies are formed. We have performed molecular simulations to systematically explore the parameters, including solvent quality, volume fraction, temperature, tether length and nano building block topology, that control the assembly process and influence the resulting

equilibrium structures. In particular, we study mono- and multi-tethered POSS cubes and POSS/polymer "telechelics" consisting of two POSS cubes connected by a single oligomeric tether, as neat materials and in selective solvents. We explore their phase diagrams, and present new results on novel nanostructures that result from microphase separation combined with the unique shape of these nano building blocks. Our computational methodology provides insight to the assembly process, and facilitates the rational design of new nanoscale materials by enabling the exploration of various assemblies and the conditions under which these novel structures are feasible. This research is part of a collaboration between the University of Michigan, University of Virginia, Vanderbilt University, and Colorado School of Mines and is funded by the National Science Foundation under DMR-0103399.

#### L11.38

**Synthesis and Characterization of Y2O3:Yb,Tm Blue Nanophosphors.** Shailaja Varma and Olivia A. Graeve; Metallurgical and Materials Engineering, University of Nevada, Reno, Reno, Nevada.

The interest in phosphor powders with nanometer dimensions has increased dramatically in the last few years. Several studies have shown that nanometer sized powders exhibit spectroscopic properties that are different from their micrometer-sized counterparts. However, the effect of particle size on the luminescence intensity of phosphors is not well understood. Even worse, there are direct discrepancies among different studies. Some have found that luminescence increases with particle size, while others have found the opposite. In an attempt to clarify the effect of particle size on luminescence intensity, Y2O3:Yb,Tm blue nanophosphors were synthesized by combustion synthesis. The synthesis process yielded ultra fine powders, which were subsequently annealed in a furnace to obtain particles of varying dimensions, from a few nanometers to 100 nm. After synthesis and annealing, several characterization techniques were utilized to determine the properties of the powders. From XRD and TEM, the particle size was determined to be in the range of 8 to 15 nm for the as-synthesized powders. Upon heat treatment the particles grew to dimensions in the range of 30 to 100 nm. From the PL measurements, it was determined that the powders were not luminescent in the as-synthesized state. However, upon heat treatment at 1273 K the powders showed an intense blue emission between 450 and 470 nm wavelength. While this phenomenon, in which luminescence is recovered upon heat treatment, has been observed in other studies, a clear relationship between particle size and luminescence has not been determined. In this work, a direct relationship between the particle size and luminescence intensity was obtained. As the heat treatment time was varied between 4 and 12 hours, the phosphors increased their luminescence intensity, showing a maximum at a heat treatment time of 8 hours. This phenomenon will be discussed and explanations given.

#### L11.39

**Nanodisperse Many-Particle-Systems: Concept, Structure-Property Relationships and Characterization Strategy.** Vladimir P Oleshko, Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Most practically important many-particle-systems (MPS) such as nanocrystalline thin films, small-domain-matter, particle-matrix-systems (metal-non-metal systems, imaging materials, granular superconductors, cluster tunnel junctions, cermets, dispersions), etc., form macroscopic compact matter and consist of a very large number of nano-sized units, that are interacting with each other. Physical interactions among clusters and/or with the embedding material mainly determine the macroscopic properties of the material. The need for knowledge about the properties of such systems arises in a variety of contexts, ranging from purely theoretical problems (small particle geometry, bonding and thermodynamics, quantization effects and electronic states in small particles, optical response of cluster matter) to numerous applications (imaging and recording systems, adsorption, catalysis, powder techniques, microelectronics, etc.). The functional properties of nanostructured matter depend on a number of parameters that describe the single cluster (atomic and molecular structure, elemental composition, size and shape), the near-order and far-order effects of a given cluster. They all have to be considered in detailed multilevel ultramicroscopic and analytical characterization, and several can be manipulated to tailor new materials with desired optical, electronic or catalytic properties. Such approach provides a logical synergism between engineering design (modeling) and characterization of MPS aimed for a better understanding of structure-property relationships. Within this concept, applications of a combination of imaging, diffraction and analytical electron microscopy (AEM) modes including (FE)-HRTEM, (cryo)-EFTEM/EELS, (cryo)-STEM/EDX/PEELS, low-voltage FE-SEM/EDX and real-time environmental TEM/EFTEM for the characterization of nanodisperse MPS will be discussed. Moreover, advanced AEM may give new insights into fundamental

structure-solid-state property relationships, local electronic and optical properties of nanostructured materials and dynamical structural and compositional transformations in-situ. Selected examples will include "giant clusters" of Pd<sub>561</sub>L<sub>60</sub>(OAc)<sub>180</sub> (L=1,10-phenanthroline), [Pd<sub>2</sub>(PPh<sub>2</sub>)H<sub>x</sub>]<sub>n</sub> and [Pt(PPh<sub>2</sub>)<sub>n</sub> (PPh<sub>2</sub> = biphenyl phosphide, n=6-10), composite multistructured tabular AgX (X=Br,I) microcrystals, Ag small particles and filaments, and TiCl<sub>4</sub>-MgCl<sub>2</sub> - supported heterogeneous Ziegler-Natta polymerization catalysts.

#### L11.40

**Virtual Synthesis of Sub-Nanoscale Materials with Prescribed Physical Properties.** Liudmila A Pozhar, MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

Recent progress in experimental fabrication and materials characterization techniques has opened a new page in development of advanced materials (such as single metal and semiconductor quantum dots (QDs), of GaAs, InAs, InP, CuCl, artificial atoms, etc.) with effective characteristic size ranging from tens to over several hundred nanometers. This presentation is focused on further advances in fundamental statistical physics, statistical mechanics and computational methods to investigate prospects of essentially three-dimensional synthesis of sub-10 nm structured nanomaterials [such as silicon-based sub-nanoheterostructure (NHS) units] with prescribed physical properties. The discussed conceptually new approach and its applications permit development of sub-nanometer scale materials in which functionality and hardware integration requirements are satisfied at the stage of the materials synthesis. The desired physical properties of such materials are achieved using predictions of a fundamental theoretical approach, the functional perturbation theory (FPT), implemented in synergy with the equilibrium statistical mechanical computations and simulations. This approach, called virtual fabrication, is the first self-consistent attempt to use fundamental theoretical predictions and computational manipulations of (1) a considered system structure, composition, chemistry and topology, and (2) processing parameters (such as the average density, composition, pressure, temperature, etc.) to ensure the desired transport properties of the processed sub-nanostructured materials. Materials design and fabrication routes so predicted can be further utilized in and tuned to the corresponding experimental efforts.

#### L11.41

**Composites of Highly Oriented Polyethylene Filled with Aligned Carbon Nanotubes by Gelation Technique.** Yuezhen Bin<sup>1</sup>, Sae Imamura<sup>2</sup> and Masaru Matsuo<sup>1</sup>, <sup>1</sup>Graduate School of Human Culture, Nara Women's University, Nara, Japan; <sup>2</sup>Faculty of Human Life and Environment, Nara Women's University, Nara, Japan.

Electric conductive materials with high modulus and high strength were developed using multi-walled carbon nanotubes (MWNTs) and ultra-high molecular weight polyethylene (UHMWPE). The composites with 0.25 to 15 wt% of MWNTs were prepared by gelation/crystallization from decalin solutions, and modified with iodine doping. The percolation field was found to be around 4wt% of MWNTs for the MWNTs-UHMWPE composites. The composite gel films could be elongated to more than 50-fold. The Young's modulus was beyond 35GPa while the draw ratio reached 50-fold. Scanning electron microscopes revealed that MWNTs with continuous networks are oriented predominantly parallel to the stretching direction. Such characteristic alignment of MWNTs plays an important role to form effective conductive paths in the high oriented composites. The co-orientation of MWNTs and UHMWPE in the stretching direction ensured that the composites possess high strength and high modulus and the electric conductivity of composites was hardly dependent upon the draw ratios. The ultra-drawn gel films were chemically modified with iodine doping. The electric conductivity of the composites increased 10<sup>1</sup> to 10<sup>6</sup>S/cm by iodine doping. At the same time, the modified composites possess extraordinary stability in electric conductivity during repeated heating cycles from room temperature to 150°C. Iodine doping was proved to be a very effective means for the improvement in electrical conductivity of polyethylene-MWNTs composites, especially for the composites with low content of MWNTs.

#### L11.42

**Oxidation Resistance of Multi-Walled Carbon Nanotubes Coated with SiC.** Yoshiaki Morisada, Masakatsu Maeda, Toshiya Shibayanagi and Yoshinari Miyamoto; Joining and Welding Research Institute, Osaka university, Ibaraki, Japan.

MWCNTs have been used to reinforce various matrixes. Such reinforcements can improve tensile strength by increasing the fracture energy. However, MWCNTs are oxidized easily above 530C in air because they consist of carbon atoms. Additionally, MWCNTs are

corroded after reacting with metals such as iron and aluminum. These properties limit the applications of MWCNTs. In this study, MWCNTs were coated with nanometer sized crystalline SiC using SiO vapor. The growth mechanism of SiC and the oxidation resistance of the SiC-coated MWCNTs were investigated. The growth of the SiC layer was controlled with the partial pressure of CO using the carbon felt placed in a crucible for SiC coating. The nanometer sized SiC particles were deposited by the reaction between SiO(g) and CO(g). On the other hand, the thin surface of MWCNT was converted to SiC when the carbon felt was not used. The oxidation durability of MWCNTs was improved by the SiC coating. MWCNTs were oxidized completely in air at 650 C for 60 min. However, about 90 mass % of the SiC-coated MWCNTs remained after the same oxidation test.

#### L11.43

**Synthesis of Mesoporous Titania as a Filler for Nafion-Based Composite Membranes for Direct Methanol Fuel Cells.** Chavalit Trakanprapai, Vincenzo Esposito, Silvia Licocchia and Enrico Traversa; Dept. of Chem. Sci. Technol., University of Rome Tor Vergata, Roma, Italy.

The recent discovery of mesostructured materials has given new perspectives in a large number of environmental-friendly applications, such as sensors, catalysis, and energy production and storage. A very interesting materials for those applications is titania. Liquid-fuelled fuel cells are a promising alternative to hydrogen-fuelled devices as portable and mobile electrochemical power sources. However, the power density and the efficiency of Direct Methanol Fuel Cells (DMFCs) are lower compared to Polymer Electrolyte Fuel Cells (PEFCs), due to the slow oxidation kinetics of methanol and the methanol cross-over through the electrolyte. An increase in the operation temperature is needed to enhance the kinetics of methanol oxidation. To solve this problem, in previous papers we have proposed the use of recast composite membranes based on Nafion containing finely dispersed nanocrystalline ceramic oxide powders such as TiO<sub>2</sub> and ZrO<sub>2</sub>. The ceramic filler improves the water retention characteristics, allowing fuel cell operation at a temperature close to 150°C. Given these performances, an increase in the specific surface area like in mesoporous oxides is expected to be beneficial for the performance of composite membranes in DMFCs. Therefore, the synthesis of mesoporous titania was studied, using micellar aggregates as templates. To avoid the high reactivity of Ti(OR)<sub>4</sub> species towards hydrolysis and condensation, the precursor selected and synthesized was a titanatrane complex (Dimethylaminotitanatrane). The formation of the mesoporous oxide in fact depends upon the relative rates of the inorganic precursor hydrolysis and condensation reactions and that of the organic-inorganic self-assembling process. The precursors and oxides were characterized by Nitrogen adsorption-desorption isotherms, TG/DTA, FTIR, FE-SEM, and XRD. The results demonstrated that high purity, mesoporous titanium dioxide was obtained with the synthesis procedure developed. The morphological observations of titanium oxide powders calcined at 350°C for 120 hours and 450°C for 6 hours showed that the powders were mesoporous, with an average pore size of about 3.5 nm. The mesoporous structure disappeared for samples fired at calcination temperatures above 450°C. These powders were used as a filler to fabricate the composite membranes with Nafion. The dispersion of the mesoporous titania in the Nafion was very good, as shown by FE-SEM observations. Preliminary DMFC investigation of such membranes at high temperature reveals a significant influence of the ceramic oxide surface area on the electrochemical behavior. At 140°C with oxygen feed, a power of about 320 mW cm<sup>-2</sup> was recorded. These results are very promising and a better tailoring of mesoporous titania particles is now in progress.

#### L11.44

**Corrosion Protection of Materials Surfaces by Applying Nanotechnology Associated Studies.** Ramazan Asmatulu, FEORC, Virginia Tech, Blacksburg, Virginia.

Corrosion - known as the destructive and unintentional attack on materials has been one of the most considered industrial problems in the world for several years. Corrosion mostly comes from corrosive ions and molecules (e.g., Cl, O, OH, H<sub>2</sub>O) existed in seawater, humid environment, acid rains, emissions (or pollutants), chemical products and industrial waste, and as well as sunlight (UV and heat). It begins at the surface and interface and decreases the lifetime of materials used in aircraft and spacecraft industry, land and sea transportation vehicles, stationary structures (house, bridge, road, furniture, etc.) and electronic and computer industries. As a result of degradation on material surfaces, these materials can lose their mechanical, other physical and chemical properties and appearance. Because of the corrosion formation on the surfaces, it is estimated that more than 5% of an industrialized nation's gross national product (GNP) is spent for corrosion preventions, replacement of corroded parts, maintenance and environmental protections. This corresponds over \$300 billion cost to the US economy per year. It is reported that there are several

ways of decreasing corrosion to improve the lifetime of materials and devices. As recently determined, some of the corrosion results are directly related to nanotechnology studies. These include nanosize film (potassium permanganate, zirconium compounds, chromium, aluminum, phosphate, nickel, molybdenum, cadmium or zinc-rich layers) formations (or conversion coating) between substrate and film, nanosize particles (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>, carbon) addition to coating systems, interfacial controls, surface treatments and combination of them. The test results obtained using nanotechnology assisted methods show that materials performances are improved 10 to 1000 times more than conventional corrosion methods. In the present paper, nanotechnology associated studies, including surface treatment methods, corrosion prevention methods (new protective coating systems), tap coating, newly developed theories, reasons of the corrosion, lifetime predictions, corrosion monitoring in nanoscale and industrial applications will be evaluated in detail. Thus, this will provide several indications to readers about new developments on corrosions and control systems.

#### L11.45

**UV Curable Polymers With Organically Modified Clay As The Nanoreinforcements.** Fawn M Uhl<sup>1</sup>, Brian R Hinderliter<sup>2</sup>, Prashanth Davuluri<sup>3</sup>, Stuart G Croll<sup>2</sup>, Shing-Chung Wong<sup>3</sup> and Dean C Webster<sup>2</sup>; <sup>1</sup>Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota; <sup>2</sup>Polymers and Coatings, North Dakota State University, Fargo, North Dakota; <sup>3</sup>Mechanical Engineering and Applied Mechanics, North Dakota State University, Fargo, North Dakota.

UV curable films are prevalent in microelectronic applications. Several advantages are associated with UV curing such as rapid cure, solvent free systems, application versatility, low energy requirements, and low temperature operation. To be used in electronics the films must possess the following attributes: high glass transition, barrier properties, low shrinkage, flexibility, and enhanced mechanical properties. The area of polymer-clay nanocomposites has been widely investigated and improved mechanical, thermal, and barrier properties were reported. Most researchers attempted nanocomposite formation by melt mixing or in situ polymerization. Little is understood on UV curable nanocomposites. This paper seeks to examine nanoclay-containing polymers using organomodified montmorillonites in UV curable systems and the effects of such clay inclusions on the properties of UV cured films. By x-ray diffraction it appeared that intercalated structures were formed. In the case of an epoxy acrylate formulation an increase in glass transition temperature was observed for formulations containing clay.

#### L11.46

**Boron Carbide Encapsulated by Nanocrystalline Ni Coating.** Jianhong He<sup>1</sup>, Yizhang Zhou<sup>1</sup>, Dean Baker<sup>2</sup>, Bill Harrigan<sup>3</sup> and Enrique J Lavernia<sup>1</sup>; <sup>1</sup>Chemical Engineering & Materials Science, University of California, Davis, California; <sup>2</sup>Powdermet, Inc., Sun Valley, California; <sup>3</sup>MMC Engineering, Inc, LA, California.

In metal matrix composites (MMCs), interface bonding between metal matrix and ceramic reinforcements plays a crucial role in performance of MMCs. Usually, most ceramic reinforcements have demonstrated a poor wettability with metals; therefore, a high temperature synthesis process for MMCs containing these ceramic reinforcements is necessary. However, a high temperature is not desirable for manufacturing of MMCs due to an increase in cost as well as potential chemical reactions at high temperature, which may lead to a degradation of MMCs. A CVD Fast Fluidized Bed process, patented by the Powdermet, Inc., enables a mass production capacity (500 lbs per lot) of ceramic powder encapsulated by metallic coating. Subsequent consolidation can be accomplished via metal/metal bonding, rather than through metal/ceramics bonding. The present investigation focuses on characterization of boron carbide particle encapsulated by Ni coating. SEM observation on powder surfaces and cross-sections indicated that B<sub>4</sub>C particles are completely encapsulated by Ni coating with a thickness of 1~5 μm. TEM examination shows the coating comprises single phase, nearly equiaxed grains with size from 10 to 100 nm, that is, synthesized coating is nanocrystalline Ni one. No apparent defects, such as pore, crack and dislocations are observed at the interface between the nanocrystalline Ni coating and B<sub>4</sub>C single crystal particle, and the interface is relatively smooth and complete, thus, capsule processing does not affect powder characteristics visibly. Using the encapsulated boron carbide powder, a Ni/Ni encapsulated B<sub>4</sub>C coating was sprayed using plasma spray technology, the results indicated that thin Ni capsule layer was persevered intact in the coating.

#### L11.47

**Solution-phase synthesis of cubic and spherical nanostructures of Cu<sub>2</sub>O.** Yuliang Wang, Yugang Sun and Younan Xia; Univ. of Washington, Seattle, Washington.

The preparation of two types of uniform and monodispersed Cu<sub>2</sub>O nanostructures – nanocubes (~50 nm in size) and nanospheres (~200 nm) will be reported in this presentation. Cupric nitrate was used as the precursor in this synthesis, and the nanostructured Cu<sub>2</sub>O particles were obtained by reducing Cu(II) in boiling ethylene glycol. Depending on the usage of surfactant (PVP), either cubic (w/o PVP) or spherical (w/ PVP) structured Cu<sub>2</sub>O nanoparticles can be selectively prepared. Electron diffraction studies on both morphologies of Cu<sub>2</sub>O indicated that the nanospheres are polycrystalline in structure while the nanocubes are single crystals. Further investigation suggested that the appearance of Cu<sub>2</sub>O nanospheres were the results of self-assembly of even smaller sized Cu<sub>2</sub>O particles (~10-20 nm) that could be served as the seeds for nanocube growth.

#### L11.48

**Synthesis of titania microspheres with nanocrystalline anatase core / rutile shell structure.** Yun-Mo Sung, Jin-Kyung Lee and Yong-Ji Lee; Materials Sci. & Eng., Daejin University, Pochun-koon, South Korea.

Titania-PEO hybrids were fabricated using sol-gel processing of Ti-isopropoxide and Poly Ethylene Oxide (PEO: M.W. of 100,000). The hybrids were aged at 60°C for 6 and 12 h, respectively, followed by annealing at 800°C for 30 min. The phase formation characteristics and morphological features were strongly dependent on the aging time and PEO. The hybrids aged for 6 h showed the formation of microspheres (1-10 micrometer) with core/shell structure. Transmission electron microscopy (TEM) analyses reveal that the core is nanocrystalline anatase and the shell is nanocrystalline rutile. The hybrids aged for 12 h showed the formation of plate-like clusters of crystals with pure anatase phase. Titania without PEO showed the formation of plate-like clusters of crystals with anatase volume fraction of 0.5. This difference in the morphological features and phase formation characteristics was considered from the perspectives of activation energy for phase formation and bonding between PEO and chelated titania molecules.

#### L11.49

**Structure Evolution and Corresponding Electrical Properties in Weakly Bound Co-C60 Mixture.** Seiji Sakai, Yonghua Xu, Tri Hardi Priyanto, Vasily Lavrentiev, Kazumasa Narumi and Hiroshi Naramoto; Advanced Science Research Center, Japan Atomic Energy Research Institute, Res. Gr. for Design of New Materials with Energy Beams, 1233 Watanuki, Takasaki, Gunma, Japan.

Mixture films between cobalt and C60 were prepared on MgO substrate by co-evaporation technique under UHV conditions. The compositions x, that is CoxC60, were changed in the range of 0.5 - 700 by controlling the deposition rates of relevant materials. The films prepared were so sensitive to the exposure for gaseous environment, except for samples with x higher than 60, and a whole analysis was performed under the inert or in-situ conditions. The composition-dependent features of dilatation and downshift of Raman peak suggest that the mixtures are composed of cobalt particles and a C60-based phase in which certain number of cobalt atoms are coordinated to C60 molecule. It is deduced that the equilibrated number of cobalt atoms in the C60-based phase is 4 atoms per molecule at most and in which an electron transfer occurs from cobalt atom to a C60 molecule. Although all the mixtures show the conducting nature basically at ambient temperature, the evaluation of their temperature dependences reveals the details: 1) the mixtures with x >= 60 corresponding to a percolation threshold for cobalt particles are metallic but 2) the mixtures between x = 4 - 60 are thermally activated where the electron hopping process between the isolated cobalt particles is supposed to be operative. The mixtures with x < 4 are also thermally activated, however, their conductive nature might be attributed to the C60-based phase.

#### L11.50

**On the development of the <111> fiber texture in nanocrystalline gold during growth and annealing.** Klaus Pagh Andreasen<sup>1</sup>, Thomas Jensen<sup>1</sup>, Jakob Haahr Petersen<sup>1</sup>, Martin Skov Jensen<sup>1</sup>, Jacques Chevallier<sup>1</sup>, Jorgen Bottiger<sup>1</sup> and Norbert Schell<sup>2</sup>; <sup>1</sup>Physics and Astronomy, University of Aarhus, Aarhus, Denmark; <sup>2</sup>Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, Germany.

The evolution during growth and subsequent annealing of the <111> fiber texture in magnetron-sputtered nanocrystalline Au films has been studied experimentally using x-ray diffraction with synchrotron radiation. To quantitatively investigate this fiber texture, grain orientation distributions were recorded in situ during growth and during subsequent annealing using Bragg-Brentano geometry. The (111) diffraction intensity was measured as a function of the sample tilt  $\chi$ , the tilt axis lying at the intersection of the film surface and the scattering plane. The width of the orientation distribution was used as a quantitative measure of the texture. The grain-orientation

distributions narrowed during annealing. The activation energy for the process behind this texture change was found to be 0.64 +/- 0.05 eV, close to the activation energy for grain boundary self-diffusion in nanocrystalline Au. This and the narrowing of the grain orientation distributions led us to suggest that the observed changes in texture originated from grain rotations and not from grain growth. Grain growth did not take place at the lower temperatures, where changes in orientation distributions were observed.

#### L11.51

**Reactive Multilayer Joining: Nanostructured Heat Sources and Products.** Jiaping Wang<sup>1</sup>, Etienne Besnoin<sup>2</sup>, Alan Duckham<sup>1</sup>, Stephen J Spey<sup>1</sup>, Michael E Reiss<sup>1</sup>, Omar M Knio<sup>2</sup> and Timothy P Weihs<sup>1</sup>; <sup>1</sup>Dept. of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; <sup>2</sup>Dept. of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

Self-propagating formation reactions in nanostructured multilayer foils produce unique bursts of energy that can be used to solder and braze a variety of materials at room temperature. By sandwiching a reactive foil between two solder or braze layers and two components, ignition of a reaction within the foil can produce enough heat to melt the surrounding solder or braze layers and thereby join the materials. Here we describe self-propagating reactions in nanostructured Al/Ni multilayer foils, and we demonstrate their use in bonding Au-coated stainless steel specimens using free-standing sheets of AuSn solder. The Al/Ni foils were magnetron sputtered onto cooled substrates and then were removed from their substrates for use as free-standing samples. The foils contained thousands of alternating layers with bilayer thicknesses ranging from 25 to 90 nm. Their heats of reaction were measured as high as 1168 J/g, reaction velocities ranged from 3.5 to 6 m/s, and their final products were nanocrystalline with an ordered B2 structure. Shear strengths of the stainless steel joints were shown to increase as foil thickness increases to 40 μm and the volume of molten AuSn rises. When the foil thickness is larger than 40 μm the shear strength remained approximately constant at 48 MPa. These strengths are significantly higher than the strength of conventional solder joints (38 MPa) that were formed using a furnace treatment and no reactive foil. The higher strengths in the reactive joints are attributed to refined AuSn microstructures with lamellar spacings near 50 nm, which develop on rapid cooling. Numerical predictions and thermal measurements are used to demonstrate the very rapid and localized heating and cooling of reactive joining, which offer the ability to join temperature sensitive materials and components without thermal damage.

#### L11.52

**Phase Characterization and Morphology Control of Electrospun Nanofibers of PANI/PMMA Blends.** Keyur Desai and Changmo Sung; Chemical and Nuclear Engineering, University of Massachusetts Lowell, Lowell, Massachusetts.

Electrospinning derived from electro spraying is a process by which sub-micron polymer fibers can be produced using an electrostatically driven jet of polymer solution. The fibers are collected as non-woven mat and offer a high surface to volume ratio. Electrically conducting organic polymers are a novel class of synthetic metals that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors. Electronically conducting polymers like polyaniline (PANI) have been studied extensively owing to their applications in energy conversion devices, sensors, electrochromic devices, electromagnetic interference shielding (EMI), electronic circuits etc. In this present study Polyaniline(PANI) blended with Poly methyl methacrylate(PMMA) has been electrospun to form conducting nanofibers. The goal of this research is to characterize the electrospun fibers of PANI/PMMA blends and study the effects of various electrospinning parameters on fiber formation and fiber size. Effects of electrospinning parameters have been studied and optimized to obtain nano fibers. Scanning Electron Microscopy (SEM) along with Transmission Electron Microscopy is being used to study the fiber morphology. The phase morphology of the fibers was investigated using TEM staining and Force Modulation Microscopy. From the TEM staining results we find that polyaniline forms aggregates in PMMA matrix along fiber length. We also used statistical tools like Design of Experiments (DOE) to optimize the process conditions and study the impact of the processing variables on the fiber morphology. The use of carbon nanotubes to form conductive pathways along the fiber length is also being explored.

#### L11.53

**In-situ Control of Oxygen Content and the Effect on PL Intensity of SiOx and SiOx/SiO2 Superlattices Grown by Physical Deposition.** Kyungjoong Kim<sup>1</sup>, Daewon Moon<sup>1</sup>, Moonseung Yang<sup>2</sup>, Jihong Jhe<sup>2</sup>, Junghoon Shin<sup>2</sup>, Seunghui Hong<sup>3</sup> and Sukho Choi<sup>3</sup>; <sup>1</sup>Korea Research Institute of Standards and Science, Daejeon, South Korea; <sup>2</sup>KAIST, Taejeon, South Korea; <sup>3</sup>Kyunghee University, Seoul, South Korea.

The size and density of Si nanocrystals are important factors to determine the energy and intensity of the photoluminescence. Substrate temperature and oxygen content are main parameters to control the size and density of Si nanocrystals. In this point, ion beam sputter deposition (IBSD) can be a good candidate for the growth of SiOx films. SiOx films were grown on p-type Si(100) by ion beam sputter deposition under oxygen gas ambient. The thin films grown at the deposition chamber could be transferred to a surface analysis chamber without exposing to the air. Therefore, the oxygen content(x) of the SiOx was directly analysed by in-situ x-ray photoelectron spectroscopy (XPS). The relative sensitivity factor (RSF)s of Si 2p and O 1s peaks were calculated by in-situ XPS analysis of the stoichiometric SiO2 thin films where x is 2. The variation of PL energy and intensity of SiOx and SiOx/SiO2 superlattice films were systematically investigated by in-situ XPS. The blue shift of PL energy with the increase of oxygen content was well correlated with the decrease of Si nanocrystalline size. The PL intensities of SOx showed maximum values near x=1.6. However, those of SiOx/SiO2 films showed maximum values near x=1.2. This could be understood as a term of averaged concentration. In the superlattices with very thin layers, PL exhibits similar tendency with those of single SiOx films where the x value is same with the average of the two layers. In the case of SiO1.2(2 nm)/SiO2(2 nm) superlattice, the average composition is equivalent with x=1.6. There was no great variance of x value for the maximum PL intensity with the increase of deposition temperature.

#### L11.54

**Synthesis of mesoporous complex framework zirconium phosphates via organic-inorganic nanocomposites: genesis of structure, adsorption and catalytic properties.** Yulia Frolova<sup>1,2</sup>, Vladislav Sadykov<sup>1,2</sup>, S. Pavlova<sup>1</sup>, S. Veniaminov<sup>1</sup>, R. Bunina<sup>1</sup>, E. Burgina<sup>1</sup>, V. Kolomiichuk<sup>1</sup>, T. Larina<sup>1</sup>, N. Mezentseva<sup>1,2</sup>, M. Fedotov<sup>1</sup>, A. Volodin<sup>1</sup> and R. Roy<sup>3</sup>; <sup>1</sup>Borsovsk Institute of Catalysis, Novosibirsk, Russian Federation; <sup>2</sup>Novosibirsk State University, Novosibirsk, Russian Federation; <sup>3</sup>Penn State University, University Park, Pennsylvania.

Nanocomposite mesoporous materials have attracted much interest in a wide variety of applications including catalysis. This work presents first results of genesis investigation of framework binary phosphates of zirconium and transition metal cations (Co, Cu, Ce) prepared via nanocomposites of starting inorganic salts with citric acid. Structural and textural features of those systems on different synthesis stages have been studied by FTIRs, SAXS, ESR, UV-Vis DRS, magnetic measurements and nitrogen adsorption-desorption isotherms. Within applied routine, nanoparticles of Zr (Ce) phosphates of a layered structure with typical sizes in the range of 18-24 Å are formed at the mixing stage. Less basic Cu and Co cations are mainly octa-coordinated with both phosphate groups of those nanoparticles and citric acid molecules. At subsequent thermal treatment, Cu and Co cations are incorporated within Zr (Ce) phosphate nanoparticles acquiring a low coordination approaching a tetrahedral one while rearranging the nuclei structure into that of a framework type. Within this framework matrix, Cu and Co cations are isolated. Removal of citric acid by heating under air at 200 - 300°C preserves the size of nanoparticles while their ordered stacking forms mesoporous structure with a narrow pore size distribution ~ 50 Å and specific surface area up to 200 m<sup>2</sup>/g after calcination at 600°C. ERS of oxygen ion-radicals O<sup>-</sup> generated by hydrogen peroxide adsorption revealed existence of coordinatively unsaturated surface sites for those systems. This feature is reflected in a high decane and NO adsorption capacity as well as ability to activate hydrocarbon molecules at heating. The binary phosphates promoted by a small amount of Pt were found to be effective catalysts of NOx selective reduction by decane in the oxygen excess not subjected to coking with a high and stable performance at high space velocities in the presence of steam.

#### L11.55

**Design of Nanoporous Polymeric Materials Via Reactive Encapsulation of Chemically Inert Solvent.** Vijay Immanuel Raman and Giuseppe R Palmese; Chemical engineering, Drexel University, Philadelphia, Pennsylvania.

Nanoporous polymeric materials are used as polymer electrolytes in fuel cells, separation membranes, templates for nanoparticle synthesis, and electroactive materials in biomedical applications. Design of nanoporous polymeric materials for these applications entail controlling the permeability through the porous materials by tailoring the pore size and pore chemistry. Porous polymeric materials are usually synthesized using phase separation techniques. In these techniques, the final pore size and structural distribution of the material depends upon the thermodynamic path that the system follows. So, even a small deviation in processing conditions can lead to vastly different porous structures and controlling the pore size is difficult in methods involving phase separation. Also,

micro/macroporous materials are usually obtained in techniques involving phase separation. A novel method of synthesizing nanoporous polymeric materials that have better pore size control than the conventional methods is employed in this work. This technique involves the synthesis of nanoporous polymeric materials by reactive encapsulation of an inert solvent using step-growth crosslinking polymerization reaction carried out until completion without phase separation. The condition of complete miscibility throughout polymerization suggests that for cross-linking systems, the network will encapsulate the solvent during reaction forming a porous superstructure whose typical pore dimensions can be controlled by the amount of solvent. So, potentially, better pore size control can be obtained by using a completely miscible system. The key structural parameters of the nanoporous materials synthesized using the reactive encapsulation technique was investigated by means of supercritical extraction and SEM and small angle X-ray scattering. Micrographs of the materials synthesized using the reactive encapsulation technique showed that porous materials of pore size less than 100 nm are obtained. SEM micrographs and SAXS showed that the reactive encapsulation technique can be employed, to synthesize nanoporous polymeric materials of desired pore structure and size by changing the solvent content. The pore chemistry of the nanoporous material synthesized by the reactive encapsulation technique was tailored by improving the hydrophilicity using a grafting technique based on Michael's addition reaction. The equilibrium water uptake of the nanoporous material, monitored by FTIR, showed a significant increase after grafting. A novel method for designing Interpenetrating Polymer Networks (IPNs) of hydrophobic and hydrophilic polymer networks is proposed. The steps involved in the design of IPNs were monitored using FTIR.

#### L11.56

Abstract Withdrawn

#### L11.57

**Metastable Phase Formation and Stimulated Transitions in Metallic Nanometer Films.** Dirk Carl Meyer<sup>1</sup>, Alexander A. Levin<sup>1</sup>, Andre Gorbunov<sup>2</sup>, Stefan Braun<sup>3</sup>, Wolfgang Pompe<sup>2</sup> and Peter Paufler<sup>1</sup>; <sup>1</sup>Dresden University of Technology, Institute of Structure Physics, Dresden, Germany; <sup>2</sup>, Dresden University of Technology, Institute of Materials Science, Dresden, Germany; <sup>3</sup>Fraunhofer IWS Dresden, Dresden, Germany.

Depending on deposition technique, thin films can exhibit an energetic state far from thermodynamic equilibrium. Due to entropic causes this is a general characteristic of nanometer multilayers. Energy supply can stimulate a transition of the film structure into other metastable states characterised by an enthalpy closer to that of thermodynamic equilibrium. Besides of the sufficient quantity of activation energy significant contribution of interphases and stressed states to the free energy of the system and geometric constraints for transport processes can favour an unconventional metastable phase formation. It is of technical interest that a number of metastable phases can be stabilised at room temperature for characteristic times in the order of years. Examples of metastable phase formation are thermally stimulated solid state reactions in metallic nanometer multilayers of Al/Co/Ni and phase formation and transition in metallic alloy films of the elemental system Fe-Cr exhibiting an extended miscibility gap at temperatures below  $\sim 725$  K under equilibrium conditions. While in the first case under appropriate conditions formation of a homogeneous textured layer of a decagonal quasicrystalline structure could be achieved, the second example illustrates a formation of unconventional phases during a pulsed laser co-deposition of restrictedly miscible elements and their transformation into other metastable phases by supplying of different kinds of activation/transport energy.

#### L11.58

**Fabrication of the various oxide nano structure materials by LPD method.** Shinsuke Yamanaka, Tsuyoshi Hamaguchi and Masayoshi Uno; Department of Nuclear Engineering, Osaka University, Suita, Osaka, Japan.

A variety of oxide nano structure materials have been prepared from an aqueous solution process, which is called the liquid phase deposition (LPD) process. In this process, because of two different reactions such as depositing the metal oxide and dissolving the starting materials (anodic alumina) occurring at the same time, we can get the nano structure materials. An anodic alumina was immersed in a metal-fluoro complex solution at various temperatures and a few hours immersion enabled us to obtain the nano structure materials of oxides such as titania, iron oxide and tin oxide. Changing the reaction conditions could control the structure of this type of materials such as rod or tubules. These oxide nano structure materials are attractive for a wide variety of application in different fields such as electrical, optical and chemical devices.

SESSION L12: Tubes, Rods and Dots

Chair: Sridhar Komarneni

Friday Morning, December 5, 2003

Room 304 (Hynes)

#### 8:30 AM L12.1

**Anomalous Magnetoresistance Behavior of Bismuth Antidot Arrays.** Oded Rabin<sup>1</sup> and Mildred S Dresselhaus<sup>2</sup>; <sup>1</sup>Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Physics, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A locally-ordered antidot array (an array of circular nanovoids) was formed in thin films of bismuth via a simple evaporation step. This architecture can be considered as an intermediate between a two-dimensional and a zero-dimensional system. Temperature and field dependence of the electrical transport in the thin film revealed the strong influence of the nanostructure of the film. The antidot array resistance decreased with temperature, and it displayed comparable transverse and longitudinal magnetoresistance. Furthermore, enhanced magnetoresistance was observed at low temperatures ( $T \sim 2$ ~K) and low magnetic fields ( $B < 1$ ~T). These surprising observations are attributed to the semimetal-semiconductor transition and localization effects in low dimensional bismuth systems.

#### 8:45 AM L12.2

**Synthesis and Structural Characterization of Si Quantum Dots for Non Volatile Memories.** Rosaria A. Puglisi<sup>1</sup>, G.

Nicotra<sup>1</sup>, S. Lombardo<sup>1</sup>, C. Spinella<sup>1</sup>, C. Gerardi<sup>2</sup> and G. Ammendola<sup>2</sup>; <sup>1</sup>Catania, CNR-IMM, Catania, Italy; <sup>2</sup>Central R&D, STMicroelectronics, Catania, Italy.

The ability to synthesize Si nanostructures is an important capability because of the possibility to obtain new functions in novel devices for microelectronics. In particular, in the non-volatile memory technology, the use of nanocrystals as storage-nodes has emerged as an important alternative to conventional floating gates, because of the high reliability associated with the discrete-trap structure. Several methods to synthesize the Si dots have been investigated in the past, but the use of CVD has demonstrated to be a convenient technique because of its immediate implementation in the ULSI processing, a good control on the deposition parameters, and because of the possibility to obtain isolated storage nodes, immersed in stoichiometric SiO<sub>2</sub>. We obtained the Si nanostructures by rapid thermal CVD of silane and investigated their formation in the range from the sub-monolayer to the complete coverage with Si, at several substrate temperatures, and post-deposition annealing temperatures. Energy filtered transmission electron microscopy is adopted to evaluate the dot size and distance distributions. This technique couples the high spatial resolution typical of the TEM analysis, to the compositional information obtainable by electron energy loss spectroscopy. Results show that for each deposition temperature and time, new Si nuclei continue to appear, even after long deposition times, when the coalescence process between the dots is present. This effect indicate the occurrence of nucleation under steady state at small sizes, close to the critical radius. However, the interdot distance distribution shows a maximum at finite distance values, and this effect increases with the post-deposition annealing process, thus indicating the dot ripening phenomenon. These effects will be shown and discussed in the framework of a continuous nucleation model, which takes into account both dot coalescence and ripening.

#### 9:00 AM L12.3

**Self-assembled Nanostructures Through Spontaneous Phase Decomposition.** Ladan Mohaddes-Ardabili<sup>1</sup>, Haimei Zheng<sup>1</sup>, Satish B. Ogale<sup>1</sup>, Manfred Wuttig<sup>1</sup>, Ramamoorthy Ramesh<sup>1</sup>, Beatrice Hannover<sup>2</sup>, Wei Tian<sup>3</sup>, Xiaoqing Pan<sup>3</sup> and Samuel E. Lofland<sup>4</sup>; <sup>1</sup>Materials Science and Engineering, University of Maryland, College Park, Maryland; <sup>2</sup>Institut des Materiaux, Universite de Rouen, Cedex, France; <sup>3</sup>Material Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>4</sup>Department of Physics, Rowan University, Glassboro, New Jersey.

The phase stability of multicomponent oxide systems is known to be sensitive to a variety of external variables, including the oxygen chemical potential. We are exploring the stability in a nominally single phase La-Sr-Fe-O perovskite system as a function of oxygen pressure, using thin film heteroepitaxy as the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Growth in reducing environments (8E10-6 Torr of oxygen) leads to the formation of a nanoscale composite of  $\alpha$ -Fe nano-pillars embedded in a matrix of a layered perovskite with a nominal composition of LaSrFeO<sub>4</sub>. The height of the pillars is equal to film thickness. The lateral size, shape and density of these ferromagnetic nano-pillars depend systematically on growth

conditions. This therefore affects the magnetic properties. High resolution Transmission Electron Microscopy results indicates that at high temperatures of deposition the pillars with 50-70 nm lateral diameter and a square-shaped section are formed. As the deposition temperature is reduced the shape evolves into octahedral and then circular section. Theoretical calculation on interface symmetry and interfacial energy is presented. We report in this paper these results as well as the result of our studies to induce a long-range translational order among these ferromagnetic nano-pillars. This work is supported partly by NSF-MRSEC under contract No. DMR-00-80008 and by an ONR MURI program under contract No. N000140110761.

#### 9:15 AM L12.4

##### **Oriented Arrays of Single Crystal Titania Nanofibers Produced by Reaction With Hydrogen-Bearing Gas.**

Sehoon Yoo<sup>1</sup>, Sheikh A Akbar<sup>1</sup> and Ken H Sandhage<sup>2</sup>; <sup>1</sup>Dept. of Materials Science and Engineering, The Ohio State University, Columbus, Ohio; <sup>2</sup>School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The processing conditions needed to achieve precise control of fine, nanoscale features in advanced materials, and those needed for large-scale mass production of such materials, often come into conflict. Processes that avoid such conflicting conditions are needed to enable the widespread utilization of advanced nanostructured materials and devices. In this paper, a simple, low-cost method for fabricating oriented arrays of single crystal titania nanofibers is reported: the reaction of dense TiO<sub>2</sub> surfaces with H<sub>2</sub>-bearing gases at modest temperatures\*. Upon exposure to a flowing 5% H<sub>2</sub>/95% N<sub>2</sub> gas mixture at 700 C, dense, polycrystalline rutile surfaces were converted into arrays of discrete oxide nanofibers with diameters of 20-50 nm and lengths of 0.1-5 μm. The nanofibers that formed from a given titania grain were oriented in the same direction. From time-sequence SEM images of the same grains, it was observed that the nanofibers formed by an etching process (not by a deposition process). During the initial stage of heat treatment, nanochannels formed on specific faces of the faceted rutile grains. The depth and interconnectivity of these nanochannels increased with time, until the channels converged to yield isolated, parallel nanofibers. Electron diffraction analyses revealed that each nanofiber was comprised of a single oxide crystal, with the fiber axis oriented parallel to the [001] crystallographic direction. Detailed characterization of the nanostructure of the fibers, and the influence of various processing parameters (e.g., specimen preparation conditions, H<sub>2</sub>/N<sub>2</sub> gas flow rate, temperature) on the nanofiber formation process, will be discussed. This reaction-based process may be readily scaled up (by continuous operation of controlled-atmosphere furnaces) to yield large quantities of low-cost, high-surface-area titania nanofiber arrays with photocatalytic, gas-sensing, electronic, and/or antimicrobial functions for a wide variety of environmental, biomedical, transportation, and chemical manufacturing applications. \*S. Yoo, S. A. Akbar, K. H. Sandhage, U.S. Patent Application

#### 9:30 AM L12.5

**Zinc Oxide Nanotripods.** Zheng Chen<sup>1,2</sup>, Zhiwei Shan<sup>1</sup>, Phillip Lee<sup>1</sup>, Olivier Manosane<sup>1</sup> and Scott X. Mao<sup>1</sup>; <sup>1</sup>Department of Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; <sup>2</sup>Department of Materials Science and Engineering, East China Shipbuilding Institute, Zhenjiang, China.

ZnO, a wide-gap (3.37eV) semiconductor oxide, has attracted considerable attentions due to its large exciton binding energy (~60 meV) and bond strength, which might make reliable high-efficiency photonic devices based on ZnO. Here we present our deterministic carbothermal reduction synthesis of ZnO nanocrystals with different morphologies (dendrites, tripod-shaped and wires) by carefully tuning the carrier gas (nitrogen) flow rate at ambient pressure involving neither catalytic nor vacuum system. The synthesis of ZnO was carried out in a horizontal furnace. ZnO nanocrystals were directly grown in a quartz tube by heating ZnO and graphite powder mixture (1:1 molar ratio) at 1100°C under a flow of high purity nitrogen as carrier gas at a rate of 10-90 sccm (standard cubic centimeter per minute). The growth time was typically 0.5-1 h. After evaporation and deposition, we found different products in different positions on the inner wall of the quartz tube. The crystal structures were analyzed using X-ray diffractometer (XRD-PHILIPS APD 3720). The morphology and size of the products were characterized using field-emission scanning electron microscope (FE-SEM, PHILIPS XL30) equipped with an energy-dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM, JEOL 2000F at 200 kV) was used to study the microstructure of the nanotripods. The energy dispersive spectrometries (EDS) of the ZnO dendrites, tripods and wires show that the atomic composition ratio of Zn/O is about 1:1. X-ray diffraction (XRD) measurements demonstrated that all the products are hexagonal wurtzite structured ZnO with lattice parameters of a = 0.3249 nm and c = 0.5206 nm. Present results prove that the morphology and the dimensions of the ZnO products

can be controlled by adjusting the carrier gas flow rate during the synthesis of ZnO via carbothermal reduction process. We have shown that the carrier gas flow rate is a key parameter which can simultaneously affect the reaction rate between ZnO and carbon, the supersaturation of Zn vapor and oxygen, as well as the growth position and temperature. In addition to ZnO dendrite and nanowires, we have successfully synthesized ZnO nanotripods by using a controlled carrier gas flow rate during synthesis. A seed-twinning mechanism has been proposed to explain the nucleation and growth of nanotripod ZnO. The special structure characters of the nanotripods may have interesting physical properties, and act as a candidate material for 3-D assembly of the nanodevices.

#### 9:45 AM L12.6

##### **Growth of Carbon Nanocones Using Three-nanometer Diameter Iron/platinum Nanoparticle-catalyst and Their Field Emission Properties.** Hongtao Cui<sup>1</sup>, Xiaojing Yang<sup>2</sup>, Larry

R Baylor<sup>1</sup>, Michael L Simpson<sup>1,2</sup>, Walter L Gardner<sup>1</sup>, Douglas H Lowndes<sup>1</sup>, Lei An<sup>3</sup> and Jie Liu<sup>3</sup>; <sup>1</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; <sup>3</sup>Department of Chemistry, Duke University, Durham, North Carolina.

Carbon nanocones have been synthesized using iron/platinum alloy nanoparticles as catalyst in a direct-current plasma enhanced chemical vapor deposition reactor. The alloy nanoparticles are monodisperse with an average diameter of three nanometers. Acetylene is used as the carbon supply gas and ammonia as the dilution and etching gas. The carbon nanocones are highly oriented perpendicular to the substrate surface, but are much smaller and have different morphology than any grown previously, with a solid and amorphous internal structure. Experimental results and modeling on field emission properties of carbon nanocones are also presented.

#### 10:30 AM L12.7

**Synthesis and Characterization of Novel Vanadium Dioxide Nanorods.** Wen Chen, Li-Qiang Mai, C. S. Jiang, F. J. Peng, Q. Xu and Q. Y. Zhu; Institute of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei, China.

Vanadium dioxides have found a wide range of applications in temperature sensing devices, optical switching devices, energy-conserving coating for windows and so on, because they undergo a phase transition at approximately 68°C from a semiconductor to a metal [1, 2]. Recently, one-dimensional nanostructure materials, such as nanotubes, nanowires and nanorods, have attracted much attention due to their unique properties originated from their high surface area and low dimensionality [3]. In the present work, vanadium dioxide nanorods have been synthesized, for the first time, using cetyltrimethylammonium bromide (CTAB) as structure-directing template in hydrothermal condition. Morphology and structure of the sample were characterized by XRD, SEM, HRTEM, and TG-DTA. The results show that the products are monoclinic (C/2m) VO<sub>2</sub> nanorods and they are 1-2 μm in length. HRTEM micrographs reveal that they indeed form bundles of agglomerated smaller filaments with diameters ranging from 20 to 40 nm besides single nanorod. This filament-like shape in the nanoscale dimension leads to the exposure of a large fraction of the atoms to the surface. Thus, these materials are promising candidates for the development of new functionalized materials. TG investigation shows that there are a weight loss of 2.21% between 250-400°C corresponding to removal of the organic residuals and a weight gain at about 430°C corresponding to oxidation of vanadium with low oxidation state. The simplicity of hydrothermal process, cheapness, and availability of raw materials are advantages favoring the scaling-up of nanorods. References [1] Hanlon TJ, Wsiker RE, Coat JA. Thin Solid Films 405 (2002) 234. [2] Guinneton F, Sauques L, Valmalette JC. J Phys Chem Solid 62(2001)1229 [3] Xia Y, Yang P, Sun Y, et al. Adv Mater 15(2003)353 Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 50172036), the Teaching and Research Award Program for Outstanding Young Professors in Higher Education Institute, MOE, P. R. China and the Science Fund for Distinguished Young Scholars of Hubei Province (Grant No. 2002AC008).

#### 10:45 AM L12.8

**Growth of Single Crystal Tungsten Nanorods by Oblique Angle Sputter Deposition.** Tansel Karabacak, Pei-I Wang, Gwo-Ching Wang and Toh-Ming Lu; Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York.

We report the creation of single crystal tungsten nanorods with unusual simple cubic β-phase. These novel nano-structures are grown by oblique angle deposition with substrate rotation (also known as glancing angle deposition or simply GLAD) through a shadowing effect, that is, a physical self-assembly mechanism. Transmission

electron microscopy (TEM) diffraction patterns from individual nanorods clearly show the single crystal structure. As evidenced by TEM diffraction and X-ray diffraction (XRD) measurements, during the oblique angle deposition, both  $\beta$ -phase W(100) and  $\alpha$ -phase W(110) islands exist at the initial stages of growth. However, at later stages of the growth we observe the dominant  $\beta$ -phase structure. This is in contrast to the sputter deposition at normal incidence where only the thermodynamically stable bcc  $\alpha$ -phase W(110) polycrystalline films were formed when the film grew to a certain thickness. We explain our results by using the shadowing and adatom mobility mechanisms: At the initial stages of growth, the  $\beta$ -phase W(100) islands grow taller due to the lower adatom mobility on these islands. The taller  $\beta$ -phase W(100) islands survive in the competition during oblique angle growth and form isolated nanorods in the later stages, while the shorter  $\alpha$ -phase W(110) islands stop growing due to the shadowing effect.

#### 11:00 AM L12.9

**Nanopipes in Transition-metal Nitride Layers.** Joanna R. Lynch and Daniel Gall; Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Nanopipes are 1-nm-wide open pores in single crystal transition metal nitride layers. They form during vapor phase deposition due to a combination of anisotropic surface diffusion and atomic shadowing effects. Their shape, orientation, and arrangement can be controlled by ion-irradiation and deposition angles. CrN, TaN, ScN, and TiN layers were grown on MgO(001) at 600-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N<sub>2</sub> and N<sub>2</sub>+Ar discharges at 3-20 mTorr. These deposition conditions result in a highly anisotropic surface diffusion with hop-rates that are 7 orders of magnitude smaller on (111) versus (001) surfaces. This anisotropy leads to kinetic surface roughening and the development of deep surface cusps which cause atomic shadowing and the formation of nanopipes that are elongated along the [001] growth direction. The nanopipes have rectangular cross-sections and form self-organized arrays aligned in orthogonal [100] and [010] directions, precisely replicating the in-plane correlation of the surface morphology. Non-normal deposition increases the level of atomic shadowing and introduces a controlled tilt to the nanopipes. Increasing the N<sub>2</sub><sup>+</sup>-ion irradiation flux or decreasing the N<sub>2</sub> partial pressure (and, hence, the steady-state N coverage) during growth provides a corresponding increase in cation surface mobilities leading to smoother surfaces, less atomic shadowing, and partial or full suppression of nanopipe formation.

#### 11:15 AM L12.10

**Polar surfaces induced growth of asymmetric nanocantilever arrays.** Xiang yang Kong<sup>1</sup>, Zhong Lin Wang<sup>1</sup> and J. M. Zou<sup>2</sup>;

<sup>1</sup>School of materials science and Engineering, Georgia Institute of Technology, Atlanta, GA, Georgia; <sup>2</sup>Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, IL 61801, Illinois.

Ionic crystals that consist of alternating layers of oppositely charged ions, stacked parallel to the polar surfaces, produce an accumulating normal dipole moment, resulting in divergence in surface energy. Crystals with polar surfaces generally have facets or exhibit massive surface reconstructions to compensate the electrostatic charge on the surface, but ZnO(0001) is an exception, which is stable and without reconstruction. Structurally, the wurtzite structured ZnO crystal is described schematically as a number of alternating planes composed of fourfold tetrahedral-coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces. In this paper, we demonstrate that the surface polarization and surface termination are important factors for determining the growth of ZnO nanostructures. The polar (0001) surfaces of ZnO result in anisotropic growth along [0001]. Longer and wider nanofinger arrays are grown from the (0001)-Zn surface, which is suggested to be a self-catalyzed process due to the enrichment of Zn at the growth front. The chemically inactive (000-1) surface typically does not grow nanobelt structure, but controlling experimental condition leads to the growth of nanocantilever arrays of mono-width and mono-length from the intersections between (000-1)-O with (01-10) surfaces. The self-catalyzed process is likely a mechanism for the growth of nanobelts without the presence of foreign metallic catalysts. The nanocantilever arrays have potential applications as nano-scale sensor arrays and tweezers arrays. [1] Pan, Z.W., Dai, Z.R., Wang, Z.L., Nanobelts of semiconducting oxides, Science 291, 1947-1949 (2001)

#### 11:30 AM L12.11

**Functionalized Carbon Nanotubes As Macromolecular Dopants For Electrically Conducting Polymers.** Mark Hughes<sup>1</sup>, Graeme A Snook<sup>1</sup>, George Z Chen<sup>1</sup>, Milo S P Shaffer<sup>2</sup>, Derek J Fray<sup>1</sup> and Alan H Windle<sup>1</sup>; <sup>1</sup>Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, United

Kingdom; <sup>2</sup>Department of Chemistry, Imperial College, London, SW7 2AZ, United Kingdom.

Electrically conducting polymers (ECPs), such as polypyrrole, polythiophene and polyaniline are frequently deposited as films via electrochemical oxidation of the relevant monomer. During deposition, an anionic dopant is typically incorporated into the ECP to balance the positive charge on the oxidized conducting polymer chains. The susceptibility of multiwalled carbon nanotube (MWNT) surfaces to functionalization makes them exciting candidates for a new class of dopant for ECPs. In this work, hydroxyl, carbonyl and carboxylic groups are attached to the surface of MWNTs via an acid-treatment process involving nitric and sulfuric acid. These functional groups give the acid-treated MWNTs a net negative charge, enabling them to provide charge balance for the oxidized ECPs, as do more conventional anionic dopants. Once deposited, the functionalized MWNTs are permanently embedded within the ECP, forming a continuous nanocomposite film. Previously, if there was insufficient anionic dopant available to ensure the deposited ECP was comprehensively oxidized, the electrical resistance of the neutral polymer prohibited further deposition. However, when using functionalized MWNTs, their electrical conductivity and high aspect ratio make it possible to grow MWNT doped ECPs in which the polymer is only partially oxidized. This phenomenon is attributed to the formation of an electrically conductive network comprising the MWNTs and the oxidized layer of ECP adjacent to the functionalized MWNT surface. The work described here relates to MWNT-polypyrrole nanocomposite films in which the MWNTs are the only dopant used during film deposition. Electrochemical impedance spectroscopy, cyclic voltammetry, scanning electron microscopy, Raman spectroscopy and a quartz crystal microbalance are used to characterize the doping behavior of the functionalized MWNTs. A comparison is also made between polypyrrole doped with embedded functionalized MWNTs and similarly prepared polypyrrole films doped using large immobile anions such as dodecyl sulfate. Finally, the effect of growing MWNT-polypyrrole films in the presence of competing dopant anions is explored.

#### 11:45 AM L12.12

**Carbon Nanotubes and Nanofibers Grown by Microwave Plasma Enhanced Chemical Vapor Deposition on Nickel Substrate.** Kalayu Gebretekle Belay, Jeremy Jackson and Yan Xin; Physics, Florida A&M University, Tallahassee, Florida.

Both carbon nanotubes and carbon nanofibers were grown on a 1.0 inch diameter thick nickel substrate by means of microwave plasma enhanced chemical vapor deposition (MPECVD) process using 20% methane and 80% hydrogen at a temperature of 750C and a pressure of 50 Torr. The substrate was pre-abraded with 1.0 $\mu$ m diamond powder and 15.0 $\mu$ m diamond paste to increase the rate of nucleation. When the substrate was taken out of the reactor the film detached itself completely from the nickel without exerting any force. The film growth was not uniform. Odd-looking structures appear juttied on one section of the substrate in a symmetrical manner. These structures were very hard and when analyzed using Raman spectroscopy and transmission electron microscope (TEM) they were observed to be multi wall carbon nanotubes (MWCNTs) and nanofibers. An attempt to measure the hardness of the film using a nano-indenter was inconclusive due to the extreme hardness of the material produced