SYMPOSIUM L

L: Continuous Nanophase and Nanostructured Materials

December 1 - 5, 2003

Chairs

Sridhar Komarneni
Pennsylvania State University
205 Materials Research Laboratory
University Park, PA 16802
814-865-1542

James Watkins
Dept. of Chemical Engineering
University of Massachusetts-Amherst
159 Goessmann Lab
Amherst, MA 01003
413-545-2569

John C. Parker
Cabot Microelectronics Corporation
870 N. Commons Dr.
Aurora, IL 60504
630-375-5534

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*Invited paper
SESSION 1: Textured Films and Composites
Chair: Sridhar Kommendri
Monday Morning, December 1, 2003
Room 304 (Hynes)

8:30 AM *L1.1
Nano-Structured Oxide Ceramic Composites by Solidification of Eutectic Melts. Makoto Yoshimura, Sumji Araki and Jose M. Caceres-Montes, 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 pyrolysis, not via melt/casting. It is believed that melt/solidified ceramic would crack during cooling due to (1) bristle nature of ceramics and (2) residual stress accumulation after the solidification. In order to prevent the accumulation of residual stresses, we have tried to make the samples by rapid solidification of the eutectic. Since the grain growth of solidified crystals can be minimized in eutectic systems, particularly ternary eutectic systems, such cracking also can be minimized. In the ternary systems of Zirconia/Hafnia-Alumina-YAG, we have succeeded to fabricate transparent nanostructured bulk ceramics by just simple solidification of the melt. The samples have no cracking and consisted of 20-100nm size crystals (z=ZrO2,HfO2), Al2O3, and YAG. Other ternary eutectic systems have given similar nano-structured composites. Amorphous transparent bulk has been obtained in several ternary systems like ZrO2-A12O3-HfO2 (for more future), ZrO2-A12O3-HfO2 [perovskites]. Those amorphous could be changed to nano-composites by appropriate annealing. Those ceramic nano-composites can be applied for wide areas, structural, functional, and cosmetic materials.

9:00 AM L1.2
Influence of Multiple Interfaces on Oxygen Ionic Conductivity in Gadolinia-doped Ceria and Zirconia Thin Films. Christian von Borstel, Matthias Banza, Volker Sembdner, Jochen Hammer, and Dietmar Plendl, University of Wuerzburg, Germany.

Ion conduction 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 conduction at low temperatures is an essential in the efficiency of these devices. It has been established previously that ceria, doped with a divalent or trivalent cation, exhibits higher ionic conductance compared to 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 ionic conductance along the interfacial directions at moderate temperatures. In our present study, we investigate a novel approach to increase the ionic 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. The ionic 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 ionic 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 High-temperature 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 (O2). Many metals which are stable in O2 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 500°C, but continues reacting with AO. Single Ag crystals (Ag100), Ag(111)) were exposed to a 5eV hyperthermal atomic oxygen, created by the laser detonation of molecular oxygen at 2950°C for 7 hours. 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 obtained Ag oxide film 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 oxide oxides, which is remarkably different from the O2 oxidation. The HRTEM investigation suggests that the formation of this structure was caused by the rapid diffusion of silver from substrate to oxide scale and [111] planes are most affected at the oxygen diffusion limit. 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 building blocks of copper oxide with a cubic morphology. Luciana Cristina Soares, Nathalie Jangou, Pauline Gac-Cubel, Jacques Lemaitre, and Henri Hofstetter, Laboratory of Powder Materials, Powder Technology Laboratory, Swiss Federal Institute of Technology, EPFL, CH-1015, Lausanne, 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 behavior. These nano-structured particles may be prepared by an oxide co-precipitation followed by the appropriate treatment. The copper oxide particles are made up of self-assembled nanocrystallites. Cobalt oxides is expected to exhibit a similar behavior due to its crystallographic structure similar to the copper oxide structure. We synthesized this material by precipitation via an oxide route followed by an adequate heat treatment. Our first aim is to understand and control the precipitation of copper oxides before combining it with cobalt oxides to make a composite. Precipitation of copper oxides has been investigated in a instrumented and well-mixed reactor by following the kinetic parameters to investigate the growth mechanism of the precipitation. The copper oxide nanoparticles seem to be the made-up of self-assembled building blocks. The precipitated nanoparticles have been further characterized 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 oxide nanoparticles from cubic shape into copper using an isothermal process under a reducing atmosphere. The nanocrystallite size is characterized as a function of time as the main challenge is to maintain the particles morphology during the reduction. Preliminary analysis of the model indicated that the experimental data the mechanism seems to involve a nucleation process followed by micrometric growth of the nuclei. An alternate route to obtain metallic copper is to start from copper oxide particles with cubic morphology. The kinetic behaviors of this transformation (Cu-oxide, 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 block 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, Material: Role for Microwave and Laser-microwave Hybrid Processes. Rustum Roy, 1Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; 2Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

This paper will point to some routes to make nanoscience useful. The commercial utility of nanoparticles is limited and cannot justify the research effort being channeled into this field. 0.5 micron powders such as the new zeolites, with nano level refinement, and for 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 mm 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 microstructure. This is clearly the most successful route to true commercial nano-structured, macroscopic product. Based on this perspective, data will be presented on recent remarkable findings in a new approach: utilizing microwave radiation to directly nano-size materials already shaped (e.g. make them X- and X-ray 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, oxides of 3d and 4f elements, including insulators like TiO2, 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 200 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 metal 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. Sangy Moon and Hye Shen; CVD Technology, Institute of New Materials, Sinfrunck, Germany.

With the advent of nanotechnology, the challenge of achieving chemical homogeneity down to the nanometer scale (lattice engineering) by conventional material processing methods remains. In fact, the chemical methods based on molecular precursors represent one of the viable alternatives for targeted synthesis of nanomaterials with different compositions and structures. If the intimate mixing of different elements present in the precursor persists until the desired ceramic or composite crystals, the typical problems of materials synthesis such as selectivity, crystallinity or segregation of one constituent and preferential hydrolysis or pyrolysis of one component can be avoided. Assembling all the elements in the right form before the material is in a single molecular compound, can augment the advantages of chemical processing. The major attributes of aforementioned single-source approach are: (i) the possibility to tune the 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 the ligand elimination mechanisms. To this end, we have developed various molecular sources and examined their single-step conversions to obtain nanostructures and films of complex oxides (Fe2O4, GdFeO3, YFeO3, ZnAl2O4, Y3Al5O12, CoFe2O4), biphase metal/oxide composites (Ge/GeO2, Ni/Al2O3), oxide-oxide composites (ZnO/Al2O3, NiAl2O4/Al2O3, ZnAl5O12/Al2O3), intermetallic/oxide composite (Ni3Sn4/Sn2O3), and semiconductor nanowires (Ge, Sn2O3). The results illustrate that a predefined reaction chemistry of the precursors enforce a remarkable control over morphology, composition and particle size. Owing to the structural features and composition controllability, the investigated nanomaterials show interesting properties. A brief account based on the above item will be presented.

11:00 AM L1.1

Correlation between magnetic and structural properties of nanostructured Cu films. Sungkyu Park1, X. Zhang2, A. Mira3, M R Fitzsimmons1, J D Thompson1, M F Hundleby2, M A Naughton3, J Shewchuk5, and O P Parkinson. Los Alamos National Laboratory, Los Alamos, New Mexico; 1University of Arizona, Tucson, Arizona.

Nanostructured Cu films, consisting of a Au/Cu/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 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 magnetic, loses its moment disordered upon a 2 ML Au underlayer. In addition, we found that the temperature induced magnetization direction change (from in-plane to out-of-plane with cooling below ambient temperature) 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. Michael Hundleby1, Amit Mir3, Ira Brewer1, Corwin Booth1, Arthur Malinowski1, Xingzhong Zhang1 and Michael Naughton3; 1Los Alamos National Laboratory, Los Alamos, New Mexico; 2Lawrence 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 in situ from magnetron sputtered targets. 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 μm. 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 normally connects a high-temperature T-independent moderate resistance regime (ρ ∼ 10 μΩ cm) with a low-temperature high-resistance regime (ρ ∼ 50 GΩ cm). This stark contrast to the monotonic, nearly temperature-independent resistivity exhibited by films with layer thickness greater than 5 nm. The anomalous behavior cannot be explained by conventional electronic interface scattering mechanisms. 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

11:30 AM L1.9

Nano-scale Fe3Al and Ag0.1 Alloy Films and their Hydrogen Interaction Characteristics: Annealing Dependence. Yulin Sercyngna4, Zhouying Fang5 and Michael A Carpenter2; 1Chemistry, University at Albany, SUNY, Albany, New York; 2School of Nanoscience and Nanotechnology, University at Albany, SUNY, Albany, New York.

Thin films of 20 nm Fe3Al and Ag0.1 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 0-5%. Temperature-dependent analyses 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 α→β phase transition. Preliminary results at elevated operating temperatures will be discussed.

SESSION 1.2: Characterization

Chair: Sridhar Komarneni

Monday Afternoon, December 1, 2003

Room 304 (Hyatt)

1:30 PM L2.1

Phase Separation in Metal Nanoparticle Arrays in Monolithic Silica-Biopolymer Aerogels. Xiping Liu, Yu Zhu, Chunhua Yao and William M. Rees; Chemistry Department, Brown University, Providence, Rhode Island.

Transparent monolithic aerogels based on silica, the biodegradable polymer chitosan, and coordinated iron ions have been employed to serve as a three-dimensional scaffold decorated with Au, Pt and Pd ions. The coordination of the metal ions and the internal gel structures 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 CO2 extraction to form the aerogels. Also in this work, it has been found that the resultant aerogels can be imaged photolytically in the two plane dimensions. The spatially controlled photolithography produces nanomaterials of Au in the range of from 20 to 40 nm for example, that constitute two dimensionally imaged reactors whose volumetric concentration also varies in the third dimension. These images microarrays of nanomaterials provide a basis for localization and detection of dyes, amine acids and protein molecules. The formation of these arrays is driven by 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-Nanoparticle inside a Fullerenol Lattice. Helge Kreuger1, P Reineke2, M Buetten3 and P Oehsen4; 1II. Physik, Universitet Gottingen, Gottingen, Germany; 2Institut fuer Physik, Universitet Basel, Basel, Switzerland; 3Department 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 C60-Si and C60-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 C60 surface is investigated. The intent is to use the fullerenol lattice as a template for the self-assembly of ultrasmall clusters (<20 atoms) and the synthesis of porous structure-free amorphous silicon. The solid-state powders were prepared by the cold cathode plasma chemical vapor deposition method. An electron microscope analysis of the resulting materials indicated the presence of fullerenes and their interconnects. The powders were subjected to both X-ray diffraction and Raman spectrometry. The X-ray diffraction showed that the fullerenes were not destroyed by the present experimental conditions. The Raman spectra confirmed the presence of fullerene L-cysteine and the intensity of the spectra for the samples containing gold increased with increasing gold concentration. The changes observed in the Raman spectra were attributed to the interaction of gold ions with the fullerene skeleton. The interaction is expected to occur at the fullerene surface and at the fullerene-fullerenol interface. The results of these studies are presented in this paper.
confinement in the Au and Si regions. The effect of region/channel size and interaction with the fullerene matrix on the luminescence spectra and electronic transitions will be discussed in detail. It has 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-C60 layers are transformed to SC at 700°C. To gain information on the thermal stability of Au, 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 channel arrays will be discussed.

2:15 PM L1.2.3

Clusters and nanocrystals represent a new class of materials that exhibit prominent optical properties. The growth of nanocrystals in the gas phase gives control not only over 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 superheated 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 nanocrystal properties. X-ray absorption spectroscopy (XAS) and photoemission (PES) were performed to investigate the electronic structure of Germanium nanocrystal films. We find that submonolayer deposition of elementary carbon nanocrystals on Si substrates strongly modifies confinement effects but that with increasing coverage the confinement affects attenuate. However, when the nanocrystal surface is passivated the electronic properties of original properties are maintained by the nanocrystal deposition and it is possible to generate nanocrystal- 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 L1.2.4
Analysis of the Optical Properties of Nanophase Sculptured Thin Films by Spectroscopic Mueller Matrix Ellipsometry. Chi Chen, Nickolas Podraza, An Iain, Gelo M Ferreira, and Collins W Robert. Materials Research Institute, 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 (-4 to -5 eV) of the fabrication and processing of inorganic surfaces and thin films [1, 2]. In our initial applications of this instrument, high speed measurements of the Mueller matrix elements in transmission and reflection for nanophase sculptured thin film structures prepared by glancing angle deposition with simultaneous substrate rotation. The Mueller matrix measurements 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 effective structure of the film and in the design of optical devices and sensors. From the 15 elements of the 4x4 Mueller matrix, the real and imaginary parts of the complex matrix ratios rxx, ryy, and rxy (six parameters in all) obtained in transmission (or mpp, mpp, and mpp 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 rxx, ryy, and rxy (or mpp, mpp, and mpp) 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 θff at the interface to the substrate (measured with respect to the transmission direction), the optical thickness of the film d, the phase retardation δθ, and the chiral pitch ρ. 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 nanocrystalline structure can be assessed using a multilayer optical model that incorporates a stepwise variation in the nanocrystal size and anisotropies with depth into the film. References [1] R. W. Collins and J. Koh, J. Opt. Soc. Am. 59, 199 (1969). [2] J. Lee, J. Koh, and R. W. Collins, Rev. Sci. Instrum. 72, 1742 (2001). [3] C. Chen, Iain 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, Materials Research Laboratory, University Park, PA 16802, USA. Phone: 418-863-1880, fax: 418-848-2326, email rwc6@psu.edu.

2:45 PM L1.2.5
Self assembled gold and silver nanoparticles on silicon nanotips as surface enhanced Raman active substrates. Saraj Chattergady, H C Lo,*, K H Chen,*, C H Hau and L C Chen, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan. 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 adsorbed molecules down to the limit of single molecule detection. In this paper we report a nanostructured Si substrate on which silver or gold nanoparticles, with less than 50 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-masking dry etching of Si substrates, which is followed by self-seeded SERS active Ag and Au nanoparticles with silver, methane, hydrogen, and argon gases. These nanotips have lengths of few microns and tip diameters about 2.2 nm. The density of these nanotips were extremely high ranging from 10^10/cm^2 to 10^12/cm^2. Gold, silver or platinum when deposited on these nanotips via ion beam sputtering self assemble into nanometer size particles over the entire surface of these nanotips. This substrate containing the nanotipcs on the nanotips are SERS active. Materials such as Rhodamine 60, 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 nanoparticles distributed on them enable the substrate to behave as reliable and reproducible SERS active even at very low concentrations (10^-12 M) of the molecules under study. The SERS enhancement factors obtained using these substrates are in the range of 10^5 to 10^8.

3:00 PM L1.2.6

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-bridging sp^3-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 alleviated 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^3-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 new edge x-ray absorption fine structure (NEXAFS) and transmission electron microscopy (TEM) measurements on a series of UNCD and MCD films provides insights toward understanding the Raman spectrum of UNCD. We find that although the sample has ~95% sp^3-bonded carbon by NEXAFS and TEM, none of the spectral features seen using visible Raman spectroscopy are attributed to sp^3 carbon. Our current film data, and 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-Materials Sciences, under Contract W-31-109-ENG-28.

3:30 PM L1.2.7

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 polydispersable 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, gallium arsenide nanoparticles, and core-shell nanoparticles, and compared the results to numerical simulations. We have found that Scherrer's analysis generally yields a crystalline size near the high end of the actual distribution, whereas the X-ray method yields a crystallite size near the high end. Together the two techniques therefore provide a more complete picture of the size distribution, including a rough measure of polydispersity. It will also be shown that in certain nanocrystalline samples, transmission electron microscopy (TEM) indicates that the 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 Thompson1, M K Miller1 and H L Fraser2, 1Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama, 2Metal and Ceramic Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA. 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 sputter 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 that there is an interfacial strain at the Ti layers to a pseudo-equilibrium concentration of approximately Ti1.57at%Nb, while maintaining a compositionally modulated interface. In contrast, the hcp Ti layers indicated little Nb interdiffusion within the layers. No unusual chemical or physical properties were noted in the APT results. 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 nanostructured systems.

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4:00 PM L2.9
Spin-dependent STM tunnelling study of the polaronic nanostructure pattern on magnetite (111) surface.
Nikolaos Berdounas, Shane Murphy, Guido Mariotti and Igor V. Shvets, Physics Dept, Trinity College, Dublin, Ireland.

Magnetite, Fe3O4, 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 nanomagnetic bi-particles are 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 annealing 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 local carbon atoms.

We described the origin of the electronic structure of the polaron 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 the significant spin-intact 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 were employed to verify the SP-STM results.


4:15 PM L2.10
Percolation in Multi-Wall Carbon Nanotube-Epoxycomposites: Interplay of processing parameters, nanotube aspect ratio and electric fields on the bulk conductivity.
Jan Sandor1, Christian A. Martin1,3, Milo S.P. Shaffer2

Matthias-Klaus Schwarz1, Wolfgang Bruhoffer1, Karl Schulte2 and Alan H. Windle1, 1Materials Science and Metallurgy, Cambridge University, Cambridge, United Kingdom; 2Chemistry College London, London, United Kingdom; 3Materials in Electrical Engineering and Optics, Technical University Hamburg-Harburg, Hamburg, Germany. 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 electric percolation thresholds in an epoxy matrix of 1% by volume, i.e., 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-stabilization 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 the 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 10-4 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 MWCNT with an aspect ratio of 290 and 2000 no 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 percolation theory are applied in the interpretation of the results. Additionally, the influences of applied electric fields during curing of the samples were studied. For both AC and DC voltages the network formation was unaltered compared to the samples filled with nanotubes. The percolation thresholds 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 behavior of carbon black in the epoxy matrix.

4:30 PM L2.11
High-resolution Analytical Electron Microscopy Investigation of Mottaseble Tetragonal Phase Stabilization in Undoped Sol-Gel Derived Zirconia Nanoceramics, Vladimir P. Oleško1, James M. Howe1, Sayajit Shukla2 and Sudip K. Seal3, 1Materials Science and Engineering, University of Virginia, Charlottesville, Virginia, 2Advanced Materials Processing and Analysis Center & Mechanical Engineerin, 3US Air Force Research Laboratory, Dayton, Ohio, Florida.

The mechanisms underlying stabilization of the metastable tetragonal (t-phase in undoped, nanocrystalline ZrO2 ceramics were studied by high-resolution field-emission analytical electron microscopy, utilizing parallel electron-energy loss (PEEL) and energy-dispersive X-ray nanospectroscopy. The sol-gel nanoceramics were sol-gel derived by hydrolysis of zirconium (IV) n-propoxide in the presence of the 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-prepared ZrO2 (R=5) contained aggregated clusters and elongated dense particles 20-40 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 calcined ZrO2 particles were spherical (40-100 nm in size) and consisted of 13.4-14.1 nm-size t-nanocrystals. The as-prepared ZrO2 powder (R=60) contained primary 4-11 nm-sized particles with an amorphous structure that formed aggregates (~200-1000 nm in size). Calcination of this sample lead to a mixture of t- and monoclinic (m) ZrO2. The as-gelagomorhized nanocrystals 8-10 nm in size. The PEEL intensity from the nanopowders matched the expected position of a direct band gap for ZrO2 between 4.5-5 eV energy losses. For the as-prepared nanopowder (R=60), the intensity threshold was less pronounced due to a number of peaks in the spin-softened spectra of the ZrO2 band structure in the low-loss and inner-shell PEEL spectra allow differentiation between the amorphous-like and nanocrystalline ceramic. Stabilization of nanocrystallites of t-phase in the amorphous ZrO2 particles with sizes 3-10 nm has been previously reported is likely due to strain-induced size refinement from surrounding growing crystals, which suppress the volume expansion associated with the metastable t-phase transformation. Local particle agglomerates of nanocrystals synthesized with a high R-value cannot suppress the t-m transformation. In this case, the
tphme may be partially stabilized due to a crystalline site effect and/or to the simultaneous presence of m-phme.

SESSION 1.3: Poster Session 1

13.1 The Effects of Cs Intercalation on the Raman Modes of Single-Wall Carbon Nanotubes in the N-doped Single-Wall Carbon Nanotubes (n-SWCNTs) and Ruth Boccheri, 1,2 Materials and Manufacturing Directorate, 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-atom vibrations [N. Bendini, et al., Chem. Phys. Lett. 339, 315 (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.

13.2 Spectroscopic Study of Pr- and Er-doped Silicon Rich Silicon Carbide in Site-Selected Films. Luis J. Fontecave, Carlos Rito, Oscar Resto and S. Zvi Weisz, Physics, University of Puerto Rico, San Juan, Puerto Rico

Endodoped SiO2, Pdoped SiC, SiO2 and Er, Pdoped Si rich SiO2 thick 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 to 1100°C. 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 11/2 → 11/2 (1532 nm) and 11/2 → 11/2 (980 nm) transitions of Er3+ in the Er-doped film. PL is reported for the 2P3/2 → 2P5/2 (650 nm) transition of Pr3+ in the Pdoped 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.

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

Although many structural models have been developed for use with well-defined surfaces, the looming 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 evolution than was previously possible. 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), was developed recently in our laboratory, in 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 movement of the substrate surface, as well as its operation with respect to the surface. It is equally useful for design of monolayer and multilayer structures, and offers a variety of parameters, such as: interatomic distance, dimension of the adsorbate/substrate unit cells, correlation 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, as a set of dynamic analysis tools was developed, allowing the 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]-Pt(111) system. Results indicate existence of distinct 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 software, 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.

13.4 Nanoparticle NIO in an SiO2 Matrix for CO Sensing Using Optical and Electrical Conductivity Transduction. Mike Poste, 1 Alex Martucci, 2 Massimo Gagliardi 2 and Carlo Cantalini 3, 1 TCEP, National Research Council of Canada, Ottawa, Ontario, Canada; 2 Dipartimento di Ingegneria Meccanica S. Materia, Universita di Padova, Padova, Italy; 3 Dipartimento di Chimica e di 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, nanoparticle NIO embedded in a porous SiO2 matrix has been studied for the application of carbon monoxide sensing. Thin films of the NIO/SiO2 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 2.5 nm with a narrow size distribution and which are homogeneously dispersed in the SiO2 matrix. When the films are exposed to CO, a fast and reversible increase in optical transmittance takes place. This effect has been studied in the wavelength range 400 nm to 900 nm and for CO concentrations from 100 ppm 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 SiO2 matrix, which is produced by the thermal post-treatment, 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.

13.5 Helical Silica Nanosprings. His-Feng Zhang, 1,2, Cheng-Min Wang 1 and Li-Sheng Wang 1, Department of Physics, Washington State University, Richland, Washington, 1 Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, Washington

Amorphous helical SiO2 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 nanomaterials based on the detailed structural characterization. Present study suggested that these nanosprings may have great potential for applications related to nanomechanical and micromechanical electronic devices.

13.6 Photoregulation of Mass Transport Using Photoresponsive Mesoporous Nanocomposite Films. Nanguo Liu, 1,2, John L. Wilson 1 and George E. Breitner, 1,2 Chemical and Nuclear Engineering, The University of New Mexico, Albuquerque, New Mexico; 1 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 photoreactive organosilica, 4,4-(3-triethoxysilyl propyl)oxydiadene (TSUA). Trasmi isomerization induced by light or heat of unsubstituted ligands contained in TSUA cause a dimensional change of ca. 3A. 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 photocathodic cell with our photoresponsive film and, using ferrocene dimethanol as a molecular probe, performed chronopotentiometry experiments with alternating UV and visible light exposure. We observed reversible optically-mediated responses indicating the reversible photoregulation of mass transport of the molecular probe.

13.7 Electrical Response to Different Gases of Nanostuctured
YCoO$_2$$_2$ and Y$_{1-x}$Sr$_x$CoO$_2$$_2$ Prepared by a Solution Method. Carlos R. Michael$^1$, Aldo Saul Gago$^2$, Chudin Carolina Lahr$^2$, and Arturo Chávez-Chavez$^2$

$^1$Physics, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico; $^2$Departamento de Química, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

In recent years, ceramics with perovskite-type structure have received a lot of attention for their applications in fields like ceramic membranes for oxygen separation and catalysts for nitric oxide reduction$^{1-3}$. Among these ceramics, the members of the solid solutions La$_{1-x}$Sr$_x$CoO$_2$$_2$ have been the most studied compounds in these fields, due to their superior physical properties. These oxides are characterized to be non-stoichiometric, with a cation in a mixed-valence state +2 and +3. For these applications, their properties are usually enhanced when the mean particle size of the powder is in the order of nanometers. In this work, samples of nanostructured YCoO$_2$$_2$ and Y$_{0.5}$Sr$_{0.5}$CoO$_2$$_2$ were prepared by a solution method, which employed the dissolution of stoichiometric amounts of Y(NO$_3$)$_3$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O and Sr(NO$_3$)$_2$·6H$_2$O in an aqueous medium containing urea. The precursor resins obtained from the solutions after heating to dryness, were analyzed by DTA and TGA, and they were also thermally decomposed in a tubular furnace in a temperature range from 300°C to 900°C in air. X-ray powder diffraction was performed in samples calcined every 100°C in order to identify the formation mechanism from an amorphous phase to the perovskite. Pure samples of YCoO$_2$$_2$ and Y$_{0.5}$Sr$_{0.5}$CoO$_2$$_2$ were obtained at 900°C for 24 h, their TEM analysis gave as a result a mean particle size of 15 nm. The electrical properties were measured on pellets and thick films using the Van der Pauw four-point probe method. Nanostructured thick films were made by the screen printing method and dried at 120°C. The films showed semiconducting behavior from room temperature to 700°C. The electrical response of these perovskites to different gases was also measured in the same temperature range, and the results were compared with the results obtained from the La$_{1-x}$Sr$_x$CoO$_2$$_2$ solid solutions.

References:


L3.8 Gas-sensing properties of SnO$_2$ nanowire array. Masayoshi Uno$^1$, Tatsuya Haraguchi$^1$, Nobuaki Yubuk$^1$, Akiko Iida$^1$, Tomohiko Nakata$^1$, Masato Egashira$^1$, Yasuhiko Shimizu$^1$ and Takuo Hyodo$^2$.

$^1$Engineering, Osaka University, Suita, Osaka, Japan; $^2$Department of Materials Science and Engineering, Nagoya University, Bunyo-machi, Nagoya, Japan.

The SnO$_2$ nanowire arrays have been prepared by modoc alumina in ammonium hydroxide solution at room temperature for a few hours. Pt, Au, and Pd electrodes were sputtered on the nanowire array at H:2 and NO$_2$ gas sensing properties of SnO$_2$ nanowire array sensors have been evaluated in dry air at 50–550°C. In the case of H$_2$, every sensor showed quick response to H$_2$ but fairly low sensitivity. In the case of NO$_2$, SnO$_2$ nanowire array sensors showed high sensitivity at 500°C, and the selectivity decreased as temperature decreased. On the other hand, Pt–SnO$_2$ sensor exhibited resistance increase upon exposure to H$_2$ at 300–400°C. This is probably due to resistance increase by the hydrogen solid solution in Pt electrode.

L3.9 A New Emulsion Method to Synthesize Adjustable and Robust Mesoporous Materials. Guangzhou Liao$^1$, Chemical Engineering, Tsinghua University, Beijing, China; $^2$Chemical Engineering, Tsinghua University, Beijing, China.

A new emulsion method to prepare adjustable, robust mesoporous materials with well-defined internal structures 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 spherical 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 spherical 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 particle size and the particle morphology although the latter should be theoretically more suitable for the optimization of the particle size for its average water droplet enveloped 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.


$^1$Material Chemistry, Kyoto University, Kyoto, Japan; $^2$PRESTO, JST, Kawaguchi, Saitama, Japan.

Mesoporous materials with the well-defined macropore gel skeletons 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 can be formed via a subcritical decomposition of gel, which the mesoporous silica gel system has been attempted. The incorporation of anionic 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 homogenous monolithic gels. Triloblock copolymer, EOPOEO, is also known to induce phase separation in tetramethoxysilane, TMS, system because of its strong hydrogen-bonding interaction between silanol groups. It was found that triloblock copolymers, L121, P123, P127, induce phase separation in BTMS systems to result in co-continuous microporous structure in limited composition ranges. The pore size distribution in the micrometer range, however, depended strongly upon the length of terminal PEG chains which were removed from the core–POO chain. That is, cylindrical pores of ca. 4 nm in diameter formed only when P123 was used as a template, while possibly lamellashaped mesopores in addition to major micropores were formed in the cases of L121 and P127, in the BTMS–P123 system, the resultant mesopores exhibited narrow distributions after the heat-treatment at 350°C, and the pore volume was well correlated with the incorporated amount of the triloblock copolymer. The three triloblock copolymers have identical lengths of PEG, 70 units, and different length of PEO, 5, 20 and 106 units for L121, P123 and P127, respectively. It is therefore presumed that the mesoporous templating in microporous BTMS-derived gels is effective only with surfactants having strong enough hydrogen bonds 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 Yamasato$^1$, Shinshiro Nagare$^2$ and Mssomo Sena$^3$.

$^1$Faculty of Science and Technology, Keio University, Yokohama, Japan; $^2$Nara Machinery Co., Ltd., Tokyo, Japan.

Nanocomposite films comprising self-assembled Ag nanodots and boron-doped glass matrix were prepared by one-step pulsed laser deposition on glass substrates. The SPR spectrum of the nanocomposite films was evaluated in terms of size distribution, volume fraction and degree of agglomeration 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 400 nm 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 achieved by systematically varying the operation parameters of PLD, e.g. gas species (N$_2$, Ar, He), pressure (between 6 mPa and 1 kPa) 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.


Octadentate tungsten sulfide clusters of the form W$_8$S$_{16}$[I · · · N or P-bonded ligand] can be viewed as building blocks for inorganic-organic networks. Such architectures have the potential for increasing electronic and magnetic properties stemming from ligand-mediated 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 isonicotinamide and isonicotinic acid that are capable of hydrogen bonding can create intermolecular forces among clusters and provide a means of non-covalently linking clusters. Linkage may also be directed by use of both ionic and relatively inert ligands. The ionic cluster compounds W$_8$S$_{16}$[bis(dihydridophosphino)ethane] and
We synthesized diethylphosphine oxide (diethene) and have been studied and can serve as starting points for the construction of dendritic structures. Our progress in these efforts will be presented and discussed.


Nanocrystalline powders of stoichiometric Fe₃Co were prepared by mechanical milling of metallic 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 diffraction, scanning electron microscopy and field emission scanning microscopy. Fine powders 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 8 nm was exhibited at a milling time of 0.5 h. Although magnetization of 1.8 T was obtained after 240 h of milling, Interestingly, a decrease in coercivity was not observed, below a grain size of 50 Å, as noted in many other soft magnetic alloys by Herzer (G. Herzer, J. Magn. Magn. Mater., 112, 298-309, 1992). This work is supported by NIST grant 60NANB20120.


A novel template synthesis of bone-shaped (dumbbell-shaped, dogbone-shaped) nanomaterial is demonstrated. Porous macroporous aluminum (PAA) templates with uniform nanochannels were fabricated using a solution based process. The structure of carbon nanotubes with stem and end diameters and length of 40 nm, 78 nm, and 5 μm, respectively, These nanocomposites, which show high performance compared to bulk composites. For example, the nanocomposite is a bone tissue and can be used as scaffolding.
chemical vapor deposition. In this experiment, Co nanoparticles play a crucial role for the growth of the crystalline GaN nanowires. On the other hand, the catalyst, usually Ni, was 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 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 Structure Formation. Yoona Lee 1, Youngnam Yoon 1, Yoo Jae Lee 2, Sang Kyu Choi 2 and Cheol Jin Lee 2, 1 Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea; 2 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 nanotubes, 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 3) 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 2H 2) 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 Hyun Lee 1, Hyun Jin Nam 1, Jungseong Lee 1, SeongWoo Rhee 2 and Duk Young Jung 2, 1 chemistry, Sungkyunkwan university, suwon, South Korea; 2 The Budak Engineering, University of California at Irvine, California. A novel method to immobilize nanocrystals of layered double hydroxide (LDH) on the Si substrates and to intercalate diacetoxyxides 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 ion exchange reaction is significantly changed in comparison with that for MgAl-LDH. The AFM results present the as-adSORbed MgAlLDH 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. 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 - Glocosaminoglycan Nano Composite Sol Under Well Controlled Condition. Yuko Ishikawa and Mamoru Senda; Faculty of Science and Technology, Keio University, Yokohama, Japan. Hydroxyapatite (HAP) - glycosaminoglycan (GAG) nano composite sols were prepared or synthesized by the ion-exchange method from Ca 10 [PO 4 ] 6 [CO 3 ] 2 or Ca 10 [(HPO 4 ) 2 ] 6 ·2SiO 2 and H 2 SiPO 4 ·H 2 O or NiH 3 [SiO 2 ] 8 ·H 2 P 2 O 7 ·4H 2 O. These soluble Ca sources were used in order to increase the number of nucleation sites for HAP on GAGs. Hydroxyl acid, chondroitin sulfate and its deacetylated product were used as GAGs. Starting materials were supplied by two kinds of processes to give solution(s) of (a) only PO 4 3- [$\text{PO}_4^{3-}$] or (b) PO 4 3- [$\text{PO}_4^{3-}$] 3 and Ca 2+ [Ca 2+] dropwise into GAG solution containing CaO·2Ca(OH) 2 to elucidate the details of the 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 crystals of HAP. The aspect ratio of the aggregates and HAP crystals was controlled by supplying processes of Ca sources. Lattice parameters of the samples prepared from Ca 10 [(HPO 4 ) 2 ] 6 ·2SiO 2 shifted towards those of chondroitin. Those from (CaH 3 [SiO 2 ] 8 ·H 2 P 2 O 7 ·4H 2 O, 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.

L3.23 Fast Deposition of Structured Coatings from Microbranches and Nanoparticles. Brian Prevo, Ruben G. Carbocell and Orin 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 at desired dip coating times. Structured coatings larger than few cm 2 are deposited in minutes from aqueous suspension volumes of approximately 10 milliters. Three different systems were studied: hexagonal crystalline, thin metallic coating 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 free 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 scalable technology.

L3.24 Self-assembly of Polymer-Coated Nanoparticles in a Block Copolymer. Gregori 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 nanoparticle species is studied with the help of a combined Small-Consistent Field Theory (SCFT) and 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 factors (A, B, and C). Effective pair interaction of coated particles immersed in block copolymer is calculated using the SCFT technique. A Pickering-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. Later, 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/2block copolymer composite material. The above approach may be instrumental in design and synthesis of ‘smart’ nanstructured materials for various applications.

L3.25 Magnetic Nanoparticle as A Solid Support in Various Reactions. Dongwoo Yoo, He-Jong Yoon, Jin-Hung 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 organic molecules, quinolymannionate salts from nitricric 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 micrometer size organic monomeric polymer support materials, compounds immobilized on nanometer size support show the high reactivity comparable to the homogeneous reactions and they can be easily separated from the reaction mixture by applying an external magnetic field. Various reactions known on the magnetic nanoparticle surface such as catalytic reaction, polymerization reactions, and other coupling reactions will be discussed to show broad application area of magnetic nanoparticle support.


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 hemihydrate (Zn2SiO4(OH)(2H2O)). A thin layer of petal-like nanocrystals with walls aligned perpendicular to the substrate was used as a buffer layer for the growth of a secondary layer of hemihydrate 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 Ce1-xZr x O2 Solid solutions made by liquid-feed flame spray pyrolysis. Min Kim, Julien Mercier and Laine M Richard, Materials science and engineering, Univ. of michigan, Ann Arbor, Michigan.

We describe here the synthesis of nanostructures in the Ce1-xZr x O2 system by liquid-feed flame spray pyrolysis (LF-SP) for applications in three-way extract catalysts (TWCs) and diesel emission control. Through the choice of the correct precursor chemistry, we are able to produce Ce1-xZr x O2 materials in the phase space. The resulting powders have typical particle sizes of < 100nm, and surface areas of up to 80m2/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. Suh Young Kim and Venkatraman Gopalan. 1Material, Penn State Univ, university park, Pennsylvania, 2Material 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 adopted. We present experimental NSOM images that show unexpected optical contrast at a parallel 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 for the far-field propagation region is used. We find that 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 equivalent line 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 preserve the propagating and evanescent field till the NSOM tip. By activating both the incident and individual plane wave, we can successfully calculate the NSOM OTF. We mathematically prove that this FDTD simulation and OTF are equivalent under the condition. Then we used this 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 Growth and Scattering of Nanoparticles during Sols-Gels Synthesis. Nan Yu1, King Lam Yung2 and Guo Xiong Nong2.

1Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China; 2State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

Sol-gel synthesis is established method for preparation of advanced materials including ceramics, catalysts and functional nanomaterials. The growth and scattering of the nanoparticles during sol-gel synthesis are influential factors that determine the final properties of the material. This phenomenon has been investigated at different length and time scales using various spectroscopic techniques[1]. However, vital information on the local structural environment (i.e., L-100 nm) is often deduced from macroscopic measurements rather than from direct observation. This paper demonstrates the use of atomic force microscopy (AFM) for in situ observation of the nanoscale morphology transformations that occur during the solgel 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 templated method based on a modification of traditional sol-gel technique. The structural evolution during the solgel synthesis of mesoporous silica, alumina and silicon-alumina catalysts were observed using AFM. The formation of fractal structure is strongly correlated to the silicon-content of the sample. Both silica and silicon-alumina samples displayed fractal growth forming intricate branched structures. The branches consisted of nanometer-sized clusters that exhibit complex structural transformations that include coarsening, outward 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. Aging at room temperature transforms the original alumina into a polycrystalline network of nanoparticles. The final metal oxide catalysts were analyzed by electron microscopy, X-ray diffraction, N2 physisorption and NMR to determine its structure and chemistry.


1Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Recent advances in the design and fabrication of microreactors, microprocessors and microelectrodes bring 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 sputtering 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 catalysts within a microchannel. Using a modified sol-gel method, TiO2 aerogel was deposited into the microchannel from a TiO2 solgel. 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 attachment to the microchannel wall and control the shrinkage of the wet gel during drying. After temperature treatment,
a complex network filled the microchannel. The structure and density of the network was dictated by the composition of the original alcoholic solution and the length of the network was tested under flow conditions and the activity of the TiO2 was evaluated for photocatalytic destruction of methyl orange dye in aqueous solution. Monolithic TiO2 with ordered and disordered monoperoxide channels were also prepared using a template method. Polymer microchannel were used as template material to create the macroporous materials. Comparison indicated that monolithic TiO2 provides lower pressure drop, while maximizing the contact area between catalyst and reaction mixture.

10.3.21  Construction of Nano-Sized Surfaces Using High-Temperature Viscous Flow of Ultra-Thin Film Silicate Glass. Shinji Kiba, Shuhei Sato, Akifumi Misaki 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 possibilities to develop new functionalities of nano-electronics. Softening behavior and viscous flow resulting from the supercooling state, which is characteristic 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 ultrathin film glass at high temperatures. The ultrathin films (about 3nm thick) of soda lime silicate glass were deposited by pulsed laser deposition using a glass target onto the ultramicro naphthyl substrates, which have atomic steps of 0.2 nm in height and ultramicro terraces of 50×100 nm in width. These naphthyl substrates were obtained by anodizing in air at 1000°C (Arg. Phys. Lett. Vol. 67 (1990) 261). 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 ultrathin film glass. It was found that the surface flattening of ultrathin film glass became remarkable just over the glasses transition temperature. Furthermore, the surface morphology of the annealed glass film reflected the nano-sized structure of the substrate surface. The nano-sized surface was used to produce a flat substrate (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 ultrathin film oxide glass in combination with the microscale heating by optical fibers may provide us with a novel nano-tool such as nano-adhesive for micromachines or a nano-scale insulator for biological devices.

10.3.32  Sintered Tantalum and Niobium Sub-micron Powders of Solid Electrolytic Capacitors. Yuri Pandele-Freedman,1 Alexander V. Gladkov2,3 and Norbert St. Sebring,2,4 Vitas: Springfield, Surfaced, Maine; 2Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv, Israel.

Sintered tantalum and niobium sub-micron powders are widely used in modern electronics as porous media of Ta and Nb solid electrolyte capacitors. Due to high surface area of the media, these capacitors demonstrate excellent specific charge per unit of their volume. At the same time, sintering process of DC 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, metallic oxide film of Ta. In the Nb capacitors, the DC leakage of the dielectric, metallic oxide film of Nb, increases gradually. Simultaneously, activation energy of conductivity gets lower and bias dependence of the capacitance becomes larger. The results of some study and electrical measurements are brought together in order to understand the difference in the capacitance degradation and failures. It is shown that a different behavior 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 oxide 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 2.8 nm on their surface. Sintering of the powder into pellets at temperature above 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 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 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 on their surface are under the discussion.

L3.30  Pb on Ge(111) 2D growth mode. Fabio Barth1,2,3, Alberto Mesmaeker4,5, Leandro Nascimento da Silva5,4,4, and Steffen Brandle4,3, 1E.M.T. INRS, Varennes, Quebec, Canada; 2TASC, INFM, Trieste, Italy; 3 Dipartimento di Fisica, Universit`a di Trieste, Trieste, Italy; 4Jozef 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 raging for a thoroughly increasing interest, both for technological applications and for purely scientific motivations. In particular, the Pb/Si system has been always considered as a model system for the singling out and characterization of the elements determining the Schottky barrier height. Nevertheless, due to the monomolecular properties of thin layers [1], merely basic scientific studies have recently brought most of the attention. According to different theoretical simulations [2,3], variations in the electronic and morphological properties of the growing metal 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 metallic Pb 2D films on Ge(111) at very low temperatures, performed by helium microscopy (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 entire 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) film. 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. Hauto, MS Thesis in Physics (2002); [2] F. K. Schulte, Surf. Sci. 55, 427 (1976); [3] P. J. Feibelman, D. R. Homan, Phys. Rev. B 59, 5613 (1984); [4] A. Crotti, D. Cretto, L. Floreano, R. Cotter, A. Morgante, F. Tommolini, 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. Reinier Job, and Alexander G. Ulyanov; Department of Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany.

Plasma hydrogenation applied on standard Cadmium silic (Cr %) 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 sub-surface regions up to about 1 μm depth, quasi 2 dimensional extended defects, so-called platelets, which are oriented in the [111]- or [100]-crystalllographic directions are also formed by such treatments. The formation of these nano-structured defects at the surface and sub-surface regions of the hydrogenated wafers was investigated after hydrogenation plasma treatment, in dependence of process conditions and substrate temperatures up to about 500°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 1300°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 the crystalline orientation will be discussed. The impact of the nano-structured defects and the silicon nano-phase formation at the wafer surface and in the sub-surface regions will be finally discussed with regard to several technological processes applied for the formation of various silicon device structures.


CrIV doped olivines (forsterite, cumite etc) emit in the 1100 to 1600 nm spectral range. Controlled ceramination procedure of an appropriate glass may produce transparent glass-ceramics with embedded nano-crystallites of optically active CrIV doped olivines. Glasses forming ability and devitrification behavior of Cr-Ge-B-O compositions is
L3.36
Long-range order and Verwey transition on the Fe$_3$O$_4$ (001) surface, Igor V. Sheets, Guido Mariotti, Shane Murphy, Nikola Berdena, Sergio F. Ceballos and Ken Jordan, Physics, Trinity College, Dublin, Ireland.

Magnetite (Fe$_3$O$_4$) 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 halfmetallic nature, which makes magnetite an interesting material for applications in spin electronics. However, the nature of the electronic transport and the metallicity of the Verwey transition at $T_V = 123$ K has not yet been clarified. We have studied the (001) surface of synthetic single crystals of Fe$_3$O$_4$. The crystals have been characterized $x = y$ by x-ray diffraction, resistivity versus temperature measurements, Hall effect measurements, and magnetization measurements. The $x = y$ surface preparation procedure consisted of a combination of $A$ and $+$ sputtering, annealing in ultrahigh vacuum (UHV) and in an oxygen partial pressure. The crystals were characterized by x-ray electron spectroscopy (AES) and low-energy electron diffraction (LEED), which showed a simple (1$\times$1) or (2$\times$2) $2\times\sqrt{8}$ mesh. Scanning Tunneling Microscopy (STM) measurements were performed at room temperature using a tip of a ferromagnetic Mn$_3$Al alloy. Atomically resolved STM images provide evidence of a surface terminated at the octahedral plane (B plane), with rows of Fe ions aligned along the [100] and [110] crystallographic axes. Two different kinds of Fe ions with a separation of 6A are imaged; the periodicity between Fe ions of the same kind is about 12A. 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 170K above the bulk Verwey temperature. The data provides evidence of a Fe$^{3+}$, Fe$^{2+}$ and Fe$^{4+}$, and Fe$^{3+}$, Fe$^{4+}$ 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$_3$O$_4$ (001) surface. The first model is based on the interaction between the conduction electrons of the Fe 3d 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, and thereby 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 correlations create 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$_3$O$_4$(001) surface.

L3.37
Abstract Withdrawn

L3.38

The Materials Research Group at Curtin University is investigating structure-property relationships for aluminoaluminates, also known as geopolymers. These polymers consist of an amorphous three-dimensional structure resulting from the polymerisation of aluminoaluminate monomers in an alkaline solution. One of the principal 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 metakaolin 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 microstructure of the material by examining the microchemistry of features in the images. The polymers were formed by mixing metakaolin 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, with the required water content. SEM analysis shows that there are two distinct phases present, which are the fully reacted polymer and residual metakaolin. The relative amounts of these two phases vary systematically with the 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 elements of the Al,O$_2$ in the residual metakaolin. Impurity elements such as Ca and Mg are found in the polymer phase, while impurities such as Fe and Ti are found in the residual metakaolin. Reference [1] Rowles, B.C.: "Aluminoaluminate geopolymers synthesised by sodium silicate activation of metakaolin", 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), Yuxin Wang$^{1,2}$, Zhigang Xu$^{1}$, Dianming Yin$^{1}$, Sergey Yarmolenko$^{1}$ and Jagannathan Sankar$^{1,2}$, College of Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina, *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 nanoindentation. The relationship between the film properties and the deposition parameters 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 to Tuning Phase Stability in NanoComposite Multilayers, Gregory B. Thompson$^{1,2}$, Arda Gen$^{1}$, Rajesh Benerji$^{1}$ and Hamish L. Fraser$^{3}$, Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama, *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 the design of functional nanocomposites. 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 and bcc Ti phase stabilities in a Ti/Nb multilayer. The Ti layers were subsequently cycled with the bcc-stabilising 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 it is now possible to engineer a specific phase to a desired nanometer thickness for the enhancement of the nanocomposite properties.

L3.41
Sil-Gel Synthesis And Magnetic Studies of Titanium Dioxide Doped With 10% M (M=Mn, Ru, Co, Ni), Ayankanni Manivannan, Gerry P Ghaspel and Mohinder 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 solgel 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 calcined below 500°C to produce the doped titanium dioxide. The dominant phase of titanium dioxide with a low angle which was confirmed by X-ray diffraction. The particle sizes for cobalt, manganese, iron and nickel, and doped titanium dioxide were determined via powder analysis to be approximately 10 nm from the XRD data of the XRD patterns. Magnetic properties of the 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. Krishna, Appl. Phys. Lett., 83 (July 7, 2003 issue).
1Department of Chemistry, University of South Florida, Tampa, Florida; 2Department of Chemistry, University of South Florida, Tampa, Florida.

Magnetic nanoparticles embedded in polymer matrix have excellent potential for electromagnetic device applications, such as EM noise reduction, storage media, recording devices, etc. Polymer composites consist of poly(styrene-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 techniques including in situ ultrasonic polymerization and melt blending. The polymer processing conditions were optimized to achieve a uniform distribution of the nanoparticles in the polymer matrix. Magnetic properties were determined using a micro-VSM 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 nanoparticles, 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 our goals is promising for electromagnetic applications of these materials. H.S. acknowledges support from NSF grant # ECS-0414947.

L3.43 Multifunctional single-crystal lake crystals. Xiang yang Kong1, Qiang Qiu2, and Jialei Wang3.
1School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA; 2School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, China.

Tunable structures in micro- and nanoscale 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, while the interior is small and dense to 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 medical 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 chemical robustness, which will be effective for penetrating bio-biochemical tissues and transporting fluid. In this paper, using a simple solid-vapor process, a novel single-crystal, microtubular structure of aluminum-rich muffite 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 microtube has the [001] growth axis, a dislocation-free volume, a thick hollow interior channel of 0.53 micrometers in width, and a thin wall of 50-100 nanometers. The ceramic microtubes are mechanically hard with potential applications for two-pass media, drug delivery, microchannel for micro-electromechanical systems and biochips, as well as optical response cavities and waveguide.

L3.44 The SrTiO3 (001) Surface: TiO2-rich Reconstructions with (2x1) and (c(4x2)) and (c(6x2)) Unit Cells. N. Asaka, R. Erman, O. Wacławski, C. H. Lin, H. J. B. Peepelmeier, M. Asta, D. E. Ellis, and L. D. Marks.

We have recently reported solutions for the (2x1) and (c(4x2)) surface reconstructions of SrTiO3 (001) obtained through high-resolution transmission electron microscopy, direct methods analysis and density functional theory calculations. The results suggest that the formation of TiO2 overlayers in which truncated TiO2 polyhedra are arranged into edge-shared structures in contrast to the corner-shared TiO6 octahedra in bulk. We present preliminary results of a third reconstruction with a c(6x2) unit cell.


Gold nanoclusters dispersed in single crystal TiO2(110) have been formed by 2MeV Au + implantation at 300 K and 575 K followed by annealing at 1275 K for 5 hours. The morphological features, size and crystallographic orientation of the Au nanoclusters with respect to the TiO2 matrix have been investigated using conventional transmission electron microscopy and electron diffractions. In particular, the interface structure between the Au nanoclusters and TiO2 was investigated. Atomic structural model of interface Au and TiO2 was established based on high-resolution transmission electron microscopy (HREM) imaging and HREM image simulation. Two types of interface models and the atomic structure of the TiO2(110) surface were presented. These were: (1) Au<110>/TiO2[001] and Au(111)/TiO2(001), and (2) Au<110>/TiO2[001] and Au(111)/TiO2(001). Au clusters are facetted along Au(112) and Au(111) or Au(220) and Au(002) planes. The precipitated Au clusters show extensive (111) twinning. The orientation relationships are the same for Au clusters grown on strictional TiO2(110) surface, indicating that lowering interfacial energy to be a governing factor for setting the interface orientation.

1School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore; 2Department 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 importance for the success of these devices as analytical instruments. In this paper, a novel amperometric biosensor with carbon nanotubes modified using carbon nanotubes for glucose biosensors, has been developed. The initial results showed that the carbon nanotubes provide suitable electrode matrices for glucose oxidation immobilization, they also increase the glucose oxidase stabilization. The biosensor stability and reproducibility were therefore 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 Maruyama1, 2, Keiji Matsuoka2, Norikazu Sakurai2, and Shigeyo Nishitani2.
1Science and Engineering, Meijo University, Nagoya, Japan; 221st Century COE program NANO FACTORY, Meijo University, Nagoya, Japan.

We successfully obtained atomically flat Ge surfaces on mesa structures with an area of 10x10 μm² by growth of phosphorus-doped Ge on Si(100) by low pressure epitaxy. Schematic of the LPE growth is shown. The use of 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. Wet etching was used 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 mesa, we tried to suppress the formation of 3D nuclei on grown surface by decreasing the super saturation. When the super saturation was enough small at the growth temperature below 340 °C, flat facets were formed on some mesas after 30 min growth. 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 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 super saturation during the LPE growth. Our results show the possibility that atomically flat Ge area beyond 100μm² will be obtained by the control of the growth condition.

L3.48 Metal Nanotubes. Young Sun and Younan Xia.
Department of Chemistry, Univ. of Washington, Seattle, Washington.
Metal nanotubes have been prepared through a galvanic displacement reaction between the silver nanowires and silver nitrate in morpholino 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. These nanotubes had 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 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. Tarac1, R. Rosario1, A. A. Garcia1, D. Gaz1, M. Haynes1, S. T. Pickeral2, B. C. Bunker2, B. I. Kim3 and J. E. Houston3, 1Arizona State University, Tempe, Arizona, 2Sandia 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 distinguished from earlier reports of optomechanical switching of molecules on surfaces. Previously we designed and demonstrated a photoswitchable layered light-triggering coating of the rings of tethered spiropyrans monolayers on glass surfaces leads to the switching of the hydrophobicity of the surface, with wetting angle changes of up to 15 degrees. Irradiating the photoactive surface with UV light triggers the spiropyran rings to close the surface, while irradiation with visible light creates 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 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 simplifying the switching of electrical double-layer forces. Potential applications of these photoresponsive 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. Yasuo Ishii1,2,3,4, Toshiaki Kawamura1,2,3,4, Masato Hongo1,2,3,4, Takumi Okada1,2,3,4, Kazuyuki Sato1,2,3,4, Ryoji Hori1,2,3,4, Masahide Nishita1,2,3,4, Kenji Yamada1,2,3,4, Kazuhiko Kikuchi1,2,3,4, Hiroshi Itou1,2,3,4, Nobuyuki Takada1,2,3,4, *Center for Applied Near-Field Optical 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 benzonic acid (benzoic acid molecules which dithiol in 2-propanol (IPA) and Xylenol 6 and ethyl vinyl acetate copolymer (EVA) compounded with organo modified montmorillonite dry was presented. The co-line data were correlated with off-line dielectric measurements, one analysis of these data yielded a wealth of dielectric relaxation phenomena. Significant differences in the dielectric relaxation phenomena were observed for clay nanocomposites in the aggregate, intercalated and exfoliated states. Macwell-Wagner interfacial polarizations were observed in the nanocomposites reflecting polarizations associated with the polymer/clay surfaces. Microstructure characterizations using TEM, X-ray and SANS observations were also carried out. Fluorescent dyes, doped into EVA copolymer, were being used as molecular probes to study the effects of microstructural transformation on their spectra. Real-time monitoring of both fluorescence and dielectric properties offers the potential for detecting microstructural character changes during processing without the need for off-line, post-processing experiments.

SESSION L4: Applications

Chair: John Parker

Tuesday, December 2, 2003
Room 304 (Hynes)

8:30 AM L4.1 Industrial Applications of Transparent Conductive Nanoparticles. Changwon Park1,2 and Hongyool Ju1, 1Dept. of Chemical Technology, Hankuk National University, Tejuon, South Korea, 2ANP Research Center, Advanced Nano Products Co., Ltd., Changwon, South Korea.

Due to the unique nature 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 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 applications, the current conducting nanoparticles show the most successful model in current industrial applications. Those particles are being massively used for electronic and display industries. High performance transparent IR blocking films are being produced using conducting particles 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 14.2
HSA-CERANAM: A New Material with a Continuous Nanopore Network. Baskireddy Nair, Merrill Wilson and Akash Akash; Ceramic Inc., Salt Lake City, Utah.

A new ceramic material called HSA-CERANAM (a trademarked abbreviation for High Surface Area CERamic 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 strength as high as 60-70 MPa and component surface areas as high as 100 sq m/g. This material, which 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 development micorreactors for applications such as hydrogen/hydrogen gas generation.

9:15 AM 14.3
Iron Oxide / Silica Nanocomposites, Michael Kroll, Markus Priebe and Guido Zimmermann; Cewin Technologies and Innovation - Advanced Nanomaterials, Degussa AG, Hanau, Germany.

Iron oxide / silica nanocomposites are produced in a pyrolytic 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 magnetization curves therefore do not show any or depending on the mean domain size just a small hysteresis. The saturation magnetization can be varied from 5 to 35 Am^2/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 250 m^2/g by controlling the size of the silica layer or the magnetic domains by adjusting the flame temperature. The superparamagnetic behaviour can be utilised in different applications. If the nanocomposite is exposed to an external magnetic field they get heated up. This behaviour is useful in applications like hyperthermia (cancer therapy) or adhesives (bonding/debonding on demand). Due to their magnetization they can be used for ferrofluids, shielding layers, receptor particles for microwaves or magnetic sinter agents or as pigments. In the presentation the visible methods for the synthesis of iron oxide / silica nanocomposites, the physical characterization with special emphasis on the magnetic properties and an outlook for future applications.

9:30 AM 14.4
Single-Walled Carbon Nanotube Rope for Gas Sensor Applications. Jianmei Lee, Minchun Chai, Kijong Hong, Hyunju Chung and Byungwoon Ryu; Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejon, Chungcheong North, 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 solvents with much lower concentration and dispersed in 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 1V characteristics across the fabricated SWNT ropes, and they showed the characteristic of a semiconductor which can be applied as gas sensors. The change of conductivity of these SWNT ropes in the presence of NO and NH3 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, Appl. Phys. Lett., 79, p. 3803 (2001).

9:45 AM 14.5
Polymer-Silicate Nanocomposites: Morphological Studies and Their Application as Electrolytes in Lithium Polymer Batteries. Mirei Kurian1, Aruna Dasgupta2, M. Mary Galvin1; 1Materials Science & Engineering, University of Delaware, Newark, Delaware; 2Polymer Research Lab, Army Research Laboratory, Aberdeen, Maryland; 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 high solubility 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 advantage 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 sufficiently light for portable power needs. Our work is focused on the development of a new class of nanocomposite electrolytes. The incorporation of Li4 exchanged mica clay sheets into a suitable polymer matrix is expected to impart the inherent favorable electrochemical 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 14.6
Nanobelts as nanocatalysts, William L. Hughes and Zhong L. Wang; Materials Science and Engineering, Georgia Tech, Atlanta, Georgia.

Semiconductor oxide nanobelts of ZnO have been synthesized and manipulated for microelectrochemical 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 synthesized by vacuum evaporation of ZnO 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 nanobelts were manipulated to have a range of lengths, exemplifying our ability to tune the resonance frequency. Structurally modified nanobelts demonstrate potential for nano-catalyst based technologies.[2] With dimensions ~35 - 1,800 times smaller than conventional catalysts, the nano-catalysts are expected to have improved chemical, and biological sensitivity for scanning probe microscopy and sensor-based applications. The ability to dimensionally control and manipulate nanobelts for catalytic devices and applications establishes a framework from which ultra sensitive catalysts will be developed.[3] [1] Z.W. Pan, Z.R. Pan, Y. Wang, Science 291 (2001) 1947-1949. [2] W.L. Hughes, Z.L. Wang, Appl. Phys. Letts., 82 (2003) 2886-2888.

10:30 AM *14.7

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 feedstock, e.g. aluminum at room temperature and pressure. We convert this material into a high-temperature (5000K), high-pressure (100 atm) plasma. By controlling the plasma quench...
rate (which in excess of 1 million K per second) we are able to control the mean particle size from sub-100s to 10μm 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. An overview of chemical and physical synthesis processes will be given with special attention to the homogenous plasma 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: electronics, microelectronics, energy storage, and aerogels. Applications include: electrical and/or thermally conducting fillers; direct write electronics; transparent optical coatings; photovoltaics; fuel cells and advanced materials for explosive, propulsion, and armor. 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 L4.5
Nanocrystalline Mixed Metal Oxides - Novel Oxygen Storage Materials
Nanophase Technologies Corporation employs a new physical vapor synthesis technique to manufacture ceria-doped 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 1000° 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 size and density distribution of 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 L4.6
Surface modification of ceramic particles using a newly developed DC plasma spray system. Kang Geun Choi1, Kyoung Seon Kim1, Hye Jin Yoon2, Bum Suk Han3, Byungok Oh4, Dae Young Lee5, Ju Ho Lee1, Yong Ho Ro2, Byoung Ho Kim1, Hoon Kang6, Dong Joo Lee7, Kim Jae Jung8, perpendicular direction, Thermal spraying, High temperature, Nanomaterials

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 2step cyclone chamber, operating at the low pressure, was adapted for dividing the particle size and disaggregating the plasma-treated particles. The enlarged plasma length up to 60cm, in the reaction tube, served as very effective in disaggregating the plasma-treated particles during cooling and to lead them to 2step cyclone chambers with a stable temperature distribution. The new thermal plasma system was applied for various ceramic powders such as Al2O3, SiC, ZrO2, and C. 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 2nd 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 nanophase in the hybrid micromolecular matrix. The membrane becomes proton conducting polymer electrolyte when doped with 13-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 proton conductivity of 2.6 x 10^-4 S/cm was obtained at 130°C when the PDS/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, Zhaofang Huang, Sinivas Nemani, Kang Sub Yim, Li-Qun Xin and Hichem Mekad; Dielectric System & Module, Applied Materials, Santa Clara, California.
A second-generation organosilane glass (OSG) low-k film for the 65nm technology node was developed with k value of 2.5±0.6, corresponding to a 15% reduction in dielectric constant, as measured from the first-generation Black Diamond® 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 organosilane molecule and small organic molecule precursors. Post deposition, the OSG films was treated by electrochemical beam etching (E-BE) and 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 dielectric 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 porosity has a narrow size distribution that peaks at 1nm, as measured by ellipsometric porosimetry. Modulus of up to 15 GPa can be achieved through by-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. The 2-step film, from 90nm to 65nm is simplified due to the similarity between the first and second-generation film properties. A single dielectric structure was fabricated using 50nm of BLOMET as an etch stop layer on the 90nm film of the new OSG film. Interline capacitance measurement and TMA Rophield simulation indicated an integrated k value of 2.6. A similar effective k value was also achieved with a dual dielectric structure. Planar capacitance measurements indicated a breakdown strength of >0.7MV/cm, and >95% yield was measured on a 9 million wafer.

SESSION L5
Properties Chair: John Parker
Tuesday, December 2, 2003
Room 304 (Hyne)

1:30 PM L5.1
Nanocrystal are organized in 2D superlattices forming either in a corner, a hexagonal network or chain like. Two superlattices of 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 Nairan 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 sp3bonded carbon atoms. DLC coatings possess properties close to diamond in terms of hardness, high thermal stability, and chemical inertness. Unfortunately, DLC exhibits poor adhesion to metal and polymers. The adhesive force of 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 modified design was adopted to incorporate metal (e.g., silver or titanium) into the DLC films during pulsed laser deposition. Atomistic structure with a resolution of 1.6 Ångstrom was performed using STM-Z contrast at
ORNL. Since scattering power or contrast depends upon atomic number squared (Z2), heavy noncarbon atoms in the DLC matrix can be studied in high-resolution TEM of the DLC/metal composites, 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 composites possess drastically lower wear resistance. On the other hand, pure DLC possesses the lowest wear resistance.

Diamond-like carbon composites also exhibit significantly enhanced adhesion. Careful analysis of the Raman data also indicates a significant change in the crystalline nature and the other parameters that are derived from the Raman measurements, indicating a reduction in compressive stress within these films. This reveals a trade-off between adhesion and wear resistance, which is expected to be beneficial for practical applications.

The chemical properties of these composites were studied using x-ray electron spectroscopy (XPS). By varying the metal concentration as a function of distance from the interface, it is possible to create a functionally graded DLC/metal nanocomposite, whereby the DLC/metal nanocomposites have multiple biomedical applications. For example, we have shown that DLC/silver composites possess antimicrobial properties against Staphylococcus aureus. DLC/transition 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.


Oxygen storage and related vacancy/interstitial migration in doped diamond-like carbon films has been a center of focus for the recent years in the area of catalyst and solid oxide fuel cells (SOFC). The high efficiency intermediate temperature range of oxygen storage from chemical to electric state is important in the reduction of the pollutants made materials like diamond-like carbon to atomic carbon, which is the case for nanocrystalline diamond films. The oxygen and impact of ionic conduction in doped-CdO films relies heavily upon grain boundary dynamics. Study of doped-microcrystalline CdO films 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 CdO 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 n.c. conductivity by impedance spectroscopy. The grain boundary analysis is carried out using the high-resolution transmission electron microscopy (HRTEM). Initial 400 diffusion measurements were done to incorporate the nanocrystalline microstructure in the carbides. The nanocrystalline films studied here are significant for their industrial applications, as they are both in the grain size range and the grain boundary structure.

2:30 PM L5.4 Thermal Equilibrium and Transport Properties of Nanocrystalline FCC Metals. Peter M Derbes and Helen 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 transformation and in the velocity-momentum space. Rev. Lett. 87205501 (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 Polyolynide Nanocrystallisation, Characterisation and Electrochemical Behavior. Samuel T Lu, A Dong Hong, Peter Y Zawalih and M Stanley Whittingham; Department of Chemistry and Chemical Biology, Columbia University, New York.

Vanadium oxide nanofibers have been prepared using poly (methyl methacrylate) (PMMA) as templating reagent. Sol-gel reaction and subsequent hydrothermal synthesis of V2O5 and PMMA resulted in Nitro VxOy (x=2, 3) nanofibers; 3.8-5.0 nm core with 24-36 nm PMMA coating. Reduction of V2O5 was done in nitrogen and oxygen at 1000 oC formed V0.7 and V2O5 nanofibers respectively. Polyoxovanadium oxynitride nanomaterials were prepared by sol-gel reaction of vanadium(V) oxycarbполидное and polyoxovanadium(VI) oxycarbполидное; V2O5 nanofibers for lithium insertion and were examined by X-ray diffraction, XPS, XRD, TGA and IR. The vanadium oxides are redox active and can electrochemically insert lithium reversibly. A specific charge of about 110 mAh/g (with respect to the nanofibers) was obtained for subsequent lithium insertion and removal with cycling. The electrochemical behavior of the vanadium oxides with polyoxovanadium is also discussed. This work is being supported by NSF grant DMR-0131963.


Ultrananocrystalline diamond (UNCD) is a very fine-grained (3-5 nm) diamond material with atomically abrupt mixed sp2 and sp3 bonded grain boundaries. Synthesized by microwave plasma-enhanced chemical vapor deposition (MPCVD) with Ar-rich Ar/CH4 plasmas, the electronic, structural, and tribological film properties of UNCD films can be tailored by doping with a controlled amount of nitrogen. These UNCD films correspond with the transformation in the film structure, whereby both the grain and grain boundary sizes increase, and the grain boundary binding structure is altered. These effects result in an n-type, highly conductive diamond 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 insights into the unique conduction mechanism of nitrogen-doped UNCD, along with conformation of the carrier concentrations, mobilities, and conductivities of this material as a function of nitrogen doping and film microstructure. [1] This work was supported by the 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 Linicin and Enrico Travessa; Dept. of Chem. Sci. Technol., University of Rome Tor Vergata, Rome, 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 the function of energy conversion. Rev. Lett. 87205501 (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.

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 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 the performance of direct methanol fuel cells (DMFC). 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 salts 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 has 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 amorphous ceramic oxides to polymeric matrices improves the electrical and mechanical performances both in DMFMs and lithium batteries. It is worth noting that the beneficial effect of nanoceramic powders was found both in protonic and Li-ion conductors. Improvement in conductivity was observed in both cases. Electrical insulation for the recording of EEG (electroencephalograms). This is to the best of our knowledge, the first report on the use of 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 nano-scale 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 Bahatskere, Marc Hamm, Milos Shafier and James Elliott 
Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom; 2Department 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 composites and the enhancement of their electrical properties. The challenge is to determine the type and size of CNTs 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 required properties such as electrical conductivity. This research primarily involves mesoscale simulations (discrete 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 Nanoparticles/Polymer Composites. Colleen Bakes, S. Iman Shah, and Khasbib Hassen. 1Materials Science and Engineering, University of Delaware, Newark, Delaware; 2Physics and Astronomy, University of Delaware, Newark, Delaware; 3Physics, Quaid-i-Azam University, Islamabad, Pakistan.

An inert gas condensation (IGC) technique was used to prepare nanoparticle-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 Fe2O3 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 100 nm. These particles were spin cast into Poly(methylmethacrylate) (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 10-20 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 evidenced 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 studied compared to the non-dispersed compressed powder, suggesting of heightened anisotropy barriers.
Select Mixed Mineralization in Block Copolymers.
Brian Joseph Mele 1, Thomas P Russell 1 and Sandra L Burkett 1.
1 Chemistry, Amherst College, Amherst, Massachusetts; 2 Polymer Science and Engineering, University of Massachusetts, Amherst.

Asymmetric diblock copolymer thin films have been used as templates for the mineralization of silica. Films of poly(styrene-block-poly(methyl methacrylate)) (PSb-PMMA) and poly(styrene-block-poly(ethylene oxide)) (PSb-PEO) were prepared in which cylindrical PMMA domains oriented perpendicular to the surface. Silicon oxide could be selectively grown in the PMMA cylinders by sol-gel phase and liquid-phase sol-gel processes using tetrachlorosilane (TEOS). Vapor-phase TEOS treatment of PSb-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 nanocores, 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 cores could be obtained. The block copolymers may act as templates for other metal oxides to create nanoscale 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, Manmohan Singh 1, Matthew J Oakes 2 and Laura B Glover 3.
1 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 collagen was carried out under simulated physiological conditions using acidic biopolymers, such as poly(aspartic acid) and poly(vinyl phosphonic acid), to form a monolithic inorganic 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 crystallizes into hydroxyapatite within the pores of hydroxyapatite. Heterochromic dye analysis shows that a liquid-phase mineral precursor of calcium phosphate can prove useful for in vitro model systems for the study of in vitro 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, Myungwhan Kim 1, Lynne A Sannaeh 1 and Jayant Kumar 2.
1 Chemistry and Physics, Center for Advanced Materials, Lowell, Massachusetts; 2 U.S. Army RDCCOM, 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 sulfonated poly(styrene latex) (PS) and carbonylated poly(methyl methacrylate) latex (PMMA) nanoparticles. This approach allows for the fabrication of relatively uniform PS and PMMA films 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 layer, with uniform coverage of the substrate. The polymeric layer was then modified by the deposition of polyacrylate to provide adequate surface charge density to enable subsequent deposition of a low refractive polymer (PS). In another approach, 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

9:30 AM L6.4
Nanostructured Hybrid Inorganic-Organic Films Formed by...
and compared, and promising applications discussed.

Spherical Mesoporous Carbon Particles from Aerosol-Assisted Mesoporous Silica Templates. John Eric Handsy, Zhiqiang Wu, Qingwan Hu, Jiebin Peng, Donald Wang, Byron McCusker, Department of Chemical Engineering, Tulane University, New Orleans, Louisiana.

Spherical mesoporous carbon particles have been synthesized using mesoporous silica as a template. The templates were synthesized using an aerosol-assisted self-assembly process. Briefly, starting with a precursor solution prepared by reacting tetraethylorthosilicate (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 silica species into ordered mesostructures. After condensation of the silica and removal of the surfactant, mesoporous silica particles are formed. The mesoporous silica particles were 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 fillers in nanocomposite materials.


Alternative cathode materials for lithium batteries have been investigated widely to replace the expensive and oxidatively unstable LiCoO2 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 Fe2+ /Fe3+ redox couple-based materials have been investigated extensively. Li,Fe2P2O4 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+ 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 discharge 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 facilitates the penetration of the liquid electrolyte into the mesoporous structure of electrodes and hence increase lithium diffusion rate. Here, we reported for the first time the synthesis of ordered hexagonal mesoporous Li,Fe2P2O4 employing cationic, cetyltrimethylammonium chloride 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 m²/g with an average pore size of 3.2 nm according to N2 adsorption/desorption analysis.

Highly Swollen Liquid Crystals as new reagents for the synthesis of nanomaterials. Eric Perret, Geertase Surendran, Mike Tukumbe, Eduardo Pena dos Santos, Patrick Kocyman, Hyd Remia and Laurence Romeu. Groupe de dynamique des Phases Condenses (CNRS), Montpellier, France; Institut Europeen des Nanomatériaux, Montpellier Cedex 9, France; Laboratoire de Chimie Physique (CNRS), Orsay, France; Centre for high Resolution TEM, Delf, Netherlands.

We present a general method to synthesize nanostuctured 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. Red-like nanomaterials are synthesized by chemical reduction in the aqueous part of the hexagonal mesophase, porous micelles of zinc are obtained by crystallization from hydrotropic phase and porous micro- and nano-fibers are obtained in the organic phase by photopolymerization or radiolysis. Hexagonal SLCs were first observed in the plane diagram of quaternary mixtures combining the amionic surfactant sodium azulene sulfonate (SAS) with an aqueous solution of rhodamine salt (NaCl), cyclohexane as a hydrophobic swelling
solvent and pentanol I as a co-surfactant. They display at room temperature a direct hexagonal phase constituted of infinite nematic cylinder columns 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 microreactors 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 microreactor that will be illustrated by the preparation of these mesophases. As an example, we show that involving small angle X-ray scattering and transmission electron microscopy will be shown.

2:15 PM L7.3

Reparation of Organic Templates in Supercritical Fluids: A Novel Approach to the Preparation of Nanostructured Metal Oxide Films. Rajaram Achat Pai and James J. Watkins, Chemistry, University of Massachusetts, Amherst, Massachusetts.

Ordered nanostructured metal oxides are of enormous interest for their applications in photonics, sensors, drug delivery, optoelectronics, and low dielectric constant films (low k) in microelectronics. The traditional approach to preparation of these materials involves the use of co-solvents and surfactants in aqueous solution. A novel technique has been successfully developed 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 injection 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 consolidation during drying. We will present results on the application of the technique to preparation of ordered mesostructured silicon/organosilicate films and their application is discussed.

2:30 PM L7.4

Porosity-Regulated Control in SBA-16 Type Mesoporous Silica Thin Films Synthesized with a Tri-Block Copolymer. Sosuke Naka1,2, Masahiko Suzuki1,2, Takao Ogura1 and Tatsuya Okubo1,2.1,2, Department of Chemical Systems Engineering, The University of Tokyo, Tokyo, 75-3 Hongo, Bunkyo-Ku, 113-8656, Japan; 2PRESTO, JST, Japan; 3Material Research and Development Laboratory, Japan Fine Ceramics Center, 2-1-Matsusaka, Asahikawa, Nagaoka, 496-8507, 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 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) and transmission electron microscopy in the characterization of mesoporous silica thin films. The effects of factors such as the spin 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 lamellar-hyper 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 N2 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).2,2 References 1. Naka et al., Chem. Mater., (communicated) 2 Murakami et al. (CPL, in press)

3:00 PM L7.5

Macroscopic Alkylene-Bridged Polydiacaphane Gels with Templated Nanopores. Kazuki Nakashima1,2, Yuki Kobayashi1, Yukimori Yamato1 and Kazuyuki Hiro1.1,2, Department of Chemistry, Kyoto University, Kyoto, Japan; 2PRESTO, JST, Kawaguchi, Saitama, Japan.

Silicon-based sol-gel systems accompanied by polymerization-induced phase separation are known to give well-defined co-continuous microstructures, including well-defined macroscopic morphologies. In pure silicon 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 siloxane liquids or bis(triethoxysilyl)alkanes. Depending on the type of templating materials used, 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 siloxane in a system reported by S. Hashimoto, D. Esposito, et al. to be a novel organic-inorganic hybrid system, are now also used as templates in bis(triethoxysilyl)methane-based systems. The EO-PO-EO type polyether copolymers were able to induce phase separation in most organic-inorganic hybrid systems, while their templating strength was dependent on the content of organic-inorganic containing parts in the silicate-based gel networks. Poly(oxyethylene) alkyl ether was effectively used to template slit shaped mesoporous systems in bis(triethoxysilyl)methane gels. These examples suggest the possibility of simultaneously controlling macro- and mesopores in poly[oxyethylene] gels in general.

3:30 PM L7.6
Synthesis of controllable mesostructured heteropoly oxometalate thin films with hierarchical structure by triblock copolymer templating. Hong Heng, Hao Shou Zhou, Yun Hui Suk, and Makoto Kunitake, EEL, AIST, Tsukuba, Ibaraki, Japan; Dept. of Materials Science, Univ. of Tokyo, Bunkyo-ku, Tokyo, Japan.

Mesoporous metal oxides, which can be prepared using surfactant-mediated synthesis method, have attracted much attention due to their potential applications such as catalytic, sensor devices, novel electrod4e-19, 28. Here we report a simple, reproducible, and versatile procedure for the synthesis mesostructured metal oxide thin films with hierarchical structure. We used 12-phosphotungstic acid (HPW12O40K8, H2O15, H2O20, PWA) and other heteropoly oxometalates as raw materials which might promise applications involving catalysis, solid electrolytes and fuel cell due to their strong Brønsted acidity and structural properties.23-25. We also used amphiphilic triblock copolymers as structure-directing agents. Mesostructured metal oxide thin films have hexagonal or cubic structures with d10 spacing of 7.7-11.2 Å in Ar. The films also have cubic structure with d10 spacing of 23 Å in Ar; 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 crystalline-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 m2/g) and show interesting electrochemical properties.

3:45 PM L7.7
Multi-Functional Responsive Particles Prepared by Aerosol-Assisted Self Assembly. Yi Yang1, Ningguo Liu1, and C Jeffrey Brinker1,2; 1Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, The University of New Mexico, Albuquerque, New Mexico; 2Sandin National Laboratories, Albuquerque, New Mexico.

Evaporation-induced self-assembly of aerosol droplets can be used as a route to create mesoporous noncomposite powders. Using the aerosol assisted self assembly, different mesostructured cerium, hydrogel-, and azobenzeno-containing noncomposite particles were prepared and their transport properties studied. Co-controlling silan nanostructured shell particles exhibited core/shell structures (dense cerium core and hexagonal ordered silica shell). The special core/shell structure may benefit the controlled release of Ce from the composite particles, a property that is critical in applying CeCl3 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 hydrogel to changes in external stimuli such as temperature, pH, and ionic strength. Pendant azobenzene-containing composites exhibited onion-skinned 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 Porosity By Wet Coating. Hidetoshi Sakaoka, Shigeki Chuya, Masahiro Fujita, and Yukio Yamaguchi; Japan Chemical Innovation Institute, Tokyo, Japan; 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 10 cm by 10 cm with high speed, say more than 1 mm/s by employing both a spin coater and a capillary tower. 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 poly styrene base (PSL) and silica nanoparticles was coated onto glass substrates by spinning. The PSL film on the silica thin film was 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 50-700nm. The ordering of pores on the silica thin film was evaluated by Voronoi polygon analysis. The ratio of hexagonal calculated as the quantity of hexagonal ordering was 98%. The average deviation of hexagonal 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 disturbed 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 Titanias Composites with Controlled Morphologies. Michael H Rett1, and Galen D. Stucky1,2; 1Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California; 2Materials Department, University of California at Santa Barbara, Santa Barbara, California.

In the last several years mesostructured nanocrystalline titania has become a particulary important material for a variety of applications in photocatalysis, batteries, photocatalysis, and photovoltaics. With respect to shape control and patterning, however, the morphologies reported so far for mesostructured titania, in contrast to mesostructured silicon and carbon materials, has been limited. 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 micro-architected 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

Current methodologies for the production of meso- and nanocomposites 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) that can be enabled 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 mesostructure on a new approach using physically spaced nanotubes in their hydrocarbon tails that allow for their facile deprecipitation of catalytically metallo-supramolecular polymerization, to produce a variety of volatile catalytic cores. Evidence will be presented illustrating surfactant organizations 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.
Effects of Deep-UV Exposure on Nanocomposite Silica Thin Films: Mechanism and Photochemical Pattern Generation. Andrew M. DietzElbaum, Gary A. Baker,1, Meri L. Amweg2,1, Chunel E. Yee,3 James H. Werner,4 Hung-Lin Wang,1 Atul N. Parikh1 and Andrew P. Schofield. Los Alamos National Lab, Los Alamos, New Mexico; 2Department 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 organosilane 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 phase 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 mesosstructured 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 mesosstructured/mesoporous films is also shown to selectively remove the mesosstructured regions, leading to patterned mesoporous structures. Surprisingly, in the process, a room-temperature liquid crystal phase is formed, offering the possibility of using density control to manipulate optical properties of the mesoporous 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. Karpov1, Viktor G. Balchenko1 and Sergey K. Gordeev1,2 1Natural Science Center, General Physics Institute, Moscow, Russian Federation; 2Central Research Institute of Materials, St.Petersburg, Russian Federation.

Some diamond and related structures such as CVD diamond thin films, DLC film, diamond nanowires, carbon nanotubes, etc. can show outstanding low-field electron emission with threshold fields of 1-3 V/Å. Many of these effects are due to the geometry of the emission sites that show the emission is often associated with diamond grain boundaries and diamond/aphthylene 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 nanowires of silicon oxide, boron nitride in cubic and hexagonal forms, as well as nanodiamond. The samples of non-diamond/pyrogen and diamond/pyrogen nanocomposite materials were prepared by the same technique, in which the matrix is pressed from nanowires and then saturated with pyrogen during a CVD process. Besides, nanowires exist in the samples that also play a role of "dielectric inclusions". The thickness of pyrogen 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/μm, 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 nanowire. 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 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 being 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 Site-Effect Characterization for Nanostructured Material in Nanodentin Test. Yongmei Wei, Ying Du, Sijie 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 better wearability, etc. These advantage properties can be measured by using the nanodentin test method. On the other hand, the experimental measurements show that the behavior of the nanostructured material strongly depends on the specimen size. 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, a new theoretical model (nanostructure function 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 indentation curvature radius with 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 nanodentin experimental results for a nanocrystalline Al-Sc alloy material.

L8.3 Synthesis and Field Emission Properties of Novel Carbon Nanowires. Jianjun Wang,1 Min Zuo1, Xia Zhou1, Xia Zhao2, Hong Ou2, B. Dennis Mason3, Brian Holloway3, Chinho Park2, Tim Anderson2 and Victor MANNING2, 1Department of Applied Science, 2College of William and Mary, Williamsburg, Virginia; 3Department of Mechanical Engineering, University of Florida, Gainesville, Florida; 4International Technology Center, Raleigh, North Carolina.

Nanometer edge carbon structures, carbon nanofibers (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 were used for generating CNFs, such as CH4-H2, C2H2-H2 and C2H2-N2-H3. Typical deposition conditions are: substrate temperature of 860°C, overall gas flow rate of 10 sccm, chamber pressure of 25-120 mTorr, and hydrogen concentration in the range of 0-80%. Scanning electron microscopy shows CNFs preferentially growing on the Ni dots with the irregular carbon fluxes standing perpendicular to the substrate. The flake edge distances are 10-15 nm and interflake spacing on a given Ni dot are on the order of 15-180 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 spectroscopy and SEM structure show a typical carbon feature with D and G peaks at 1350 and 1580 cm-1, respectively. Intensity ratio of these two peaks, I(D)/I(G), varies with hydrogen 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 3.43 eV, which are near that of pure graphite. Preliminary results of field emission testing, including field emission spectroscopy, LE curves, Fowler-Nordheim plots and stability curves, indicate that this structure could act as a conductive, robust, edge emitter.

New process for the preparation of Fe-Pt nanowires has been developed through sonochemical oxidation and electrodeposition technique. Aluminum thin film sputtered on ITO thin film on a glass surface was decomposed into alumina by sonochemical oxidation technique. The anodic alumina layer was removed by strong anodization of the glass surface. The barrier layer at the bottom of the nanowires was removed by acid etching to attain DC field assisted electro deposition. Fe-Pt nanowires were 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/inch².

8.5 Nanocomposites Prepared by Laser Ablation of Microparticles (LAM) and Subsequent Thin Film Deposition
Weijie Wang, Daniel T. O Brien, Jonghoon Baeck, Michael F. Becker, John W. Kato and Desadero Kolar; 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 electrospraying NPC collection cell that allows precise control of NP size. The electrospraying cell is essentially an electrostatic aerosol collection 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, a glass-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 electrical cell. Within the voltage range studied (0-1.000V), the NP mean size was controlled from 5nm to 60nm. The structure and optical transmission of PLD AlN films deposited without NP was strongly dependent on substrate temperature (room temperature to 900°C) and ambient condition (argon or nitrogen gas) during the deposition. Adding nitrogen and increasing the substrate temperature improved the stoichiometric composition of the film and also its optical transmission. 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. 00362S-0209-2001 and an NSF GOALI under Grant No. CTS-9978926.

18.6 FE-SEM Observation of Formation Processes of Anodic Porous Alumina on a Si Substrate Using Infrared Absorption Spectroscopy
Yasuo Kimura 1,2*, Hirokazu Shikiri, Hino Ishii 1,2, Satoshi Ono 1,2, Kongo Ikuyama 4,5 and Michio Ninomiya 1,2,3; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan; 2CREST, Japan Science and Technology Corporation, Sendai, Japan; 3Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai, Japan; 4Department 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. Electrochemical etching 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 deposited on a silicon substrate. However, it is necessary to prepare 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 of porous alumina on a Si substrate using infrared absorption spectroscopy in the multiple reflection geometry (MIR-IRAS). In particular, we focused on anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. 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 anodic oxidation near the interface between an Al film and a Si substrate. We investigated formation processes of porous alumina on a Si substrate using infrared absorption spectroscopy in the multiple reflection geometry (MIR-IRAS).
nanostructured cadmium chalcogenide thin films have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) 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 nanorods can be controlled by the template mesostructure. Optical and band-gap properties of the nanostructured thin film scanning 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.

1.8.10 Effects of DC and AC Magnetic Fields on Grain Growth in Electrodeposited Nanocrystalline Nickel. Takahiro Matsuishi,1 Takahiro Yamaoka,2 Yuan Zhang,3 Tomomi Watanabe1 and Gino Palumbo5; 1Nanomechanics, Tokushu University, Sendai, Japan; 2Integrarnel Technologies, Torcon, 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 some metal-amorphous 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. NanoNi sheets of 99.9% purity was produced by the electrodeposition technique. The average grain size was 4nm. The annealing was conducted at 573K (0.377T), ferrimagnetic temp.) and 680K (0.47m, paramagnetic temp.) in a vacuum of 6x10^-3 Pa for 2min -5hrs with a direct current (DC) magnetic field up to 6T or an alternating current (AC) magnetic field of 0.3T 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 (0.377T) 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 1hr of annealing at 680K, 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. A most important observation is 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.

1.8.11 Synthesis and Characterization of Nanocrystalline Silicon Films Prepared By PECVD. Katerina Vukal and Viktor Vitko; radiophysics, Kiev national university, Kiev, Ukraine.

Nanocrystalline silicon films (no 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 (111) phase nanocrystals system. The structural and optical properties are observed by Fourier Transform Infrared spectroscopy (FTIR). Atomic force microscopy (AFM) imaging demonstrates the developed surface deposited films, which is column-like. The observed photoluminescence at room temperature depends on film thickness.

1.8.12 Synthesis of ultrafine oxide powders by hydrothermal method. Dariel Meskin,1 Alexander Burkin,2 Yuri Kolokol,2 Alexander Barashchikov,2 Buht Churagulov1 and Nikolai Oleynikov1,2, 1Department of Chemistry, Moscow State University, Moscow, Russia Federation; 2Institute 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 avoid the hydrothermal treatment but the reaction mixture appears the liquid medium under action of powerful ultrasound. Hydrotherm-thermal 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 Co3O4, has allowed to considerably increase the conversion degree and to achieve the smallest particle size, 60-70 nm (with ultrasound) contrary to 600-650 nm (without ultrasound). It is important that the Co3O4 samples obtained by hydrothermal-ultrasonic synthesis are characterized by mesoporous structure. Ultrasonic treatment for the hydrothermal processing of amorphous gel of zirconia and titania hydroxides promotes the substantial growth of the rate of crystallization process. In the resulting zirconia and titania with the particle size 4-17 nm were obtained. The use of ultrasound for the hydrothermal treatment of amorphous gel of zirconia and titania hydroxides promotes the substantial growth of the rate of crystallization process. In the resulting zirconia and titania with the particle size 4-17 nm were obtained.

1.8.13 Separation of Copper and Lead using Selective Ordered Mesoporous Silica Adsorbents. Louis E. King, Ping Liu, 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 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 Cu2+ and Pb2+ 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-NH2 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-NH2 adsorbents. Single component adsorption isotherms for different copper salts were obtained. The results obtained that copper adsorption on OMS-NH2 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.


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, 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 and 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. However, monolithic structures are favored rather than fine particles for strict structural control. In this context, pore formation derived via sol-gel methods has emerged as a very promising technique for tailoring the photonic strength. The macroporous structures can be controlled by changing the separation parallel to the sol-gel transition. Based on this concept, Nakashima et al. found that monolithic macroporous silica gels with controlled pore structure have been successfully prepared from systems containing titanium oxide. Rattle-type titania has a large refractive index of ~2.8 and very low absorption in the visible region. Hence, strongly scattering and weakly absorbing materials are realized for the visible light, and localization effects are anticipated. In spite of all this advantage, few works have been performed on porous titania because the kinetics of hydrolysis and polycrystallization in the system containing titanium oxide is too fast to control the reaction, compared to that in the system started with silica. 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 titania alkoxide. After the heat treatment of titania gel at 1000°C, the crystal structure of titania is transformed from anatase to rutile. In addition, the macroporous network is maintained even after the heat treatment. We show that the macroporous ratio-type titania is very strongly scattered and weakly absorbing. Besides, macroporous titania with a large surface area due to the interconnected pore structure are widely applicable to electrode materials, gas sensors, and chromatography.


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 thermal evaporation/conденсation 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 from 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.

18.16 Hydrothermal Synthesis of Sodium Manganese Oxide (G2). Volodymyr Slivnyak, G. D. Stiev (Gh. Jones) and 3 T Tunnel Structure. Xianfeng Shen, Yufeng Sun, Jin Liu, Jun Cui, Francis S. Galasso, and Steven L. Shk., Department of Chemistry, University of Connecticut, Storrs, Connecticut; Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Sodium manganese oxide OMS nanomaterials with a 3D tunnel structure have been synthesized using Na2CO3 as a carbon template. Na2CO3 and K2CO3 were first prepared in a redox reaction of MnO2 and KMnO4, followed by a hydrothermal treatment at 175–240 °C for 2 days. HRSEM showed the nanofibers morphology of the synthesized 2D manganese oxide OMS materials. The 2D manganese oxide has thermal stability up to 500 °C. The average pore size of about 3.0 nm. The average pore size of about 3-23 nm and the pore volume is about 0.1 cm3/g. XRD and XRD measurements were also used to characterize the synthesized 2D manganese oxide.

18.17 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 of magnetic materials with nanoscale size and shape 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 aluminum 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 and magnetic behavior of magnetic particles have been studied. The paper presents our experimental results from investigations in which screening transmission electron microscopy with atomic number contrast (STEM-Z) and electron energy loss spectrometry (EELS) were used to understand the atomic structure of Ni nanoparticles and interface between the nanoparticles and the surrounding matrixes. It was interesting to learn from EELS measurements at interfaces of individual grains that Ni in aluminum matrix does not form an ionic bond indicating the absence of metal-oxide bond. Introduction of the TiN met alloy oxide bond, in turn, suggests the absence of any dead layer of Ni nanoparticles even in an oxide matrix.

18.18 Brimble-like Mesostructured Nickel Oxide Fiber Clusters. JieXian M. X. Chong, Guoyue Xu, and Weixing Fang, 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 fiber clusters were synthesized by using organic surfactants (sodium dodecyl sulfate or sodium dodecyl sulfate) as templates, and nickel salts as inorganic precursors, via the S-L route in alkaline solution. The as-prepared samples were characterized by means of XRD, FT-IR, SEM, TEM and TG/DTA techniques. XRD pattern of NO/SDS shows a hexagonally packed mesostructure, corresponding to the d-spacing 28A. FT-IR spectra indicate that the presence of the surfactants in the synthesized samples. The several influential factors (pH, surfactant concentration and different nickel sources) of the mesostructure formation were studied. The SEM image of mesostructured NO/SDS composite shows there were some brimble-like fiber clusters on the surface of the samples. These brimble clusters were composed of ellipse or flat pipe fibers. The diameter of fiber pipes varies from 200 nm to 600 nm, and the length of these varies from 1 nanometer to 100 nm. We believed that mesostructure could be synthesized followed by "optimized templating mechanism" during the interaction between SDS and nickel species, and the mesostructure grow along some orientations in the size of microns. 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 electrochemistry.


Low-k dielectrics for future ULSI can be engineered by incorporation of insulating silicate matrix. One promising class of low-k dielectrics is spin-on-glass films with nano porosity induced by deposition of a thermal oxidation. These dielectric generating materials (sacrificial pores). 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 desired because pore by secondarily ion transmission electron microscopy (TEM). The average pore size is about 3 nm and the pore volume is about 0.1 cm3/g. XRD and XRD measurements were also used to characterize the synthesized 2D manganese oxide.

18.20 Development and characterization of the nanostructured diamond-like carbons films. Wai Lai Yang, Koichi Sekiguchi, Kenju Nishiura and Ken Ho Auh, Computer Processing Research Center.
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. Hence they have a limitation in 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 nanoscale 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 inorganic silica were embedded in DLC matrix for the nanostructured DLC films. The relationship between the microstructure and physical properties will be investigated.

L2.8.1
Mean Inner Potential of Nanostructured Noble Metal Catalysts, Satoshi Ishikawa, Tomoki Akita, Kazuyuki Okazaki, Masatada Okumura, Koji Tanaka and Masanori Kobayashi, 1 Special Division of Green Life Technology, National Institute of Advanced Industrial Science and Technology, Tokyo, Japan; 2School 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 caused by the change of the electronic structure of the gold particle or the interface between the gold and the oxides, however its detail has not been clarified yet. We measured the mean inner potential of gold particles supported on TiO2 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 almost the same as reported for Pt. When the size is <5nm, the mean inner potential is higher than Pt (experimental: 21-25V, calculated: 25-30V). When the size is <5nm, it begins to decrease above 30V, its the mean inner potential is higher than Pt (experimental: 21-25V, calculated: 25-30V) when the size is <2nm. It indicates that the electronic structure of the gold particles vary from that of the bulk gold as the size of the gold particles reduce due to the nano-size effect or the interaction at the interface, while the mean inner potential is sensitive to the electronic state of the outer valence electron. On the other hand, the behavior of the platinum catalyst is different from that of gold catalysts. When the size of the platinum particle on the TiO2 support is >1nm, the mean inner potential of platinum is the same as that of the bulk (>25V). In case of the particle with the size <1nm, it begins to decrease above 30V. The size effect is lower than in the case of gold particles with the size <3nm. It is suggested to be due to the difference of the interaction with TiO2.

L2.8.2
Novel Allotropes Fullerene-Like and Nanotubular BN Structures, V. Vladimir Pokropivny, 1 Richard Parch 2 and Alex Pokropivny3,


Abundance of allotropes forms of boron nitride (E-phase, etc.) are known to exist many years ago, the densities of which are intermediate between that of graphite like BN and a diamond like zircoboride boron. 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 (or C24N24, C24N48) which have been supposed to Cu2D, a "hyperdiamond" with C24N24 molecules in a superhard diamond lattice, and a body-centered cubic fullerite Me2B2N12 (doped with the small donor metal impurities Me=Li, Be, etc.) with the density &#61545;1.8 and 0.819 g/cm3 higher than the graphite have been predicted [1]. Crystal-chemistry analysis in a couple with quantum-chemistry MINDO calculation of the B12N2, B3N24, B6N36 fullerenes and (6,0) and (6,6) BN-nanotubes have permitted us to establish the structures of above unconvetional cubic and hexagonal phases of boron nitride, the analogs of "cubic graphite", a-carbyn, b-carbyn, chianite and other unconventional hexagonal forms of carbon are suggested, that will demonstrate the nanoparticles, zeolites and such phases contain two dimensional lattices of cylindrical nanochannels in their structure, that may be utilized in special molecular sieves. In result of size effects, appearing at &#61545;~d, the unusual optoc and other properties are expected to be observed on novel materials on base of such fullerenes-like forms of boron nitride that will find novel perspective applications. [1] VV Pokropivny, et al., J Solid St. Chem. 154, 214 (2000).

L2.8.3
A Model of New VUV NLO Materials Based on Borate. A Novel Noncentrosymmetric Borophosphate Compound, BeB2O5, Zhengshen He4 and Hiroshi Moriyama5, 1Materials & Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; 2Department of Chemistry, Toho University, Funabashi, Japan.

The model compounds formulated as M2+3A2+3(B2O3)3+PO4 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 the borate, borophosphate, and borophosphosilicate group theory. For example, a novel noncentrosymmetric borophosphate compound BeB2O5 has been synthesized by solid-state reaction. The borophosphate compound BeB2O5 is a new kind of material and contains the B2O3 anionic group in its basic structural unit, which should play an important role for SHG coefficients. In fact, BeB2O5 powder was found to have the significant SHG effect.

L2.8.4
Fabrication of carbon nanofiber films for electrochemical capacitors, Chi-Chieh Hsieh, Jin-Ming Chen, Rong-Rong Kuo and Yung-Hsue Huang, Industrial Technology Research Institute, Chutung, Taiwan.

High-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 CNF having a mean diameter of 80-100nm were grown at 800°C, using decomposition of toluene as carbon precursor, and Ni-electrodeposited substrate as catalyst. X-ray absorption experiments showed that the CNFs had a BET surface area of 120 m2/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 capacitor-like character. The double-layer capacitance of the capacitor almost maintained a constant value of about 15 μF/cm2 at different current densities. 1, 2, 10, 30, 50 mA/cm2, and confirmed that the distributed capacitance effect of CNFs, which is expected, was negligible, which was agreement with CV results. Finally, charge-discharge cycling showed that the capacitor fabricated with the CNFs exhibited astounding cyclability (~15 μF/cm2) and excellent Coulombic efficiency (~95.6 %) during 200 cycles.

L2.8.5
Mesoporous Silica Film Preparation By Novel Supercritical Fluid Extraction Of Organics. Scientific Paper, Tokuhiro Hirano1, Yoshito Fujimoto3 and Yoshitaka Nagase2,

1Electronics Research Lab., Kobe Steel Ltd., Kobe, Hyogo, Japan; 2Chemical & 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 electronic 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 constants, due to the high temperature or interfacial tension during the process. In this study, supercritical fluid extraction (SFE) technique by using supercritical CO2 (sc-CO2), 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-CO2 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 the SFE with and without hydrogen peroxide solution. In the case that hydrogen peroxide solution is introduced into surfactant solution of CH3OH or CH3OH bond, 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 performed only by pure sc-CO2. 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 of 2.9 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 experiments, the films were annealed in a vacuum chamber, which is equivalent to C-H and C-N bonds in CTAB molecule, are observed. After the films are processed to the SFE, the intensity of Cls is decreased, which result from CTAB extraction, however, the increase of the Cls 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 so-CO₂. It is also suggested that CTAB is decomposed completely when the weight reduction, thus, the organic template can be extracted by so-CO₂. This research was supported by grants from NEDO of Japan.

LS. 26
Anisotropic Luminescence of Individual CdS Quantum Dot Ensembles. Jinf Q1,2, Chunlin Mao1, John M White1 and Angela M Belcher1,2. 1Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, 2Department 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 distribution of QDs comprising of a QD regarding to the exciting 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 PL emissions were performed after a cold treatment 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. 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 excitation. The direction 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.

LS. 27
Controlled Assembly of Carbon Nanotubes Fibers by Dielectrophoresis. Jing Tang1,2, Bo Guo1, Hainizi Geng1, Orlin D Velev1, Lu-Chang Qin1,2 and Otto Zhou3. 1University of North Carolina, Chapel Hill, North Carolina, 2National Institute for Materials Science, Tsukuba, Ibaraki, Japan, 3North 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 fiber with variable lengths from micrometer to over 1cm. The CNTs within the fiber are bonded by van der Waals force and are aligned along the fiber axis. The method affords fine control of the fiber length and is capable of parallel fabrication of a large number of fibers using the same source. The short CNTs fibers can potentially be used as the probes for scanning probe microscopes and the conductors in electronic circuit. [1] J. Wang, B. Guo, H. Geng, O. D. Velev, L. C. Qin, and O. Zhou, Adv. Mater. in press.

LS. 28
Micro-Structure and Micro-Structure of A Silica Thin Film with Semiconductor and Metallic Nanoparticles. A. S. B. G. Ng, E. Y. Ng, A. Biggstyle, B. Simonsy,2, G. Xiemartiraks1 and C. J. Brinker. 1Space Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada, 2University of New Mexico, Albuquerque, New Mexico.

Silica thin films with nanometer-scaled voids organized in a ordered array with controllable hydrophilicity may be highly desirable for future semiconductor devices. We present here a thorough characterization of the meso-structured porous silicon thin film formed on a (100) Si substrate. In addition to the meso-structure, we also present a comprehensive investigation on the micro-structure. The film presented was fabricated by solvoll evaporation-induced solgel and self-assembly processes (EISGSA), with methyl triethoxysilane (MTES, Si(OCH₃)₃) as the silicon precursor and a poly(vinylpyrrolidone) (PVP) solution 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 angle tilting to four zone axes, as well as the calculation of plane spacings and angles for comparison of the experimental values with corresponding theoretical ones. The TEM examination concluded that the meso-structure is a pseudo bodycentered cubic (bcc) rather than face-centered cubic (fcc); the bcc meso-structure with a slight distortion was further assigned to bodycentered 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 small-angle X-ray scattering (GISAXS). Furthermore, two types of dislocations were observed by TEM. One was an edge dislocation, with the Burger vector b = [110] and the dislocation line direction x = [100]. The other was a dislocation dipole with the Burger vectors b = [111,111,111] on a (111) 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, X-ray scattering by synchrotron X-ray (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, given the size of the mesopores a few cm (the volume of 100 nm) 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 silica film from the meso-structure on the porosity of the film from its meso-structure.
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 temperature of solvent inside and outside the nanotube under pressure were also considered.

L.3.1

Nanocomposite Research Laboratory, Lehrstuhl fu\"{}r Materialwissenschaften, Technische Universit\"{}at Darmstadt, Konsensor 2, D-64243, Kiel, Germany.

Smart Materials Group, CAESAR, Ludwig-Erhard-Allee 2, D-53117, Bonn, Germany.

Future GHz driven mobile communication handsets and portable information terminals need new requirements for further miniaturization and lower insertion losses for inductive components instead of using microstrip components. 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. To overcome these two losses, mixtures of magnetic nanocomposites protected in insulating polymer matrices are promising candidates and could play important roles particularly in such high magnetic field applications with higher cut-off frequencies in the GHz regions. Appropriately volume filled isolated magnetic nanoparticles dispersed three dimensionally (3D) in an insulating polymer matrix possess good potential to generate quite high saturation magnetization required to shift ferromagnetic resonance in the GHz range along with significantly minimized eddy current losses due to the surrounding highly insulating layers. 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 nanocomposites in organic host. However, there is no easy synthet 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 3D dispersed FeNi-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 show a saturation magnetization of the nanoparticles of nearly 2 Tesla matching with the corresponding bulk ferromagnetic resonance appears to occur at around 6 GHz based on the complex permeability measurements.

L.3.2
Polymer Nanocomposites with Surface Modified Magnetic Nanoparticle, Young-june Kim and Jin-Kyu Lee, Chemistry, Seoul National Univ., Seoul, South Korea.

The surface of Fe ferrite magnetic nanoparticles prepared by a known co-precipitation method was modified with deliberately prepared carboxylic organic molecule, quaternary ammonium salts from nitrilotriacetic acid (NTA). The modified Fe 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 ferrite is preferably located in a specific block. These polymer-Co ferrite magnetic nanocomposites could also be fabricated in thin films by spin-casting method. Synthesis and characterization results of these nanocomposites will be discussed.

L.3.3
Nonlinear magneto-optical Kerr effect in optical third harmonic generation from magnetic granular films exhibiting giant magnetoresistance. Evgenia Mikhailova Kim, Tatyana Vladimirovna Murrina and Olga Andreievna Akipovets, Physics Department, Moscow State University, Moscow, Russian Federation.

Magnetic nanomaterials such as multi layered 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 results in both magnetic and nonmagnetic 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 $\text{Co}_x\text{Ag}_{1-x}$, $\text{Co}_x\text{Cu}_{1-x}$, and $\text{Co}_x\text{Al}_{1-x}$ for the first time, to our knowledge. Nonmonotonic dependencies of the magnetoresistance and NOMOKE magnetic contrast of the volume fraction of the magnetic component $x$ are found. The nonlinear-optical studies were performed using the uncoupled output of a Q-switched Nd:YAG Nd[3] laser at the wavelength of 1064 nm with a pulse width of about 10 ns, repetition rate of 5 Hz. 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 $\text{Co}_x\text{Ag}_{1-x}$, $\text{Co}_x\text{Al}_{1-x}$ and $\text{Co}_x\text{Cu}_{1-x}$ composition were prepared by co-deposition of Co and Ag at [200 K] 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 400 nm. 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 off-plane current configuration and three different external magnetic field application. To study the crystallographic symmetry of the samples the x-ray diffraction and the THG and THG intensity were measured, which showed the existence of a mirror plane in the film structure. Magnetooptical THG 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 dependencies of the SHG magnetic contrast observed recently. The THG interferometry did not reveal magnetooptical changes in the third harmonic phase. [1] T.V. Murrina, T.V. Murrina, A.F. Krasov, J. Gudle, D. Schumacher, G. Mavratsy, A.A. Nikulin, O.A. Akipovets, Surface Science, 482-485 (2001).

L.3.4
Nanoflyer onto carbon nanotubes, Krzyzstof KK Kosiol, Milo SP Shaffer and Alan H Windle, Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom; Department of Chemistry, Imperial College, London, United Kingdom.

There is a possible range of 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 use the surface of carbon nanotubes, but only a few have succeeded in covalently grafting macromolecules. Perhaps surprisingly, the application of this technique has focused 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 monoacryl 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 scallops of different nanotube diameters can be functionalised and analysed the grafted material with electron microscopy, Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and thermogravimetry (TGA).

L.3.5
The determination and removal of metal impurities in carbon nanotubes, Krzysztof KK Kosiol, Francis Talakin, Milo SP Shaffer and Alan H Windle, Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom; Department of Chemistry, Imperial College, London, United Kingdom.

The determination of the metal 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 crystalline parameters, multi-walled carbon nanotubes are produced by a chemical vapour deposition (CVD) technique which can contain significant
The importance of films composed of different nanocomposites 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 nanomaterial components were considered: CdSe nanocrystals capped by TOPO, γ-Fe2O3 (magnetite) nanocrystals capped by oleic acid and Au nanocrystals capped by dodecanethiol. Electrophoretic deposition from mixtures of CdSe and γ-Fe2O3 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 noble nanocrystals. As the density of the Au dots 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 microelectronics and high density magnetic memory devices. This work was supported by the MRSEC program of the National Science Foundation, Award No. 0213574.

L8.36
TEM and DOE Optimization Studies of Electrosyn Polycarbonate Nanofibers, Ningning Katsusari 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 (tetrahydrofurane) and DMF (dimethylformamide) has been performed. Polycarbonate is selected because it is a promising thermoplastic material, used in injection molded materials. 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 11 inches) 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 such as GAIA Blue and Scion imaging. The surface morphology of the electrosyn 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 Minisat software to find the most important parameter for uniform nanofibers. The optimum conditions of distance, viscosity and voltage result in nanofibers smaller than 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 41 inches 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. Shiqing Rob Hui, Jinhao Dang, Jeff Roth, Huimin Chen and Danny Xue; US NanoCorp, Inc., Willington, Connecticut.

Nanostructured components have shown promising results for improving the electrode performance in many electrochemical systems. Fuel cells, metal-air secondary batteries, solid-state chemical sensors, and electrochemical 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). Suitable materials were employed in the fabrication 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. Ismail1,2,3, Yuqi Xin1,2, Ming Xiang1,2,3, Ralph O’Brien1,2,3 and Irving P. Herman1,2,3; 1Applied Physics and Applied Mathematics, Columbia University, New York, New York; 2Chemical Engineering, Columbia University, New York, New York; 3Materials Research Science and Engineering Center, Columbia University, New York, New York.

The high growth temperatures typically needed when growing diamond films using chemical vapor deposition (CVD) with H2/CH4 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/CH4 plasma chemistries that give rise to C2 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 grow microcrystalline diamond. In this work we have examined the temperature dependence of UNCD growth over temperatures ranging from 400-850 °C. Different diamond seeding procedures (including mechanical polishing, ultrananocrystalline diamond powder suspension) as well as bias enhanced nucleation were employed to promote 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 plasma. A combination of SEM, UV Raman, HETEM and NEXAFS analysis indicate that the UNCD films grow with relatively high growth rates at temperatures as low as 400 °C. The high nucleation density provided by the seeding procedure, the choice of substrate, and the high secondary nucleation density resulting from the C2 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-438.

1.41 Preparation and Mechanical Properties of Nanostructured Tungsten Carbide Alloy Strengthened by Carbon Nanotubes. Guochun Dai, Xinjie Wu, and Zhongyan Li, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104; 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 carburned by C2H2 instead of CO and a fraction of decomposed carbons are in situ converted to carbon nanotubes. In this way, the composite powders of nanostructured tungsten carbide and carbon nanotubes have been in situ prepared. The composite WC-Co powders are then hot pressed into bulk alloy which shows a exceptionally high microhardness up to 3307 kg/mm2. 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 WC grain growth inhibitor on the mechanical properties of the nanostructured WC-Co hard alloys was also studied in detail. The synthesis process of nanostructured WC-Co powders from the reduction of amorphous tungsten tetrabromide by C2H2 mixture gas, including the effect of process parameters such as temperature and gas pressure on the final product phases will also presented, together with XPS studies of the surface characterization of these composite powders.

1.42 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 microscopic 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 microscopically disordered structures, with special 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 motion as the boundary is swept across the lamellae. The net motion of the grain boundary toward the transverse region, even though both parallel and transverse orientations are linearly stable. This behavior is 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.


In recent years, federal regulations have become stricter on Hazardous Air Pollutants (HAPs) and Volatile Organic Compounds (VOCs), creating a demand for low-cost, high-performance coatings. Inorganic solvent-based coatings create minimum VOCs and virtually no HAPs, making them ideal material in industry. They are, however, not as well developed for in situ organic 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 nanocomposite 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 consist of 3-Glycidoxypropyltrimethoxysilane (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.

1.44 Nanostructured polymer coatings for enhanced ultraviolet protection. Phanbhuon Kurhong, Steven B. Wanner, Prabh K. Puri, Yong K. Kim, and Steven B. Wanner, School of Materials Science and Engineering, 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 are deposited onto the fabric substrate. Nanocoatings are prepared by dispersing zinc oxide and titanium dioxide in acrylic solutions. The nanocoated structures 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 affected by nanoparticles will be explored 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.


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 200 nm. The nanofibers were surface treated with 0.005% 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 disperse the nanofibers into the formic acid/nanoparticle dispersion. The 15% w/v solution of nylon-ferrite system was then electrosprun using a point to plate geometry, with field strength of 1.5 kV/cm and a solution flow rate of 3 ml/h. Using similar spinning conditions, virgin nylon-polymer solution was also electrosprun. SEM analyses were carried out on both electrosprun samples. The diameter of the virgin nylon fibres was found to range from 35-110 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 viscosity of solution due to the ferrite particles. The SEM micrographs of the electrosprun ferrite-nylon system indicated the absence of nanofibers on the fiber surface, leading 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 nanofibers within the polymer fibers, XRD and TEM studies are in progress.

1.46 Morphological Influence of Layered Silicates on Nylon 6 Nanocomposites and Clays. Ganes Iyan, Prabh K. Puri, Yong K. Kim and Steven Wanner, Textile Science Department, University of Massachusetts Dartmouth, N. Dartmouth, Massachusetts.

Nylon 6/clay nanocomposites are synthesized using a synthetic hectorite (Laponite ® Na4) and a natural montmorillonite (Cloisite ® Na+) clay by in-situ intercalative polymerization method. In the course of the in-situ polymerization process, pre-intercalation of clay platelets is employed by the insertion of α-caprolactam monomer, and hence, silicate surface of the platelets remained unmodified. X-ray diffraction studies on montmorillonite powder, pre-intercalates, and nanocomposites show that pre-intercalation process increases the basal space from 10A to 16A and polymerization process delaminates the lattices resulting no distinguished basal reflection. In contrast to
montmorillonite, lignite platelets do not exhibit well-defined lamellar reflection both in powder and nanocomposite forms. It is suggested that the dispersion is due to the d[100] spacings 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 thin films of lignocellulose show that it has a lower crystallinity order than that of montmorillonite. Because in-situ intercalation polymerization is a powerful method to achieve highly dispersed clay, it is not appropriate to compare the dispersion of the two platelets in their nanocomposites. Nevertheless, preferred textural arrangement of montmorillonite platelets after polymer deaccretion indicates that montmorillonite platelets have stronger electrostatic interactions than that of lignite. It is also observed that the residues of lignite, montmorillonite and lignite/montmorillonite containing nanocomposites have different morphologies. The difference in continuity and brittleness of lignite and montmorillonite clays is attributed to different aspect ratio and surface charges, which may influence the continuous network formation of clay aggregates. The present research is directed to better understand the influence of clay morphology on flame resistance of lignite and montmorillonite nanocomposites, especially in terms of their reduced heat release and mass loss rates as observed from cone calorimeter.

L.8.47 Continuous Nanocrystalline Ionic Silver Halide Optical Fibers with Reduced Optical Scattering.
Leonid N. Buvina, Evgeni Dinnov, Andrei Okhrimchuk, Nelid Lisickova, Vladimir Sagorodnev, Oleksa Sereed.

The single crystals of silver halides of solid solutions AgCl:AgBr with high purity and homogeneity were grown by Bridgeman technique. Severe deformation and dynamic recrystallization in nanocrystalline silver halide optical fibers were produced by equal channel multiformation. Nanostructured 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 interferometric 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 losses less than microcrystal optical fibers made with extrusion of single crystal. The nanocrystalline silver halide optical fibers with losses lower than 1 dB/m in the region from 2 to 20 mkm are demonstrated. Influence of vacancy pores with nanodimensions on boundaries and hirerference in nanograin on optical losses, measured in nanocrystalline ionic materials, will be discussed. Mechanical properties of nanocrystalline and microcrystal silver halide fibers will be compared. Application of nanocrystalline silver halide optical fibers in remote spectroscopic chemical sensing and laser medicine will be presented.

L.8.48 Xe Synthesis of CoPt-SiO2 and Ru-Pt-SiO2 Nanocomposite Films.

In this study, Co or Fe ions were implanted at an extraction voltage of 35 kV into thermally grown SiO2 on Si substrates at a dose of 4×1016 ions/cm2 using a metal vapor arc ion source. The resulting ion dose to doses ranging from 1.5×108 to 3×1010 ions/cm2 were performed at an extraction voltage of 50 kV. Characterization of the films was performed using Rutherford backscattering spectroscopy, x-ray diffraction, transmission electron microscopy, and vibrating sample magnetometry. Under implant conditions, it was found that Fe1-x+Pt1-x+SiO2 and Co1-x+Pt1-x+SiO2 nanocomposite films with 0 ≤ x ≤ 0.54 and 0.3 ≤ x ≤ 0.51 were obtained. The Co and Fe im-planted 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: CUGHK4216/08E).


Carbon/Nafion® nanocomposite thin films developed through a low-cost procedure were used for high-sensitivity, high-throughput laser desorption–ionization (LDI) mass spectroscopy targets for small molecule detection. The nanocomposite films were spin cast onto glass or steel substrates from a solution mixture of Nafion® polymer and amorphous carbon nanoparticles (average size of 30 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® was replaced with another polymer. Hence the role of Nafion® is understood to be more than gluing the carbon particles together, it also serves as an efficient ionization enhancer. In fact Nafion® (perfluorosulfonic acid/tetrafluoroethylene copolymer in the acid (H+) 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® 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, analysis 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 mDa and below) background noise in conventional matrix-assisted LDI MALDI mass spectroscopy. Our nanocomposite targets do not produce any background unless fragmentation of Naefion® 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. Resonance with the matrix allows detection down to femtograms. The signal intensity was found to increase with carbon content in the nanocomposite. On the other hand, one of a weak dependence to ionization lower 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® enhances ionization. Furthermore, we did not observe any hydrocarbon or other contaminant collection on our target surfaces when they were left in laboratory conditions 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., ~2 S/cm for the film with equal polymer and carbon weight content) also enables electronic biasing of the analyte during LDI.

L.8.50 Spinodal Morphology and Thermal Stability of PP/ZnO Nanocomposites.
Sandeep Raul, Prabha Puri, 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 procedure, 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 microscopy confirmed the composite samples to be 1% higher than the ZnO 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.

L.8.51 Contact Compression of Self-Assembled Nano- and Matrix-free Laser Desorption–Ionization Mass Spectroscopy Targets.

Carbon/Nafion® nanocomposite thin films developed through a low-cost procedure were used for high-sensitivity, high-throughput laser desorption–ionization (LDI) mass spectroscopy targets for small molecule detection. The nanocomposite films were spin cast onto glass or steel substrates from a solution mixture of Nafion® polymer and amorphous carbon nanoparticles (average size of 30 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® was replaced with another polymer. Hence the role of Nafion® is understood to be more than gluing the carbon particles together, it also serves as an efficient ionization enhancer. In fact Nafion® (perfluorosulfonic acid/tetrafluoroethylene copolymer in the acid (H+) 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® 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, analysis 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 mDa and below) background noise in conventional matrix-assisted LDI MALDI mass spectroscopy. Our nanocomposite targets do not produce any background unless fragmentation of Naefion® 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. Resonance with the matrix allows detection down to femtograms. The signal intensity was found to increase with carbon content in the nanocomposite. On the other hand, one of a weak dependence to ionization lower 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® enhances ionization. Furthermore, we did not observe any hydrocarbon or other contaminant collection on our target surfaces when they were left in laboratory conditions 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., ~2 S/cm for the film with equal polymer and carbon weight content) also enables electronic biasing of the analyte during LDI.
Many practical applications of nanoporous materials, most notably in the area of catalysis, separation, ion exchange, fuel cells and sensor technology, have been exploited in recent years using neutral inorganic (zeolite) materials. Much less work, however, has focused on anions as structure-directing agents in the construction of inorganic hosts. Our research involves the solvothermal synthesis and solid-state characterization of new nanoporous and low dimensional 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 nanoporous materials. Host structures are obtained by modifying new compounds, one member being a cationic, two-dimensional layered material \( \text{P}_{3}\text{SiF}_{6}\text{NO}_3 \) and BING-5: State University of New York at Stony Brook. (structure type 5). We have quantitatively exchanged the interlayer nitrate groups of \( \text{P}_{3}\text{SiF}_{6}\text{NO}_3 \) for dichromate, chromate, permanganate, benzoate and salicylate anions under ambient aqueous conditions. The material maintains or slightly expands its nanoscopic layered-to-layer distance. BING-5 is stable to 450°C, which is vastly superior to inorganic anions 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. Sung-Woo Ryou, Juan Antonio Gonzalez, Metin H. Acar and Anne M. Mayes; Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Baroplastic core-shell nanoparticles were obtained by microemulsion polymerization. Nanoparticle baroplastics can be processed and recycled at the normal 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 rubber 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. The incorporation of inorganic components, such as silica or gold, into the particles core is explored as a means to obtain baroplastic nanocomposites.

L8.56 Nanoengineering of Extended ZnO Film Structures. Z. Ryan Tire, Louise J. Crisciti, Jun Liu, Randall T. Oginn, Timothy J. Borchardt, Paul G. Clem, Matthew J. Medved, David Lindsay 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 thin-film ZnO film structures ranging from the energetics and structure of various molecular and anionic surfactants and their interactions with the primary growth surfaces of zinc oxide were performed in support of the experimental work. Using bulk 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 solution used was an extension of the approach developed by Yagupsky and colleagues [Z. Yagupsky, et al., J. Phys. Chem B 2001, 105 (3350-3352)]. The process utilizes a temperature driven thermal decomposition of a Zn-hexamethylenetetramine complex that produces a pH change. The pH shift, in turn, causes the hydrolysis and precipitation of ZnO. Under these 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.

L8.57 Polydiacetylenic Microcrystals with Highly Ordered

Many practical applications of nanoporous materials, most notably in the area of catalysis, separation, ion exchange, fuel cells and sensor technology, have been exploited in recent years using neutral inorganic (zeolite) materials. Much less work, however, has focused on anions as structure-directing agents in the construction of inorganic hosts. Our research involves the solvothermal synthesis and solid-state characterization of new nanoporous and low-dimensional 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 nanoporous materials. Host structures are obtained by modifying new compounds, one member being a cationic, two-dimensional layered material \( \text{P}_{3}\text{SiF}_{6}\text{NO}_3 \) and BING-5: State University of New York at Stony Brook. (structure type 5). We have quantitatively exchanged the interlayer nitrate groups of \( \text{P}_{3}\text{SiF}_{6}\text{NO}_3 \) for dichromate, chromate, permanganate, benzoate and salicylate anions under ambient aqueous conditions. The material maintains or slightly expands its nanoscopic layered-to-layer distance. BING-5 is stable to 450°C, which is vastly superior to inorganic anions 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.

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L8.57 Polydiacetylenic Microcrystals with Highly Ordered
Mesostructures and Polydiacetylene/Silica Nanocomposites 
Thereof, Shelin Pang, Byron P. McCauley, Xinxin Li, Xingxing Ji and Yanzhong Lin. Engineering, Tulane University, New Orleans, Louisiana.

Nanosized 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 nanocomposites of polydiacetylene sodium (PDA-S) and silica nanoparticles 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 thermochemical transition behaviors, such as irreversible red to blue, reversible blue to red, and irreversible red to orange changes at different temperature ranges. The thermochemical behavior 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 thermochromically yellow or pink PDAsilica nanocomposites with disordered mesonets in the presence of water have been easily prepared. The nanocomposites were characterized in detail by fourier transform (FT-IR) spectroscopy, 13C solid-state nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), thermomechanical analysis (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 L5: Polymer Systems and Membranes
Marian James Wurkin, Thursday Morning, December 4, 2003, Room 304 (Hynes)

8:30 AM L5.1
Hierarchically Ordered Multi-Component Block Copolymer/Particle Nanoparticle Composites.
Michael Rainer Bockstaller and Edwin Lerner Thomas, MIT, Cambridge, Massachusetts.

The effective control of the spatial organization and connectivity of nanomaterials is an important prerequisite for the technological utilization of nanomaterial research. The simultaneous self-organization of block copolymers in the presence of preformed nanoparticles provides an approach to engineer 2D and 3D nanostructures that facilitate control of the structural characteristics of the segregated component which becomes important when applications require the control of shape related properties of nanomaterials. In this contribution we demonstrate that chemical complementarity of the nanoparticles and geometrical characteristics of the block copolymer matrix allow effective control of the particle topology within the composite. Different composite morphologies can be distinguished, that is homogeneous distribution, interfacial segregation or centered alignment of the particles within a polymer domain. The different microstructural environments of the segregated component that results from the small particles present result in distinctly different physical properties of the composite and render these materials interesting for a variety of applications.

9:00 AM L5.2
Extending Nanoscale Block Copolymer Self-Assembly Approaches to High Temperature Ceramics.

Nanotechnology 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 SCN are particularly challenging since their polymeric precursors are often difficult to obtain and ill-defined. Nanotechnology of such materials is expected to open up completely novel material properties and forms not obtained from bulk materials at high temperature stability or mechanical properties. Here, to the best of our knowledge, we demonstrate for the first time the ability to nanostructure SiC-type ceramics by blending an organo precursor polymer with the amphiphilic block copolymer polystyrene-block-poly(maleic anhydride) (PS-b-PEO). The PS-b-PEO is used as a structuring directing agent for a polysilane, commercially known as Ceraset. Selective swelling of the PEO microdomains of the block copolymer with the silane oligomer results in a cooperative self-assembly of block copolymer and Ceraset into nanostuctured morphologies. Different silica nanoparticles similar to those used to create these block copolymer systems are observed by systematically increasing the polysilane to block copolymer weight fraction. The structure is permanently set by crosslinking the silane 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 hierarchically nanostructured high temperature SiC-Ni-type ceramic materials.

9:15 AM L5.3
Micromechanics of PS/PB/PS Triblock-Copolymer Films with Lamellar Morphology, theodora tranetopoulou and Mary C Boyce; Mechanical Engineering, MIT, Cambridge, Massachusetts.

Thermoplastic elastomers (TPEs) are 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 ordered, single-crystal lamellae 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 the micromechanical finite element unit cell model of a polyurethane triblock copolymer. The orientation behavior of lamellar morphology subjected to tensile loading at different directions to the lamellae plane. Various morphological imperfections, common for this family of diblock copolymeric materials, are studied, including surface morphological imperfections, layer misalignment, and paired-edge dislocations. These structural imperfections provide initiation sites for potential deformation instabilities, such as layer buckling, micromechanical 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 ordered chp-particle lamellar block copolymers. Representative unit cell models of single-crystalline 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 L5.4
Gold Nanoparticle Filtration Through a Nano-structured Polymer Membrane. Allon Hochberg, Aryan Akthakul, Francesco Stellacci and Anne M. Myers; 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 membranes 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 in an organic solvent and that this size is controlled 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 filtering efficiency, the membrane can be used to select specific nanoparticle distributions. This work demonstrates that the graft copolymer membranes could produce nanoparticles of low size diversity in a convenient and reproducible manner. The current separation techniques, such as chromatography. Nanoparticles of such narrow size distributions are necessary for many applications in nanoscale electronic and optical devices as well as investigations of the frontier of multi-body particle physics.
Sequential, Orthogonal Fields: A Path to Long-Range, 3-D Order in Block Copolymer Thin Films. Ting Xu, James T. Goldsmith 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 was imposed normal to the flow. These two fields were 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 10.6
Kyoung-M. Choi1 and John A. Rogers2.
Bell Labs, Lucent Technologies, Murray Hill, New Jersey. 1Materials 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 developed a new version of stiff, chemically modified PDMS elastomer that is developed specifically for nano-scale 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 phototransistor, 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 10.7
Kiranmamori1, Jeffrey L. Bink1 and James M. Tour1, 4Chemical Engineering, Rice University, Houston, Texas; 2Department of Chemistry, Department of Mechanical Engineering and Material Science, and the Center for Nanoscale Science and Technology, Rice University, Houston, Texas; 3CNI 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 habit 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 use of surfactants to mediate the interactions. End-capped 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 and the fabrication of small features in 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 probes using different scanning calorimetry and isothermal and non-isothermal studies demonstrated dramatically increased kinetics of crystallization indicative of the nucleating characteristics 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 10.8
Facile Production of Well-Exfoliated Polypropylene–Clay Nanocomposites via a Novel, Solid-State Shear Pulverization Method. Kosmas Kasisis1, Laura M. Dykes1, Wesley R. Burghardt1,2 and John M. Tolskelsen1, 2Department of Chemical Engineering, Northwestern University, Evanston, Illinois. 3Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

There is great scientific and technological interest in developing polymer-clay nanocomposites that are stronger, lighter, and cheaper than their bulk counterparts. To produce such nanocomposites, the clay is typically dispersed using high-energy mechanical processing methods. However, many of these methods are expensive and impractical for large-scale production. This presentation will discuss a novel, facile, and inexpensive method for preparing polypropylene-clay nanocomposites. In this method, polypropylene is extruded in a twin-screw extruder under vacuum to thoroughly deagglomerate and adjacent clay platelets. The deagglomerated clay is then incorporated into PP using a novel shear pulverization method. 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 novel processing method called solid-state shear pulverization (SSP) can yield well-dispersed and compatibilized polymer blends, overcoming many problems associated with melt mixing of blends. Here we have demonstrated that SSP 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 more passes through a twin-screw extruder. However, when the clay was vacuumed after being 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 SSP to achieve dispersion in systems that are not totally organic/micromeric, and suggests a broad array of applicability of SSP. 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 2D 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 'lying 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 SSP) the presence of a solid-like plasma in shear storage modulus at low frequencies. This is signature of significantly dispersed polymer-clay systems.

11:00 AM 10.9
Organic-Inorganic Biodegradable Nanofibers. Vahid Khrisripar3,4, Cheryl Casper5, John Rinkfort6 and Darrin Pochan3,4
1Materials Science and Engineering, University of Delaware, Newark, Delaware; 2Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

In this investigation we have explored the possibility of making new polymers of rigid polymer layered silicate nanocomposites via an electrospraying process. The elastomeric-biocompatible/biodegradable polymer matrices with incorporation of organoclays. Commercially available organic-inorganic 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 electrospraying a suspension of organoclay/diluoromethane with Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polymer, as the polymeric matrix. We have shown that decreasing the amount of miscibility of the precursor decreases the degree of exfoliation and randomly distributed the silicate layers throughout the matrix. Polished light microscopy shows a high degree of biorthogonality suggesting that the polymer chains in as spun fibers are well aligned. Conventional transmission electron microscopy (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 daigmbular peaks from WAXS Scanning. 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 L0.10

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

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

New liquid crystalline nanoparticles have been synthesized by reaction of cyanophenyl derivatives with polyhedral oligomeric silsesquioxanes (POSS). Several liquid crystalline nanoparticles can be made by varying the aliphatic spacer of the cyanophenyl derivatives. A representative synthesis involves the reaction of n-1-butyl bromide with 6-bromohexanol in the presence of sodium hydroxide and tetraethyl orthosilicate. The proceeding product is then reacted with 4,4'-dihydroxy-2,2'-biphenylcarboxylate in the presence of potassium carbonate and acetone. The cyanophenyl terminated alkyl is then reacted with octanal POSS® via a hydrosilation reaction employing a Kinetest’s catalysis. The LC POSS® nanoparticles were then compounded into thermotropic polyester liquid crystalline polymers (LCPs) as well as a “frustrated” LCP based on 4,4’-biphenylacrylic and aliphatic diis. 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 one LC nanoparticle into a frustrated LCP. It is proposed that the LC nanoparticle will help to “unfrustrate” the LCP. The thermal stabilities, glass transition temperatures, and the moduli of these LCP/LC nanoparticle composites will be reported.

11:30 AM L0.11

**Nylon-6/Clay Nanocomposites Probed by Dielectric Relaxation Spectroscopy.** Yichun Liu, Anthony J. Bar, Naosuke 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 and interpret 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 length of relaxation time distribution is carried out by fitting raw data with the modified Cole-Cole function in which the electrode effect has been taken into consideration. DRS results reveal the existence of three glass transition related relaxation modes. Above the Tg of bulk Nylon-6, filled systems exhibit a shorter relaxation time as a result of a depressed crystallinity. At very low temperatures, a suppressed chain dynamics is detected below the Tg 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 Tg. 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 L0.12

**Glass Transition Temperature Behavior of Alumina/Poly(methyl methacrylate) (PMMA) Nanocomposites.** Benjamin J. Ash, Linda S. Schaller* and Richard W. Siegel.

SUNY-Binghamton, Binghamton, New York; Materials Science and Engineering Department, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Alumina/poly(methyl methacrylate) (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 (Tg) of the nanocomposites dropped by 25°C when compared to the neat polymer. Further addition of filler did not lead to additional Tg reductions. This novel thermal behavior is shown to vary with particle size, but this dependence disappears when normalized by specific surface area. The nanocomposite Tg 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 responsible for the Tg reduction in polymer ultrathin films. The results also point to a drastically increased scope of the so-called interaction zone (IZ) and its “far-field” effect on the entire matrix.

**SESSION L10: Modeling and Theory**

**Chair: Rima Tannenbaum**

**Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.**

Metallic fragments, or metalloids (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 diffusion 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 mirror 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(2-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 that are directly responsible for the overall rate of the process. The rate of decomposition of the precursor nanoclusters, and thus the traditional assumptions regarding the process of the nanoclusters are not correct. The formation of cobalt oxide nanoclusters with an average size above the detection threshold of dynamic light scattering (~3 nm) and TEM (~2-8 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 evidenced by the common and parallel induction period observed in the formation of the cobalt oxide nanoclusters and the transformations that occur in the outer functional groups of PMMA. It is therefore clear that the aggregation and stabilization processes occur only after the reactive metallic fragments, i.e. metalloids, have reached a critical size and a distinct surface structure.

**2:00 PM L10.2**


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 polycrystal with a 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 phase enhance both the stress and free energy of grain boundary diffusion fluxes and grain-boundary sliding. Second, dislocations generated as a result of grain-rotation induced grain coalescence and grain-boundary deformation are observed to contribute to the deformation.

2:15 PM L10.3
On Molecular Dynamics Simulation of Metal Clusters and their XRD and ELNES Spectra. Gregorio D'Agostino and Micheal Gasco; ENEA, Roma, Italy.

The present paper reports on classical molecular dynamics of close-packed 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 accounted for classical 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, truncted-decahedra and kochedra) and cobalt (fcc and hcp basis) of different sizes. Caloric curves have been evaluated and showing well known co-existence region and lowering of melting temperature (melting) stable structures were brought out. Their minimum energy configurations and phonon distributions have been evaluated by direct diagonalization of the dynamic matrix. Low temperature quantum free energies and related Debye-Waller factors have also been derived by simulated phonon spectra by 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 surfaces whereas at higher temperature Debye-Waller factors become relevant.

2:30 PM L10.4

A nanocomposite of multiwalled functionalized carbon nanotube and poly(3-methylithiophene) has been synthesized for selective sensing of halogenated methanes. TGA analysis of the composite showed two phase transitions at about 300 °C and 350 °C with a weight percent loss of about 38% at 200 °C and 100% loss at 750 °C. The IR spectrum of the nanocomposite showed peaks due to both the components. When the nanocomposite is exposed to CHCl3, 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. To confirm the performance of the nanocomposite sensors have been constructed with functionalized carbon nanotubes or poly(3-methylithiophene) or the blend. The nanocomposite showed high sensitivity for chloroform and very little for carbon tetrachloride and methanol. Whether 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 analysis with indication potential 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 CHCl3 from a mixture of CH3 and CCl4 suggests its potentialities for industrial applications.

2:45 PM L10.5
Molecular Modeling Computer Simulation of Organic Polymers: A Novel Computer Simulation Technique to Characterize Nanostructured Materials. Sarah G. Schafer1, Hubert Kuhn1,2, and Guenter Schmid1; 1Institute of Inorganic Chemistry, University of Essen, Essen, Germany; 2AI Cove - Molecular Dynamics GmbH, Gelsenkicker, Germany.

Complex nanostructured self-assemblies such as colloidal suspensions, micelles, immiscible mixtures, microemulsions, etc., represent a challenge for modelling techniques due to the presence of different time scales in their dynamics. We have recently successfully applied a novel computer simulations technique, Descriptive Potential Dynamics (DPD), to model the behavior of diblock polymers at the water/water 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 nanostructured systems such as surfactants and polymers. 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 biocompatible phase of C12E8 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 "hopping-effect", a concentration-dependent shift in composition 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 of great importance for the interpretation of complicated experiments or even to obtain experimentally unobservable data. E. Rykina, H. Kuhn, H. Rehage, F. Mueller, J. Poppa, Angew. Chem. Int. Ed., (2002), 41(6), 983.

3:00 PM L10.6
Predicting the Morphologies of Confined Copolymer/Nanoparticle Mixtures. Anna C. Bailie, Joe Youn Lee and Zhenguo Song; 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 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 films. We illustrate this point using a model diblock copolymer and symmetric diblock and show that the wall confinement can be exploited to promote the self-assembly of the system into particle nanowires that extend throughout the films and are separated by nanoscopic 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 entropic effects.

3:30 PM L10.7

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 structure band gap structure is the 3D cubic structure having Fibonacci symmetry (89, 89). Moreover, there is no systematic approach to discovering champion photonic crystal 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 allows 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 Weyl sites. Three of these fundamental geometries display complete band gaps – including two: the 3D-R with Fibonacci symmetry and a group 21 structure with Fibonacci symmetry that have not been reported previously. By using this systematic approach we were able to open gaps between 53, 54, 55, 56 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. Mahanta; Physics and Astronomy, Michigan State University, East Lansing, Michigan.

The geometries and electronic properties of guest alkali atoms in the crystalline zeolite 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/mnl and consists of 32 Si and 60 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 6.02% larger than the corresponding experimental ones. The ITQ-4 system found with all atoms in the simulation. Possible positions of the alkali atoms inside the channel are optimized by energy and force minimization process. For 4 Ca atoms/unit cell (2 atoms/channel), it was found that the Ca atoms form a zigzag chain along the channel, which is consistent with the previous calculations [1], where a C2/m space group symmetry was assumed. Experimentally Petkov et al. [2] find zigzag chains of Ca atoms along the channel. However, the plane containing the Ca atoms is found to be nearly perpendicular to 2 which is found theoretically. We are reaming their geometries by looking at other configurations and comparing directly the pdf [pair distribution function] [2] using the theoretical models with experiments.

Results with employing different atomic models (such as Na, K) and for different atomic configurations are being investigated. [1] Z. Li et al., J. Am. Chem. Soc. 2003, 125, 6650. [2] V. Petkov et al., Phys. Rev. Lett., 2002, 89, 75502.

4:00 PM L10.9


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-connected complexes of organic molecules which are interconnected by various organic links, such as pyrrole, bipyrindine, and metal porphyrins. We have performed first-principles density functional, and molecular dynamics analysis of Zn-porphyrin based molecular boxes in their electronic, electronic, 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 atomic 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. Lillian P Dawid, Matt-Jose Caturia, Alfonso Kubota, BalaTadgh, Teresa Diaz de la Rubia, James Shackleford, Sikkim Ramshirsh, and Stephen Garofalini. Department of Chemical Engineering and Materials Science, UC Davis, Davis, California; Lawrence Livermore National Laboratory, Livermore, California; Department of Applied Physics, University of Alicante, Alicante, E-03080, Spain; Department 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 Reuston 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 nanoamorphous nature of fused silica, influencing applications that depend on its structure under these conditions, from applications 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-7405ENG-48.

4:30 PM L10.11

Multi-scale modelling of carbon nanotubes. James Elliott, How Smithsoon, Marc Haron and Alan Wiedl, 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 working on 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 carbon 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 Dionicio G. Vlahos, Department of Chemical Engineering and Center for Catalytic Science and Technology (CST), 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 nanotubes. These systems challenge modeling approaches on several levels, including the strong energetics of the confined diffusion, the energetic anisotropy of the diffusion sites, the influence of nanoscale 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 threedimensional single crystal lattice. 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 validated 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 Komaravolu, John Parker and James Watkins
Thursday Evening, December 4, 2003
8-10 PM
Exhibition Hall D (Hynes)

L11.1 Solvent Effect on the Morphology of the Mesoporous TiO2. Jung, J., Leewil, W. and Wen-Yen, Chiu. Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan; 2Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; 3Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan.

Mesoporous TiO2 particles in various shapes were synthesized by a modified sol-gel reaction using amorphous 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 amorphous block copolymer in an organic solvent, followed by the growth of TiO2 via the condensation of the surface-anchored precursor and free titanium isopropoxide monomer. The structures of these mesoporous TiO2 materials were investigated by BET and XRD techniques. The sol-gel reaction on the shape and porosity of the TiO2 particles will be presented.
L11.2 Carbon nanotube deposition on the surface of metal wire by inductively coupled UHF microplasma CVD. Yoshiki Shimizu, Toshiki Sanuki, Naoto Koshizaki, and Kazuo Teshima.

We have deposited carbon nanotubes (CNTs) on the surface of metal wires such as copper and nickel using a configuration of UHF microplasma CVD. At high 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 0.001 mm diameter was placed. During the CVD process, the wire was moved around the quartz capillary. In cases 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. The CNTs, with the certain conditions of the gas flow rates and UHF power, were grown perpendicularly on the whole surface of the metal wires.

L11.3 HRTEM Characterization of Self-Assembled Manganese Oxide Thin Films. Kate Laubner's, Jikang Yuan's, Jeanette Villegas's, and Steven L. Shiib's.

The formation of pure inorganic membranes is becoming increasingly important in nanoelectronics science. This work describes the formation of inorganic free-standing thin films without the use of polymeric additives. These inorganic films have applications as selective ion sensors, and in separation and ion-exchange processes. The free-standing thin films (15 - 50 nm 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 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). The powder X-ray diffraction and TEM micrographs show the lamellar morphology of the film. The results suggest that the formation of the thin 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 TEM data show that the films are composed of OMS-2 (cryptomelane) fiber bundles, arranged in ordered layers. Synthesis OMS-2 consists of mixed valent MnO6 octahedra, sharing corners and edges to form tunnel structures. OMS-2 is a 2D structure with tunnel dimensions of 0.064x0.44 nm. The individual nanofibers aggregate together into bundles, which form the film matrix. The individual fibers and the corresponding bundles have an average diameter of 150 and 340 nm, respectively. Cross-sectional TEM brings out the long direction of the fibers. Additionally, EELS analysis provided data related to the electronic environment of the manganese species.


We have engineered nanoscale porosity in oxide thin films using electron beam evaporation and substrate control motion of the Glancing Angle Deposition technique. The films consist of high aspect ratio (~10 to 30) columns separated by longitudinal pores of diameter ~100 nm or less, oriented perpendicular to the substrate. This anisotropic architecture comprises high surface area, high porosity films with exceptional control of the porosity of the pores, or grains. To demonstrate sensor capability we have sandwiched these nanostructured SiO2, SiO, and Al2O3 films between porous metal electrodes to fabricate parallel plate capacitive humidity sensors. The sensors display extremely quick response times of down to 25 ms, and a capacitive response to change in humidity of approximately 4 orders of magnitude. The mechanisms responsible for the capacitive response will be discussed, and investigations of the sensors in an interrogated rather than parallel plate electrode arrangement will also be reported.

L11.5 Nanostructured Ferrite Thin Films Prepared by Atmospheric MOCD. Takashi Shima and Yong-Chang Chang. College of Engineering, Lungwha University of Science and Technology, Taoyuan, Taiwan.

In this presentation, we will report synthesis of ferrite films with nanostructure by MOCD. We also discuss the magnetic properties of films were closely related to film nanostructure. In this project, a MOCD process has been successfully developed to deposit polycrystalline zinc iron ferrite, Cu19Zn37Fe2O4 films at temperatures from 300 to 1000 °C, with zinc acetyacetonate, Cu(acac)2, iron acetylacetonate, Fe(acac)3, and oxygen as reactants, using a horizontal cold wall atmospheric reactor. AES and XPS results showed that the films had an intermixed structure. In situ magnetic measurements using a SQUID indicated that these CVD films were polycrystalline spinel ferrite, with grain orientations on (111), (311), and (220) (depression générale d=1.6 Å, 2.10 Å, 2.52 Å, 2.97 Å, with (311) being the preferential grain orientation for Cu19Zn37Fe2O4 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 distinct shaped and grain-dimension of 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, (2-8 Oe), internal magnetic permeability (μ) 3.2 ± 1.0 emu/Oe, saturation magnetization (Ms) 3.0 × 10-6 T orthogonal to remanent magnetization (Mr). 1.60 ± 0.02. SQUID results also show that both μ and Ms are related to grain size, and deposition temperature. μ and Ms achieve the largest value at 400 °C film. The unit saturation magnetization is 2.95 emu/cm3 (4 emu/g), and remanence magnetization is 21.6 emu/cm3 (4 emu/g).

L11.6 Optical Properties of ZnO/Al2O3 Nanostructured Thin Films. John M. Harrison, Masashi Matsumura and Renato P. Camm, 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 nanomaterials. 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 concentration, conductivity, and mechanical properties. However, 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 containing ZnO nanocrystals in Al2O3 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/Al2O3 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 growth matrix species that often cause contamination in PLD systems 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 plasma. NBPLD delivers a beam of sized-selected nanoparticle nanocrystals 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 layered of Al2O3 containing well-separated, size-selected ZnO nanoparticles with areal densities between 1.0 x 10^6 cm^-2. ZnO nanoparticles were deposited during the ablation of a Zn target at 0.3-0.7 Torr in the NBPLD source using a KrF excimer laser (248 nm) at fluences of 1.5-2.5 mJ/cm² while deposition of Al2O3 was achieved by ablation of aluminum targets at 510.3 mJ/cm² in a 10^-4 Torr 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 ZnO nanoparticles and samples in which the nanoparticles were encapsulated by Al2O3 deposition. Photoluminescence measurements on these films will also be presented in relation to the study of the luminescence of various ZnO films. Our main focus is on the identification of size effects and interference phenomena in these nanostructured ZnO samples. (Funding: NSF-DMR-0116088).

L11.7 The effects of crystallinity on the Er3+ photoluminescence properties of Er-doped nc-Si/Si02 superlattices. Ji-Hong Jhe, Moonseung Yang, Jung H. Shin, Kyungkong Kim, and Dreuwon Min. PHYSICS, KAIST, Taejon, Korea.

In this study, we have measured the photoluminescence properties of Er-doped nc-Si/Si02 superlattices. The samples were grown by atmospheric MOCD and have a period of 100 nm and a thickness of 1000 nm. The Er3+ ions were introduced by the MOCD process and their concentration was controlled by varying the Er3+ precursor concentration. The photoluminescence properties of the samples were measured by exciting the samples with a He-Cd laser at 325 nm. The photoluminescence spectra were recorded in the range of 500-1200 nm. The results showed that the photoluminescence intensity of the Er3+ ions increased with increasing Er3+ concentration. The photoluminescence properties were also influenced by the crystallinity of the samples. The samples with higher crystallinity showed stronger photoluminescence intensity. This indicates that the crystallinity of the samples plays an important role in the photoluminescence properties of Er-doped nc-Si/Si02 superlattices.
Si-based optoelectronic devices. Despite the large advances, the Er3+
mesencefficiencyachievedisstillratherlowtolowethereduction
can be achieved at room temperature. Recently, silicon-rich silicon
oxide (SiRSox), which consisted of Si nanocrystals (nc-Si) embedded
in SiO2 matrix, appears as one promising candidate for host material
and by using SiRSox, it is also possible to obtain both the high excitation
efficiency of Si and the high luminescence efficiency of SiO2.
Unfortunately, the size and density of nc-Si and the location of Er
atoms, which are key parameters for obtaining efficient Er3+
mesence, are difficult to control. However, such parameters can be
controlled in Si/SiO2 multilayer superlattices. In this work, the
effects of crystallinity in the Er3+ luminescence properties of
Er-doped nc-Si/SiO2 superlattices were investigated. The Er-doped
SiOx/SiO2 superlattices were deposited by UHV ion beam
sputtering method and were subsequently annealed at 550 or 1100 °C.
After annealing, Er atoms were well confined in SiO2 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 Er3+ luminescence from Er-doped nc-Si/SiO2 superlattices and further detailed discussion about the Er3+
luminescence properties will be presented.

L11.8 Comparison of conventional and microwave sintering on the
barium titanate nanocrystals made by Ambient Condition Sol
(ACS) process. Pererk Bashlane, Jake Jokisjarvi, Bertrand I Lee and
Sunit B Bhadrir, Clemson University, Clemson, South Carolina.

Barium titanate is an important material in the electronics industry. Its
dielectric constant and low dielectric loss factor over a wide
range of temperature and frequency make it desirable as a dielectric
material for surface mount capacitors. The properties of ceramic
powders 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
heating on the phase transition of barium titanate crystals was studied.
Microwave treatment was found to produce tetragonal phase
barium titanate. The crystal structure, crystallite size, phase
transition and morphology of the powder samples were analyzed by
XRD, Raman, DLS, DSC, TGA and SEM.

L11.9 Aerosol-Assisted Nanocomposite Materials. John Eric Hampeye, Jeshin Pung1, Qiangyu Hu1, Donghai Wang1, Byron McCaig2, C. Jeffrey Brinker2 and Yunfeng Lu3
1Department of Chemical Engineering, Tulane University, New
Orleans, Louisiana; 2Direct Fabrication Department, Sandia National
Laboratories, Albuquerque, New Mexico.

Silica nanocomposite particles have been synthesized by an
eosol-assisted self-assembly process. Constituents such as inks
spheres, fluorescent dyes, organic ligands, catalyst particles, and
metal oxide nanoparticles were added to the precursor solution
prepared using tetraethoxysilane (TEOS), ethanol, surfactant 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°C. The solvent evaporates from the droplets, leaving
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 Logem1, Pascal Massie2, Brian Devel1,
Andrew Skolnick1, Raja Francis2, Anna Luong2, Daniel Ratt3, Yves Grammont4
and Randolph N. Silver6.1, 2, 3, 4Chemistry, University of Florida, Gainesville,
Florida; 2Chemistry, University of Bordeaux I, Bordeaux, France;
3Chemistry, University of Calcutta, Kolkata, 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 (PS4=PPE4), where n=8 and is
the number of branches (x) of the block copolymer) or a dendrimer-like star, PS4=PPE6. Both experiments demonstrated the
ability of the films to be stable with PS anchoring the PEO to the
interface. The presence of a pseudophase at a pressure of 10
mN/m was found to depend on the amount of PEO present. In
addition, backbone and brush regions were also observed in the
carried-out experiments, where the pressure was varied from 20
mN/m. Both experiments showed that the surface films readily flow at pressures below the pseudophase 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 Pyranyl Nanocrystals and Novel Oxygen Sensing
Capabilities of an Associative Polymer. Bryce A. Jones1, Sung
Dog Kim1 and John M. Tofteland2, 3Department of Chemical Engineering,
Northwestern University, Evanston, Illinois; 2Dept. of Materials
Science and Engineering, Northwestern University, Evanston, Illinois.

Unusually large melting point depression 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 involve in controlled growth of small particles, or similar nanoscale
materials, in the case of the Py-PDMS-Py system, nanocrystals form
in a novel manner within nanogragates of pyranyl units that are
strongly immiscible in PDMS. For 5,000 g/mol and 7,000 g/mol
Py-PDMS-Py, physical gels with the pyranyl 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 no SAXS peaks are seen at room temperature; however, after annealing for 12 hours at 268 K, multiple
melting peaks are evident at 278-303K. 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 on 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. Vishal Anil Kumar Mangalda and Sunit B Bhadrir, Jasmine Lee
Sunit B Bhadrir; 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 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 varistor ceramic Bi2Ti3O9 powders for comparative study. Silver was added from 0% silver at 5 wt% interval 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
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
Bi2Ti3O9 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 Monostructured/Mesoporous Silica Nanotubes, Sheng Wang and Gary D. Stucky. 1, 2
1 Chemistry and Biochemistry, Univ. of California, Santa Barbara, Santa Barbara, California; 2Materink, University of California, Santa Barbara, Santa Barbara, California.

Well-ordered monostructured/mesoporous silica nanofibers have been synthesized in a quiescent dilute aqueous cationic surfactant/silica precursor rection 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.


Compared to Chemical Vapor Deposition (CVD), Spin-On Dielectric (SOD) can provide superior gap-fill capability, but tend to form comparatively less uniform films in critical dimensions (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 hydrophobic sol-gel mixture (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 tetramethyl orthosilicate, and were subsequently surface-modified with methyltrimethoxysilane and dispersed in an organic solvent. The resultant silica nanoparticles were spherical with particle densities in the range of 2.00–2.16 g/cm³, mean particle diameters in the range of 10–16 nm and narrow particle size distributions. Films spun coating on patterned silicon wafers were annealed 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 solubilization method using reactive plasma treatment and HSQ resin dispersed in a solvent, a dense silica 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 thickness of both the nanoparticle coating and the dense silica dioxide films have been examined by high-resolution scanning TEM using a scanning electron microscope. A focused ion beam (FIB).

L11.15 Development of Improved Routes towards Preparation and Surface Modification of Iron Oxide Nanoparticles, Lingyan Wang, 1 Jie Luo, 1 Li Hao, 1 Minato Tominga 3 and Chuan-Jie Zhou 4, 1State Key Laboratory of Light Elements Chemistry, SUNY-Binghamton, Binghamton, New York; 2Kumamoto 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. Iron-oxide/EPR ferritin was used for the preparation of iron oxide nanoparticles. The preparation involves thermal removal of the protein shell from ferritin. In the second approach, iron penta-carboxylate compounds are used for the preparation of iron oxide nanoparticles by thermal decomposition as controlled temperatures and under different catalytic 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 systems will also be discussed.

L11.16 Probing nano scale dynamics in glassy polymers near glass transition temperature, kenanwonzor, samanthaham and Nathan Iarleof, 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 glassy polymer polyisoprene (PVAc) near Tg. Using ultra high vacuum (UHV) and capacitance scanning probe microscopy (SPM) techniques, nano scale probing of thermal noise fluctuations in a glassy polymer can be reduced 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 covariate, correlation matrix of the octaves. Statistical analyses of these thermal noise fluctuation ions 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.


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 and the polymer matrix. Most of these nanocomposite/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 also strengthen 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 nanotube in matrix. Our research consists of simultaneous purification, opening, shortening and carboxyl functionalization of carbon nanotubes using acid treatments. Carboxyl functionalized nanotubes will be further treated for methylene benzene carbonation, which is compatible with polymer substrates. Two approaches for preparation of nanocomposites are under consideration, which consist of sandwiching functionalized carbon nanotubes between two ultrathin polymer films and other approach in 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 In2O3 Nanocubes, Bin Cheng, 1, Lei Zhang 2 and Edward T. Samulski 1, 3, 4, 5 Chemistry, University of North Carolina, Chapel Hill, North Carolina; 6Curriculum of Applied and Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

Bin Cheng, Lei Zhang, and Edward T. Samulski. 1, 2Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290 *To whom correspondence should be addressed, etsmulski@unc.edu. Forced hydrolysis of In(OH)3 from different precursors was studied in detail. The composition of the final precipitates was identified as In(OH)3: In(OH)3, and In(OH)3. Small size (~ 40 nm) and regular shaped In2O3 nanocubes were successfully obtained for the first time by carefully controlled hydrothermal conditions. The composition, crystal structure and morphologies were characterized by XRD, SEM, AFM, TEM, and SAED. The photoluminescence of the as-prepared novel nanostructure of In2O3 was also measured.

L11.19 Spherical Nanoparticle Ordering in Block Copolymers, John M. Poplawski and Mary E. Galvin: Materials Science & Engineering, University of Delaware, Newark, Delaware.

Theoretical work by Bulmash 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 compositions of the copolymer and the inclusion matrix, a variety of structures can be obtained. Our investigations have initially centered around utilizing two differently sized particles of the same chemical composition. We have additional ongoing studies of alternate particle systems. Our work investigates these possible systems as well as the use of the enthalpy (modified by the inclusion of surfactants) and entropic needs of the system to obtain order.

L11.20
Highly Reproducible Synthesis of Thermally Stable 2D Hexagonal Mesostructured TiO2. Sungyeon Cho1, Marc Mann1, Neil Coombs2, Naveen Chopra1 and Geoffrey A. Ozin1, 1Chemistry, University of Toronto, Toronto, Ontario, Canada; 2Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

Non-siliceous mesoporous materials are of considerable interest, as they usually also possess optical, electronic, magnetic and catalytic properties compared with pure siliceous mesoporous materials. In particular, high surface area mesostructured titania (TiO2) is a very interesting material, with respect to its potential use in controlled delivery, chemical sensor, optical, electronic, photocatalytic, or energy conversion applications. Recently, the synthetic approach based on the EISA (Evaporation Induced Self-Assembly) method, which makes use of ethoxylated surfactant mesoporous precursors, has enabled tri-block copolymers as templates to be 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 mesostructured "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 titania. This synthetic approach was based upon the well-documented EISA method using the nonionic amphiphilic tri-block-copolymer, Pluronic P123 (PEO20POP20PEO20) as the templating agent. Titanium ethoxide (Ti(EtO)4) was chosen as the inorganic precursor, HCl is 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(OEt)4 precursor in P123 templating composition to be the basic solution. Relatively crack-free transparent thin films were prepared by spin coating followed by controlled aging of the films. The obtained mesoporous titania thin and thick films produced by such modified conditions have a highly ordered 2D hexagonal structure, narrow pore size distribution (H type hysteresis), and high specific surface area of over 200 m²/g. Moreover, this structure composed of channel walls containing nanocrystalline titania was stable even up 400°C. Thin film samples are currently under consideration as the centimeter-scale structures as determined from optical microscopy. Characterization of mesoporous titania samples were performed by Polarization Optical Microscopy (POM), powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), X-ray absorption spectroscopy, and Thermogravimetric analysis (TGA).

L11.21 Structural characterization of Ni-doped and Co-doped carbon aerogels prepared by ion-exchange method. Adelin P Santos1, Nassir S Demir2, Gene Dresselhaus3, Mikled S Dresselhaus3, Ted F Bausman3 and Joe H Satchler1, 1Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94551 (U.S.A) and Materials Science Center, Centro de Desarrollo de Tecnología 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 nanospheres (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/cm³), extremely high surface areas (600-800 m²/g), and an intrinsic disorder of the system, with a great number 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 framework as whole such as the mesostructure, 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 aerogels systems synthesized by an innovative technique developed by Bausman et al. at Lawrence Livermore National Laboratory (LLNL). The method is based on the use of a solgel precursor derivative containing an ion-exchange moiety which enables a uniform placement of metal species on ion-exchange sites on the organic skeleton. Different metal-doped aerogel can be prepared by 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 Halton1, Doug D Perovic1, Kai Landström2 and Geoff A Ozin1, 1Department of Chemistry, University of Toronto, Toronto, Ontario, Canada; 2Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

Periodic mesoporous organosilica (PMOs) are polyisocyanosilanes structurally similar to a self-assembled supramolecular surfactant template to create a periodic array of nanoscale channels [1]. Silsesquioxane precursors of the type [EO]3Si(OEt)6 (EO is a linear alkoxy chain with an ethylene oxide backbone) can be used to introduce functionality into the channel wall of the mesopore. 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-brided organics such as methylene, ethene, ethylene, 1,4-benzene and tri-brided organics such as 1,3,5-benzene. Evaporation-induced self-assembly (EISA) [2] has been used to create a catonic 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 XRD, HR-TEM, ATR-IR, SEM, 29Si and 13C NMR, and ellipsometry. The mechanical properties of the films have been measured using nanindentation. Measurements have been made of the dielectric constant (κ) by parallel plate capacitance, which have been found to be consistent with organic content and value as low as 2.0. These PMO films may be attractive as low dielectric layers also because they are hydrophilic and demonstrate good mechanical and thermal stability. 1Asea, et al. Nature 419, 865-871 (2002). 2Lu et al Nature 380, 364-368 (1997).

L11.23 Photoluminescence from the Silicon Surfaces Treated by Various Ionized Gases and Annealing Processes. My-Cher Jung, Young Ju Park, Changho Ko, Moonseup Han, Chulyoung Han, Sung Ho Jun and Kyoungmann Park, 1Dept. of Nano Science and Technology, University of Seoul, Seoul, South Korea; 2Dept. of Physics, University of Seoul, Seoul, South Korea; 3Nano-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 characteristic of nanocluster silicon layer formed by two times of ionization/oxidation and successive annealing process on silicon surface. Cluster-like structures were firstly formed on the ionized N2 gas at room temperature and low pressure. Atomic force microscopy and X-ray photoelectron spectroscopy analyses show that nanometer-scale SiN nanoclusters 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 islands in the secondly 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 emission wavelength with the ionized N2 gas 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.


A biodegradable polymer, Nedacl, 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 1, Amol Chande 1, Dong Seong Kim 1, Changsoo Sung 2 and James E. Whittem 1, 2. Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts, 2Department 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 alkamethins, Th (CH2)n-SH (Th = 3-thiophene with n = 2, 3, 9, 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). TEM demonstrates the formation of gold particles covered with thiophene-functionalized alkamethins. The peak position and peak-to-peak distance of Au 4f spin-orbit-coupled double indicate zero-valent gold, and the SS 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 alkamethins. TEM images of the functionalized gold nanoparticles show that the size of particles is in the range of 2-8 nanometers. Optical properties of the gold nanoparticles dispersed in different solvents have been investigated using UV-vis spectroscopy. The 6(3thiophenyl)hexanethiol functionalized gold nanoparticle well disperses in chloroform and toluene, and shows surface plasmon (SP) bands with maximum intensity at 500 and 520 nanometers, respectively. However, the intensity of the SP bands shift to 650 and 690 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 Order 1,2 and Nathan Insel 1,2. Physics Department, Northeastern University, Boston, Massachusetts, 2Nanomaterials 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 and glass dynamics. Scanning Force Microscope (SFM) has been used to map dissipation across a surface, yielding localized information on the dissipation in glassy polymer polymers. A new technique of scanning probing techniques including phase imaging and local force spectroscopy combined with Hertzian dynamics allows local probing of dissipation, yielding insight into the cooperativity of rearranging regions (CHR). We also present analysis of methods of probing dissipation and polymer nanoparticles using SPM techniques continued from previous studies of nanoparticles.


Recent advances in intrinsically conductive polymers have created new opportunities in a broad range of electronic and electrical applications. Through redox or, in some cases, proton doping of the conjugated electronic structure, polymers can be prepared with metallic conductivities up to 105 S/cm. They have found application in a broad range of technologies from batteries and solar cells to computer electronics. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDT/PSS), is widely used in the form of a film in a wide range of applications, e.g. LCD. Because of its high conductivity (0.8 to 3000 S/cm), this study, PEDT in fiber form was explored. Successively, PEDT/PAN nanocomposites were produced using the electrospinning process. The electrical conductivity of the electrospun fibers was found to increase as the fiber diameter decreased. By using PEDT polymer in fiber form, the application of PEDT is expected to expand in the area of biocompatibility and 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. Toshiko Ohadgo Salahin and Scott R.J Oliver; Chemistry, Binghamton University, Binghamton, New York.

Our efforts into the solvothermal (non aqueous synthesis) of new nanomaterials 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 unique unplaced methodology of microstructure directing agents (SDAs), focusing on nanoscopic species that have the potential to act as SDA such as, BF4, PF6 and CF3SO3H. These SDA are able to direct the structure as well as introduced specific charges on the synthesized materials. We also modified 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 3D, 1D, 2D and 3D compounds with interesting materials properties, which will be discussed along with their synthesis and structure.

L11.29

Nowadays the demands placed upon the tools 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 minimised 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 TiAlN 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 high-temperature oxidation resistance when aluminium 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 TiAlN make it ideal candidate for applications such as milling, hobbing, tapping, stamping and punching. MoS2 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 TiAlN matrix with the lubricating properties of MoS2 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 X-ray photoelectron spectroscopy. The tribological properties were evaluated by pin-on-disc (P-0D) tribometer. The adhesion was estimated by scratch test and the hardness was measured by nanoindentation. The coatings examined had a very low friction coefficient (typically below 0.09) and volumetric wear rates against 100Cr6 steel. The weight of the friction pair is usually 5000 N. The relationship of deposition parameters to structure and properties is discussed. To the authors knowledge, this is the first paper describing quaternary TiAlN matrix with inclusions of MoS2.

L11.30
Comparative Effects of Nanoparticle Morphology on Properties of Polymer Nanocomposite Films. Elizabeth A. Welch, Michael Shokr, Christopher Thellen, Danielle Froio, Axel Rodrigo, David Ziegler, Jo Ann Ratto and Walter Zukas; US Army RDAE Command (Prox), Nurdik Soldier Center, Nurdik, 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 material is the subject of much speculation. The electrical and mechanical properties of EGN/polymer nanocomposite films have been studied. Barrier and mechanical properties of EGN/polymer nanocomposite films have been compared to similar nanocomposite films having either comparable filler morphology 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 permittivity resistance to water, oxygen, and selected organic peroxides.

**L1.1.31**

**Structural Analysis of a (CoRe27, Re5(5nm)/(Co2nm)/(Re0.6nm)) Sandwich Grown on Al2O3, Wenxin Xu1, Timothy Cherkovski2,3, Lance E. DeLong2 and David Lederman2; 1Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky, 2Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 3Department of Physics, West Virginia University, Morgantown, West Virginia.

The structure of a (CoRe27, Re5(5nm)/(Co2nm)/(Re0.6nm))2 sample grown on magnetron sputtering was thoroughly analyzed via x-ray diffraction (XRD), x-ray reflectivity (XRR) and transmission electron microscopy (TEM). Prior to the superlattice growth, the Re seed layer was annealed at 1000 °C to remove residual stresses and to enhance the 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 Al2O3 are approximately 0.42, 0.43, 0.26, 0.44, and 0.24, 0.44 nm, respectively. The lattice spacings of Al2O3 correspond to α/2 and α/β, respectively. Interestingly, both high resolution and 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 further away from the substrate. A high magnification analysis indicates 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 microscopic magnetoplasmonic measurements will be presented in light of these new structural data. This work was supported in part by NSF-EPSCoR.

**L1.1.32**

**Development of Electron Beam Cured Low-k Dielectrics by Plasma Enhanced Chemical Vapor Deposition (PECVD) for 65nm Technology**, Kang Su Yim, Yi Zheng, Li-Xin Qin, Alex Demos, Helen Armer and Hichem Mounaf, blanket Division, Applied Materials, Sunnyvale, 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 the mechanical properties but these have met with limited success. This paper presents electron beam (EB) treatment for the production of porous dielectric films. The films are deposited using a trimethylsilyl (TMS) or tridecylsilyl (TDS) precursor in a low-pressure, high-energy, electron beam (EB) after deposition. EB treatment 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 > 8.5 MV/cm. For a k=2.0 film, electron beam treatment at very low dose causes a drop in k. The bottom k < 0.05 below the as-deposited k, and further increases in ebeam dose cause k to rise. Hardness increases monotonically with increasing e-beam dose. Hence, the e-beam 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 e-beam dose induces film densification, resulting in higher k and hardness. Mechanical property enhancement is also verified by cross sectional SEM pictures, which confirm higher density. EB treatment improves all measured properties (k, h, M, E). EB-induced film structure changes were studied using FTIR and NMR. The intensity of H-H and Si-CH3 peaks reduces after EB treatment, indicating a loss of methyl components from the film. High quality of Si-O stretching peak at 1100 cm-1 is slightly increased, indicating that a more cross-linked Si-O network structure is formed at the expense of depletion of CH3 components. NMR analysis shows the same change of film structure. Film porosity as measured by microporous porosimetry (MPS) showed 7.18% micro fractions and nano-scale pores <1 nm. EB treatment reduces pore size, and higher e-beam dose compresses the film. A single dumbbell structure was fabricated using 5nm of nitrogen-doped silicon carbide as an electron stop layer and 10nm of silicon carbide. The k of the IDL layer for this structure was extracted using interplanar capacitance measurement and TMA Raman simulation, and the resulting integrated k value was 2.6. Single dumbbell structure measurements data show significant improvement in the IDL layer design. A 0.15μm thick silicon dioxide film was grown with a 1.6μm thick silicon nitride film. A 2-level metal dual-dumbbell structure was fabricated. This structure had a leakage current of 56-11 A/cm² at an electric field of 0.5MV/cm. Long time bias (up to 8 million volts) were tested, and this was 99.9%. No damage to the MOSFET has been observed at 3x1.63 Amp current.

**L1.1.33**

**Effect of film composition and structure on the diffusion barrier properties of metal alloy layers formed by electron deposition**, Artur Kolo1, Nick Petrow1, Nihal Li2, Marina Polynskaya2, Jason Schner2 and Igor Ivanov2. Blue29, Inc., Sunnyvale, California, 3KLA-Tencor, San Jose, California.

Despite the numerous advantages of the use of copper as an interconnect material in ultra-large scale (ULS) microelectronic devices, the technology faces several problems such as metal-copper adhesion, high chemical reactivity, and considerable diffusion of copper in silicon. In particular, the poor adhesion of copper to SiN, SiC, SOI raises significant reliability problems. One of the promising ways to overcome this shortcoming was the application of metal alloy coating 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 Cu-Ni-P and refractory metals, which can be formed using electron plating method. The corrosion protection and barrier properties of this layer depend largely on their microstructure and composition. These properties can be altered by the deposition condition and composition of the electron deposition bath. In the expected range, we focused on determining a process and resultant deposit itself. Nanodots, growth mechanism of copper-oxide layer together with selectivity and barrier properties of the alloy system was characterized with the use of scanning electron (JEOL), atomic force microscopy (KLA-Tencor) and Auger-electron spectroscopic (Phi) techniques.

**L1.1.34**


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 exothermic character imposes a thermodynamic limitation to the conversion of ethylbenzene that can be retained (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 alkali contamination, but their surface areas are extremely low (about 0.5 m²/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 m²/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-SiO3. Platelet GNF showed a selectivity of 54% 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.

**L1.1.35**


There has been growing interest in the miniaturization of chemical reactors for portable applications. Solid-liquid (SL) microreactors offer the potential of addressing some of the problems associated with current microfabricated flow systems. 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 nanoparticles. Some 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 Pt nanoparticles was deposited onto the microchannel wall of silicon-based microreactors. The thin-film catalyst was synthesized by two sol-gel methods. In the first method, H₃PtCl₆ was dissolved in 1,3-butadiene to make a Pt solution, then it was mixed with an alumina sol. The liquid mixture was infiltrated into the microreactor, 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 into the microchannel by infiltration of the microreactor layer. The surface and the fracture-section of the Pt/Al₂O₃ layer were observed by scanning electron microscopy. The thickness of the catalyst layer varied from 0.5 to 1.0 μm. The effect of the volume of the injected liquid precursor and the geometry of the microchannel.

The BET surface area of the amorphous Al₂O₃ support was 480 m²/g, and the diameter of most pores was in the range of 3 to 4 nm. Particle size distribution of the Pt on Al₂O₃ was obtained by transmission electron microscopy. The results 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/Al₂O₃ catalyst were tested for preferential oxidation of CO by O₂. This reaction is a critical part of fuel processing for proton exchange membrane fuel cell applications for removing CO from H₂-rich reformate. Simulated reformate 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


Mo doped vanadium oxides have found a wide range of applications because of their selective oxidation as well as the unique interaction between V₂O₅ and MoO₃ 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 vanadium. 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 microstructures and properties 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 VNTs, the interdistance between oxide layers in the (VₓMoₓ)O₄ nanotubes 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 microstructure and electrochemical performance of (VₓMoₓ)O₄ 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 16 (2002) 8. [2] Najjar M., Applied Catalysis A, General 157 (1997) 239. [3] Chen W., Xu, Q., Mai L. O., Hu Y. S., Zhi Yang, J Mater Chem 12 (2002) 1996. Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 51771626), 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. 2002A008).

### L11.37 Self Assembly of Tethered Silesiquatocene “Nanocubes” into Nanostructured Materials: A Molecular Simulation Study

**Galbraith, C. A., R. Chen.** Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 2Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Nanomaterials composed of organic/inorganic nanoscale building blocks hold much promise for providing innovative materials with superior properties. Recent experiments have demonstrated that polymer-mediated self-assembly of polyethylene oxide/silanesilsequioxane (POS) micelles 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 POS micelles can be achieved by manipulating POS-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 organic linker 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 “tethers”, connecting two POSS units by a single organic linker, 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 nanomaterial building blocks. Our results provide insight to the assembly process, and facilitate the rational design of new nanoscale materials by enabling the exploration of various assemblies and the conditions under which these novel structures are formed. This research is a collaboration between University of Michigan, University of Virginia, Vanderbilt University, and Colorado School of Mines and is funded by the National Science Foundation under DMR-1012399.

### L11.38 Synthesis and Characterization of Y203/Yb,Tm Blue Nanophosphors: Shinjiya Varma and Olin A. Grewe.

**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 nanometer to 10 μm. 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 nanosynthesized 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 Nanodispersive Many-Particle Systems: Concept, Single-Particle-Property and Many-Particle System. Strategy

**Vladimir P. Oleksii, Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.**

Most practically important are many-particle systems (MPS) such as nanocrystalline films, small-domain matter, particle-matrix systems (metal-nanometal systems, imaging materials, granular superconductors, cluster tunnel junctions, cermets, dispersed composite systems, etc.), form matter, and systems that 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 matrices, applications in Larmor precession 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 structural, electronic model, size and shape), the nearneighbor 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, electrical, magnetic, mechanical, etc. properties. Such approach provides a logical synergism between engineering design (modeling) and characterization of MPS aimed for a better understanding of the processes and their control. Within this concept, applications of a combination of imaging, diffraction and analytical electron microscopy (AEM) modes including (FE)-HRTEM, (cryo)-EFTEM/PEELS, (cryo)-STEM/EIDX/PEELS, low-voltage FEI/EIDX and realtime electron microscopy (AEM) for the characterization of nanodispersive 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 morphological transitions in crystalline materials will be discussed. Examples will include "giant clusters" of Pd-82.5%O (X = Ag, Cu, Au) (1-1.18 pm thiolene), [Pd2(μ-Cl)2H2]+, and [P2(μ-Cl)2]2+ (μ-Cl = bidentate phosphine, μ2-Cl = 2-Cl) composite multistructured tubular AgX (X = Br, I) nanotubes. As small particles and thin films of Ag and TiCl4-MgCl2 supported heterogeneous Ziegler-Natta polymerisation catalysts.


Recent progress in experimental fabrication and materials characterization techniques has opened a new page in development of advanced materials (such as single crystal and semiconductor quantum dot QDs) for optoelectronic and infrared (IR) optical devices. Based on chemical reactions of MoO2, InCl5, and C6H5ClO (carbon tetrachloride), MoO2 nanocrystals with an effective particle size ranging from tens to over several nanometers. This presentation is focused on further advances in fundamental statistical physics, statistical mechanics and computational methods to investigate properties of essentially three-dimensional synthesis of sub-10 nm structured nanomaterials [such as silicon-based sub-nanometric structures (NMS) 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 as one of such structures were predicted by a fundamental theoretical approach, the functional perturbation theory (FPT), implemented in synergy with the equilibrium statistical mechanics 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 inorganic and amorphous nanomaterials. Materials design and fabrication route 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 Techniques. Yuewen Liu1, Sae Imamura2, and Masaru Matsuo1.1. Graduate School of Human Culture, Nara Women’s University, Nara, Japan; 2. 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 (MWN Ts) and ultra-high molecular weight polyethylene (UHMWPE). The composites with 0.25 to 15 wt.% of MWN Ts were prepared by gelation/crystallization from decalin solutions, and modified with iodine doping. The percolation field was found to be around 4 wt.% of MWN Ts. A fits for UHMWPE composites. The composite gel films could be elongated to more than 50 fold. The Young’s modulus was beyond 35 GPa while the draw ratio reached 50 fold. Scanning electron microscopy revealed that MWN Ts with continuous networks were oriented dominantly parallel to the stretching direction. Such characteristic alignment of MWN Ts plays an important role to form effective conductive paths in the high oriented composites. The co-orientation of MWN Ts and UHMWPE in the stretching direction ensured that the composites possess high modulus and high strength, 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 by 10/8 fold 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 proved to be a very effective means for the improvement in the electrochemical of polyethylene MWN Ts composites, especially for the composites with low content of MWN Ts.

L11.42 Oxidation Resistance of Multi-Walled Carbon Nanotubes Coated with SiC. Yoshiaki Morkin, Masakazu Muto, Toshiaki Shihoyangi and Yoshinori Miyamoto. Joining and Welding Research Institute, Osaka University, Higashi, Japan.

MWCNTs have been used to reinforce various matrices. Such replacement materials can improve the fatigue fracture energy. However, MWCNTs are oxidized easily above 300 °C 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 structurally sized crystalline silicon 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 SiC coated MWCNTs was improved by the SiC coating. MWCNTs 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.


The recent discovery of mesoporous 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 material for those applications is titanium. Liquid fuel cells are a promising alternative to hydrogen-fueled devices for portable and mobile electrochemical power sources. However, the power density and the efficiency of Direct Methanol Fuel Cell (DMFCs) are lower compared to Polymer Electrolyte Fuel Cells (PEMFCs), due to the slow kinetics of methanol oxidation at the anode catalyst. To achieve high power density of DMFCs, 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 mesoporous titanium on Nafion membrane-based DMFCs, finely dispersed non-crystalline titanium dioxide oxides such as TiO2 and ZrO2. The ceramic filter 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 titanium was studied, using micellar aggregates as templates. To avoid the high density of Ti (OH)4 species at high density hydration and condensation, the precursors selected and synthesized was a titanium complex (Dimethylaminotitanate). The formation of the mesoporous oxide in fact depends on 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 filter to fabricate the composite membranes with Nafion. The dispersion of the mesoporous titanium in the Nafion was very good, as shown by FE-SEM observations. Preliminary DMFC investigation of these membranes at high temperature revealed a significant increase of the catalytic area surface on the electrochemical behavior. At 140 °C with about 30 g load recorded. These results are very promising and a better tailoring of mesoporous titanium particles is now in progress.


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 usually comes from corrosive ions and molecules (e.g., Cl, O, OH, H2O) existed in seawater, humid environment, acid rains, emissions (e.g. pollutants), chemical products and industrial waste, and as sunlight (UV and heat). It begins at the surface of materials and decreases the lifetime of items 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, 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 prevention, replacement of corroded parts, and environmental protections. This corresponds over $800 billion cost to the US economy per year. It is reported that there are several
ways of decreasing corrosion to improve the lifetime of materials and devices. As recently determined, some of the corrosion processes are directly linked to nanotechnology studies. These include: nanocrystalline film (potassium permanganate, zinc compounds, chromium, aluminium, phosphate, nickel, molybdenum, cadmium or zinc-rich layers) formation (or conversion coating) between substrate and film, nanocrystalline particles ($SO_2$, $AI_2O_3$ and $ZrO_2$ carbon) addition to coating systems, interfacial controls, surface treatments and combination of them. The test results obtained using nanotechnology assisted methods show that the wear performance of 1000 times of conventional methods is reduced by the present paper, nanotechnology assisted studies, including surface treatment methods, corrosion prevention methods (new protective coating systems), top coating, new 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 corrosion and control systems.

L1.1.45
UV Curable Polymers With Organically Modified Clay As The Nanoinfillaments. Fam M Uli1, Brian R Hindle2, Prashanth Dwivadi3, Stuart G Cred2, Shing-Chung Wang3 and Dean C Webster2. 1Center for Nanoscience Science and Engineering, North Dakota State University, Fargo, North Dakota, Polymers and Coatings, North Dakota State University, Fargo, North Dakota, 3Mechanical 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, enhanced mechanical, thermal, and barrier properties were reported. Most research reports on nanocomposite formation by melt mixing or in situ polymerization. Little is understood on UV curable nanocomposites. This paper seeks to examine nanohydrating polymers using organically modified montmorillonites in UV curable systems and the effects of such clay incursions 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.

L1.1.46
Boron Carbide Encapsulated by Nanocrystalline Ni Coating. Jianhong He1, Yuhang Zhou1, Dean Baker2, Bill Harrigan3 and Enrique J Lomino1, 1Chemical Engineering & Materials Science, University of California, Davis, Davis, California, 2Powdermet, Inc., Sun Valley, California, 3MMC 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 wetting ability with metal, therefore, a high temperature synthesis process for MMCs requires using these ceramic reinforcements in 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 CVI Fast Fluidized Bed process, patented by the Powdermet, Inc., enables a mass production capacity (5000 lbs per lot) of ceramic powder encapsulated by metallic coating. Subsequent consolidation can be accomplished via metal/metal bonding, rather than through metal/ceramic 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 B4C particles are completely encapsulated by Ni coating with a thickness of 1-2μm. TEM examination shows the coating comprises single phase, nearly equaxed 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 nanocrystalline Ni coating and boron carbide/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 carbide B4C coating was prepared by plasma arc spraying process. This indicated that thin Ni capsule layer was persevered intact in the coating.

L1.1.47
Solution-phase synthesis of cubic and spherical nanostructures of Cu2O. Yuhang Wang, Yuhang Sun and Yousun Xin, Univ. of Washington, Seattle, Washington.

The preparation of two types of uniform and monodispersed Cu2O nanostructures (nanocubes (~50 nm in size) and monospheres (~200 nm) will be reported in this presentation. Copper nitrate was used as the precursor in this synthesis, and the nanostructured Cu2O 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) Cu2O nanoparticles can be selectively prepared. Electron diffraction studies on both morphologized Cu2O indicated that the nanospheres are polycrystalline in structure while the nanocubes are single crystals. Further investigation suggested that the reaction mechanism of Cu2O formation were the results of self-assembly of even smaller sized Cu2O particles (~1k 20 nm) that could serve as the seeds for nanocube growth.

L1.1.48
Synthesis of titania microspheres with nanocrystalline anatase core / rutile shell structure. Yun Mo Sung, Je-Kyung Lee and Yong-Ji Lee, Materials Sci. & Eng., Daejeon University, Pohang-kooen, South Korea.

Titania-PEO hybrids were fabricated using sol-gel processing of Ti-isopropoxide and Poly Ethylene Oxide (PEO: M.W. of 180,000). 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 (1-11 micrometer) with core/shell structure. Transmission electron microscopy (TEM) analyses reveal that the core is nanocrystalline anatase and the shell is microcrystalline rutile. The hybrids aged for 12 h showed the formation of plate-like clusters of crystals. Titania without PEO showed the formation of plate-like clusters of crystals with an anatase volume fraction of 0.5. This difference in the morphological features and phase formation characteristic was considered from the perspective of activation energy for phase formation and bonding between PE and chelated titania molecules.

L1.1.49

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 0.5-0.70 by controlling the deposition rates of relevant materials. The films prepared were so sensitive to the exposure to 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 downsweep 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, which is most and in which electron transport occurs from cobalt atom to a C60 molecule. Although all the mixtures synthesized, 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 while the electron hopping process between the isolated cobalt particles is supposed to be operative. The mixtures with x ≥ 60 are also thermally activated, however, their conductive nature might be attributed to the C60-based phase.

L1.1.50
On the development of the $\langle 111 \rangle$ fiber texture in nanocrystalline gold during growth and annealing. Klaus Pagh Andreasen1, Thomas Jensen 2, Jakob Hashir Petersen 3, Martin Skov Jensen1, Jacques Chevallier 4, Jorgen Bottiger 4 and Norbert Schilling 5; Physics and Astronomy, University of Aarhus, Denmark, 1Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, Germany.

The evolution during growth and subsequent annealing of the $\langle 111 \rangle$ fiber texture in nanocrystalline gold was 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 subsequent annealing using Bragg-Brentano geometry. The $\langle 111 \rangle$ 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...
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 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 of SiOx was directly analyzed by in-situ x-ray photoelectron spectroscopy (XPS). The relative sensitivity factor (RSF) of Si 2p and O 1s peaks were calculated by in-situ XPS analysis of the stoichiometric SiO2 thin films where x = 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 nanocrystallites. The PL intensities of SiOx showed maximum values near x = 2.2. However, those of SiOx/SiO2 films showed maximum values near x = 2.5. This could be understood as a term of averaged concentration. The superlattices with very thin layers, PL exhibits similar tendencies to those of single SiOx films where the x value is same with the average of the two layers. The results of the SiO1.2/2(2 nm)/SiO2(2 nm) superlattice, the average concentration is equivalent to x = 0.6. There was an increase of x = 0.9, the maximum PL intensity with the increase of deposition temperature.

L11.52 Phase Characterization and Morphology Control of Electrospun Nanofibers of PANI/PMMBl Blends. Keyur Desai and Changmoo Song; 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 to produce thin fibers. The fibers are collected on a grounded collector and form a high surface to volume ratio. Electrically conducting organic polymers are a novel class of synthetic materials which combine the chemical and mechanical properties of polymers with the electrical and/or electronic properties of conducting materials. Electrospinning is the technique of conducting polymers like polyaniline (PANI) have been studied extensively owing to their applications in energy conversion devices, sensors, electronic 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 nanofibers. 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 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/SiO2 Superlattices by Physical Deposition. Kyungjoong Kim1, Daewon Moon2.

Moonseung Yang2, Jihong Jie2, Junghoong Shin2, Seunghee Hong3 and Sikho Choi3.

1Korea Research Institute of Standards and Science, Daejeon, South Korea; 2KAIST, Daejeon, South Korea; 3Kyunghee 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 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 of SiOx was directly analyzed by in-situ x-ray photoelectron spectroscopy (XPS). The relative sensitivity factor (RSF) of Si 2p and O 1s peaks were calculated by in-situ XPS analysis of the stoichiometric SiO2 thin films where x = 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 nanocrystallites. The PL intensities of SiOx showed maximum values near x = 2.2. However, those of SiOx/SiO2 films showed maximum values near x = 2.5. This could be understood as a term of averaged concentration. The superlattices with very thin layers, PL exhibits similar tendencies to those of single SiOx films where the x value is same with the average of the two layers. The results of the SiO1.2/2(2 nm)/SiO2(2 nm) superlattice, the average concentration is equivalent to x = 0.6. There was an increase of x = 0.9, 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. Yulin Floven1,2, Vladimir Sadykov1,2, Stavros Kallimahis3, Volodymyr Sereda4,5,6, Benjamin7, E. Bergins8, V. Kolomietsik9, T. Larkin10, M. Messori11, A. Volodin10, I. Tarekova12, Slavisa13, and J. C. Y. Yung12.

1State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, People's Republic of China; 2China National Innovation Foundation for Fundamental Research, Beijing, People's Republic of China; 3Chemical Laboratory of the K. N. Maksimov Institute of Inorganic Chemistry, Novosibirsk, Russian Federation; 4Novosibirsk State University, Novosibirsk, Russian Federation; 5Penn 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 (Cu, Co, 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 PTIRS, SAXS, ESR, UV-Vis DRS, magnetic measurements and nitrogen adsorption-desorption isotherms. Within applied routine, nanoparticles of Zr (Ce) phosphates acquire a low coordination approaching a tetrahedral one while ranging into this of a framework type. Within this framework matrix, Cu and Co cations are isolated. Removal of citric by heating under air at 200 - 300°C preserves the size of nanoparticles while their ordered stacking forms mesoporous structure with the lowest pore size distribution parameters. Electrically conducting nanoparticles of polyaniline (PANI) have been studied extensively owing to their applications in energy conversion devices, sensors, electronic 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 nanofibers. 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 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.


Nanoporous polymeric materials are used as polymer electrodes 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 solvent-mediated precipitation techniques. In these techniques, the final pore size and structural distribution of the material depends upon the thermodynamic pull that the system follows. So, even a small deviation in processing conditions can lead to very 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 nanoscale structures of materials that have better porous size control than the conventional methods is employed in this work. This technique involves the synthesis of nanoscale porous materials by reactive encapsulation of an inert solvent using step-growth crosslinking polymerization technique 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 supramolecular structure. The porosity and pore dimension can be controlled by the amount of solvent. So, potentially, better porous size control can be achieved by using a completely miscible system. The key structural parameter of the resulting porous material 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 were obtained. SAXS results showed that the reactive encapsulation technique can be employed to synthesize nanoscale porous materials of desired pore structure and size by changing the solvent content. The post-chemistry of the nanoscale porous materials 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 nanoscale porous 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.

L1.1.06
Abstract Withdrawn

L1.1.07
Metastable Phase Formation and Stimulated Transitions in Metallic Nanometer Films. Dirk Carl Meyer1, Alexander A. Levin1, Andrei Gortunov2, Stefan Braun, Wolfgang Pomper1, and Peter Pausch1.

L1.1.08
Fabrication of the various oxide nanostructure materials by LDPE method.

SESSION L1.2: Tubes, Rods and Dots
Chair: Sridhar Kommeni
Friday Morning, December 5, 2003
Room 304 (Hyne)

8:30 AM L1.2.1
Anomalous Magnetoresistance Behavior of Biannular Antidot Arrays. Oded Rubin1 and Mildred S Dresselhaus2; 1Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Physics, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A locally-ordered antidot array (an array of circular nanowires) 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 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 ($T=2\text{-}K$) and low magnetic fields ($B=1\text{-}T$). These surprising observations are attributed to the semimetals semiconductor transition and localization effects in low dimensional bismuth systems.

8:45 AM L1.2.2
Synthesis and Structural Characterization of Si Quantum Dots for Non Volatile Memories. Rosaria A Popegi1, G. Nicotra1, S. Lombardo1, C. Spinelli1, C. Gerardi2 and G. Amorendola2; 1CNR-IMM, Catania, Italy; 2Centrale R&D, STMicroelectronics, Catania, Italy.

The ability to synthesize Si nanostructures is an important capability because of the possibility to obtain new functionalities which is novel device for non-volatile memories, or even nanoelectronics. 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 of the deposition parameters, and because of the possibility to obtain isolated storage nodes, immersed in stoichiometric SiOx. 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 distances between them. 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 confluence process between the dots is present. This effect indicates the occurrence of nucleation under steady state as 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 L1.2.3
Self-Assembled Nanostructures Through Spontaneous Phase Decoherence. Ljudmila Malehovskaya-Aranchuk1, Huiwei Zheng2, Surish B. Ogale3, Manfred Wittig2, Ramamoorthy Ramesh1, Beatrice Honig5, Wei Tran3, Xiaogao Pan5 and Samuel E. Lofflard3; 1Materials Science and Engineering, University of Maryland, College Park, Maryland; 2Institut des Matériaux, Université de Rennes, Cedex, France; 3Material Science and Engineering, University of Michigan, Ann Arbor, Michigan; 4Department 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$_2$Sr$_2$Fe$_2$O$_7$ perovskite system as a function of oxygen pressure, using thin film heterogeneity as the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Growth in reducing environments ($80\text{torr}$ 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 La$_2$Sr$_2$Fe$_3$O$_7$. 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 indicate that at high temperatures, the carrier gas flow rate and ZnO film parameters such as film thickness, doping concentration, and substrate temperature significantly influence the growth of ZnO nanostructures. The growth rate is affected by the thermal stability and morphology of the ZnO nanostructures. This effect can be controlled by adjusting the carrier gas flow rate during the synthesis of ZnO via carbotermal reduction process. We have shown that the carrier gas flow rate can be simultaneously affect the reaction rate between ZnO and carbon, the stabilization of ZnO nanotubes using a controlled carrier gas flow rate during synthesis. A seed-twinning mechanism has been proposed to explain the nucleation and growth of ZnO nanotubes. The special structure feature of the ZnO nanotubes 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 Nanocanes Using Three-dimension Diameter Iron/platinum Nanoparticle-catalyst and Their Field Emission Properties. Hongsao Cui¹, Xingjiao Yang², Larry R Bugtry², Michael I Simpson²,²,¹, Walter L Gardner², Douglas H Lowndes², Lei An², and Jie Liu². ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ³Department of Chemistry, Duke University, Durham, North Carolina.

Carbon nanocanes have been synthesized using iron/platinum alloy nanoparticles as catalyst in a direct-current plasma enhanced chemical vapor deposition reactor. The as-synthesized nanocanes 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 nanocanes are highly oriented perpendicularly to the substrate surface, but are much smaller and have different morphology than any previously reported carbon nanotubes. A possible mechanism for the formation of the amorphous internal structure. Experimental results and modeling the field emission properties of carbon nanocanes are also presented.

10:30 AM L12.7

Vanadium dioxide has found a wide range of applications in thermoelectric sensors, optical switching devices, and energy-saving coatings. The present work is focused on the synthesis and characterization of vanadium dioxide nanorods. The morphology and structure of the sample were characterized by XRD, SEM, and TEM. The results show that the products are monocrystalline (C/2ms) V2O5 nanorods and they are 1-2μm in length. The TEM 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 nanorod diameter dimension leads to the exposure of a large fraction of the atoms to the surface, making these materials promising candidates for the development of new functionalized materials. The TEM investigation shows that there are a weight loss of 2.1% between 240-400°C corresponding to the oxidation of the organic residual 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 application of this material.

10:45 AM L12.8

We report the creation of single crystal tungsten nanorods with unusual simple cubic β-phase. These novel nanostructures are grown by oblique angle deposition with substrate rotation [also known as gloating angle deposition (GLAD)] through a physical 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 β-phase W(100) and α-phase W(110) islands exist at the initial stages of growth. However, at later stages of the growth we observe the dominant β-phase structure. This is in contrast to the sputter deposition at normal incidence where only the thermodynamically stable bcc α-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 mechanism. At the initial stages of growth, the β-phase W(100) islands grow taller due to the lower adatom mobility on these islands. The taller β-phase W(100) islands survive in the competition during oblique angle deposition and form isolated nanorods in the later stages, while the smaller α-phase W(110) islands stop growing due to the shadowing effect.

11:00 AM L12.9


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 misorientated surface diffusion and atomic shadowing effects. The shape, orientation, and arrangement are controlled by ion-irradiation and deposition angles. CN, TN, SnN, and TIN layers were grown on MgO at 1100°C by ultra-high-vacuum magnetron sputtering. Atomic and molecular nitrogen was used as a reactive gas. Erionite-type structures result in highly misorientated surface diffusion with hop-rates that are 5 orders of magnitude smaller on (111) versus (001) surfaces. This misorientation leads to kinetic surface roughening and the development of deep surface corrugation, which produces atomic and molecular shadowing and the formation of nanotubes that are elongated along the [001] growth direction. The nanotubes have rectangular cross-sections and form self-organized arrays aligned in orthogonal [100] and [011] directions, precisely replicating the in-plane correlation of the surface morphology.

Non-normal deposition increases the level of atomic shadowing and introduces a controllable tilt to the nanotubes. Increasing the N2+ ion bombardment flux decreases the N2+ partial pressure (and, hence, the steady-state N2+ coverage) during growth provides a corresponding increase of self-shadowing in atomistic surface mobility leading to smoother surfaces, less atomic shadowing, and partial or full suppression of nanotube formation.

11:15 AM L12.10

Polar surfaces induced growth of asymmetric nanocantilever arrays, Xiangkun Kong,1 Jun Lin Wang1, and J. M. Zuo2.

1 School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2 School 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 accumulated normal dipole moment, resulting in divergence in surface energy. Crystals with polar surfaces generally have facets or edges or massive surface constructions to compensate the electrostatic charges 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 sequence of alternating planes composed of fourfold tetrahedral-coordinated O2 and Zn2+ ions, stacked alternately along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (0001)-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 nanocantilever 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 (0001)-O surface typically does not grow nanobelts structure, but controlling experimental condition leads to the growth of nanocantilever arrays of monoclinic and monochorith from the intersections between (0001)-O with (011)-O surfaces. The self-catalyzed process is likely a mechanism for the growth of nanobelts without the presence of foreign metallic catalysts. The nanocantilever array applications as nanosensor arrays and tweezers arrays.

11:30 AM L12.11

Functionalized Carbon Nanotubes As Macromolecular Dops For Electrically Conducting Polymers, Mark Hughes1, George S. Chen1, Miao S. P. Shaffer2, Derek J. Fray3, and Alan H. Windle4; 1 Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, United Kingdom; 2 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 electrophoretic 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 multivalled carbon nanotube (MWNNT) surfaces to functionalization makes them exciting candidates for a new class of dopant for ECPs. In this work, hydroxyl, carboxyl and carboxylic groups are attached to the surface of MWNNTs via an acid-treatment process involving nitric and sulfuric acid. These functional groups give the acid-treated MWNNTs a negative charge, enabling them to provide charge balance for the oxidized ECPs, as do more conventional anionic dopants. Once deposited, the functionalized MWNNTs 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 completely oxidized, the electrical resistance of the neutral polymer prohibited further deposition. However, when using functionalized MWNNTs, their electrical conductivity and high aspect ratio make it possible to grow MWNNT doped ECPs in which the polymer is partially oxidized. This phenomenon is attributed to the formation of an electrically conductive network comprising the MWNNTs and the oxidized layer of ECP adjacent to the functionalized MWNNT surface. The work described here relates to MWNNT-polypyrrole nanocomposite films in which the MWNNTs 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 MWNNTs. A comparison is also made between polypyrrole doped with acid-treated MWNNTs and similarly prepared polypyrrole films doped using large immobile anions such as dodecyl sulfate. Finally, the effect of growing MWNNT-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, Kaushik Ghosh, B. T. Tchekalev, Jeremy Jackson and Yin 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 750°C and a pressure of 50 Torr. The substrate was pre-cleaned with 1.0 μm diamond powder and 15.0μm 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 jettisoned on one section of the substrate in a symmetrical manner. These structures were very hard and when analyzed using Raman spectroscopy and transmission electron microscopy (TEM) they were observed to be multi wall carbon nanotubes (MWNNTs) and nanofibers. An attempt to measure the hardness of the film using a nano-indentor was inconclusive due to the extreme hardness of the material produced.