SYMPOSIUM L

L: Continuous Nanophase and Nanostructured Materials

December 1 - 5, 2003

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Symposium Support
Advanced Nano Products Co. Ltd., Korea
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Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 788
of the Materials Research Society
Proceedings Series
SESSION 1: Textured Films and Composites
Chaired by Sridhar Komarneni
Monday Morning, December 1, 2003
Room 304 (Hynes)

8:30 AM *L.1
Nano-Structured Oxide Ceramic Composites by Solidification of Eutectic Melts, Masahiro Yoshimura, Sumji Araki and Jose M Chaleron-Mondragon, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Generally, most of polycrystalline ceria has to be made from fine powders via their shape forming and sintering or their precursors via pyrolyzing, not via melt/casting. It is believed that melt/solidified ceramic would crack during cooling due to (1) brittle nature of ceramics and (2) residual stress accumulated after solidification. In order to prevent the accumulation of residual stresses, we have tried to make the samples by rapid solidification of the eutectic systems. Since the grain growth of solidified crystals can be minimized in eutectic systems, particularly ternary eutectic ones, this cracking also can be minimized. In the ternary systems of Zirconia (Hafnia)-Alumina-YAG, we have succeeded to fabricate transformable, nanostructured bulk ceramics by just simple solidification of the melt. The samples had no cracking and consisted of 20-100 nm size crystals - ZrO2-9H2O, Al2O3, and YAG. Other ternary eutectic systems have given similar nanostructured composites. Amorphous transparent bulk have been obtained in several ternary systems like ZrO2-A12O3-H2O (40mol%), ZrO2-H2O electrolyte, ZrO2-H2O [perovskites]. Those amorphous could be changed to nano-composites by appropriate annealings. Those ceramic nano-composites are applied for wide areas, structural, functional, and coating materials.

9:00 AM L.1.2


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 ionic conductivity and are tolerant to lower temperatures is essential to improve the efficiency of these devices. It has been established previously that ceria, doped with a divalent or trivalent cation, exhibits higher ionic conductivity compared with yttria-stabilized zirconia, the major component currently used in fuel cells. In a recent study, a nanoscale lamellar structure of calcium and barium fluoride was found to exhibit considerably higher ion conductivity along the interfacial directions at moderate temperatures. In our present study, we investigate a novel approach to increase the ionic conductivity 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 utilizing 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 oxygen ion conductivity, as relatively low temperatures, was found to increase with increasing number of layers in these films. Detailed studies on the influence of multiple interfaces on oxygen ion conduction in these layered oxide films are currently underway.

9:15 AM L.1.3
Formation of Nanosized Metal Grains and Oxide Created by Oxidation of Ag Single Crystals with Hyperthermal Atomic Oxygen, Long Li and Judith C. Yang, Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Atomic oxygen (AO) is considered as a more reactive oxidizing species than molecular oxygen (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 continually reacts with AO. Single Ag crystals (Ag[100], Ag[111]) were exposed to a 5eV hyperthermal atomic oxygen, created by the laser detonation of molecular oxygen at 320°C for 7 hours. Our 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 oxidized layers by high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), and x-ray diffraction (XRD) revealed that this "oxide scale" is composed of nanomaterial polycrystalline silver grains (5-100nm) and nanosized silver oxides, which is remarkably different from the O2 oxidation. The HREM investigation suggests that the formation of this structure was caused by the rapid diffusion of silver from the substrate to oxidize scale, and the first [111] planes are exposed at the material surfaces. Our results indicated that AO could be used to create oxide films containing randomly distributed nanosized metal clusters in an oxide scale.

10:00 AM L.1.4
Assembly of nano-domain building blocks of copper oxalate with a cubic morphology, Lucia Cristina Sorin, Nathalie Jongen, Patrice Rebuffat, Jacques Lemoine, and Henrys Hoffmann, Institute of 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 nanocomposite particles may be prepared by an oxalate co-precipitation followed by the appropriate treatment. The copper oxalate particles are made up of self-assembled nanocrystallites. Cobalt oxalate is expected to exhibit a similar behavior due to its crystallographic structure similar to the copper oxide structure. We synthesized these material by precipitation via an oxalate route followed by an adequate heat treatment. Our first aim is to understand and control the precipitation of copper oxalate before combining it with cobalt oxalate to make a composites. Precipitation of copper oxalate has been investigated in a instrumental and wellcontrolled reactor by following the kinetic parameters to investigate the growth mechanism of the precipitation. The copper oxalate nanoparticles should be made up of self-assembled building blocks. The precipitated particles have been further characterised using various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD). The second aim is to control the transformation of copper oxalate nanocomposites of cubic shape into copper using an isothermal process under a reducing atmosphere. The nanocrystal size is characterised as a function of time as the main challenge is to maintain the particles morphology during the reduction. Preliminary analysis of the model indicates that in 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 oxalate with a cubic morphology. The kinetic analysis of this transformation (Cu-oxalate, Cu-oxide, Copper) will be also presented. The paper will discuss in detail possible mechanism of the particle formation by selforganization of nanosized building blocks and their influence on the morphology as well as on the kinetics of decomposition.

10:15 AM L.1.5
Post Forming Nano-izing of Macroscopic, Technologically Useful, Materials: Role for Microwave and Laser-microwave Hybrid Processes, Rustam 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 nanostructure useful. The commercial utility of nanopowders is limited and cannot justify the research effort being channelled into this field. However, the advances in the 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 (benign 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 dies (10 m. in dia. x 1.5 m. thick), containing 3 or 4 crystalline phases, 1.5 nm in size, is a classic cases. But it is made by forming and shaping the finished product first and then heat treating to introduce the desired nanostructure. This is clearly the most successful route that exists. The true commercial nano-structured, macroscopic process. Based on this perspective, data will be presented on recent remarkable findings on a new approach: utilizing microwave radiation to directly nano-size materials already shaped (~make them 10-2000 times smaller). 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 4d 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 1500W AC magnetic field at 2.45 GHz. Laser and Laser-microwave combinations have also produced similar effects. While the laser decrystallization has been achieved even in single crystals (diamond) and the metal in solid samples, the microwave effects so far have mainly been in compacted powders.

10:45 AM L.1.6
Molecule Derived Nanomaterials: Chemical Concepts for
Composition, Morphology and Particle Size Control. Sung H. Moon and Hoo Shen; CVD Technology, Institute of New Materials, Shapingba, China.

With the advent of nanotechnology, the challenge of achieving chemical homogeneity down to the nanometer scale (lattice engineering) by the conventional material processing methods rather imperative. In view of the practical implications of nanomaterials there is a current need to develop strategies for a controlled growth of nanomaterials. Although it is difficult to divide high-throughput procedure, the chemical methods based on molecular precursors represent one of the viable alternatives for targeted synthesis of nanomaterials with different compositions and microstructures. If the intimate mixing of different elements present in the precursor persists until the desired ceramic or composite crystallizes, the typical problems of material synthesis such as selective crystallization or segregation of one constituent and preferential hydrolysis or pyrolysis of one component can be avoided. Attributing all the elements, required to form the material, in a single molecular compound, can augment the advantages of chemical processing. The major attributes of the so-called single-source approach are: (i) the possibility to tune the cation ratio in the precursor, (ii) phase formation at low temperatures since the atoms are chemically linked, no diffusion of ions is necessary and (iii) low organic contamination due to the liquid/gas elimination mechanisms. To this end, we have developed various molecular sources and examined their single-step conversions to obtain nanoparticles and films of complex oxides (FeO4, GdFe3O4, YFe3O4, Zr2Al2O7, YCaAl2O5, CoFe2O4), biphase metal/oxide composites (GeO/GeO2, Ni/A12O3), oxide-oxide composites (ZrO2/A12O3, NiAl2O4/A12O3), and metal/oxide composite (Ni3Sn4/SnO2), and semiconductor nanowires (Ge, SnO2). The results illustrate that a defined reaction chemistry of the precursors ensures a remarkable control over morphology, composition and particle size. Owing to the structural and compositional versatility, the investigated nanomaterials show interesting properties. A brief account based on the above lines will be presented.

11:00 AM L1.7
Correlation between magnetic and structural properties of nanostructured Co films. Sungyong Park1, H. Zhang1, A. Mira1, M R Fitzsimmons1, J D Thompson1, M F Hundley1, M A Nastasi1, J Showalter1, M F Hall1, Los Alamos National Laboratory, Los Alamos, New Mexico.

Nanostructure multilayers, consisting of a Au/Co/Au/Co (111) architecture on Si(111) substrate, were grown by molecular beam epitaxy in order to study the influence of the interfacial strain on the magnetic properties of the Co layer. The magnetization of an 8 ML Co layer changes from out-of-plane to in-plane when the thickness of the Au underlayer is dropped from 6 ML to 2 ML. We will show that this is due to the difference in 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 highly strained by nitride buffer layers, is partially relaxed with a 2 ML Au layer. In addition, we found the temperature induced magnetization direction change (from in-plane to out-of-plane with cooling below ambient temperatures) for the sample with a 2 ML Au layer and the related mechanism will be discussed.

11:15 AM L1.8
Anomalous Electronic Transport Properties in Nanoscale Cu-Nb Bilayer Films. Michael Hunde1, Amir Mira1, Felix Busser1, Corwin Booth3, Artur Malinowski1, Xinghang Zhang1 and Michael Nastasi1; 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 using magnetron sputtering techniques. 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 nm. For individual layer thicknesses between 2 and 5 nm extremely large, hysteresis-free quantum is present between 150 K and 250 K in both the resistivity and Hall coefficient. The transport normal mode connects a high-temperature T-independent moderate resistance regime (ρ = 10 μΩ cm) with a low-T high-resistance regime (ρ > 10 Ω cm). A stark contrast to the monotonically new, temperature-independent resistivity exhibited by films with layer thickness greater than 5 nm. The anomalously large hysteresis-free quantum is present by most traditional electronic transport 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

Thin films of 20 nm Fe3-xAlxO4 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 of 0.5-50%. Temperature 0.1°C and 1 second exposure 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 by X-Ray Diffraction (XRD) data. Each film showed a significant increase in response time at the α-γ phase transition. Preliminary results at elevated operating temperatures will be discussed.

SESSION 2.2: Characterization
Chair: Nirav Kommena
Monday Afternoon, December 1, 2003
Room 304 (Hyres)

1:30 PM L2.1
Phenomena of Metal Nanoparticle Arrays in Monolithic Silica-Hybrid Polymer Aerogels. Xuefeng Liu, Yu Zhu, Chunhua Yao and William M. Riesen; Chemistry Department, Brown University, Providence, Rhode Island.

Transparent monolithic aerogels based on silica, the bimodified polymer Chitosan, and coordinated iron ions have been employed as a three-dimensional scaffold decorated with Au, Pt and Pd ions. The coordination interacts with the metal ions and the internal gel characteristics control the diffusion rates of ions in the gels so that concentration gradients in one or several of the ions are established in the thickness of the monolith that is produced by supercritical CO2 extraction to form the aerogels. Also in this work, it has been found that the resultant aerogels can be imaged photolytically in two dimensional plane. The spatially controlled photolysis produces nanoparticles, [Au(n) in the range of from 20 to 40 nm for example, that constitute two dimensionally imaged sierag whose volumetric concentration also varies in the third dimension. These images microcavities of aerogels provide a basis for localization and detection of dyes, amino acids and protein molecules. The formation of these arrays and the control over the spatial, light intensity, frequency and exposure, and distribution of ions in the initial aerogel also will be presented.

2:00 PM L2.2
Creation and Characterization of Gold- and Silicon-Nanoparticles inside a Fullerene Lattice. Helge Kroger1, P. Reinke2,1, M Buetter2,2 and P Oehlendorf1,2; 1II. Physik, Universitat Gottingen, Gottingen, Germany; 2Institut fuer Physik, Universitat Basel, Basel, Switzerland.

Fullerenes have been doped with a variety of elements, mainly alcohols 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 fullerene lattice as a template for the self-assembly of ultrasmall clusters (<20 atoms) and the synthesis of porous structures beyond the percolation threshold. Photodetector spectroscopy (PES) was employed to study the electronic properties of the material and interfaces. It supplied information on the barrier heights and fullerene-Si/Au interaction. PES also provides an indirect measure of the cluster size, respectively the extension of the Si or Au regions embedded in the insulating fullerene. The shift of the core level as a function of cluster size was quantified independently of other experiments. The extension of the Au and Si regions is directly controlled by the element concentration and since both, Si and Au interact strongly a function of cluster size quantified independently of the films takes place. The size of the Si and Au regions and electronic 

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confinement in the Au and Si regions. The effect of region/chamber size and interaction with the fullerene matrix on the luminescence spectra and electronics 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 SiC at 700°C. To gain information on the thermal stability of Au nanodots, the as-prepared fullerene surface the layer growth is observed with low electron energy diffraction (LEED) and photoelectron spectroscopy. The feasibility of producing regular three dimensional chamber arrays will be discussed.


Clusters and nanocrystals represent a new class of materials that exhibit properties distinct from their monomeric or bulk counterparts. The production of these nanomaterials in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation, which is typically not possible in other growth modes. The clusters are condensed out of superatmospheric 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 photoelectron microscopy (PES) were performed to investigate the electronic structure of Germanium nanocrystals. We find that submonolayer deposition changes the electronic structure and modifies the properties of the nanocrystals, particularly in the case of the core levels. 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.

3:30 PM L.2.4 Analysis of the Optical Properties of Nanoparticle Sculptured Thin Films by Spectroscopic Mueller Matrix Ellipsometry. Chi Chen1, 2, Nicholas Podraza1, 2, An Iain1, 2, Golo M. Ferreira1, 2, and Collins W. Robert1, 2.

1MateriScience, The Penn State University, University Park, Pennsylvania. 2Department of Physics, The Penn State University, University Park, Pennsylvania.

A multichannel ellipsometer in the dual rotating-compensator configuration has been designed and constructed recently for applications in real time Mueller matrix ellipsometry (~2 to 5 eV) of the fabrication and processing of nanoscopic surfaces and thin films [1]. In our initial applications of this instrument, high speed measurements were performed for Mueller matrices in transmission and reflection for nanoparticle sculptured thin film structures prepared by glancing angle deposition with simultaneous substrate rotation. The Mueller matrix calculations become 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 efficiency of the structural integration the film and the optical devices and sensors. From the 15 elements of the 4x4 Mueller matrix, the real and imaginary parts of the complex matrix elements rpp, rps, and rps (six parameters in all) obtained in transmission (or rpp, rps, and rps obtained in reflection) can be extracted [2]. Multiple independent methods for computing these ratios yield results in excellent agreement. The methods first described by Berreman [4] have been applied to analyze rpp, rps, and rps (or rpp, rps, and rps) and extract structural parameters and optical properties of the films for a nanoparticle chiral thin film, for example, analysis of the transmission amplitude ratios provide the film thickness d, the azimuthal Euler angle φ atan the interface to the substrate (measured with respect to the vertical direction), the number of layers L, and the chirality P. In addition, the optical properties can be determined, including the two principal indices of refraction associated with the form birefringence of the local unimodal structure. Finally, deviations of the film from a perfect chiral nanomaterial can be assessed using a multilayer optical model that incorporates a stepwise variation in the azimuthal Euler angle and unequal uniformities with depth into the film. References [1] R. W. Collins and J. Koh, J. Opt. Soc. Am. A., 12, 1737 (1995). [2] S. Lee, M. W. Collins, and R. W. Collins, Rev. Sci. Instrum., 72, 1742 (2001). [3] C. Chen, Iain An, and R. W. Collins, Phys. Rev. Letter, 90, 217402 (2003) [4] D. W. Berreman, J. Opt. Soc. Am. 52, 902 (1972). Corresponding author: Robert W. Collins, The Penn State University, Material Science Laboratory Research Laboratory, University Park, PA 16802, USA: phone 1-814-8631880, fax: 1-814-8652296, email: rw6@psu.edu.

2:45 PM L.2.5 Self-assembled gold and silver nanorods as surface enhanced Raman active substrates. Soumya Chatterji, H. C Lo1, K. H Chen2, C. H Hsu1 and C. L Chen3, 1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Surface enhanced Raman spectroscopy (SERS) has evolved as a powerful and sensitive tool for detection and identification of a wide range of adsorbate molecules down to the limit of single molecule detection. In this paper we report a nanostructured Si substrate on which silver and gold nanoparticles, with less than 100 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 deposition of Si substrates with ECR evaporation with silicon nitride, hydrogen, and argon gases. These nanotips have lengths of microscopically uniform particles of ~20 nm. The density of these nanorods were extremely high ranging from 10^13/cm^2 to 10^14/cm^2. Gold, silver or platinum when deposited on these nanorods via ion beam sputtering self-assemble into nanometer size particles over the entire surface of these nanotips. This substrate containing the nanorods is termed SERS active. Nanorods such as Rhodamine 6G, BPE and even carbon nanotubes, adsorbed on these substrates show SERS reproducibly. The large surface area of the nanorods and extremely high density of the nanorod substrates is distributed on the substrate to behave as reliable and reproducible SERS active even at very low concentration (10^-12 M) of the molecules under study. The enhancement factors obtained using these substrates are in the range of 10^6 to 10^8.


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 diamond and amorphous diamond is not straightforward. This is due to the resonantly enhanced signal of the non-bonded sp^2-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, ultranano crystalline diamond (UNCD) is an ideal material to probe the effect of the nanostructure and sp^2-carbon content, because the fine grain size (3-8 nm), large number of grain boundaries, and ability to produce a microcrystalline (MCD) or UNCD film structure by varying the deposition parameters. Comparisons of the visible and UV Raman analysis with near edge x-ray absorption fine structure (NEXAFS) and transmission electron microscopy (TEM) measurements on a series of MCD and UNCD films provide important insights toward understanding the Raman spectrum of UNCD. We find that although the sample has ~55% sp^2-bonded carbon by NEXAFS and TEM, none of the spectral features seen using visible Raman spectroscopy can be attributed to sp^2-carbon. Our current work shows that the visible Raman spectra provide information solely on the bonding structure of the disordered carbon at the grain boundaries of UNCD. This allows us to understand the changes in the Raman spectrum of UNCD grown under different conditions, where the Raman signal is found to change drastically with little concurrent change in the nanostructure of the film. This work was supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.


Existing techniques for determining the mean crystallite size in nanocrystalline materials include electron microcopy Scheerer analysis of x-ray diffractograms, dynamic light scattering, and transmission x-ray absorption fine structure (EXAFS). When applied to samples containing a polydisperse distribution of nanocrystals 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 analysis generally yields a crystalline size near the high end of the actual distribution, while the Rietveld method yields a crystalline size near the low end. Together the two techniques therefore provide a more complete picture of the size distribution, including a rough measure of polydispersion. It will also be shown that in certain nanocrystalline samples, transmission electron microscopy can provide further insights into the nature of the crystallites, making EXAFS a valuable adjunct in these cases as well.

3:45 PM 12.8
Atom Probe Tomography of Thin Film Multilayers.
Gregory B Thompson, M K Miller and H L Fraser, Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama; Metal and Ceramic Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 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 led to a compositional interdiffusion in the Ti layers to a pseudo-equilibrium concentration of approximately Ti15.5Nb85. The Ti layers while maintaining a compositionally modulated interface. In contrast, the hcp Ti layers indicated a limited Nb interdiffusion within the layers. He no interdiffusion was observed within the Nb layers.

Thermodynamic volumetric free energy modeling has shown that this unexpected Nb interdiffusion has helped to facilitate the bcc phase stability in this system to a larger critical layer thickness than previous predictions. The coupling of APT results to the pseudomorphic bcc Ti phase demonstrates the capability APT has in quantifying the compositional characteristics in these types of multilayered nanocomposite systems.

Research at the SHALE User Center was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00 PM 12.9
Spin-dependent STM tunnelling study of the polaronic nanostructure pattern on magnetite (111) surface.
Nikolai Berdineau, Shane Murphy, Guido Marzotto 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 bicrystals is formed in 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 lattice strain. We deduced the details of the electronic structure of the polaronic pattern. Spin-polarized (SP) STM with magnetic tip was employed to study the electronic and magnetic properties of the nanostructure pattern. SP-STM results demonstrate significant interdiffusion 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 can be employed to explain the SP-STM results. 1. Berdineau,N., Murphy,S., Marzotto,G., Shvets,I.V., Formation of a strain-induced polaronic superlattice on a magnetite (111) surface, 2003, submitted to PRB.

4:15 PM 12.10
Percolation in Multi-Wall Carbon Nanotube-Epoxy Composites: Compositional dependence of percolation parameters, nanotube aspect ratio and electric fields on the bulk conductivity.
Jan Sandel, Christian A. Martin, S. Milo S. Shaffer.

Matthias-Klaus Schwarz1, Wolfgang Brabec2, Karl Schier1 and Alan H. Windle3, 1Materials Science and Metallurgy, Cambridge University, Cambridge; 2Chemistry, Imperial College London, London, United Kingdom; 3Materials in Electrical Engineering and Optics, Technical University Hamburg-Harburg, Hamburg, Germany; 4Polymer Composites, Technical University Hamburg-Harburg, Hamburg, Germany.

In a recent study we have shown that the use of aligned CVD-grown multi-wall carbon nanotubes (MWCNT) leads to electrical percolation thresholds in an epoxy matrix of about 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 insitu 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(-3) 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 ratio were produced and analysed with regard to the electrical properties. For Nb in the range of 290 and 2900 the Nb formation 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 computer theory are applied in order to explain the results. Additionally, the influences of applied electric fields during curing of the samples was studied. For both AC and DC voltages the network formation was measured during the power on in the samples between electrodes sputtered onto optical microscopy slides and bulk samples. Light microscopy was applied to follow the network formation as a function of the applied field. The results are compared to the behaviour of carbon black in the epoxy matrix.

4:30 PM 12.11
High-resolution Analytical Electron Microscopy Investigation of Motastable Tetragonal Phase Stabilization in Undoped Sol-Gel Derived Zirconia Nanoceramics. Vladimir P. Olesiuk1, James M. Howe1, Sayajit Sukhia1 and Sudip A. Seal2,1Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; 2Advanced Materials Processing and Analysis Center & Mechanical Materials Aerospace Engineering Department, University of Central Florida, Orlando, Florida.

The mechanisms underlying stabilization of the metastable tetragonal (t-phase in undoped, monoclinic crystalline ZrO2 ceramics were studied by high-resolution field-emission analytical electron microscopy, utilizing parallel electron-energy loss (PEEL) and energy-dispersive X-ray microspectroscopy. The as-prepared ZrO2 ceramics were sol-gel derived by hydrolysis of zirconium (IV) n-propoxide in the presence of trace amounts 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 200x500 nm in size that appeared amorhous. 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 (400x600 nm in size) and composed of 15-30 nm sized t-phase crystallites. The as-prepared ZrO2 powder (R=60) contained primary 4-11 nm sized particles with an amorhous structure that formed aggregates (~50-100 nm in size). Calcination of this sample lead to a mixture of t- and monoclinic (m) ZrO2 agglomerated nanocrystals 8-10 nm in size. The net PEEL intensity from the nanopowders matched the expected position of a direct band gap for ZrO2 between 4-5 eV energy losses. For the as-prepared nanopowder (R=60), the intensity threshold was less pronounced due to a number of geometric factors. The spectra of the ZrO2 band structure in the low-loss and inner-shell PEEL spectra allow differentiation between the amorhous-like and monoclinic/tetragonal ZrO2 ceramics. Stabilization of nanocrystallites of t-phase in the amorphous ZrO2 particles with sizes 3-10 nm has not previously reported is likely due to strain-induced size confinement from surrounding growing crystals, which suppresses the volume expansion associated with the metastable t-m phase transformation. Local spherical agglomerates of 10-50 nm nanoparticles synthesized with a high R-value cannot suppress the t-m transformation. In this case, the
tphase may be partially stabilized due to a crystalline size effect and/or to the simultaneous presence of m-phase.

13.1 The Effects of Cs Intercalation on the Raman Modes of Single-Wall Carbon Nanotubes. Brham Alkim1, Xiaofeng Du1, and Ruth Pechter1, 2. Materials and Manufacturing Directorate, AFRL, WPAFB, Ohio; 2. ASC MSRC, AFRL, WPAFB, Ohio.

It was previously shown that alkali metal doping of single-wall carbon nanotubes results in low-frequency peaks assigned to modes involving both radial motions of the tubes and alkali-atom vibrations [N. Bendib, 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.


Endoped Si3N4, Pedoped Si3N4, P-doped Si rich SiO2 thin films are prepared. Photoluminescence (PL) spectra for visible and infrared are obtained for each as-deposited film. The samples are annealed by steps to different temperatures within the range 600°C-1100°C for 30 minutes at each annealing temperature. PL spectra are obtained at each step and their characteristics are studied. The best annealing temperature for the PL of the rare earth (RE) ions is obtained. PL is reported for the 3T1/2→3H1/2 (1332 nm) and 6T1/2→6H1/2 (980 nm) transitions of Er3+ in the Er-doped film. PL is reported for the 3F4→3H6 (650 nm) transition of Pr3+ for the Pr-doped film. The Er:Pr-co-doped film exhibits PL from both rare-earth ions. The PL spectra of the films are compared with one another to determine how the co-doping with both rare-earth ions affects the PL of each.


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

13.4 Nanoparticle NO in an SiO2 Matrix for CO Sensing Using Optical and Electrical Conductivity Transduction. Mike Post1, Alex Martucci2, Massimo Guglielmi3 and Carlo Cantalini1, 2. National Research Council of Canada, Ottawa, Ontario, Canada; 3. Dipartimento di Ingegneria Meccanica S. Mattioli, Università di Padova, Padova, Italy; 4. Dipartimento di Chimica e dei Materiali, Università 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 NO imbibed in a porous SiO2 matrix has been studied for the application of carbon monoxide monoxide sensing. Thin films of the NO/SiO2 composite have been prepared using solgel techniques and a dip coating method. A range of NO concentrations (10% to 40% NO) in the matrix have been prepared, and these have been subjected to a series of controlled post treatment at selected temperatures in the range 500°C to 900°C. TEM imaging reveals NO nanoparticle of size ~2.5nm with a narrow size distribution and which are homogenously dispersed in the SiO2 matrix. When the films are not preheated above 200°C and exposed to CO, a fast and reversible increase in optical transmittance takes place. This effect has been studied in the wavelength range 410nm to 910nm and for CO concentrations from 100ppm to 1%. Reported here will be a description of the apparatus used for the in-situ CO exposure experiments and the results of the optical transmittance study. The relationship which exists between the sensor response characteristics and the degree of densification in the SiO2 matrix, which is produced by the thermal post-treatment, will 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.


Amorphous helical SiO2 nanoparticles (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 nanowires was performed. A growth model was proposed for the formation of these novel nanostructures based on the detailed structural characterization. Present study suggested that these nanoparticles may have great potential for applications related to nanomechanical and nanoelectronic devices.


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

13.7 Electrical Response to Different Gases of Nanostuctured...
YCoO$_{2+y}$ and Y$_{1-x}$Sr$_x$CoO$_{2+y}$ Prepared by a Solution Method. Carlos R. Michel$^1$, Aldo Saul Grago$^1$, Chudin Cristina Lacer$^2$ and Arturo Chavez-Chavez$^3$, $^1$Physics, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico, $^2$Inorganic Chemistry, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

In recent years, cobaltates with perovskite-type structure have received a lot of attention for their applications in fields like ceramic membranes for oxygen separation and cathodes for nitric oxide reduction$^{1-2}$. Among these cobaltates, the members of the solid solution La$_{1-x}$Sr$_x$CoO$_{2+y}$ have been the most studied compounds in this field, due to their superionic properties. These oxides are characterized to be non-stoichiometric, with cobalt 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 nanocrystalline YCoO$_{2+y}$ and Y$_{0.9}$Sr$_{0.1}$CoO$_{2+y}$ 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$_3$)$_2$ in an aqueous media containing urea. The precursor resins obtained from the solutions after heating to dryness, were analyzed by DTA and TGA, and they were also thermally decomposed in a tubular furnace in a temperature range from 300°C to 900°C in air. X-ray powder diffraction was performed in samples calcined every 100°C in order to identify the formation mechanism from an amorphous phase to the perovskite. Pure samples of YCoO$_{2+y}$ and Y$_{0.9}$Sr$_{0.1}$CoO$_{2+y}$ 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. Nanocrystalline thick films were made by the screen printing method and dense pellets using a slurry containing urea as a sintering agent to prevent the formation of a semiconductor behavior from room temperature to 700°C. The electrical response of these perovskites to different gases was also measured in the same temperature range, and the results were compared with those obtained from the La$_{1-x}$Sr$_x$CoO$_{2+y}$ Refs. 1: Hwang K., Goedcough J.B. J. Electrochem. Soc. 138, (5) E203 (2001). 2: Kimerling Hansen K., Skou E.M., Christensen H. J. Electrochem. Soc. 147, (5) 2007 (2000).

L3.8 Gas-sensing properties of SnO$_2$ nanno electrode array. Masanori Uno$^1$, Tawiyoshi Hamauchi$^2$, Nobuhiko Yabuki$^1$, K. Akido$^1$, I. Ieda$^1$, Tomonori Nakata$^3$, Mokoto Egashira$^3$, Yasuhito Shimizu$^3$ and Takaaki Hyodo$^1$, $^1$Department of Materials Science and Engineering, Nagasaki University, Sasebo, Japan, $^2$Department of Materials Science and Engineering, Nagasaki University, Bunkyo-machi, Nagasaki, Japan.

The SnO$_2$ nanno electrode arrays have been prepared by spraying aminon in ammonium hexafluoroorominate solution at room temperature for a few hours. Pt, Au, and Pd electrodes were sputtered on the tin oxide nanno electrodes. H$_2$ and NO$_2$ gas sensing properties of SnO$_2$ nanno electrode sensors have been evaluated in dry air at 350°C or 500°C. In the case of H$_2$, every sensor showed quick response to H$_2$ but fairly low sensitivity. On the other hand, Pt, Au and Pd sensors showed high sensitivity at 500°C, and the sensitivity 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. Guangzhong Li$^1$, Chemical Engineering, Tsinghua University, Beijing, China$^2$, Chemical Engineering, Tsinghua University, Beijing, China.

A new emulsion method to prepare adjustable, robust mesoporous materials with controllable pore sizes has been developed in the present work. The synthetic conditions including emulsion types, PEG chain lengths, PEG concentrations, duration of aging, and the time when the swelling agents were added to the crystallization solution 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 nearly spherical shape with decreased size and less agglomeration. The results showed that the interior and exterior structures of the particles were both controlled very well with an emulsion as the preparation condition. The particles prepared with the new method were uniform and compared to those with the hydrothermal method and not prone to agglomerate. Compared the results of c/w emulsion with those of w/o emulsion, it could be seen that the former was superior for both in the particle morphology although the latter should be theoretically more suitable for the optimization of the particle size for its averge water droplets 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.

L3.10 Controlled Hierarchical Pore Structures in Ethylene-Bridged Polybisquinoxalines Gels. Kazuki Nakamish$^1$, Yuki Kobayashi$^2$, and Kazuhiro Hira$^1$. $^1$Material Chemistry, Kyoto University, Kyoto, Japan; $^2$PREFST, JST, Kawaguchi, Saitama, Japan.

Beautiful examples of supramolecularly templated bridged polybisquinoxalines 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 has been performed via spinooidal decomposition of gelation bis(trimethylethyl)ether of BTME system has been attempted. The incorporation of cationic surfactant such as CTAB unexpectedly turned out to be ineffective to induce the phase separation which leads to the formation of micrometer-range co-continuous morphologies, as far as the starting composition is chosen to form homogeneous monolithic gels. Triloblock copolymer, EOPOEO, is also known to induce phase separation in tetramethoxysilane, TMOS, system because of its strong hydrogen-bonding interaction between silanol groups. It was found that triloblock copolymer, L121, P123, and F127 induce phase separation in BTME systems to result in co-continuous microporous structure in limited composition ranges. The pore size distribution in the nanometer range, however, depended strongly upon the length of terminal PEO chains used for preparing the core PPO chain. That is, cylindrical pores of ca. 4 nm in diameter formed only when P123 was used as a template, while possibility lamellishaped mesopores in addition to major micropores were formed in the cases of L121 and F127, in the BTME-F127 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 copolymer have identical lengths of PEO, 70 units, and different lengths of PEO, 5, 20 and 106 units for L121, P123 and F127, respectively. It is therefore presumed that the mesoporous templating in monomeric BTME-derived gels is effective only with surfactants having strong enough hydrophobic segments 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. Yukihiro Yamamoto$^1$, Shinjiro Nagare$^2$ and Masaomi Senna$^3$, $^1$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 substrate of the thickness of 20 µm. The SPR spectrum was evaluated in terms of size distribution, volume fraction and degree of assembly of Ag nanodots. Characteristics of the nanoComposite films were monitored quantitatively by measuring the changes in the Ag surface plasmon resonance (SPR) absorption, by using transmission UV/Vis spectroscopy. Properties of SPR at around 400nm were examined in terms of the structure and distribution of the dots, as well as the dielectric properties of the matrix. Control of these properties was elucidated by systematically varying the operation parameters of PLD, e.g. gas species (N$_2$, Ar, He), pressure (between 6mPa and 1kPa) in the chamber. Optimization of operational conditions given above, and target preparation for controlled dot assembly, and hence sharp and strong plasmon resonance was explored.

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

Octahedral tungsten sulfide clusters of the form W$_x$S$_y$Se$_z$ (L = n- or P- based ligand) can be viewed as building blocks for inorganic-organic networks. Such architectures have the potential for creating electronic and magnetic properties stemming from linker-mediated cluster-cluster interactions. Two new approaches to network formation via ligand-ligand interactions and varying ligand binding strengths to direct linkage of clusters. Use of ligands such as xanomalonamide and xanomalonate that are capable of hydrogen bonding can induce intermolecular forces among clusters and provide a non-covalently linking clusters. Linkage may also be directed by use of both labile and relatively inert ligands. The inert cluster compounds W$_x$S$_y$[bis(diphenylphosphino)methyl]ethane] and
We have synthesized and characterized various nanomaterials that have been used in numerous studies for their unique properties and potential applications. These materials include magnetic nanoparticles, semiconductor nanocrystals, and carbon nanotubes, among others. The synthesis and characterization of these materials are crucial for understanding their physical and chemical properties. In this section, we will discuss the magnetic properties of FeCo nanocompounds and the development of a new method for fabricating ultrathin film nanomaterials. We will also explore the potential applications of these materials in various fields, such as catalysis, electronics, and medicine. The synthesis and characterization of these materials are complex processes that require careful control of various parameters.

1.3.3 Magnetic Properties of Nanocrystalline Fe₃Co Materials. Maziar Shariati, Shahriar Shafiei, Iraj Haji, and Trung Pham, Institute of Chemical Engineering, Dartmouth College, Hanover, New Hampshire.

Nanocrystalline powders of stoichiometric Fe₃Co were measured using a commercial vibrating sample magnetometer. The particles were characterized using X-ray diffraction and scanning electron microscopy (SEM). The results showed that the particles were well dispersed and had a high magnetic moment. The magnetic properties of the Fe₃Co nanoparticles were found to be dependent on the synthesis method and the size of the particles.

1.3.4 Beam-coupled Nanomaterials for Nanocomposites Application. Terry T. Xu, Frank T. Fisher, and Rodney J. Roust, Department of Mechanical Engineering, Northwestern University, Evanston, Illinois.

A novel beam-coupled nanocomposite process is described. This process involves the coupling of laser beams with nanoscale components to create composite materials with unique properties. The process is well suited for the fabrication of nanocomposites with high mechanical and thermal stability.

1.3.5 Preparation and Oxidation Activity of Gold Cluster/Aerogel Nanocomposites. Nupur Tal 1, Koji Fujiki 1, Junichi Murakami 1, and Masakata Haruta 1, 2, 3, 4, 5 Institute for Structural and Engineering Materials, AIST Chubu, Nagoya, Aichi, Japan; 1, 2, 3, 4, 5 Institute of Materials Research, Tohoku University, Sendai, Japan.

Golden clusters have been used as catalysts in various applications, including hydrogenation, oxidation, and reduction reactions. In this study, we investigated the effect of gold cluster composition on the oxidation activity of gold cluster/aerogel nanocomposites. We found that the nanocomposites had a high activity for the oxidation of organic compounds, which was attributed to the combination of gold clusters and aerogels.

1.3.6 Synthesis and Characterization of GaN Nanowires by Chemical Vapor Deposition Using Co Catalyst. Young Heon Kim 1, Seung Chul Lyu 2, Moon Youl Jung 3, and Cheol Jin Lee 1, 4; 1 Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; 2 Department of Nanotechnology, Hanyang University, Seoul, South Korea.

Gallium nitride (GaN) nanowires are one of the most promising materials for high-frequency and high-power electronic devices. In this study, we investigated the growth and characterization of GaN nanowires using chemical vapor deposition (CVD) with Co as a catalyst. We found that the nanowires had a high crystalline quality and a high density, which makes them suitable for various electronic applications.
chemical vapor deposition. In this experiment, CNTs grow on Si substrates and controlling the growth of CNTs is done by chemical vapor deposition (CVD).


One of key factors for growth of carbon nanotubes (CNTs) using thermal chemical vapor deposition (CVD) is transition metal as catalyst. Nanoparticles, which serve as catalyst for CNT growth, should be formed from metal layer with a shape of thin film, by pre-treatment processes such as thermal annealing or ammonia (NH3) 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. CNT nanoparticles with a uniform size of 8 nm were synthesized by thermal decomposition process and colloidal solution was 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 mole concentration of the colloidal solution. CNTs with a uniform diameter were synthesized on the Co nanoparticles by thermal CVD of acetylene (C2H2) 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 Solventothermal Ion-exchange of Layered Double Hydroxide Nanocrystals. Jong Hyeon Lee, Hyejin Nam, Jungseong Lee, SeongWoo Rhee and Duk Young Jung. Chemistry, Sungkyunkwan University, Suwon, South Korea; The Ohio State University, Columbus. Ohio, USA.

A novel method to immobilize nanocrystals of layered double hydroxide (LDH) on the Si substrates and to intercalate dicarboxylic ions into interlayer space of fixed LDH nanocrystals by solventothermal treatment is described. The orientation-controlled LDH crystal assembly on solid substrates is considered as nano-sized chemical actuators, chemically controllable by altering anion species utilized. The AFM and XRD studies for the immobilized LDH crystals provide us with snapshots of the intercalation reaction followed by the anisotropic layer expansion. The basal spacing after the anion exchange reaction was significantly changed in comparison with the SrMgAl-LDH. The AFM results present the as-synthesized 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, and their measured diameters of LDH crystals remain constant. The heights of anion exchanged MgAlLDH crystals dramatically expanded, corresponding to the ratio of basal spacing values based on the X-ray diffraction data. The results gave several viewpoints 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 - Glyceromaminoglycan Nano Composite Sol Under Well Controlled Condition. Yoko Ishikawa and Masanori Soma; Faculty of Science and Technology, Keio University, Yokohama, Japan.

Hydroxyapatite (HAp) glyceromaminoglycan (GAG) nano composite sol was prepared or silica sols by a modification method from CA(Si2)2 or CH3(3)(SiCO)8(2)Ca and H3(3)(SiOPO4)(2) or NH4(Si4)(3)8(2) HIPO4(4)8 These soluble Ca sources were used in order to increase the number of nucleation sites for HAp on GaAs. Hydrolytic acid, chondroitin sulfate and its deacetylated product were used as GAGs. Starting materials were supplied by two kinds of processes to give solution only by PO4(4)2(2)8 or, by PO4(4)2(2)8(3)8 and Ca(3)2(8)3(8) dropwise into GAG solution containing Ca(3)2(8)3(8) to elucidate the details of nucleation mechanism of HAp. Morphology of the aggregates and crystallize size as well as lattice parameters of the HAp were examined by TEM and XRD. Rietveld refinement observed needle like aggregates of crystallite of HAp. The aspect ratio of the aggregates and HAp crystallite size was controlled by supplying processes of Ca sources. Lattice parameters of the samples prepared from Ca(Si2)2 shifted toward those of chondroitin. These from (CH3(3)[3]COO)8(2)Ca, however, corresponds to theoretical values of HAp. The results of FT-IR spectra and the changes of rheological property indicate the electrostatic interactions between negatively charged functional groups of GAGs and HAp.

L3.22 Preparation And Control Of The Microstructures Of Protein Thin Film Deposited Via Laser Ablation And Colloidal Chemical Routes. Segur Nakayama, Ichiro Takatori, Sanshiro Nagao and Masanori Soma; Faculty of Science and Technology, Keio University, Yokohama, Japan; Nara Machine Co., Ltd., Tokyo, Japan.

Protein thin film (mainly silk fibroin) was prepared by pulsed laser deposition (PLD) and dip spin coating. Microstructures of the deposited film, i.e. film thickness, surface roughness, crystallinity, were studied by TEM, AFM, and thin film XRD. Hot pressing conditions for target preparation and PLD conditions with a uniform diameter were selected in order to obtain high crystallinity. The as-deposited film was examined by FTIR. The PLD film properties were compared with those deposited with colloidal chemical routes in terms of their microstructures, interactions with the substrate, and the surface chemical states.

L3.23 Fast Deposition of Structured Coatings from Microswarm and Nanoparticles. Brian Prevo, Ruben G. Carbonell 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 devise 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 advantage afforded by this technique are improved process efficiency and reduced material consumption at scaled dip coating techniques. Structured coatings larger than 1 m2 are deposited in minutes from aqueous suspension volumes of approximately 10 microliters. Three different systems were studied: layered colloidal crystals, thin metallic colloidal coatings and structured porous nanoparticle coatings obtained via microsphere templating. The governing mechanism of particle deposition is convective assembly at high volume fractions. The most accessible and easily controlled process parameters are the deposition speed and particle volume fraction. Varying these parameters provided the means to control and tune coating thickness, structure and properties. A volumetric flow balance incorporating the evaporating solvent and assembling particle fluxes was used to derive 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. Grzegor Sigalow and Anna C. Balaz; Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Self-assembly in a nanocomposite material that consists of an AB block copolymer filled with coated spherical nanoparticles is studied with the help of a combined Small-Constant 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, and enthalpic forces. As a result of the effective pair interaction of carbon particles immersed in block copolymer is calculated using the SCFT technique. A Pickard-type iterative procedure is improved by using variable iteration steps and some elements of the conjugate 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 system is analyzed using DFT approach. We know how, 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-fill/block copolymer composite material. The above approach may be instrumental in design and synthesis of ‘smart’ nanostructured materials for various applications.

13.25

Magnetic Nanoparticle as A Solid Support in Various Reactions. Dongwook Ye, Ting-Jong Yoon, Jin-Jung Han and Jin-Kyu Lee; School of Chemistry and Molecular Engineering, Seoul National University, Seoul, South Korea.

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

13.26

Hydrothermal synthesis of ZnO on Silicon and Alumina. Cheong T. H. S. Choy, S. Ting, And Y. C. Y. Choy; Chemistry, National University of Singapore, Singapore, Singapore.

Hydrothermal synthesis of ZnO on silicon, C-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 solutions due to the growth of hemimorphite (Zn2Si2O7·(OH)) (H2O) Crystall. A thin layer of petal-like nanocrystals with aligned perpendicular to the substrate was used as a so-called buffer layer for the growth of a secondary layer of hemimorphite crystals. On alumina or sapphire substrate however, pure ZnO nanorods which exhibit sharp exciton emission peaks in the photoluminescence spectra could be grown.

13.27

Ce:LiF:Zr x O2 Solid solutions made by liquid-fed flame spray pyrolysis. Mi Kim, Julien Marder and Liane M Richard; Materials science and engineering, Univ. of Michigan, Ann Arbor, Michigan.

We describe here the synthesis of nanoceramics in the Ce: LiF:Zr x O2 system by liquid-fed flame spray pyrolysis (LF-FSP) for applications in three-way exhaust catalysts (TWCs) and diesel emission control. Through the choice of the correct precursor chemistry, we are able to produce Ce: LiF:Zr x O2 materials within the space phase. 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.

13.28

Beyond Imaging: Detailed Simulation of NSOM images. Sungmin Kim and Venkatraman Gopalan; 1Materi. 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 nonparallel ferroelectric domain walls in a lithium niobate (LiNbO3) single crystal. To simulate these images, Finite Difference Time Domain (FDTD) method is applied near the NSOM tip area in the near-field light propagation region, and the Beam Propagation Method (BPM) method is used in the far-field propagation region. The fiber 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 excitation wave. The phase of the OTF is found via the FDTD approach. The OTF is calculated for each individual plane wave, we can successfully calculate the NSOM OTF. We mathematically prove that this OTF simulation and OTF are equivalent under this condition. Therefore, we can calculate the field distribution under the sample surface, we can extract final image by using OTF. The agreement between theory and experiments is excellent. The local refractive index profile across the wall is extracted also.

13.29

Growth and Generation of Nanoparticles during Sol-Gel Synthesis. Nar Yoo 1, King Lam Yung 2, and Guo Xiong 2, 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 an established method for preparation of advanced materials including ceramics, catalysts and functional nanomaterials. The genesis and growth of the nanoparticles during sol-gel synthesis are affected by factors that determine the final properties of the material. This phenomenon was 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] was often deduced from indirect methods, rather than from direct observation. This paper demonstrates the use of atomic force microscopy (AFM) for in situ observation of the nanoscale morphological transformations that occur during the solgel process. Recently, it has been reported that mesoporous metal oxide catalysts with narrow pore size distribution at mesopore region could be prepared using a new templateless method based on a modification of traditional sol-gel technique. The structural evolution during the sol-gel synthesis of mesoporous silica, alumina and silica-alumina catalysts were observed using AFM. The formation of fractal structure is strongly correlated with the silica-content of the sample. Both silica and silica-alumina samples displayed fractal growth forming intricate branched structures. The branches consisted of nanometer-sized clusters that exhibit complex structural transformations that include coarsening, osydal 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 amorphous alumina into a polydisperse 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.

13.30

Incorporation of Functional Metal Oxide Materials in Chemical Microsystems. Nan Yoo and King Lam Yung; Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Recent advances in the design and fabrication of microreactors, microreactors and microreactors 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 easy scale-up through replication. This enables rapid product deployment to the marketplace as well as raising a significant competitive edge. One of the important issues in chemical microsystem is the proper incorporation of functional nanoparticles (e.g., catalysts, adsorbents, and membranes) within the microchannel architecture. Metal and metal oxide thin films can be deposited using traditional microfabrication methods of thermal deposition, chemical vapor deposition and sputter coating. However, in 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 facile incorporation of mesoporous TiO2 catalysts (silicon microchannel). Using a modified sol-gel method, TiO2 aerogel was deposited into the microchannel from a TiO2 colloidal. Precise control over the sol-gel process within the confined environment of the microchannel is a must. Synthesis conditions were adjusted to obtain better aerogel adhesion to the microchannel wall and control the shrinkage of the wet gel during drying. After temperature treatment,
a complex aerogel network filled the microchannel. The structure and density of the aerogel network was dictated by the composition of the original aerogel. The length of the microchannel was tested under flow conditions and the activity of the TiO(2) was evaluated for photocatalytic destruction of methyl orange dye in aqueous solution. Monolithic TiO(2) with ordered and disordered nanopores were also prepared using a template method. Polymer microspheres were used as template material to create the macroporous materials. Comparison indicated that monolithic TiO(2) provides lower pressure drop, while maximizing the contact area between catalyst and reaction mixture.

L3.31


Very few attempts have been made to investigate nano-scale behavior of glass at high temperatures, but glass materials controlled at the nano-scale have possibility to develop new functionalities of nano-electronics. Softening behavior and viscous flow resulting from the supercooling state, which is 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 5μm thick) of soda lime silicate glass were deposited by pulsed laser deposition method using the glass target onto the ultrasmooth sapphire substrates, which have atomic steps of 0.2nm in height and ultrasmooth terraces of 50~100nm in width. These sapphire substrates were obtained by annealing in air at 1000°C (Argi Physics. Lett. Vol. 67 (1980) 216). 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 becomes remarkable just over the glass transition temperature. Furthermore, the surface morphology of the annealed glass film reflected the nano-structured structure of the sapphire substrate. The nano-structured surface was verified by scanning electron microscopy (SEM) from the halation pattern of the reflected 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 micro-scale 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.

L3.32

Sintered Tantalum and Niobium Sub-micron Powders of Solid Electrolyte Capacitors. Yuri Pareskev-Freeman 1, Alexander Gladkikh 2, 3, Yavuz-Sengur 2, Surfof, Maine; 2Wolfin Applied Materials Research Centre, Tel Aviv University, Tel Aviv, Israel.

Sintered tantalum and niobium sub-micron powders are widely used in modern electronic as porous modes of Ta and Nb solid electrolyte capacitors. Due to high surface area of the mode, these capacitors demonstrate excellent specific charge per unit of their volume. At the same time, several factors such as the DC leakage of the dielectric, anodic oxide film of Ta, 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 this contribution and differences in the capacitance, performance and failures. It is shown that a different ability of Ta and Nb metal powder to formation and decomposition of oxygen solid solution during high temperature processing may be critical for stability of the interface between metal anode and oxide dielectric. Both Ta and Nb original powders are very clear 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 20nm on their surface. Sintering of the powder into pellet at temperature about 1200°C dissolves oxygen from the amorphous surface oxide into the powder metal; and this effect is strong due to a high surface to volume ratio. After sintering, in the case of Ta, oxygen remaining 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 dense, with lattice parameter close to its original value. The effects of dissolving of oxygen and phase transformations in the sintered Ta and Nb powders on structure, current-voltage, current-temperature, and capacitance-voltage characteristics of the dielectric oxide film formed of their surface are discussed.

L3.33

Pb on Ge(111) 2D growth mode. Fabio Rateo 1, 3, Alberto Merlini 1, 3, Laura Fronzetti 4, 3, Federico Bradey 2, 3.

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The study of the 2D Frank-Kasper de Merwe growth mode of thin metallic films on insulating substrates has been receiving a continuously increasing interest, both for technological applications and for purely scientific motivations. In particular, the Pb on Ge(111) system has always been considered as a model system for the singling out and characterization of the elements determining the Schottky barrier height. Nevertheless, due to the anomalous properties of thin layers [1], merely basic scientific studies have recently been carried out, mostly of the attention. According to different theoretical simulations [2, 3], variations in the electronic and morphological properties of the growing metallic film are expected to be, 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 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 structural surface and of the statistics of the island distribution, during the whole stage of the growth process. As an example, the physical model we adopted allows to obtain a convincing determination of the most interesting geometrical features of the topmost exposed layers in the deposited Pb on Ge(111) films. The interpretation of the experimental data and of the subsequent analysis clearly points to the appearance of structural QSEs, likely driven by the occurrence of electronic QSEs. [1] F. Rateo, Ms Thesis in Physics (2002); [2] F. K. Schulte, Surf. Sci. 55, 427 (1976); [3] P. J. Feibelman, D. R. Hamann, Phys. Rev. B 29, 4603 (1984); [4] A. Crottini, D. Creto, L. Floriano, R. Goret, A. Morgante, F. Tumminni, Phys. Rev. Lett. 79, 1527 (1997); [5] C. S. Lent, P. I. Cohen, Surf. Sci. 139, 121 (1984).

L3.34

Structuring Of Silicon Wafer Surfaces On The Sub-100 nm Scale By Hydrogen Plasma Treatments. Reinhart Job and Alexander G. Uybach. Department of Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany.

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

L3.35


Cr(V) doped olivines (forsterite, candeite etc) emit in the 1100 to 1600 nm spectral range. Controlled ceramization procedure of an appropriate glass may produce transparent glass-ceramics with embedded nano-crystallites of Cr(IV) doped olivines. Glass forming ability and devitrification behavior of Cr-Ge-B-O compositions is
studied using Differential thermal analysis and X-ray diffraction. Surface crystallization of Cr(VI)/Cr2O3 showed was observed for a number of Cr-GO oxide composites. We are studying the kinetics of the nucleation and growth process of Cr(VI) doped laser crystallites, in Gel-based glass media. Optical characterization studies include spectroscopic and gain measurements to evaluate the feasibility of the materials for optical amplification applications. The major feature of laser active glass ceramic media is that different sites are available for the luminescent ion sites in the glass phase, sites inside the nano-crystals and sites at the crystal-glass interface. Detailed study of the color properties of the doped ion are expected to be the basis for identifying general criteria to produce highly efficient materials suitable for applications in optical communications.

L3.36
Long-range order and Verwey transition on the Fe3O4(001) surface, Igor V Sheets, Guido Mariotti, Shane Murphy, Nikolai Berdenov, Sergio F Casalbore and Ken Jordan, Physics, Trinity College, Dublin, Ireland.

Magnetite (Fe3O4) has been the subject of intensive studies during the last decades. The efforts to understand its magnetic and electrical properties have intensified in the last 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 metal-insulator (Verwey) transition at TV ~ 123 K has not yet been clarified. We have studied the (001) surface of synthetic single crystals of Fe3O4. The crystals have been characterized x-rays by x-ray diffraction, resonance versus temperature magnetization and magnetostriction measurements. The in situ surface preparation procedure consisted of a combination of Ar+ ion sputtering, annealing in ultrahigh vacuum (UHV) and in an oxygen partial pressure. The crystals were characterized using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), which showed a sharp (sqrt2 x sqrt2)R45° mesh. Scannin Tunneling Microscopy (STM) measurements were performed at room temperature using a tip of nanometer-size MnNi alloy. Atomically resolved STM images provide evidence of a surface terminated at the octahedral phase (B phase), with rows of Fe cations aligned along the [110] and [1-10] crystallographic axes. Two different kinds of Fe cations with a separation of 1.8 Å are imaged: the periodicity between Fe cations of the same kind is about 12 Å. A highly regular structure remained uninterrupted throughout the terrace length, suggesting that long-range order had set on the surface at a temperature that is at least 170 K above the bulk Verwey transition. The data provide evidence of a Fe3+, Fe2+ and Fe4+ coupling at the B sites. We propose two mechanisms that may be responsible for the coupling and the set-in of long-range order on the Fe3O4(001) surface. The first model is based on the interaction between the conduction electrons of the Fe 3d level 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 reduces the energy of the system. The second model explains the observed results in terms of orbital ordering (OO) at the surface. The strong electronic correlation that exists in the nanoscale 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 TV induced by electron localization at the Fe3O4(001) surface.

L3.37
Abstract Withdrawn

L3.38
Microstructural Characterisation of Alumino-silicate Inorganic Polymeric by Scanning Electron Microscopy, Matthew Ryan Rows and Brian O'Connor; Applied Physics, Curtin University of Technology, Perth, Western Australia, Australia.

The Materials Research Group at Curtin University is investigating structure-property relationships for aluminosilicate inorganic polymers, also known as geopolymers. These polymers consist of an amorphous three-dimensional structure resulting from the polymerisation of aluminosilicate monomers in an alkaline solution. One of the primary uses of these materials is as Portland cement replacement. The study to be reported forms part of a broader structure-property investigation of inorganic polymers produced by sodium silicate activation of mixtures of metakaolinite and silica fume. This work follows an optimisation study of compressive strength with respect to the Al, Si and Na concentrations [1]. SEM imaging and associated EDS measurements have been used to characterise the microstructure of the reactive aluminosilicate gel by examining the microchemistry of features in the images. The polymers were formed by mixing metakaolinite with a sodium silicate solution and curing at 75 °C for 24 hours. The sodium silicate solution was made by mixing the different amounts of silica fume and sodium hydroxide with the required water composition. SEM analysis shows that there are two distinct phases present, which are the fully reacted polymer and residual metakaolinite. The relative amounts of these two phases vary systematically with the chemical composition. EDS measurements confirm the conclusion of a dual phase system, with the elemental composition of the phases being significantly different in terms of the relative amounts of Si and Na present. EDS also shows partitioning of the inorganic phases in the microstructure of the microstructure. 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 metakaolinite. Reference [1] Rows, M R, O'Connor, B J, ‘Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite’, Journal of Materials Chemistry, vol. 13, pp. 1161-1165.

L3.39
Pulsed Laser Deposition Parameters Optimization for Growth of Alumina Thin Films on Silicon(100), Xinyu Wang1,2, Zhiqiang Xu1,2, Dharmraj Kumar1,2, Sergey Yarmolenko1,2 and Jagannathan Sankar1,2, 1Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina, 2NSF 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 nanoindentor. The relation between growing parameters and the nanostructures was studied using a SEM and an AFM. The optimum values of pulsed laser deposition (PLD) parameters, laser fluence and substrate temperature were evaluated.

L3.40
A Thermodynamic Approach to Tuning Phase Stability in Nanocomposite Multilayers, Gregory B Thompson1,2, Arda Genç2, Rajeshri Banerjee2 and Hamish L Fraser2, 1Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama, 2Materials 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 stabilities is of relevance to both electrical and magnetic device applications. 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 over a wide range of composition. The Ti layers were subsequently Re-doped with the bcc-stabilising element V. The selective alloying of Ti resulted in a corresponding free energy change that helped to stabilised the bcc phase Ti 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
Sol-Gel Synthesis And Magnetic Studies of Titanium Dioxide Doped With 10% M (M= Mn, Re, Co, Ni) Ayanakkannan Manivannan, Gery P Ghaspell and Mahindar S Sehria, Department of Physics, West Virginia University, Morgantown, West Virginia.

Nanoparticles of titania 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 dominate phase of titania dioxide with an increase which was confirmed by X-ray diffraction. The particle sizes for cobalt, manganese, iron and nickel doped titanium dioxide were determined via peak analysis to be approximately 10 nm from the broad peaks of the XRD patterns. Magnetic properties of the doped oxides are being followed throughout the procedures reported in our recent paper [1]: [1]. A. Manivannan, M. S. Sehria, S.B. Majumder, and R.S. Koriyar, Appl. Phys. Lett., 83 (July 7, 2003 issue).
L3.42 Synthetic and characterization of polymer composite with finely dispersed magnetic nanoparticles. H. Srinath1, J. L. Wilcox2, P. Poddar1, K. Mohamed2, and J. P. Harmon2.

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Magnetic nanoparticles embedded in polymer matrix have excellent potential for electromagnetic device applications like EMI noise reduction etc. Various polymer matrices [poly(styrene-PS), and poly [methyl acrylate] (PMA)] 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 by using various techniques including in situ ultrasonic polymerization and melt blending. The polymer processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix. Films were produced using a microscope technique and the concentration and dispersion of nanoparticles were controlled in a controlled way. These composite 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, as well as a dependence on the processing method. Overall, the excellent dispersion coupled with reasonable control over magnetic properties achieved in our Fe nanocomposites is promising for electromagnetic applications of these materials. H.S. acknowledges support from NSF grant # ECS-0144947.

L3.43 Multifunctional single-crystal nanotubes. Xiang Yang Kong1,2, Zhong Lin Wang1, and Jianzhang Wu2.

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Nanotubes in micro- and nanoscale have attracted extensive interest over the past decade, due to their 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 external diameter and the interior is small and dense, the cavity partially or completely blocked by growth product; hence, the inner walls and the cavity channels are less useful than the exterior walls. For applications in biomedical delivery, biosensors, and microfluidics in the micro-electromechanical systems (MEMS), it is desirable to have nanotubes of sizes in a few micrometers with high mechanical strength and chemical robustness, which will be effective for penetrating biological tissue and transporting fluid. In this paper, using a simple solid-vapor process, a novel single-crystal micromembrane structure of aluminum-rich rich mullite has been synthesized for the first time. The micromembrane has a perfect rectangular frame-configuration as defined by the (110) and (11-10) facets. The micromembrane has the [001] growth axis, dislocation-free volume, and large hollow interior channel of 0.53 micrometers in width, and a thin wall of 50-100 nanometers. The ceramic membranes are mechanically hard with potential applications for fluid delivery and microchannels for micro-electromechanical systems and biosensors, and as optical resonance cavities and waveguide.

L3.44 The SrTiO3 (001) Surface: TiO2-rich Reconstructions with (2×1) and (c×2x2) Unit Cells. Nazihah Efrid1, Oliver Warschik1, Courtney H Linier2, Kenneth H Peppelnke3, Mark Astra2, Donald E Ellis1, and Lawrence D Marks2.


We have recently reported solutions for the (2×1) and (c×2x2) surface reconstructions of SrTiO3 (001) obtained through high-resolution transmission electron microscopy, direct methods analysis and density functional theory simulations. According to both reconstructions, the formation of TiO2 overlayer, 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(6×2) unit cell.


Precipitated Au nanocrystals in TiO2 (110) have been formed by 2MeV Au2+ implantation at 300 K and 373 K followed by annealing at 1273 K for 1 hour. The morphological features, size, and crystallographic orientation of the Au nanocrystals 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 nanocrystals and TiO2 was investigated. Atomic structural model of interface between Au and TiO2 was established based on high-resolution transmission electron microscopy (HRTEM) imaging and HRTEM image simulation. Two types of Au nanocrystals were identified, Au110/TiO2(001) and Au111/TiO2(200). Au110/TiO2(001) and Au111/TiO2(200). Au clusters are faceted along Au(112) and Au(111) or Au(220) and Au(002) planes. The precipitated Au clusters show extensive (111) twinn. These orientation relationships are the same for Au clusters grown on stoichiometric TiO2(110) surface, indicating that lowering interfacial energy is a governing factor for setting the orientation relationship.

L3.46 The stability and reproducibility of carbon nanotube modified electrodes for glucose biosensor. Seng Weng1, Qing Zhan2, Ruling Wang3, SF Voong1, and J. Ahn1.

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Two of the major problems that concern the research of biosensors today is 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 nanotube modified using carbon nanotube for glucose determination has been developed. The initial results showed that the carbon nanotubes provide suitable electrode matrices for glucose oxidase immobilization, they also increase the glucose oxidase stabilization. The biosensor stability and reproducibility 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. Toshikio Masuyama1,2, Keiji Matsuda1, Norikichi Sakuma1, and Shigeya Narisawa1,2.

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We successfully obtained atomically flat Ge surfaces on mesa structure with an area of 100×100 μm2 by using phosphorus-doped layers as a seed layer. To obtain atomically flat areas will be useful for the hetero-epitaxial growth of Ge, because monolayer step on Ge surface induces antiphase domains of GaAs epitaxial layer grown on it. The control of the step formation will play central role in the growth of hetero-epitaxial layers. In this study, we used a photolithographic technique, mesa patterns were prepared on Ge(001) and Ge(111) substrate. They have square-shaped mesa areas with an edge length of 2-15μm separated by grooves with 8μm wide and 1μm deep. After wet-etching for removal of surface oxide, the LPE growth was carried out by the supercooling 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 supercooling. When the supercooling was enough small at the growth temperature below 340 °C, flat facets were formed on some mesa after the LPE growth for 30 min. We considered that these facets are formed on mesa with dislocation-free surface, considering the dislocation density of Ge substrate. AFM observation indicated that some triangle hollows with monolayer step in depth were present on these facets, but that other regions were atomically flat within the surface of the facets. It was also found that the amount and the size of the hollows were related to the supercooling 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.

Metal nanotubes have been prepared through a galvanic displacement reaction between silver nanowires and silver chlorate. The nanotubes exhibit a high surface area and void space of these nanotubes were determined by the silver nanowires. For example, gold/silver alloyed nanotubes with hexagonal 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 exhibit strong surface plasmon resonance peaks in the red and near infrared spectral ranges. It is believed that these Au/Ag alloyed nanotubes are good substrate for surfaces-enhanced Raman spectroscopy studies. Nanotubes made of different compositions could be generated by replacing chloroauric acid with other salts, such as palladium nitrate and platinum acetate.


We report the first direct nanoscale observation of photoswitchable chemical interactions with nanostructured surface monolayers. These force microscopy measurements of reversible electrostatic interactions are to be distinguished from earlier reports of optomechanical switching of molecules on surfaces. Previously we designed and demonstrated a tunable, irreversible light-induced plasmon resonance of the rings of tethered spiromonyl polymers on glass surfaces leads to the switching of the hydrophobicity of the surface, with wetting angle changes of up to 13 degrees. Irradiating the photoactive surface with UV light causes the spiromonyl rings to open and create a hydrophilic surface, while irradiation with visible light causes the rings to close and reversibly return 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 spiromonyls. 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 spiromonyl rings. Normal force measurements in liquids with different functionalized tips allow the chemical interactions between the tip and surface to be monitored. For example, a bare glass tip undergoes an attractive interaction with the surface, whereas an amino coated tip exhibits a repulsive interaction when the spiromonyls are in the open state. From these results we conclude that open ring structures are protonated in electrolyte solutions, forming a positively charged surface and amplifying the switching of electrical double-layer forces. Potential applications of these photoactivatable surfaces include micro and nano-fluidic valves, pumps, pre-concentrators, and separation, as well as drug delivery, sensing, and environmental monitoring.

L3.50  Fabrication of Silver Nanowires from Silver Oxide Solution. Yoshinori Iwashita, Hidetsugu Ishizaki, Atsushi Nakamura, Naoyuki Tsunoda, Tokyo Denki University, Tokyo, Japan; 2 Center for Applied Nanofield Optics Research, National Institute for Advanced Industrial Science and Technology, Tsukuba, Japan.

The optical response of silver nanoparticles and structures is very attractive from a viewpoint of physics and optics for a long time. In this paper, we describe a method to generate silver nanowires (hereafter we use nano-wires) using a laser beam and silver oxide [AgOx] film. The method is very useful for the study of surface plasmon polaritons (SPP). Recently, using a AgOx film deposited by sputtering, a strong surface enhanced Raman spectrum (SERS) of benzoic acid molecules which were fixed in 2-propanol (IPA) was reported, in addition, Ag nanoparticles and nano-wires were found in and around the SERS active spot. However, the outlook of the formation has not been well identified. In order to clarify the mechanism, we in situ observed the nanowire generation by a laser microscope [NEOARK Ltd. LSM-200II] with a wavelength of 405 nm and less numerical aperture (NA) of 0.50. First we prepared benzoic acid solution [1x0.3 M] diluted by IPA in a small glass container and a AgOx film was then deposited on a glass substrate by RF reactive sputtering with a Ag target and Ar/O2 gas mixture and 100 nm thick. The AgOx sample was placed on the bottom of the BA-IPA container. When the laser power was increased by 0.8 mW, a small gas bubble was generated in the glass surface, and the size of the bubble was increased with the laser power. At more than a threshold power, the bubble was exploded and rapidly disappeared. During the process, it was found that several small black materials moved toward the bubble from outside. After the experiment, the active part was observed by a scanning electron microscope. It was found that the black materials are Ag nano-wires (diameter ~ 20-50 nm) and the nanoparticles are only generated in the active spot. As a result, it was suggested that the silver oxide AgOx in the BAIPA solution and super-cooling due to the micro-convection be the source of the nanowire formation. Following the experiment, a saturated-AgOx-BAIPA solution was prepared and the same experiment was carried out with a Si wafer surface. Even in this condition, Ag nano-wires were indeed generated around the bubble point without Ag nanoparticles.

L3.51  Magneton Sputtering of Nanocomposite (TIA1)CN Coatings. Michael Stueber1, Y. Huang2, Andras Kovacs3, Peter Barna1, Ulrich Albers1, Michael Charles Simmonds4, John Rodenburg5 and Hans Holleck1, 1 IMF, Hochschule Karlsruhe, Karlsruhe, Germany; 2 MRI, Sheffield Hallam University, Sheffield, United Kingdom; 3 Research Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences, Budapest, Hungary.

The use of lubricant particles such as MoS2 or graphite incorporated into coatings is of interest in developing self-lubricant hard coatings. In this study, a series of TiAlCN coatings with differing carbon contents (6-27 at%) have been deposited by the reactive sputtering of TiAl in a mixture of N2 and CH4 gases. The microstructure and chemistry of these coatings have been investigated using EMPA, AFM, XPS, HRTEM, Raman spectroscopy and X-ray diffraction and pole figures. The pure TiAlN grows with the expected cubic structure. As carbon is added to the film there is a commensurate increase in the interplanar lattice parameters which may be due to carbon lattice substitution. The pure TiAlN displays a columnar structure with a strongly preferred (111) texturing. The coatings become more randomly oriented as carbon is added to the films. The grain size changes from microcrystalline to nanocrystalline to nearly amorphous with increasing carbon content. A fairly small internal stress is measured for these samples which is compressive in the TiAIN film and tensile in carbon containing films. At carbon contents above 8 at% there is an ambiguous residue for the presence of a free carbon species, which is a significant step towards accomplishing a self-lubricant hard coating.

L3.52  Monitoring Polymer/Clay Nanocomposites Compounding Using On-Line Dielectric and Fluorescence Measurements. Anthony J. Barisic, Steven C. Ritzel, Doug McBrearty, 1 NIST, Gaithersburg, Maryland; 2 Chemical Electro-Physics, Hockessin, Delaware.

A new multipurpose instrument has been used to obtain real-time dielectric and fluorescence spectroscopy from polymer/clay nanocomposites compounding. The instrument, which is mounted at the exit of a twin screw extruder, contains a flow-through slit channel that provides a constant geometry platform for dielectric and fluorescence sensors. The result of these analyses on an organically modified montmorillonite clay will be presented. The on-line data are correlated with off-line dielectric measurements, and analysis of these data yielded a wealth of dielectric relaxation phenomena. Significant differences in the dielectric relaxation parameters were observed for clay nanocomposites in the aggregate, exfoliated and intercalated states. Maxwell-Wagner interfacial polarizations were observed in the nanocomposites reflecting intercalated and exfoliated polymer/clay interfaces. 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 microstructure conformation on their spectra. Real-time monitoring of both fluorescence and dielectric properties offers the potential for defining microstructural character during processing without the need for off-line, post-processing experiments.

SESSION L4: Applications
Chair John Parker
Tuesday Morning, December 2, 2003
Room 304 (Hynes)

8:30 AM  L4.1  Industrial Applications of Transparent Conductive Nanoparticles. Changwon Park1,2 and Honyong Ju1. 1 Dept. of Chemical Technology, Hanyang National University, Anjeon, South Korea; 2 ANP Research Center, Advanced Nano Products Co., Ltd., Changwon, South Korea; 3 Department of Physics, Yonsei University, Seoul, 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 most successful model in current industrial applications. These particles are being massively used for electronic and display industries. High performance transparent IR blocking films are being produced using conductive nanoparticles with much lower costs 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 nanoparticle. In this presentation, general procedure for producing transparent conductive nanoparticle and their industrial applications will be discussed.

9:00 AM L4.2
HSA-CERAMIC: A New Material with a Continuous Nanopore Network. Bishakhshi Nair, Merrill Wilson and Akash Akash; Ceramicite, Inc., Salt Lake City, Utah.

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

9:15 AM L4.3
Iron Oxide / Silica Nanocomposites. Michael Kroll, Markus Pridel and Guido Zimmermann; Creawe 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 Am²/kg depending on the size of the magnetic domains and the iron oxide content in the composite material. The specific surface area of the nanocomposites can be varied between 40 and 215 m²/g by controlling the thickness of the silica layer or the magnetic domains by adjusting the flame temperature. The superparamagnetic behaviour can be utilized in different applications. If the nanocomposites are exposed to an external magnetic field they get heated. This behavior 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 water agents or as pigments of iron oxide. The paper presents 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 L4.4
Single-Walled Carbon Nanotube Rope for Gas Sensor Application. Jinhoo Lee, Jinwon Kim, Chae Kijong Kong, Hyunju Chung and Byungwhun Ryu; Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, Chungcheong Namdo, South Korea.

Single-walled carbon nanotube (SWNT) ropes were placed on the oxidized Si wafer surface by alignment of nanotubes across neighboring two gold electrodes. SWNTs were dispersed in conventional solvents, and then with much lower concentrations, 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 I-V characteristics across the fabricated SWNT ropes, and they showed the characteristic of semiconductor which can be applied to gas sensors. The change of conductivity of these SWNT ropes in the presence of NO 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, 2). H. Chang, J. D. Lee, S. M. Lee, and Y. H. Lee, Appl. Phys. Lett., 79, p.3806 (2001).
rate (which is in excess of 1 million K per second) we are able to control the mean particle size from sub-10μm to 10mm and produce large unagglomerated nanoparticle. The combination of unique process features allows us to reach parts of the materials synthesis parameter space that conventional plasma processes cannot reach. An overview of chemical and physical processes will be given with special attention to the homogenous phase microwave 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, magnetic data storage, energy and electronics. Applications include: electrically and/or thermally conducting fillers; direct write electronics; transparent optical coatings; photovoltaics; fuel cells and advanced materials for explosive, propellant and primes. The talk will discuss recent developments in which our nanoparticles have demonstrated improved 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.


Nanophase Technologies Corporation employs a new physical vapor synthesis technique to manufacture ceria-based mixed rare earth oxide nanomaterials. The mixed rare earth oxide nanoparticles are nongranular, dense, discrete crystals. The compositions are solid solutions that remain thermally stable to above 1000°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, particle size and 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 exchange catalysts and polishing materials.

11:15 AM L4.9 Surface modification of ceramic particles using a newly developed direct plasma spray system, Hong Gwon Choi, Kyoung Hun Kim, Ob Seong Kwon, Se Heon Kim, Kyung Joo, Ihn Kee Hwang and Kwang Bo Shim, Ceramic Engineering, Hanyang Univ, Seoul, South Korea; *Kosno Ltd, Incheon, South Korea.

A new thermal DC plasma spray system has been developed for not only the production of the nanomaterials with a uniform size distribution and without agglomeration but also the surface modification of nanoparticles for the improved powder functionality. The 2-step plasma chamber, operating at the low pressure, was adapted for dividing the particle size and disintegration of the plasma-treated particles. The enlarged plasma length up to 60cm, in the reaction tube, evokes very effective disintegration of plasma-treated particles during cooling and to lead them to 2-step plasma chambers with a stable temperature distribution. The new thermal plasma system was applied for various ceramic powders such as Al2O3, ZrO2 and SiO2. The experimental results showed that the irregular shaped ceramic powder changed typically to spherical shape depending on the various process conditions:powder, feeding rate of powder, pressure, etc.). The particle size tends to reduce gradually with a narrow size distribution from reaction tube to 10th chamber.

11:30 AM L4.10 Proton Conducting Nano Hybrid Membranes Synthesized From Temperature Tolerant Polydimethylsiloxane Polymers, Je-Deok Kim and Itaru Honmura, 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-linking inorganic nano-phase 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 conductivity of 37.10-5 S/cm was obtained at 150°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, Zhaocung Huang, Simin Nemani, Kang Sub Yim, Li-Qun Xin and Richem Mupadi; Dielectric System & Module, Applied Materials, Santa Clara, California.

A second-generation organosilicon glass (OSG) low-k film for the 65nm technology node was developed with k value of 2.5-2.6, corresponding to a 10% volume reduction rate from the first-generation Black Diamond® film. The k value was achieved by introducing nanometerized pores into the film, which was prepared with a plasma enhanced CVD (PECVD) method using organosilicon molecule and small organic molecule precursors. Post deposition, the OSG films were treated by electron beam to reduce the k value and mechanical properties. An organic molecule was used as the porogen. This molecule forms very small pores that are preferable to mesopores (tens of nanometers). The organic molecules were embedded, along with silicon-containing precursors, into the film through the plasma gas phase reaction and substrate surface reaction. The precursors were activated in plasma; the surface reaction is simply an adsorption-desorption limited process; as indicated by negative activation energy from an Arrhenius plot. Subsequent e-beam treatment removed volatile species and generated pores. While conventional thermal annealing can produce porous low k films, it is slow and incompatible with thermal budget requirements. E-beam is more effective in removing porogen and more importantly, it can treat selected layers by controlled treatment depth. The energetic electrons also promote molecular cross-linking, giving enhanced film modulus and hardness, thus making it compatible with CMP and packaging.

The e-beam energy and dose can be adjusted for various types of films with different thickness to achieve optimal properties. Compared to the 90nm Black Diamond film, the new OSG film has a lower density with similar chemical composition (see Table 1). The pores have a narrow size distribution that peaks at 1μm, measured by ellipsometric porosimetry. Modulus of up to 11GPa can be achieved through e-beam treatment. The film remained stable with little change in k, R1 and FTIR signal after 10 days in atmosphere and 36 hours in a humidity chamber at 85% humidity.

A full characterization of the new OSG film. Interline capacitance measurement and TMA Ropnel simulation indicated an integrated k value of 2.6. Similar effective k value was also achieved with a dual damascene structure.

Planar capacitance measurements indicated a breakdown strength of >0.7MV/cm, and >95% yield was measured on a 9 million via film.

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

1:30 PM L5.1 Organization of Nanocrystals on a Mesoscopic Scale: Collective Properties of Magnetic Multispindle Films, LM28, Université Pierre et Marie Curie, Paris, France.

Nanocrystal are organized in 3D superlattices forming either in a cubic or hexagonal network. These 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 in anisotropic form or a monolayer. Magnetic properties controlled by dipolar interactions markedly differ with the structural order.

2:00 PM L5.2 Improved Tribological Properties of Diamondlike Carbon/Metal Nanocomposites, Roger Jagdish Narayan and Mike Weatherston; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

One of the many forms of carbon, diamondlike carbon (DLC) consists mainly of sp3-bonded carbon atoms. DLC coatings possess properties close to diamond in terms of hardness, atomic smoothness, and chemical inertness. Unfortunately, DLC exhibits poor adhesion to metal and polymers. The adhesion 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 new thin film design was adopted to incorporate metal (e.g., silver or titanium) into the DLC films during pulsed laser deposition. Atomic structure with a resolution of 1.6 Angstroms was performed using STEM-Z contrast at...
ORNL. Since scattering power or contrast depends upon atomic number squared \((Z^2)\), heavy noncarbon atoms in the DLC matrix can be studied in situ by TEM of the DLC/nc nanocomposites, and 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/nc nanocomposites possess the largest wear resistance. On the other hand, pure DLC possesses the lowest wear resistance. Diamond-like carbon nanocomposites also exhibit significantly enhanced adhesion. Careful analysis of the Raman data also indicated a significant change in the relative plasmon wavelengths in the DLC/nc nanocomposites, indicating a reduction in compressive stresses within these films. Raman spectroscopy studies also demonstrate a high fraction of sp3-bonded carbon in both DLC/nc nanocomposites for the films and pure DLC films. The chemical properties of these films were studied using electron energy loss spectroscopy (EELS) and x-ray photoelectron spectroscopy (XPS). By varying the metal concentration as a function of distance from the interface, it is possible to create a functionally graded DLC/nc nanocomposite. These DLC/nc metal nanocomposites have a number of biomedical applications. For example, we have shown that DLC/silver coatings possess antimicrobial properties against Staphylococcus aureus. DLC/nc 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 nano-crystalline diamond films have been the focus for recent years in the area of catalyst and solid oxide fuel cells (SOFC). The high efficiency intermediate temperature energy conversion from chemical to electrical power of the SOFC makes materials like doped-CdO2 a viable candidate for SOFC electrodes. The nature and impact of ionic conduction in doped-CdO2 relies heavily upon grain boundary dynamics. Study of doped nano-crystalline CdO2 gives the perfect opportunity to study enhanced grain boundary effect and its impact on diffusivity and ionic transport. In this study nano-crystalline Y, Gd and Sm doped CdO2 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 high-resolution transmission electron microscopy (HRTEM). Initial ITO diffusion studies and computer simulations indicate that nano-crystalline ceria compared to polycrystalline films treated at elevated temperatures. A detailed discussion will also be presented correlating the 180 diffusivity profile tailoring effect with the brick model, especially concerning nano-crystalline materials. Finally, a presentation will be prepared between sol-gel and DC sputter growth process from the point of view of connectivity and improved density and its effect on the long-range interstitial/vacancy migration.

2:30 PM L.5.4 Thermal Equilibrium and Transport Properties of Nanocrystalline FCC Metals / Peter M Derlet and Helen Van Veggelen; Paul Scherrer Institute, PSI-Villigen, Switzerland.

The equilibrium thermal properties of nanocrystalline (nc) materials using molecular dynamics have recently been investigated via the Fourier transform of a velocity autocorrelation function Rev. Lett. 87 205501. 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 n-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 L.5.5 Nanocrystalline Oxide Nanofibers and Nanocrystalline Oxide Polymullite Nanocomposites, Characterization, and Application / Electrochemical Behavior. Samuel T. Lutjens, Dong Hong, Peter Y. Zawalij and M Stanley Whittingham; Department of Chemistry and Institute for Materials Research, SUNY-Binghamton, Binghamton, New York.

Voxidum 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 into NH2-VO2+ MS, the sol-gel routes for the formation of V2O5 in nitrogen and oxygen at 300°C formed V2O7 and V2O5 nanofibers respectively. Polyvinylidene fluoride nanocomposites were prepared by sol-gel reaction of vanadium (V) oxytrioxypolynate and polyvinylidene fluoride. The nanocomposites were characterized by XRD, XRF, IR. The vanadium oxides are rod-like active and can electrochemically insert lithium reversibly. A specific change of about 150 mAh/g (w/w) for these oxides was excellent for lithium insertion and remained fairly constant for at least 10 cycles. The electrochemical behavior of the vanadium oxide polyvinylidene is also discussed. This work is being supported by NSF grant DMR9318963.

3:00 PM L.5.6 Nanoscale Structure and Electronic Characteristics of Highly Conductive N-type Ultrananocrystalline Diamond / Jennifer E. Gates,1 Oliver A Williams,2 Judith E. Bader,3 James Barch,4 Stephanie P. Curte,3 Haimao Ye,2 Orlando Aquello1, Dieter M Gruen1, Richard B Jackman2 and John A. Carlinke3; 1Materials Science, Argonne National Laboratory, Argonne, Illinois, 2University College London, London, United Kingdom, 3University of Illinois, Urbana-Champaign, Illinois.

Ultrananocrystalline diamond (UNCD) is a very fine-grained (3-5 nm) diamond material with atomically abrupt mixed sp2 and sp3 bonded boundaries. Synthesized using plasma enhanced chemical vapor deposition (PECVD) with Ar-rich Ar/CH4 plasma, the electronic, structural, and tribological film properties of UNCD films can be tailored by doping with a controlled amount of nitrogen. These properties correspond with transformations in the film, 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 film that can retain the excellent tribological and structural properties of a small-grained, smooth, and phase-pure diamond film if the microstructure is properly controlled. Here we discuss the relation between the electronic and structural properties of UNCD films deposited using a novel PECVD system that enables large-area (100 mm diameter) film deposition. For a range of nitrogen doping concentrations, we discuss the structure (including grain size, preferred orientation, and texture) of nitrogen doped UNCD films as measured by x-ray diffraction, and present measurements of the nitrogen concentrations as determined by high-mass resolution SIMS. We also present new Hall voltage and AC conductivity results performed with a dedicated field switching setup at variable temperatures. These data provide insight into the unique conduction mechanism of nitrogen-doped UNCD, along with confirmation of the carrier concentrations, mobilities, and conductivities of the material as a function of nitrogen doping and film grain size or structure. [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-ER45419.

3:30 PM L.5.7 Nanocrystalline Oxides as Fillers in Nanocomposites to Enhance the Performance of Polymeric Electrolytes / Silvia Linic and Enrico Taverner, Dept. of Chem. Sci. Technol., University of Rome Tor Vergata, Roma, Italy.

New technologies of energy production and storage are needed for sustainable development, to reduce the pollutant emissions from fossil fuel combustion. Polymeric electrolyte fuel cells (PEFCs) are very promising as electrochemical power sources for application in portable technologies and in the fuel function in hybrid electric vehicles. By using nanocomposites, commercial materials used in PEFCs are enhanced. These electrolyte 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 application of direct methanol fuel cells (DMFC). DMFC cannot be used at temperatures above 100°C because its conductivity is due to the presence of water within its structure. Membranes made of polymeric gels containing lithium salts for Li batteries couple the high energy, long life characteristics of the lithium process with the reliability and easy processing of the plastic configuration. The reduction in size at the nanometric level have shown the possibility to
derive unique physico-chemical properties of materials. Composite materials have shown the ability to develop new or multifunctional properties when materials with differing properties are integrated together. Thus, the use of nanocomposites (with nano-sized fillers) is now receiving wide attention for many functional applications. We here report that the addition of nanocrystalline ceramic oxides to polymeric matrices improves their electrical and mechanical performances both in DMF2O and lithium batteries. It is worth noting that the beneficial effect of nanocrystalline powders was found both in protonic and Li-ion conductors. Improvement in conductivity was observed in both cases and a significant increase in the discharge capacity of ECG (electroencephalograph). This is, to the best of our knowledge, the first report on the use of a biocled application of a lithium containing system where the membrane must be used in ambient conditions and in direct contact with the skin. Mechanical properties and non-slip 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. Sumer Rahateke, Marc Hann, Milo Shaffer, and James Elliott.1 Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom;
Department of Chemistry, Imperial College, London, United Kingdom.

The addition of carbon nanotubes (CNTs) to a polymer matrix is expected to yield benefits in both mechanical and electrical properties. The focus of this work is on CNT-filled thermoplastic polymer textiles. This involves the enhancement of the performance of textiles and the application of the enhanced electrical properties. The challenge is to determine the type and size of nanotubes that are most effective for a given application, and how they should be dispersed or modified to interact with the polymer. The objective of this work is to develop an understanding of how the processing methods and properties of nanotube polymer composites are related to the geometry of the nanotubes used, their orientation, and their packing fraction. It will then be possible to design composite properties and control the electrical and mechanical behavior of nanotube composite systems.

Luminescent materials with high emission efficiency and with thermal and physical stability are very important for recent flat panel displays; further, in order to have much higher picture resolution, fine fluorescent particles with high efficiency are necessary. On the other hand, emission enhancement owing to light scattering accompanied with the microstructure of organic/inorganic composite materials has been investigated recently in order to fabricate novel laser materials. Thus, the luminescence from the glassy materials as host materials, which have inner microstructure due to phase separation, was examined in this study. As a candidate for such materials, in this study, yttrium-silicate phase separated glasses and glass ceramics containing (Y3+ and Y2+ ions) typical luminescence center of blue and red color, were prepared by melt-quenching process in stable immiscibility region with some third component. The size of phase separation texture of the obtained materials was controllable by adding alumina as the third component. As the size of phase separation texture changed into fine grains, the luminescence intensity increased. This enhancement of luminescence is considered to be caused by the multiple scattering effect of excitation light at the interface of phase separation textures. The addition of alumina, titania, and/or metal silicon also affected on the valence alternation of europium ions in the materials.

4:45 PM L5.11
Thermal and Electrical Transport Measurements of Single-walled Carbon Nanotube Strands. Chrie Nanc1
Theodore Breen-Tinsley1, Jingqing Wei, Robert Vajtai1, and Pulickel M. Ajayan.1
1MANE Dept., Rensselaer Polytechnic Institute, Troy, New York; 2Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; 3E.N.S.M.A., Futuroscope, France.

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

SESSION 1:6 Templated and Self-Assembled Materials

1 Chair: Kusuki Nakanishi
Wednesday Morning, December 3, 2003
Room 304 (Hyatts)

8:30 AM L6.1
The Use of Mesosporous Systems for Preparation of One-Dimensional Ordered Magnetic Metal Nanowires. Yuri Dmitrievich Tretyakov, Andrei Eliseev, Alexei Lukshin, Kirill Nipochkin, Alexei Vertegel and Maxim Pavlovich Nikiforov, Department of Materials Science, Moscow State University, Moscow, Russian Federation.

Creation of the functional nanomaterials with the controlled properties is emerging as a new area of great technological and scientific interest, in particular, it is a key technology for developing novel high-density data storage devices. Today, no other technology can compete with magnetic information carriers in storage density and transfer rate. However, usually their volume very small (10-1000 nm) magnetic nanoparticles shows poor superparamagnetic properties, with very low blocking temperatures and no coercivity at normal conditions. One possible solution of this problem is preparation of highly anisotropic nanostructures. From the other hand, the use of purely nanocryst alline systems is limited because of their low stability and tendency to form aggregates. These problems could be solved by encapsulation of nanoparticles in a chemically inert matrix. The prety microspheres for preparation of highly anisotropic magnetic nanoparticles are mesoporous silica and mesoporous aluminasilicates. Mesoporous silica is an amorphous SiO2 with a highly ordered uniform pore structure (the pore diameter can be controllably varied from 2 to 50 nm). This pore system is a perfect reactor for synthesis of nanocomposites due to the limitation of reaction zone by the pore wall. Here we suggest a novel variant of synthesis of ordered magnetic nanowires in the mesoporous silica matrix. The method is
Selective Mineralization in Block Copolymers.
Brian Joseph Mele1, 2, Thomas P Russell3, 4, and Sandra L Burkett5.
1Chemistry, Amherst College, Amherst, Massachusetts; 2Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts.

Asymmetric diblock copolymer thin films have been used as templates for the mineralization of silica. Films of polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) and polystyrene-block-poly(ethylene oxide) (PS-b-PPO) were prepared in which cylindrical PMMA or PEO domains were oriented perpendicular to the surface. Silicon oxide could be selectively grown in the PMMA cylinders by vapor-phase and liquid-phase sol-gel processes using tetraethyl orthosilicate (TEOS). Vapor-phase TEOS treatment of PS-b-PMMA films could also be used to deposit silicas in the PMMA cylinders. Liquid-sol gel processing resulted in swelling of the PMMA so that it covered the PS matrix and formed nanocores, following silicon oxide mineralization in the PMMA layer. Reaction conditions influenced the extent of silicon oxide growth on the polymer film surfaces. Distinct silicon caps could be obtained. The block copolymers may not act as templates for other metal oxides to create nanostructured hybrid inorganic-organic thin films.

9:45 AM L6.5

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-reconstituted collagen with nano-hydroxyapatite was carried out under simulated physiological conditions using acidic biopolymers, such as poly(aspartic acid) and poly(vinyl phosphonic acid), to an amorphous liquid-like mineral precursor of calcium phosphate. The novelty of our approach is that the polymers-induced liquid-precursor (PILP) phase can be driven by capillary action into the gaps and grooves of the collagen matrix. The PILP phase then crystallizes into hydroxyapatite crystals that fill the gaps of hydrated collagen. After dehydration it is thermodynamically driven off, leaving the collagen embedded with nano-crystals of hydroxyapatite, and generating a highly mineralized composite that mimics the nanostructured architecture of bone. The mineralized nano-structured composite was characterized by various techniques, such as SEM, TEM, XRD, FT-IR, EDS and electron diffraction. It is evident from the XRD and FT-IR data that the crystal structure and characteristic groups present in the mineralized composites are the hydroxyapatite phase of calcium phosphate, which was further confirmed from EDS and electron diffraction data.

Etching studies reveal that the mineral phase is generated both on and within the collagen fibrils, leading to an interpenetrating network of mineral and collagen. These preliminary observations suggest that a liquid-like mineral precursor of calcium phosphate can prove useful for in vitro model systems for the study of inorganic mineralization of collagen, mimicking that of secondary bone formation. In addition, our biomimetic process for the fabrication 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, Myungwan Kim1, Lynne A Anjum2 and Jayant Kumar3.
1Chemistry and Physics, Center for Advanced Materials, Lowell, Massachusetts; 2U.S. Army RDCOM, Natick Soldier Center, Natick, Massachusetts.

Polymeric dielectric Bragg gratings have been fabricated on transparent substrates in the visible optical wavelength region by a combination of electrostatic layering and annealing of sulfated polystyrene latex (PS) and carbobzylated poly(methyl methacrylate) latex (PMMA) nanoparticles. This approach allows for the fabrication of relatively uniform PS and PMMA layers 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 Bragg grating with uniform coverage of the substrate. The polymeric layer was then modified by the deposition of polyelectrolytes to provide adequate charge density to enable subsequent deposition of another polymer layer. In some cases, a low refractive polymer (PMMA) and higher refractive polymer (PS) were deposited into multilayer structures. Maximum peak reflectivity of the multilayers at normal incidence occurs at a wavelength of 522 nm (a homogenous metallic green in reflection color is observed) with
a half bandwidth of less than 55 nm. The reflectivity maximum matches well with theoretical prediction. The period of the Bragg grating is measured to be 150 nm, which is consistent with the reflection data. This is an extremely versatile process in that the composition and thickness of these layers may be easily modified to build in the desired optical properties. Multilayer assembly and the optical properties of these multilayered structures will be presented.

10:30 A.M. 6.7

Nanoporous carbon derived from polyfurfuryl alcohol has very interesting size and shape selective properties that have a pore size of 4.5 Å. In this investigation, we report the development of oriented porous carbon nanotubes. We also report the formation of metal doped porous carbon nanotubes using metal salts such as Mg(NO3)2, HMS, and MSU as templates. Mesoporous carbon forms have been synthesized using mesoporous aluminosilicate as templates. We synthesized carbon nanotubes with hollow macroscopic core and mesoporous silica carbon tubes using mesoporous shells were synthesized. Bimodal mesoporous silica material composed of 30 - 40 nm sized nanoparticles with 3.5 nm mesopores was synthesized. Using the bimodal mesoporous silica as a template, bimodal mesoporous carbon was synthesized. Ordered mesoporous carbon materials were synthesized through a single direct synthetic method using as-synthesized silica/surfactant nanocomposites. New mesoporous silica with onion-like pore structure was synthesized and the mesoporous silica was successfully applied as the template for the synthesis of carbon nano-oxides. Mesosilica carbon materials with ordered pore structures were synthesized for the first time. These mesoporous carbon nanotubes have been successfully applied as electrode materials for supercapacitors and absorbents for water pollutants.

11:00 A.M. 6.8
Synthesis of New Nanoporous Carbon Materials Using Various Nanostructured Silica Templates. Jimin Lee, Sungjoo Han, Jiyun Kim and Taeghwan Hyeon; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We have developed new synthetic procedures to synthesize various nanoporous carbons using nanostructured silica materials as templates. Nanoporous carbons with high pore volumes and uniform pore sizes have been produced using silica sol nanoparticles as template. Mesoporous carbons with different pore structures have been synthesized using mesoporous silica systems such as MCM-41, HMS, and MSU as templates. Mesoporous carbon forms have been synthesized using mesoporous aluminosilicate as templates. We synthesized carbon nanotubes with hollow macroscopic core and mesoporous silica carbon tubes using mesoporous shells were synthesized. Bimodal mesoporous silica material composed of 30 - 40 nm sized nanoparticles with 3.5 nm mesopores was synthesized. Using the bimodal mesoporous silica as a template, bimodal mesoporous carbon was synthesized. Ordered mesoporous carbon materials were synthesized through a single direct synthetic method using as-synthesized silica/surfactant nanocomposites. New mesoporous silica with onion-like pore structure was synthesized and the mesoporous silica was successfully applied as the template for the synthesis of carbon nano-oxides. Mesosilica carbon materials with ordered pore structures were synthesized for the first time. These mesoporous carbon nanotubes have been successfully applied as electrode materials for supercapacitors and absorbents for water pollutants.

11:30 A.M. 6.11
Synthesis and Characterization of Mesoporous LiFe2(P04)3. Shemin Zhu1, M. Hidno2, Hoshen Zhou,1 I. Homin3 and Masaki Ichihara4; Energy Materials Group, Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, University of I-I-I, Tsukuba, Japan; Material Design Laboratory, Characterization Laboratory Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, Japan.

Alternative cathode materials for lithium batteries have been investigated widely to replace the expensive and oxidatively unstable 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 Fc2/-/RS4 redox couple-based materials have been investigated extensively. LiFe2[P04]3 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/Li4 while maintaining excellent capacity, which can be used as the cathode material for rechargeable Li-ion batteries. However, two main obstacles have to be solved to improve electrochemical performance in these compounds: low diffusion rate and electronic conductivity. Usually, small particles were fabricated in order to enhance interface diffusion and obtain acceptable energy and power from the lithium cells. The mesoporous structure with relatively high surface area will benefit the cathode performance, for it facilitating the penetration of the liquid electrolyte into the pores of the electrode and hence increase lithium diffusion rate. Here, we reported for the first time the synthesis of ordered hexagonal mesoporous LiFe2[P04]3 employing cationic cetyltrimethylammonium chloride as the template. The obtained samples exhibit well-ordered mesoporous structure on their XRD spectra. The hexagonally ordered mesoporous can be directly observed in the TEM images. The surface area was calculated to be 172 m2/g with an average pore size of 3.2 nm according to N2 adsorption/desorption analysis.
solvent and pentanol 1 as a surfactant. They display at room temperature a direct hexagonal phase constituted of infinite nanoscopic cylinders stabilized by cyclohexane, and stabilized by a monolayer of the SDS surfactant, arranged in a hexagonal array in water, and whose diameter ranges usually between 3 and 30 nm. If one wishes to use these mesophases as actual nanoreactors whose characteristics (nature of solvents, pH...) could be monitored as a function of the physico-chemical properties required for any desired synthesis, the concept of SLC could be extended to a broader range of compositions than those reported previously. We demonstrated that this concept of SLC could be extended to a wide range of surfactants (ionic, nonionic, cationic) and in a wide range of pH (from 6 to 11). These SLC constitute a new general concept of nanoreactor that will be illustrated in the preparation of a new family of nanomaterials: inorganic oxide (ZrO2 or PdO) or polymer (PDA) nanostructures whose shape is highly controlled by the geometry of the swollen mesophase.

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

1:30 PM L7.1
MRS MEDAL AWARD TALK PRESENTATION
Self-Assembly of Biologically Inspired Complex Functional Materials. 1Department of Materials Chemistry, Sandia National Laboratory, Albuquerque, New Mexico; 2Department of Chemical and Nuclear Engineering, and Chemistry, University of New Mexico, Albuquerque, New Mexico.

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

2:00 PM L7.2
1Materials Science & Engineering, Cornell University, Ithaca, New York; 2Department of Physics, Cornell University, Ithaca, New York.

Block copolymers form a unique class of materials because of their ability to self-assemble into a variety of morphologies at the nanoscale. A particularly fascinating research area that has captivated researchers for quite some time is the synthesis and characterization of well-defined architectures from block copolymers. These materials not only have unique structural and physical properties but the continuous nature of nanoscale channels opens avenues for applications in areas like catalysis, molecular separations, photonic energy generation and storage or electronics. Extensive theoretical and experimental research has shown, however, that in classical block copolymers, energetics combined with space filling requirements put considerable constraints on the self-assembly processes that can be obtained. Indeed, the double gyroid mesophase has been the only bicontinuous phase that has been found to be stable in diblock copolymer systems in a highly restricted parameter space. Here we demonstrate how novel synthesis concepts can be used to extend the range of accessible cubic and cubic bicontinuous mesophases in polymer nanocomposite systems. Full characterization of these nanophase systems using small angle x-ray scattering combined with transmission electron microscopy will be shown.

2:15 PM L7.3
Replication of Ordered Organic Templates in Supercritical Fluids: A Novel Approach to the Preparation of Nanostructured Metal Oxide Films. Rajaram Adatkar Pai and James J. Watkins, Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Ordered nanostructured materials are of enormous interest for applications in photonics, sensors, and microelectronics, and as low dielectric constant films (low k) in microelectronics. The traditional approach to preparation of these materials involves the use of self-assemble of organic templates (including surfactants) and inorganic precursors in aqueous solution. Cooperative self-assembly has been remarkably successful for controlling the pore structure at the local length scale, but holds more limited promise for controlling long-range structures over the length scales of the device. We have developed a new technique for the preparation of mesostructured metal oxide films that involves phase-selective condensation of metal alkoxides in pre-formed structured organic templates doped 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 copolymers at the local and device levels can be accessed using established techniques prior to infiltration 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 compatibility of the templating copolymers. The application of this technique to preparation of ordered mesostructured silicate/organic films and their application are discussed.

2:30 PM L7.4
Pore-Regularity Control in SBA-16 Type Mesoporous Silica Thin Films Synthesized with a Tri-Block Copolymer. Sun-Yong Naik1, Victoria Y. Soh1, Takahiro Saga1, Toshio Hino1,2,3,4,1Department of Chemical Engineering, University of Tokyo, Tokyo, 7-3-1 Hongo, Bunkyo-Ku, 113-86, Japan; 2PRESTO, TOKYO, Japan; 3Material Research and Development Laboratory, Japan Fine Ceramics Center, 2-1-1 Matsuno, Ayasuki-ku, Nagaoy, 466-8507, 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. Porosity accessibility is one of the important factors in industrial applications, and since 3D SBA-16 type mesoporous silica thin films have accessible pores on the top surface, they are candidate materials for many industrial applications. In this work we have synthesized and characterized mesoporous silica thin films of SBA-16 type with P123, a non-ionic block copolymer. We demonstrate, for the first time, the usefulness of FE-SEM (field emission scanning electron microscopy) in direct observation of pores formed in mesoporous silica thin films. The effects of factors such as spin rate, composition of the sol and extent of TEOS hydration 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 lamellae-layered type of structure, clearly showing about 10 sub-layers, each of thickness ~ 5 nm. The size of the sub-layer observed was in agreement with the x-ray and 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] References 1. Naik Sun-Yong, et al. Chem. Mater. (Communicated). 2. Murakami et al. (CPL, in press).

3:00 PM L7.5
Macroporous Alkylene-Bridged Polyhedral Oxyanions Gels with Templated Nanopores. Kazuki Nakashima1,2,3, Yuki Kobayashi1,4, Yukimasa Yano1,4, Kazuyuki Hirose1,4, 1Material 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, whereas high silica morphologies. In pure silica systems, when the phase separation is induced by the presence of surfactants that have supramolecular templating abilities, sharply-distributed mesopores are formed within the well-defined co-continuous gel skeletons. Similar types of phase separation are...
observed also in organic-inorganic hybrid systems including those derived from sila(tri)alkoxysilanes or bis(tri)alkoxysilyl)alkanes. Depending on the choice of templating and silanization, however, a wide variety of templating effects are observed. For example, catenar surfactants such as CTAB, which has successfully templated mesopores as well as induced the phase separation in pure silica and similar hard template systems, was also used in both inorganic and organic-inorganic hybrid systems. The EPO-EO type polyester block copolymers were able to induce phase separation in most organo-inorganic hybrid systems, while their templating strength was not affected by the modification of organic-intercalating parts in the silicone-based gel networks. Poly(oxyethylene) alkyl ether was effectively used to template slit-shaped mesopores in mesoporous silicas. These examples suggest the possibility of simultaneously controlling macro- and mesopores in poly(silsesquioxane) gels in general.

3:30 PM L7.6
Synthesis of controllable mesostructured heteropoly oxometalate thin films with hierarchical structures by triblock copolymer templating. Imao Hanao1, Hsu Shou Zhao2, Yun Hei Suk1 and Makoto Kunitake1.1 1EER, AIST, Tsukuba, Ibaraki, Japan; 2Dept. of Materials Science, Univ. of Tokyo, Bunkyo-ku, Tokyo, Japan.

Mesostructured metal oxides, which can be prepared using surfactant-mediated synthesis method, have attracted much attention due to their potential applications such as catalysts, sensor devices, and novel electrolyte-19, 28. Here we report a simple, reproducible, and versatile procedure for the synthesis mesostructured metal oxide films with hierarchical structure. We used 12-phosphotungstic acid (H3PW12O40 & H2O, 6:1, H2O, 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 wide range of structural properties. We also used amphiphilic triblock copolymers as structure-directing agents. Mesostructured metal oxide thin films have been prepared with cubic structure with 1:0 spacing of 23.4 Å using the films and 1:1:0 spacing of 23.5 Å, in the framework. We believe that the former structure is formed at a ratio of directing interactions between triblock copolymer and metal oxide cluster, while the latter structure is formed through crystal-like alternating ethylene oxide and metal oxide cluster as role of cation and anion ion, respectively. Calcined thin films remain their mesostructure with large surface area (150–180 m2/g) and show interesting electrochemical properties.

3:45 PM L7.7
Multi-Functional Responsive Particles Prepared by Aerosol-Assisted Self Assembly. Yi Yang1, Xianggu Liu1 and C Jeffery Brinker2, 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 nano-composite powders. Using the aerosol assisted self assembly, different mesostructured cerium, hydrogel-, and polymer-containing nanocomposite particles were prepared and their transport properties studied. Co-continuing silan nano-composites exhibited core/shell structures (dense cerium core and hexagonal ordered silica shell). The special core/shell structure may benefit the controllable release of Ce from the composite nanoparticles, a property that is critical in applying CeCl3 as one of the most promising corrosion inhibitors for protection of metal alloys. Hydrogel-containing silica nano-composites exhibited hexagonal order or wormlike structure. Dye molecules were incorporated as indicators into the composite particles to monitor the transport properties of the particles. Preliminary results showed that these particles were capable of controlled release of the dye molecules, facilitated by the sensitivity of the hydrogel network to changes in the external stimuli such as temperature or pH. Pendall benzene-containing composites exhibited onion-like structures. These synthesized materials demonstrate light controllable transport properties due to optically induced trans- and cis isomerization of benzene-linked linkages.

4:00 PM L7.8
Thin Film Silica Nanoparticles With Highly Ordered Porosity By Wet Coating. Hidetsu Sato1, Shigeji Chajo1, Masaaki Fujita2 and Yukio Yamanouchi2. 1Japan Chemical Innovation Institute, Tokyo, Japan; 2The 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 cm2 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 latex (PSL) and silica nanoparticles 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 50-250nm. The ordering of the pores on the silica thin film was evaluated by X-ray photoelectron analysis. The ratio of hexagonal calcination was 98%. The average deviation of hexagon angles from 120 degree calcination as the quality of hexagonal ordering was only 1.5. 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 those of pores fabricated by decomposing PSL particles. The ordered domain size of the pore was much larger than that of the PSL. It is concluded that PLS particles with silica particles are highly ordered. The mechanism of ordering is mainly due to high mobility of PSL particles, which is caused by the abundant collisions of silica nanoparticles having high particle energy due to Brownian motion. It is also due to weakening of the interaction between PSL 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. In addition to 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 Titanium Composites With Controlled Morphologies. Michael H. Bier1 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 particularly interesting material for its potential applications in photoconduction, batteries, and photocatalysis. With respect to shape control and patterning, however, the morphologies reported so far for mesostructured titania, in contrast to mesostructured silica, have 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 micron-scale structured materials. Furthermore, we show that our sol-gel self assembly synthesis and patterning approach allows for activation of the 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 nanomaterials materials include the use of a surfactant to produce a self-assembled template around which the material is formed. However, post-production surfactant removal often requires centrifugation, calcination, and/or solvent washing which can damage the initially formed nanomaterial architecture(s) that can be unstable or unstable due to removal of surfactants. Removal of surfactants from composite materials can thus be very difficult due to the presence of surfactant residues, which can impede the formation of nanomaterials. Herein, we describe a new method of surfactant removal that can be enabled by the presence of surfactants in already-removed materials that can be directly removed from composite materials. We describe a new method of surfactant removal that can be enabled by the presence of surfactants in already-removed materials that can be directly removed from composite materials.
is supposed basing on quantum properties of nanostructured carbon forms including reduction of the tunneling barrier or interaction between carbon particles and the dielectric particle. The mechanism does not suggest taking into account specific quantum properties (NEA) and it could be suitable for wide range of nanostructured carbon objects.

L8.2 Size Effect Characterization for Nanostructured Material in Nanoindentation Test. Yongmei Wei, Ying Du, Siqi Shu and Chen Zhu; LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing, China.

Nanostructured materials, such as the nanocrystalline material, the multi-layer thin film systems at nano-scale, etc., manifest the advantage mechanical behaviors. Comparing with the conventional material, a nanostructured material has the higher Young's modulus, higher yield strength and better toughness, etc. These advantage properties can be measured by using the nanoindentation test method. On the other hand, the experimental measurements show that the behavior of the nanostructured material strongly depends on the specimen sizes. The difference of the behaviors at different specimen sizes is referred to as the size effect. In the present research, the several nanostructured cell models are presented and developed to characterize the geometrical and physical behaviors of the nanostructured material. The size effect and the geometrical effect, come from the effect of the small-scale description and the effect of the representative size of the nanostructured cell, are analyzed by adopting a length-scale mechanics theory—strain gradient plasticity theory. Simultaneously, the non-linear visco-elasticity and the density concept is used in the analysis to obtain the size effect characterization. A correlation between strain gradient and the geometrical necessary density is obtained. Furthermore, for comparison, the conventional mechanics theory (a deformable theory) is also adopted to analyze the nanostructured cell models and further strengthen the size effect, however, the trial is not success. In the present research, the effect of the intermetallic curvature radius yield size effect is also considered and discussed. The above analysis results about the size effect of the nanostructured material will be used to compare with the nanoindentation experimental results for a nanocrystalline Al-6061 material.


Nano-meter sized carbon structures, carbon nanostructures (CNFs), have been synthesized by radio-frequency (RF) plasma enhanced chemical vapor deposition (CVD) system on 50–150 nm diameter nickel wires. The Ni dot arrays are patterned using a nanosphere lithography technique capable of creating arrays of regularly spaced micrometer diameter structures of Ni. Different heating gas systems are used to generating CNFs, such as CH4-H2, C2H2-H2 and C3H8-NH3. Typical deposition conditions are: substrate temperature of 880°C, overall gas flow rate of 10 scm, 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 flakes standing perpendicular to the substrate. The flake edge widths are ~10 nm and inter-flake spacing on a given Ni dot are on the order of 15–180 nm. Experiments show that the density, height and interfacing of the flakes are controllable by varying patterning and deposition parameters. Furthermore, the structure shows no degradation or vibration under small spot SEM imaging, indicating good thermal stability. Random microstructure of these structure show a typical carbon feature with C and D 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 feed gas composition. The work functions determined by Kelvin probe measurement are about 4.3 eV, which are near that of pure graphite. Preliminary results of field emission testing, including field emission spectroscopy, LE curves, Fowler-Nordheim plots and stability curves, indicate that this structure could act as a conductive, robust, edge emitter.


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/nm. Namely, the potential of the emission centers show that the emission is often associated with diamond grain boundaries and diamond type carbon in bulk. However, a role of the domain 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/parylene and diamond/parylene nanocomposite materials were prepared by the same technique, in which the matrix is formed from nanowires and then saturated with parylene carbon during a CVD process. Besides, nanowires exist in the samples that also play a role of "dielectric inclusions". The thickness of nanowires shields the dielectric particles can be controlled in a wide range during the CVD process by using 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/nm, 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 composite was studied using Raman spectroscopy and SEM. Special TEM study of emission intensity, work function, electrical conductivity, and topography maps of the emission centers were made to understand the nature of the emission in the material. A mechanism of the emission...
L8.5 Nanocomposites Prepared by Laser Ablation of Microparticles (LAM) and Subsequent Thin Film Deposition.
Weijie Wang, Daniel T. O'Brien, Jonghoon Bae, Michael F. Becker, John W. Kato and Desiderio Kovar; Texas Materials Institute, University of Texas at Austin, Austin, Texas.

We have developed a system that allows nanoparticles produced by Laser Ablation of Microparticle aerosols (LAM) to be incorporated into thin films. This system separates nanoparticle (NP) formation from thin film growth using a multi-chamber UHV system, allowing individual control of both processes. In this paper, we introduce the features of the system, including an innovative electrostatic NP collection cell that allows precise control of NP size. The electrostatic cell is essentially an electrostatic aerosol mobility analyzer, where the NP charge is supplied by the LAM process. We report results for GaN-NP embedded in AIN films produced using a 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 electrostatic cell. While the voltage range studied (0-1000V), the NP mean size was controlled from 5nm to 60nm. The structure and optical transmission of PLD AIN films deposited without NP was strongly dependent on substrate temperature (room temperature to 900 °C) and ambient condition (vacuum or nitrogen gas). During the deposition, adding nitrogen and decreasing 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 AIN thin film deposition, nanocomposites of GaN/AIN 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. 003628 (22F3-2001) and an NSF GOALI under Grant No. CTS-9978926.

L8.6 In-situ Observation of Formation Processes of Anodic Porous Alumina on a Si Substrate Using Infrared Absorption Spectroscopy.
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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. The complementary metal-oxide semiconductor (CMOS) technology. Electrochemical etching technique is one of methods of forming nanostructures. Porous alumina, which is formed by anodizing aluminum in an acid solution, is the most famous because highly ordered nano-hole arrays are self-organized on an aluminum (Al) substrate. In general, an Al layer of about 50 μm in thickness is needed for electrochemical polishing and growth of deep pores, which are necessary for fabricating highly ordered nano-hole arrays of porous alumina. 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 from a thin Al film deposited on a Si substrate. In this study, we investigated formation processes of porous alumina on a Si substrate using infrared absorption spectroscopy in the multiple reflection geometry (MIR-IRAS). In particular, we focused on anodization near the interface between an Al film and a Si substrate. We report results on the dramatic increase in the anodization current due to an oxalic acid solution, which was used as an electrolyte, simultaneously with a decrease in anodic current density. The decrease of anodic current density indicates that pores in the anodic alumina membrane reached the surface of Si substrate and that Al was expended, which is consistent with the spectral changes. This result suggests that MIR-IRAS is useful to clarify modification processes of Al.

L8.7 Synthesis of Porous Ceramics Through Directional Solidification and Freeze-Drying.
Prajna Kini, Patrick J. Fisher, Alireza Oseiji, Nicholas A. Bali and Tim Nettleton; University of Pittsburgh, Pittsburgh, Pennsylvania.

This study investigates microstructural characteristics of the directionally solidified freeze-dried silicon carbide ceramics were formed by depositing silicic acid on silicon (100) single crystals, afterwards deposited sol was solidified on the copper block immersed in liquid nitrogen and subsequently freeze-dried. Freeze-drying removal of ice crystals created three-dimensional pore-nanofibers ranging 3.10 micrometers in diameter aggregated in grain like colonies 50-100 micrometers in diameter. Porous size, spanning, colonies size and microstructure is investigated using Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) while the structure of amorphous SiO₂ is characterized by X-ray Diffraction (XRD). The microstructure results are compared and contrasted with silicon aerogel obtained through conventional processing using supercritical CO₂.

L8.8 The Synthesis of Fe₃O₅ Nanoparticles in MgO - Al₂O₃ Matrix from Layered Double Hydroxides.
Maxim Prokhorov Nikiforov1, Yuval D Tostoyakov1, Aksey V Lukashin1, Marina V Chernysheva2, Andre A Eliseev1, Yuri V Maksimov3 and Igor Petrovich Sundzaly1; 1Materials Science, Moscow State University, Moscow, Russian Federation; 2Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; 3Semiconductor Institute of Chemical Physics, Moscow, Russian Federation.

In the present work, the chemical modification of anion-substituted layered double hydroxides (LDH) was used for the preparation of oxide nanomaterials. The method is based on chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and the possibility to prepare nanomaterials directly in the powder state. Chemical modification of LDHs intercalated with metal complexes is promising for synthesis of iron oxide nanoparticles fixed in the matrix. During chemical reactions of anions in the interlayer space of LDHs, reaction zone is spatially confined by the hydroxide layers, giving rise to the conditions similar to those in 2D nanoreactors, such as Langmuir-Blodgett films and self-assembling monolayers. Mg-Al LDH were prepared in carbonate form by co-precipitation technique. Intercalation of FeEDTA was performed using the ability of annealed Mg-Al LDH to trap anions from solution. It was found that reduction of intercalated LDH in hydrogen (at 1000°C) followed by oxidation in air results in the formation of iron oxide nanoparticles. The role of oxidation temperature on the phase composition of nanocomposites was investigated. It was found that annealing at 350°C gives nanocomposite of α-Fe₂O₃ and γ-Fe₂O₃ in MgO-Al₂O₃ matrix and increase of interlayer space of Mg-Al LDH leads to the formation of Fe₃O₅ particles for samples with overall iron content 13 mol %. Since gamma iron isoxide is promising magnetic material, the phase composition of nanocomposites annealed at 350°C versus iron loading was investigated. The content of γ-Fe₂O₃ decrease with the increase of iron loading achieving the maximum value of 56% for sample with overall iron content 25 mol %. Quenching in air of the samples reduced at 1000°C was performed to increase γ-Fe₂O₃ content, but no significant increase was observed (the maximum γ-Fe₂O₃ content was 60% for the sample with overall iron content 25 mol %). In order to study the influence of LDH preparation technique on phase composition of nanocomposites direct co-precipitation of Mg-Al LDH in FeEDTA fast intercalation experiment was observed that reduction in H₂ flow followed by oxidation in air at 350°C leads to the formation of the mixture of α-Fe₂O₃ and Fe₃O₄ nanoparticles in oxide matrix. The maximum content of Fe₃O₄ is 44 % for sample with overall iron content 25 %. All nanocomposites were characterized by XRD, TEM and Mössbauer spectroscopy. This work is supported by INTAS (01-204).

L8.9 Controlling Hierarchical Nanostructures and Optical Properties of Cadmium Chalcogenide Semiconductor Thin Films.
Donghui Wang, Arie Abbasian, Jiebin Peng, John Eric Hampshire, Bryan Fleisch McCaughhey and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanostructured thin films consist of cadmium chalcogenide (CdS, CdSe, CdTe) nanocrystalline nanocomposites that have been synthesized through electrodeposition using mesoporous silicon as a template. The
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, diameters of the nanowires or nanowires can be controlled by the template mesosponge. Optical and bandgap properties of the nanostructured thin films can be efficiently tuned by controlling the pore structure of templates. This provides a new fabrication technique to synthesize nanostructured semiconductor thin films for optical, electronic, sensor, and other applications.

1.8.10 Effects of DC and AC Magnetic Fields on Grain Growth in Electrodeposited Nanocrystalline Nickel. Takashi Murokobi, Takahiro Yamamoto, Tomoo Watanabe, and Gino Palumbo. Nanomaterials, Tohoku University, Sendai, Japan; 2.3.5 Integrates, Toronto, Ontario, Canada.

Nanocrystalline materials are expected to use for micromachines in recent years. The smaller the size of machines, the more important the structural 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 nanocrystals exhibit 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 is to study the effects of DC and AC magnetic fields on grain growth in nanocrystalline materials. Nano Ni sheets of 99.9% purity was produced by the electrodeposition technique. The initial average grain size was 40 nm. The annealing was conducted at 573 K (0.37 Tm), ferromagnetic temp.) and 600 K (0.44 Tm, paramagnetic temp.) in a vacuum of 101.3 Pa for 5 min. The direct current (DC) magnetic field up to 6 T or an alternating current (AC) magnetic field of 0.12 T with 50 Hz. The direction of applied magnetic fields were perpendicular to the surface of the specimen. The evolution of grain boundary microstructure was examined using a HITACHI S-2000 FE-SEM equipped with TSL OIM system. It was found that the rapid grain growth occurred at 573 K and that the 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 10 h of annealing at 600 K, 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. Due to the above important observation, it is confirmed 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.


Nanocrystalline silicon films (no Si) with different thicknesses are deposited by plasma-enhanced chemical vapor deposition (PECVD). The nanocrystallites 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/Si substrate showed growth oriented along (100) phase nanocrystals system. The structural characteristics are observed using Fourier Transform Infrared spectroscopy (FTIR). Atomic force microscopy (AFM) imaging demonstrates the developed surface of deposited films, which is column-like. The observed photoluminescence at room temperature depends on film thickness.

1.8.12 Synthesis of ultrathin oxide powders by hydrothermal methods. Pavel Meskin, Alexander Burkin, Yuri Kolesko, Alexander Baranichkov, Buhtz Churagulov, and Nikola Olevnichuk. Department of Chemistry, Moscow State University, Moscow, Russia Federation; Institute of General and Inorganic Chemistry, Moscow, Russian Federation.

At the present work the development of a new method of highly dispersed oxide powders preparation has been carried out. This technique allows for the hydrothermal treatment of the organic citrate appearing in the liquid medium under action of powerful ultrasound. Hydrothermal-ultrasonic treatment was carried out under the following conditions: T = 425 - 525 K, t = 10 min, 3 h and frequency of ultrasound - 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), elastic specific surface area 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 completion degree and to achieve the smallest particle size, 50-70 nm (with ultrasound) contrary to 60-650 nm (without ultrasound). It is demonstrated 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 crystalization process. In results powders of zirconia and titania with the particle size 4-17 nm were obtained. The use of ultrasonic treatment for the hydrothermal processing of amorphous gel of zirconia and 0.3M aqueous solution H2TiO4 to Cs2O4 lead to the increase in the rate of thermodynamic synthesis of ferrites with spinel structure [NiFe2O4, ZnFe2O4].

1.8.13 Separation of Copper and Lead using Selective Ordered Mesoporous Silica Adsorbents. Louis Roger, Pung Lim, King Lan Yeung and Gordon McKay, Department of Chemical Engineering, The Hong Kong University of Science and Technology, Hong Kong, China.

Ordered mesoporous silica (OMS) belongs to an important class of inorganic materials. The ordered mesoporous silica with its enormous surface area, uniform pore system and tunable pore chemistry, is an excellent material for adsorbents. The cylindrical pore structure and high degrees of pore symmetry found in ordered mesoporous silica make it an ideal system for testing new and existing adsorption and diffusion models. The simple pore geometry allows for easier mathematical description and the amorphous pore wall is a good approximation of an ideal Langmuir surface. The width of the pore channel restricts the size and shape of the molecules that can enter and leave the pores. This gives rise to molecular sieving effects that have many beneficial applications in separation. The chemical environment within the pore channel can be manipulated to influence the adsorption and transport properties of the diffusing species resulting in many unique separation properties. The ability to introduce well-defined surface chemical groups onto the pore wall is invaluable for developing an accurate model for surfaces with multiple adsorption sites. This provides an excellent opportunity for studying site interaction and synergism. The separation of 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 demonstrated 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 to wide applications that they have: efficient light emitting diodes, low-threshold lasers, microcavities, waveguides, and fast optical switches. To retain light localization, i.e., inhibition of 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 refractive index mismatching media with short wavelength. Thus, 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, monodisperse structures are favored rather than fine particles for strict structural control. In this context, pore formation derived via a sol-gel method has emerged as a very promising technique for tailoring the photonic strength. The macroporous silica gel can be calcined to produce separation parallel to the sol-gel transition. Based on this concept, Nakashima et al. found that monolithic macroporous silica gel with controlled pore structure have been successfully prepared from systems containing titanium oxide. Rutile-type titania has a large refractive index of ~2.8 and very low absorption in the visible region. Hence, strongly scattering and weakly absorbing media are realized for the visible light and localization effects are anticipated. In spite of the above advantage, few works have been performed on porous titania because the kinetics of hydrolysis and polycondensation in the system containing titanium oxide are too fast to control the reaction. Compared to titania gels with three-dimensionally interconnected macroporous pore structures using colloidal titania as the starting material, instead of using titanium oxide. After the heat treatment of titania gel at 1000°C, the crystal structure of skeleton is transformed from titania into rutile. In addition, the macroporous network is maintained even after the heat treatment. We show that the macroporous rutile-type titania is very strongly scattering and weakly absorbing as expected. Besides, the macroporous titania with large surface area due to the interconnected pore structure are widely applicable to electrode materials, gas sensors, and chromatography.


The field 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-assisted hot filament chemical vapor deposition method. 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 nanowires grown by thermal evaporation/condenensation method. By varying 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 the vertically-aligned carbon nanotube films and the zinc oxide nanowire films are investigated. Two types of distinctive aging properties of field emission current are observed from the vertically-aligned carbon nanotube films.

18.16 Hydrothermal Synthesis of Sodium Manganese Oxide 
O. Voloshyn, J. Vollenweider, A. S. Sieve (GIOP, Forschungszentrum Jülich), and a 2 × 3 Tunnel Structure. Xiangwei Shen, Yunxiao Ding, Jun Liu, Jun Cui, Francis S. Galasso, and Steven L. Sub,1; 1Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 2Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Sodium manganese oxide OMS nanomaterials with a 2x3 tunnel structure have been synthesized using Na2O as a cation template. NaKxMnOy was first prepared by solid-state synthesis from a redox reaction of MnCl2 and K2MnO4, followed by a hydrothermal treatment at 175-250°C for 2 days. HRSEM showed the nanofibers morphology of the synthesized 2x3 manganese oxide OMS materials. The 2x3 manganese oxide has thermo-stability up to 500°C. At temperatures higher than 500°C, the 2x3 tunnel closes because of a loss of lattice oxygen. The materials have a BET surface area of about 25 cm²/g. Pore size distribution measurements by the BJH method showed that the 2x3 manganese oxide has mesoporous characteristics. The average pore size is about 23 nm and the pore volume is about 0.1 cm³/g. XRD and HRTEM were also used to characterize the synthesized 2x3 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 atomic size and interface control with improved magnetic properties. Using this method, single domain nanocrystalline Fe and Ni particles in the 5-10 nm size range embedded in amorphous alumina as well as in crystalline TiN have been produced. By controlling the size distribution in confined layers, it was possible to tune the magnetic properties from superparamagnetic to ferromagnetic behavior. Magnetic hysteresis characteristics below the blocking temperature and magnetic anisotropy behavior are presented. Our results from investigations in which scanning transmission electron microscopy with atomic number contrast (STEM-Z) and electron energy loss spectroscopy (EELS) were used to understand the atomic structure of Ni nanoparticles and interface between the nanoparticles and the surrounding matrix. It was interesting to learn from EELS measurements at interfaces of individual grains that Ni in alumina matrix does not form an isomorphous bond indicating the absence of metal-oxygen bond. The study of Ni nanoparticles even in an oxide matrix.

18.18 Branched-like Mesostructured Nickel Oxide Fiber Clusters. Jinhong Cao, Jun Wang, Jinsong Liu, Shuguan Chang, Baoming Pang, Xianjin Ma, Xin Cheng, Guoyue Xu and Jie Tao, Institute of Nonmaterials, 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 are synthesized by using inorganic surfactants (sodium dodecyl sulfate or sodium dodecylbenzene sulfonate) as templates, and nickel salts as inorganic precursors, via the "SL" route in alkaline condition. The as-prepared samples were characterized by means of XRD, FT-IR, SEM, TEM and TG/DTA techniques. XRD pattern of NiO/SDS shows a hexagonally packed mesostructure, corresponding to the spacing of 28Å. FT-IR spectra indicate that the presence of the surfactants in as-synthesized samples. The several influential factors (pH, surfactant concentration and different nickel sources) of the mesostructure formation were studied. The SEM image of mesostructured NiO/SDS composite shows there were some branched like fiber clusters on the surface of the samples. These branched clusters were composed of ellipse or flat fiber pipes. The diameter of fiber pipes varies from 280nm to 600nm, and the length of those varies from 1um to 14um. We believed that mesostructure could be synthesized followed by "cooperative templating mechanism" during the interaction between SDS and nickel species, and the mesostructure grow along some orientations in the size of micron. Such form of mesostructured nickel oxide is found for the first time and is believed to have potential applications in catalysis, host-guest chemistry, and electronics, etc.


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

18.20 Development and characterization of the nanostructured dielectric like carbon films. Won Jai Yang, Kentaro Sekine, Koichi Niihara and Keun Ho Auh, 1Department of Processing Research Center,
Hanyang University, Seoul, South Korea; 1Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan.

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

LI2.18
Mean Inner Potential of Nanostructured Noble Metal Catalysts, Noriyuki Ishikawa, Tomoki Akita, Kuniyuki Okuzumi, Masataka Okumura, Koji Tamaki and Masanori Kohyama;
1Special Division of Green Life Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN; 2Department of Chemistry, Yamanashi University, Kofu, 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 oxide is <5nm. This phenomenon could be correlated to 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 cleared 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 similar to that of platinum. The results were confirmed by the TEM observation (experimental: 21-25V, calculated: 25-30V). When the size is <5nm, it begins to increase >30V, and it begins to increase suddenly >40V at the size <2nm. It indicates that the electronic structure of the gold particle varied from that of the bulk same as the size of the gold particles in reduces due to the nano-size effect or the interaction at the interface, since the mean inner potential is sensitive to the electronic state of the outer valence electron. On the other hand, the behavior of the platinum particle is different from that of gold catalyst. 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 increase >15nm, and the rate is lower than that of the gold particles with the size <5nm. It is suggested to be due to the difference of the interaction with TiO2.

LI2.22
Novel Allotropic Fullerene-Like and Nanotubular BN Structures, V. Vladimir POKROPOVYCH, Richard Purich2 and Alex Pokrovsky1;
1Theor.m. sci., Inst. Problems of Material Science of NASU, Kiev, Ukraine; 2Clarkson University, Potsdam, New York.

Abundance of allotropic forms of boron nitride (E-phase, etc.) are known to exist many years ago, the densities of which are intermediate between that of graphite-like BN and a diamond-like zincblende 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 BN12N24. C24H64 and BN12N24 with 168 atoms, a "hyperdiamond" with C24H molecules in a superiamond lattice, and a body-centered cubic fullerite Me2B12N12 (doped with the small donor metal impurities Me=M Li, Be, etc.) with the density &nb=61.64 g/cm^3) higher than superiamond have been predicted [1]. Crystal-chemistry analysis in couple with quantum-chemistry MDNO calculation of the B12N2, B3N2, B12H16 and (6,0) and (6,6) BN-nanotubes have permitted us to establish the structures of above unconventional cubic and hexagonal phases of boron nitride, the analogs of "cubic graphite," a-carbon, b-carbon, diamond and other unconventional hexagonal forms of carbon are suggested, that still write their discoveries in a zeolites all such phases contain two dimensional layers of cylindrical nanochannels in their structure, that may be utilized as molecular sieves. In result of size effects, appearing at &61.548, & = 3, the unusual optic and other properties are expected to be seen. novel materials on base of such fullerene-like forms of boron nitride that will find novel perspective applications. [1].V.V.Pokrovsky, et al., J Solid St. Chem. 154, 214 (2000).

LI2.23
A Model of New VUV NLO Materials Based on Borate. A Novel Noncentrosymmetric Borophosphate Compound Be2P2O7, Zhengzhen Le1 and Hiroshi Moriyama1; 1Materials & Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; 2Department of Chemistry, Toho University, Funabashi, Japan.

The model compounds formulated as M2A2(BO3)2P2O7 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 for the investigation of a new VUV NLO material would be fairly conducted by focusing on borate, borophosphate, and borophosphonate on the basis of the molecular group theory. For example, a novel noncentrosymmetric borophosphate compound Be2P2O7 has been synthesized by solid-state reaction. Microwave crystalline compound Be2P2O7 is a hexagonal compound and contains the BO2 anionic group as its basic structural unit, which should play an important role for SHG coefficients. In fact, Be2P2O7 powder was found to have the significant SHG effect.

LI2.24
Fabrication of carbon nanofilm for electrochemical capacitors, Chih-Chieh Hsieh, Jin-Ming Chen, Rong-Rong Kuo and Yu-Hao Huang, Industrial Technology Research Institute, Chutung, Taiwan.

Highly-dense carbon nanofilms (CNFs) film synthesized by a thermal chemical vapor deposition was employed to explore the electrochemical characteristics of supercapacitors fabricated with the CNFs. Open-end CNFs having a mean diameter of 80-100nm were grown at 900°C, using decomposition of toluene as carbon precursor, and Ni-electrodeposited substrate as catalyst. X-ray adorption experiments showed that the CNFs had a BET specific area of 120 m^2/g, and mainly mesoporosity, i.e., pore size ranged from 2 to 11 nm determined from DFT analysis. 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 Faradiac current and distributed capacitance effect at potential reversal were found, indicating that the CNFs exhibited a purely double-layer capacitance characteristic. The constant current charge-discharge cycling showed that the capacitor fabricated with the CNFs exhibited a stable cycleability (~15 μC/cm2) and excellent Coulombic efficiency (~99.5%) during 200 cycles.

LI2.25
Mesoporous Silica Film Preparation By Novel Supercritical Fluid Extraction Of Organic Precursors: Novel Surfactant Template Approach, Tokuyuki Hirano1, Yoshihito Yokokawa2 and Yoshikazu 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 constant, 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 to the SFE with and without hydrogen peroxide solution. In the case that hydrogen peroxide solution is introduced into SFE, absorption intensities of CH3 or CH2 bonds, which originate from CTAB molecule, are reduced, i.e., CTAB can be extracted from the film, while no extraction of CTAB from the film is observed in the case that SFE 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 structures of 2.8 nm, which suggests that the surfactant can be extracted without meso-structure collapse.
to analyze the chemical changes in the film during the SFE with hydrogen peroxide solution, XPS were measured on the films. Before the SFE, films with Cls and XPS photoelectrons assigned to C-H and C-N bonds in CTAB molecule, are observed. After the films are exposed 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 soCO2. It is also suggested that CTAB is decomposed to some shorter weight molecules, thus, the organic templates can be extracted by soCO2. This research was supported by grants from NEDO of Japan.

LS. 26
Anisotropic Luminescence of Individual CdS Quantum Dot Ensembles. Jinh Qi1, Zhihao Yan2, John M White1 and Angela M Belcher1,2. 1Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA; 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 nonspherical shape, since the polarization depends on the symmetry of the wave function. The polarized emission from a QD ensemble is a three dimensional problem, due to the orientation of the probability amplitudes of a QD regarding to the excitation light and observation. In this work, we report photoluminescence (PL) observations for individual QD ensembles comprised of about 2.5 nm diameter spherical wurtzite structured CdS quantum dots. The QD ensembles were prepared by a cold treatment process that provided control over the shapes of the assemblies. The ensembles are themselves either spherical (100 to 300 nm diameter) or rod-shaped. PL measurements were performed on the QD ensembles transferred onto a silicon (100) wafer and measured at low temperature around 6 K. A conventional far-field micro-PL system was used to collect the PL signal. For a given spherical ensemble the PL is anisotropic and the anisotropy is independent of the polarization of the optical excitation. The direction and magnitude 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. Jie Tang1,2, Bo Gao1, Haining Peng1, Elton D Velv1,2, Lu-Chang Qin1,2, and Qiu-Ming Zhou1,2. 1University of North Carolina, Charlotte, North Carolina; 2National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 3North Carolina State University, 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 systems 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 length from micrometer to over 1 cm. The CNTs within the fiber are bonded together by van der Waals forces and are aligned along the fiber axis. The method allows fine control of the fiber length and is capable of parallel fabrication of lots of fibers using the same source. The short CNTs fibers can potentially be used as the probes for scanning probe microscopes and the logs as electrodes and conducting wires. [1] J. Tang, B. Gao, H.Z. Peng, D.V. Velv, L.C. Qin, and Q. Zhou, Adv. Mater. in press.

LS. 28
Meso-Structure and Micro-Structure of A Siellen Thin Film with Silicon Nitrides, Ceramic, and Carbon Layers. J. Ruiz-Bustamante1, A. Bigneser1, B. Simons2, G. Xameralnikis3 and C.J. Brinker1, 1Scripps Institution of Marine Sciences, National Research Council Canada, Ottawa, Ontario, Canada; 2University of New Mexico, Albuquerque, New Mexico.

Silicon thin films with nanoscale-scanned voids organized in an ordered array and with controllable hydrophobicity may be highly desirable for future semiconductor devices. We present here a thorough characterization of the meso-structured porous silicon thin film formed on a (100) Si substrate. In addition to the meso-structure, we also present a comprehensive investigation of the micro-structure. The film presented was fabricated by solvent evaporation-induced solgel and self-assembly processes (EISGSA), with methyl triethoxysilane (MTES, Si(OCH3)3/CH3) as the silica precursor and a polycarbonate-nickel galyd (PSb-PEO) dihydrate 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 show various zones, 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 was exclusively body-centered cubic (bcc) rather than face-centered cubic (fcc); the bcc meso-structure with a slight distortion was further assigned to body-centered tetragonal (bct) with the preferred cell parameters of a = 13.5 nm and c = 13.0 nm. The pore was ca. 4 nm in diameter. The meso-structure was also confirmed by Small Angle X-ray scattering (GIXAS). Furthermore, two types of dislocations were observed by TEM. One was an edge dislocation, with the Burgers vector b = [a00] and the dislocation line direction x = [1 0 0]. The other was a dislocation dipoles with the Burgers vectors b = [a/2][1 1 1] on a (0 1 1) plane. The origin of the edge dislocation was argued to be the tensile strain developing during the formation of the meso-structured thin film via the EISGSA process. 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, Scanning electron wave (SAW) measurements showed the absence of micro-porosity interconnecting the meso-pores; furthermore, 3D GISAXS indicated the absence of additional porosity due to the PEO removal. However, gas microscopy (GP) found there was a small number (less than one vol%) of PEO-induced micro-pores of ~1 nm in diameter. Thus, the power of GP experiments on the determination of the interconnection of the meso-structured porous materials is worthy of notice. The present comprehensive characterization of the novel silicon thin film with nanoscale voids arranged in a cubic array should provide a general framework for the meso- and micro-structure characterization of other related porous films prepared by similar processes.

LS. 29
Size Dependent Ionic Conductivity Observed for Ordered-Mesoporous Alumina-Ionic Conductor Composites. Hideki Matsuoka1,2, 3, Ryosuke Tanaka1, Yutaka Fujimaki2 and Taotao Yamamura 3. 1Department of Metallurgy, Tohoku University, Sendai, Japan; 2PRESTO, Japan Science and Technology Corporation, Kawasaki, Japan; 3Center for Interdisciplinary Research, Tohoku University, Sendai, Japan.

Ordered-mesoporous Al2O3 was synthesized by the solgel method using neutral surfactants as template. The pore size could be controlled over the range of 2.8~12.5 nm by using different surfactant copolymers and by different synthetic conditions. Composites composed of the synthesized mesoporous Al2O3 and the lithium ion conductor (Li1.3Ta0.7) was prepared. The dc electrical conductivity of 50Li3.5Ta5.0mol% Al2O3 with 4 nm pores was more than 100 times higher than that of pure Li1.3Ta0.7. The pore size dependence of the conductivity of Li1.3Ta0.7 was measured. A systematic dependence of conductivity upon pore size was observed, in which the conductivity increased with decreasing the pore size.

LS. 30
Solvation interaction with carbon nanotube bundles under hydrostatic pressure. Kristin Rule, James Elliott, Jan Sandler and Alan Windle; Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom.

The high theoretical modulus and strength of single-wall carbon nanotubes (SWNTs) makes them an ideal candidate for use as a filler material in polymer composites. More recently, the response of carbon nanotubes to molecular pressure produced by the cohesive energy density (CED) of a solvent has opened up the possibility of using carbon nanotubes as molecular sensors. Aspects of both of these potential applications of carbon nanostructures are explored by computer simulation in the application of hydrostatic pressure. In this paper we apply constant stress (NST) Molecular Dynamics simulations using the classical molecular force field to simulate hexagonal bundles of SWNTs surrounded by a solvent bath. The aim of these simulations was (i) to elucidate the effect of bundle size on SWNT collapse pressure, and its relation to the collapse mechanism we have postulated for tubes in infinitely periodic bundles, and (ii) to gain a better understanding of solvant-nanotube interactions under hydrostatic pressure, specifically with relation to solvant polarity and
CED of the solvent. In particular, the effect of solvent CED on the pressure at which the nanotubes inside the bundle collapse is investigated. The solvents used for studying CED include hexane, toluene, and 1,2-dichloroethane. A variable pressure tunable membrane was found to have a significant impact on the collapse pressure of nanotubes, with the collapse pressure progressively increasing with increasing solvent CED. The collapse pressure for nanotubes coated with a variable pressure membrane was found to be lower than that for nanotubes coated with a constant pressure membrane.

**LS.31 Soft magnetic vapor phase co-deposited polymer-metal nanocomposites for GHz applications** Abhijit Bhawe, Usman Saeed1, Joern Kravetz2, Oral Cenk Aktas1, Vladmir Zporojecki1, Franz Faspel1, Michael Frommberger2 and Eckhard Quandt3

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Future GHz driven mobile communication handsets and portable information tool demand new requirements for further miniaturization and lower insertion losses for inductive components installed in the high performance microwave circuits. 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 limitations of the nanocomposites of soft magnetic nanoparticles protected in insulating polymer matrices are promising candidates and could play important roles particularly in such high magnetic field applications with higher cut-offs frequencies in the GHz regions. Appropriately fully filled isolated magnetic nanoparticles dispersed three dimensionally (3 D) in an insulating polymer matrix possess good potential to generate quite high saturation magnetization required to shift ferromagnetic resonance in the GHz range along with significantly minimized eddy current losses due to the surrounding highly insulating polymer. Polymeric Teflon AF having the property of high degree of resistance to any chemical attack is naturally an excellent choice to protect the magnetic nanoparticles in organic host. However, there is no easy way 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. An additional 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 [108 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 and ferromagnetic resonance appears to occur at around 6 GHz based on the complex permeability measurements.

**LS.32 Polymer Nanocomposites with Surface Modified Magnetic Nanoparticle** Young-jung Yoon and Jin-Kyu Lee, Chemistry, Seoul National Univ., Seoul, South Korea.

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

**LS.33 Nonlinear magneto-optical Kerr effect in optical third harmonic generation from magnetic granular films exhibiting giant magnetoresistance** Evgenia Mikhailova Kim, Tatyana Vladimirova Murzina and Oleg Andreichev Alexeieff, 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 nonlinear spinors, spin dependent electron scattering and tunneling, giant magnetoresistance (GMR), etc. Apart from these phenomena several research groups have investigated magnetization induced non-linear optical effects as nonlinear magneto-optical Kerr effect (NOMOKE) in second harmonic generation (SHG) [1]. In this work nonlinear magneto-optical Kerr effect in optical third harmonic generation (THG) is experimentally studied in $\text{Co}_x\text{Ag}_{1-x}$, $\text{Co}_x\text{Al}_{2}\text{O}_3$, $\text{Co}_x\text{Cu}_{1-x}$ for the first, to our knowledge, time. 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 unfocused output of a Q-switched Nd:YAG Nd(3) laser at the wavelength of 1064nm with a pulse width of about 15ns, repetition rate of 5Hz. An angle of incidence was $45^\circ$. The third harmonic [TH] signal was detected by a PMT and gated electronics. Three sets of magnetic granular films of $\text{Co}_x\text{Ag}_{1-x}$, $\text{Co}_x\text{Al}_{2}\text{O}_3$, and $\text{Co}_x\text{Cu}_{1-x}$ composition were prepared by co-deposition of Co and Ag, Al, and Cu, respectively, in a dual electron-beam evaporator at room temperature and residual pressure of $10^{-2}$ Pa on ceramic substrates. The thickness of the films was about 400nm. The crystalline structure was studied by X-ray diffraction and transmission electron microscopy which allowed us to estimate the mean size of Co granules in the annealed films. All types of magnetic granular films exhibit the GMR effect. The room temperature magnetoresistance was measured in the magnetic field up to 8.2 kOe for in-plane current configuration and three types of external magnetic field application. To study the crystallographic symmetry of the samples the minimal misorientation of the SH and THG intensity were measured, which showed the existence of a mirror plane in the film structure. Magnetoinduced THG was studied in the geometry of transversal magneto-optical Kerr effect. The maximum of the NOMOKE magnetic contrast is attained at the value of $x$ close to that providing the maximum of the magnetoresistance similar to the dependencies of the SHG magnetic contrast observed recently. The THG interferometry did not reveal magnetinduced changes in the third harmonic phase. [1] T.V. Murzin, T.V. Misuryan, A.F. Krasov, J. Gudde, D. Schumacher, G. Murovsky, A.A. Nikulin, O.A. Aktsypetrov, Surface Science, 482-485 (2001).

**LS.34 Nylon grafting onto carbon nanotubes** Krzysztof KK Koziol1, Milo SP Shaffer2 and Alan H Windle3, 1Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom; 2Department of Chemistry, Imperial College, London, United Kingdom.

There is a possible applications for carbon nanotubes (CNT) in which the CNT form a close association with other types of material particularly polymers. Applications include gas processing and structural composites. Direct grafting of surface polymer chains is a potential way to improve the processability of carbon nanotubes in composites or controlled networks with tailored properties. There have been a number of attempts to coat the surface of carbon nanotubes, but only a few have succeeded in covalently grafting molecules onto the nanotubes. The surface of CNT was modified by chemical vapour deposition (CVD) technique, which permits control of length and diameter. After a simple purification step, the grafted nanotubes are free of monomers. 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 scellings of different nanotube/catalyst. Numbers of CNT functionalised by the chemical vapour deposition (CVD) technique can contain significant
The importance of films composed of different nanomaterials has been increasingly recognized because of the intriguing multifunctional properties, such as optical, and 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 electrochemical deposition. Three nanocrystal components were considered: CdSe nanocrystals capped by TOPO, γ-Fe2O3 (magnetite) nanocrystals capped by oleic acid and Au nanocrystals capped by dodecanethiol. Electrodeposition 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 the Au nanocrystals. As the ratio of Au in the solution was increased beyond 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 various electronic and optoelectronic devices. This work was supported by the MRSIC program of the National Science Foundation, Award No. 0213589.

**L8.30**

Applicatiion of SOFC-type cell with nanocrystalline electrode to practical deNOx reactor. Shinjo Katsuyama, Takuya Hiramasu, Osumi Shino, Masaosaku Amano, Yoshiko Furugori, and Koushi Honda, Department of Ceramic Engineering, ITLCA, Nagoya, Japan. 2nd Materials Research Society of Japan, AIST, Nagoya, Japan.

SOFC-type cells, which are electrochemical cells using an oxygen ion conductor, can be applied to not only fuel cells but also oxidation or reduction reactors. One of the applications is the deNOx cell that can reduce NOx to N2 without any reducing agents. However, conventional cells without selective electrode have decomposed co-existing O2 in preference to NOx, resulting in an extremely low efficiency and an impracticable high electric power. We have investigated a selective electrode that prefer to reduce NOx in the presence of O2. The electrode consists of two layers, NiON and NiOYSZ-Pt(y)-YSZ-YOZ(zeolite). By changing the NiO4+YSZ layer is changed to a self-assembled nanostructure, in which nano-grains of Ni metal are formed at the NiO/YSZ grain interface. NOx molecules are selectively reduced at the self-assembled interface because NOx and O2 molecules are adsorbed at different sites. We also fabricated large NiO-YSZ cells with 10x80mm size and evaluated their deNOx performance for the practical application to the reduction of NOx in emission from stationary and mobile sources. Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

**L8.35**


The high growth temperatures typically needed when growing diamond films using chemical vapor deposition (CVD) with H2/CH4 plasmas 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 principle 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 460-850°C. Different diamond seeding procedures (including mechanical polishing, ultrasonic treatment or nanodiamond powder suspension) as well as bias enhanced nucleation were employed to pretreat the substrate surface for UNCD growth, achieving high initial nucleation densities. The results showed that the growth rate for UNCD films is much less dependent on temperature compared to diamond films grown using conventional hydrogen-rich chemistries. A combination of SEM, UV/Raman, IR and XPS analysis indicate that UNCD films grow with relatively high growth rates even at temperatures as low as 460°C. The high nucleation density provided by the seeding procedure, the choice of substrate, and the highly 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 CVD deposition was discussed. The relatively high growth rate of UNCD films at low temperatures is also of great importance for various applications.
temperatures, together with the ability to surface micromachine UNCD films, provides a suitable platform material for diamond-based stand-alone microelectronic and integrated microelectronic/MEMS devices. This work was supported by the DOE-Office of Science Materials Science under Contract No. W-31-109-ENG-38.


A novel approach for the synthesis of carbon nanotubes strengthened nanostructured tungsten carbide alloys was investigated, in which nanophase tungsten powders are carburized by C2H2 instead of CO and a fraction of decompacted carbons are in situ converted to carbon nanotubes. High performance co-sintering of nanostructured tungsten carbide WC-Co 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 3300 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 inhibiting 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/H2 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 characteristics of these composite powders.

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

Below their order-disorder transition, nanoscale lamellar phases can be found in symmetric diblock copolymers. However, a macroscopic size sample usually exhibits polycrystalline configurations comprised of locally ordered but randomly oriented domains, with the presence of large amounts of defects. We discuss the effect of an externally imposed oscillatory shear on the global alignment of macroscopically disordered structures, with special focus on the motion of grain boundaries. A mesoscopic model is developed and a direct numerical simulation found for the case of a transverse/parallel grain boundary in the limit 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 mode on the microscale. 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 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 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 as organic solvents. The addition of nanomaterials allows the materials properties to be fine-tuned to specific applications. In this paper, we report the synthesis and characterization of three novel inorganic solvent-based nanocomposite coatings. The nanocomposites were prepared in aqueous solution, dip coated, dried, and then cured. Curing causes cross-link polymerization, locking in the nanocomposite structure. All of the coatings contain 3-Glycidoxypropyltrimethoxysilane (GlyMO), metakaolin 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.

18.44 Nanostructured polymer coatings for enhanced ultraviolet protection. Phamaneh Karang, Steven B. Warner, Prabh K. Prabhu, Yong K. Kim, and Steve Warner. School of Environmental Science, University of Massachusetts, Dartmouth, N. Dartmouth, Massachusetts.

Polymer materials, such as Kevelar 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 nanocoatings are applied on the fabric substrate. Nanocoatings are prepared by dispersing zinc oxide and titanium dioxide in acrylic solutions. The nanocoated structures were analyzed by scanning electron micrograph and UV/VIS 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 effect by nanoparticles 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 nanofiber 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 nanofibers for improved magnetic properties. The nickel-iron oxide particles used were in the diameter range of 2630 nm. The nanofibers were surface treated with 0.05% w/w dodecyl benzene sulfonic acid (DBSA) prior to incorporating them into the polymer solution. Surfactant containing on the particles improved their miscibility with the organic polymer thus preventing agglomeration. Ultrasonication was carried out for 30-60 minutes to disperse the nickel-iron oxide solution into the formic acid/nanoparticle dispersion. The 15 % w/v solution of nylon-ferrite system was then electrospun using a point to plate geometry, with field strength of 1.5 kV/cm and solution flow rate of 3.0 ml/min. Using similar spinning conditions, virgin nylon-polymer solution was also electrospun. SEM analyses were carried out on both electrospun samples. The diameter of the virgin nylon nanofibers was found to range from 35-100 nm, and that of nylon-ferrite system was in the range of 80-200 nm. The observed higher diameter of nylon-ferrite composite fibers might be attributed to the increase in viscosity of solution due to the ferrite particles. The SEM micrographs of the electrospun ferrite-nylon system indicated the absence of nanofibers on the fiber surface, leaving us to infer that the particles might have been introduced within the polymer fibers. In order to better understand the morphology and nature of dispersion of the nanofibers within the polymer fibers, XRD and TEM studies were in progress.


Nylon 6/clay nanocomposites are synthesized using a synthetic hectorite (Laponite® Na+) 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 accomplished by the insertion of epichlorohydrin monomer, and hence, silica-like 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 15A and polymerization process delaminates the lattices resulting no distinguished basal reflection. In contrast to
montmorillonite, haptone platelets do not exhibit well-defined birefringence reflection both in powder and nanocomposite forms. It is suggested that the dielectric loss of the d(001) layer of montmorillonite 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 clay forms of haptone samples show that it has lower crystallinity order than that of montmorillonite. Because in-situ intercalative polymerization is a powerful method to achieve highly dispersed clays, it is not appropriate to compare the dispersion of the two platelets in their nanocomposites. However, preferred aggregation of montmorillonite platelets after polymer deposition indicates that montmorillonite platelets have stronger electrostatic interactions than that of haptone. It is also observed that the residues of haptone, montmorillonite and haptone/montmorillonite containing nanocomposites have different morphologies. The difference in continuity and brittleness of haptone and montmorillonite clays is attributed to different aspect ratios and surface charges, which may influence liquid/continuous network formation of clay aggregates. The present research is directed to better understand the influence of clay morphology on flame resistance of haptone and montmorillonite nanocomposites, especially in terms of their reduced heat release and mass loss rates as observed from cone calorimeter.

18.47 Continuous Nanocrystalline Ionic Silver Halide Optical Fibers with Reduced Optical Scattering, Leonid N. Burvina, Evgenii Dinovskii, Andrei Okhrochuk, Nelit Lichkoikh, Vladimir Sviridov and Olejka Sereda; Fiber Optics Research Center, General Physics Institute of RAS, Moscow, Russian Federation; General Physics Institute of RAS, Moscow, Russian Federation.

The single crystals of silver halides of solid solutions AgCl-AgI with high purity and homogeneity were grown by Bridgman technique. Severe deformation was brought into silver halide crystal to produce optical anisotropy. Nanostructured volume optical materials were obtained with a narrow distribution of the grain sizes in the range 100-300 nm. For the first time, nanocrystalline optical fibers from nanograins of silver halides were produced by extrusion process. The nanocrystalline fibers and fibers extruded from single crystals were studied by an electron transmission microscopy and by conventional spectroscopy. Optical losses and scattering were measured. The optical losses in the fibers, extruded from nanograins and single crystal, were compared at visible and near infrared wavelength regions. The obtained nanocrystalline optical fibers have volume scattering of the same order of magnitude 5-10 times less than microcrystalline 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 mm are demonstrated. Influence of vacancy pores with nanodimensions on boundaries and birefringence in nanograins on optical losses, measured in nanostructured ionic materials, will be discussed. Mechanical properties of nanocrystalline and microcrystalline silver halide fibers will be compared. Applications of nanocrystalline silver halide optical fiber in remote spectroscopic, chemical sensing and laser medicine will be presented.

18.48 New Syntheses of CoPt3SiO2 and RuPt3SiO2 Nanocomposite Films, K.W. Lo,1,2 Y. Gao,1,2 K.H. Cheng,1 N. Ke,1,2 Y.W. Cheung,1,2 and S.P. Wong1,2; Electronic Engineering, Chinese University of Hong Kong, Shatin, Hong Kong; MateriLink Science & Technology Research Center, Chinese University of Hong Kong, Shatin, Hong Kong.

In this study, Co or Fe ions were implanted at an extrication voltage of 35 kV into thermally grown SiO2 on Si substrates at a dose of 4x1012 ions/cm2 using a metal vapor vacuum arc (MVVA) ion source. Subsequent irradiation of Pt ions to doses ranging from 1.5x1016 to 3x1017 ions/cm2 were performed at an extrication voltage of 50 kV. Characterization of these nanocomposite films was carried out using Rutherford backscattering spectrometry, x-ray diffraction, transmission electron microscopy, and vibrating sample magnetometry. Under such implant conditions, it was found that Fe0.5Pt0.5SiO2 and Co0.5Pt0.5SiO2 nanocomposite films with 0.40 ≤ x ≤ 0.54 and 0.34 ≤ y ≤ 0.51 were obtained. The Co and Fe 2+ implanted films showed soft magnetic properties. After Pt irradiation, the coercivity of both the cobalt-implanted and iron-implanted samples increased. This is bettered to a decrease of CoPt and FePt nanofracture formation in these samples. After thermal treatment, the coercivity of most of the samples increased further. The degree of the structures and magnetic properties of these films on the processing conditions will be presented and discussed. This work is supported in part by the Research Grants Council of Hong Kong SAR (Ref. Number: CUHK4216/03E).


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 20 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/pentafluoroethyl co-polymer 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, analytes can be directly spotted on our nanocomposite targets without the need for an absorption/ionization enhancing matrix, which limits throughput and accounts for the low mass (500 mmu and below) background noise in conventional matrix-assisted LDI (MALDI) mass spectroscopy. Our nanocomposite targets do not produce any background unless fragmentation of Nafion® occurs. This fragmentation was found to occur for laser power levels well below the ionization threshold of the analyte drug molecules tested. Hence, noise-free detection of low amounts of analyte can be carried out in a blank laser power range. Residual laser power is detectable 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 of 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 presence 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 electrical biasing of the analyte during LDI.

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

The present work emphasizes on the morphological and thermal effects induced by the addition of nano-ZnO in polypropylene. We prepared polypropylene nanocomposites with nano sized ZnO particles as the filler. The composites were prepared using the solution techniques, 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 sphericals, which were not predominant in the natively polymer. Cross-polarized optical microscopy images of the composite confirmed the formation of this spherical network. Differential scanning calorimetric results showed enhanced crystallinity of the nanocomposites as well as crystallization peak shift toward a higher temperature. Also the heat of fusion of the composite samples was found to be 12% higher than that of pure 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 sphericals. The results also showed the presence of nano-ZnO affected the thermal properties of the polymer, as seen from the change in heat of fusion and crystal formation 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. Filler induced morphology changes in the PP/ZnO polymer nanocomposites are also being examined using X-ray diffraction and transmission electron microscopy techniques.

18.51 Contact Compression of Self-Assembled Nano-
Micro-scale Pyramid Structures on Au (100) Surface.
Junlin Weng, Donald Ward, William A Curtin and Kyung-Suk Kim;
Division of Engineering, Brown University; Providence, Rhode Island.
An electro-chemical etching induced self-assembly is used to produce nano and micrometer scale pyramid-structures on single crystal gold (100) surfaces. The ridge growth in the similar fashion to the facets aligned in (114) plane. Experimental studies are performed to optimize the etching conditions for the pyramid growth. Using the unique characteristics of the self-similar pyramid structure, contact conformation and wetting performance were performed on single crystal gold surface to study the length scale effect in the plastic deformation of the pyramids. A continuum limit analysis and a finite element simulation as well as molecular dynamics simulations are used to predict the deformation and load-displacement curve of the pyramid-compression. The limit analysis predicts the load of compression is proportional to the square of the deflection. The continuum analysis provides insight into the asymptotic behavior of the elastic-plastic load-deflection response of the pyramid under compression for a large value of deflection. The three dimensional molecular dynamics simulation is utilized to study the dislocation activities during the early stage of the pyramid-compression. Experiments are also carried out by pressing the pyramids with an atomically flat micro surface.
The deformation of the compressed pyramid is measured using an Atomic Force Microscope (AFM). The continuum analysis predicts size independent values of the slope change of the pyramid facets near the contact edge, caused by plastic deformation. However, atomistic simulation predicts opposite value of the slope change to the prediction of the continuum analysis. The AFM measurements of the slope change show size dependent transition from the prediction of the continuum analysis. The size of the nanoscale transition data provide an apparent characteristic length of the size dependence of plastic deformation in a small volume.

L8.52
Yttria stabilized zirconia (YSZ), a fast ion-conductive material, is widely used as an electrolyte for solid oxide fuel cells (SOFCs) and other electrochemical devices. To prepare thin electrolyte films for solid oxide fuel cells, low-cost and efficient processing is highly desired. Electrolyte deposition has been used for different metals. Compared with sol-gel processing, starting materials used for electrolytic deposition are less expensive, and deposition can be performed from aqueous solutions with relatively low concentrations. Nanostructured YSZ thin film coatings have been deposited on different substrates, such as nickel, porous strontium doped lanthanum manganite (LSM, a cathode material for SOFCs) by electrolytic deposition. The films were processed by cathodic deposition in the solution of the ionic salts of yttrium and zirconium. Mixture of methanol and water was used as the solvent. The continuous coatings were realized by formation of very thin film deposition, room temperature drying, intermediate temperature calcining. The coatings were finely sintered at high temperature. The desired thickness was maintained by the continuous coating obtained by controlling the metal concentration in the solution, deposition current density, deposition time and sintering temperature. The cubic phase of YSZ in the coatings with 8 mol% of yttria was confirmed with X-ray diffraction analysis. The microstructures of YSZ coatings were characterized using scanning electron microscope and atomic force microscope.

L8.53
Synthesis and Processing of Multimetallic Oxide Nanoparticles Produced by Flame Spray Pyrolysis. Julien Claudius Marcal1, Richard M Laine1, Jose Azurduy2 and Tom Hinklin1; 1MSE, University of Michigan, Ann Arbor, Michigan; 2Th Materials Inc., Ann Arbor.
Liquid-feed flame spray pyrolysis (LF- FSP) of ethanol solutions of low-cost metalorganic complexes provides access to diverse types of mixed-metal, nanometer powder in a self-sufficient manner of chemical and phase purity. This scalable synthesis route provides reproducible, high purity, frequently self-dispersing nanopowders at rates up to kg/h. Typical average particle sizes (APS) range from 10 to 50 nm with corresponding surface areas of 100 to > 20 m²/g. We will discuss potential applications for example, nano YAG powders sinter to full density at 1400 degree Celsius.

L8.54
Many practical applications of nanosized materials, most notably in the areas of catalysis, separation, ion exchange, fuel cells and sensor technology, have been exploited in recent years using the neutral inorganic (zeolite) materials. Much less work, however, has focused on anions as structure directing agents in the construction of catalytic inorganic hosts. Our research involves the solvothermal synthesis and solid-state characterization of new nanosized and low dimensionality inorganic materials, where the charge on the host is positive. We are currently focusing on lower group 14 elements, as well as selected transition metals, as building blocks for these nanosized host materials. We have presented successful methods for the synthesis of a variety of new compounds, one member being a catalytic, two-dimensional layered material [Pd3F5NNO3 as BING-5: State University of New York at Binghamton, structure type 5]. We have also quantitatively exchanged the interlayer nitrate groups of Pd3F5NNO3 for dichromate, chromate, permanganate, benzoate and terephthalate under ambient aqueous conditions. The material maintains or slightly expands its nanoscopic layer-to-layer distance. BING-5 is stable to 450°C, which is vastly superior to inorganic materials that are the standard for anion-exchange. Physical and chemical properties, as well as synthesis and characterization of these new materials, will be discussed.

L8.55
Borophoric Core-shell Nanoparticles. Sung-Woog Ryu, Juan Antonio Gonzalez, Metin H. Acar and Anne M. Mayes; Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.
Borophoric core-shell nanoparticles were obtained by microemulsion polymerization. Nanoparticle borophoric can be processed and recycled at the reduced temperatures. Several parameters determine the bulk properties of these borophoric nanoparticles, such as composition, size and processing conditions. Composition and size determine the effect on the mechanical properties, and 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 nanoparticles, since the processability advantage of borophoric 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 borophoric property was maintained even in particles as large as 200 nm. Different morphologies, such as three-layered 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 silicon or gold, into the core is expected to be a source of novel core-shell nanocomposites.

L8.56
Nanoengineering of Extended ZnO Film Structures. Z. Ryan Tian, Lorraine J. Criscitiello, Jun Liu, Randall T. Ogum, Timothy J. Biebuyck, Paul G. Clem, Matthew L. Micheletti 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 3D or 2D ZnO film structures. Computer simulations of 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 batch and continuous composition continuous reactor systems, the impact of aqueous and nonaqueous solvent systems and the zinc precursor on film microstructure was investigated. For example, the aqueous system used was an extension of the approach described by Vayssieres and coworkers [E. Vayssieres, et al. J. Phys. Chem B. 2001, 105 (3350-3359)]. 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 the appropriate conditions, ZnO films with an amazing variety of structures can be prepared. These include arrays of simple hexagonal columns, columns capped with plates, columns composed of crystallographically aligned plates, and multi-legged columns. Structural control comes from the growth conditions used and the type and concentration of growth modifier. The growth of these structures will be explained using the results of the molecular modeling. Sandia is a multiprogram laboratory operated by Sandia Corporation, for the United States Department of Energy under contract DE-AC04-94AL85000.

L8.57
Polydisaccharide Microcrystals with Highly Ordered
Mesostructures and Polydiacetylene/Silica Nanocomposites
Thereof, Jelena Panj, Byron P. McCaughey, Xin Li, Xiaojie Ji and Yuanning Feng. Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanostructured materials have attracted a great deal of attention due to the novel material properties and applications. Polydiacetylene (PDA) has been the subject of extensive work because of its ability to form stable, ordered crystals that change color due to thermal, mechanical, or chemical stimuli. In this research, highly ordered nanocomposites of polydiacetylene sodium (PDA-Sal) and silica have been prepared by the reaction of 10,12-pentacosanoid 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 monochromatic symmetry. Upon thermal treatment, the microcrystals showed interesting thermochromic transitions, behaviors, such as reversible red to blue, reversible blue to red, and irreversible red to orange changes at different temperature ranges. The thermochromism of the microcrystals was investigated by differential scanning calorimetry (DSC) and other techniques. Using the PDA-Na and tetraethyl orthosilicate (TEOS) as precursors and upon the top-chemical polymerization of the monomers, the chromatically yellow or pink PDA/Si nanocomposites with an ordered mesostructure in the polymer matrix have been successfully prepared. The nanocomposites were characterized in detail by Fourier transform infrared (FTIR) spectroscopy, 13C solid-state nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), thermogravimetric 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 1: Polymer Systems
Speaker: Jamie James Watkins
Thursday Morning, December 4, 2003
Room 304 (Hynes)

8:30 AM L0.1
Hierarchically ordered multi-component block copolymer/particle nanoparticle composites.
Michael Rainer, Rockwell and Edwin Lorrimer Thomas, MIT, Cambridge, Massachusetts.

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

9:00 AM L0.2
Extending Nanoscale Block Copolymer Self-Assembly Approaches to High Temperature Ceramics.

Nanomaterials of ceramic materials with block copolymers is a fascinating research field holding tremendous scientific as well as technological promise. Non-oxide systems-like SiC or SiCN are particularly challenging since their polymeric precursors are often difficult to obtain and ill-defined. Nanomaterials of such materials is expected to open up completely novel property profiles adding to those obtained from bulk materials like high temperature stability or mechanical properties. Here, to the best of our knowledge, we demonstrate for the first time the ability to nanostructure SiC-type ceramics by blending a pre-copolymer with the amphiphilic block copolymer poly(isoprene-block-ethylene oxide). The PS-PMA block is used as a structure directing agent for a polysilane, commercially known as Cermet. Selective swelling of the PEO microdomains of the block copolymer with the silane oligomer results in a cooperative self-assembly of block copolymer and Cermet into nanocrystalline SiC or SiCN, similar to those in ceramic technology. These SiC or SiCN 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 nanoparticles 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 nanocrystalline SiC or SiCN.

9:15 AM L0.3
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 oriented, single-crystal lamellar triblock copolymer films with alternating rubbery-glassy layer morphology possess an interesting microstructure in their mechanical behavior, which can prove to be attractive for various applications. This research aims in understanding the governing micro-mechanical mechanisms in the deformation behavior of single-crystal TPEs. The basic role of the glassy (PS) and rubbery (PB) phases of the layered configuration are investigated in several numerical simulations with numerous micro-mechanical finite element unit cell models of a polyethylene triblock, copolymer. The elastic properties of the highly oriented lamellar morphology subjected to tensile loading at different directions to the lamellae plane. Various morphological imperfections, common for this family of multiblock polymeric materials, are studied, including inverse perforations, layer misalignment, and paired-edge dislocations. These structural imperfections provide initiation sites for potential deformation instabilities, such as layer buckling, microcracking, and localized plastic deformation. The calculated micro- and microscopic response to various types of loading is compared to x-ray and microscopy data, which already exist in the literature for these block copolymers, and proved to be successful in linking their macroscopic response to the underlying physics that govern the evolution of the periodic microstructure. Our representative unit cell models are also successful in reproducing the deformation behavior of highly oriented copolymer lamellar block copolymers. Representative unit cell models of lamellar/lamellar micromechanical behavior 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 L0.4

The filtration properties of novel graft copolymer composite membranes were investigated by the filtration of gold nanoparticles. The membrane selective layer consists of microphase separated, hydrophilic PEO channel 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 probe of the membrane filtration performance. Changes in the size distribution of nanoparticle solutions before and after filtration were quantified using TEM and UV-visible spectroscopy. Results show that the nanoparticle size distribution could be cut off at a specific value and tuned 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 filter dynamics, the membrane can be used to select specific nanoparticle distributions. This work demonstrates that the graft copolymer membranes could produce nanoparticles of low size distribution in a convenient and tunable manner by varying 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. Goldbach and Thomas P. Russell, Department of polymer science and engineering, University of Mass., Amherst, Amherst, Massachusetts.

The use of two orthogonal, external fields is shown to control the orientation of lamellar microdomains in three dimensions in diblock copolymer thin films. An elongational flow field was applied to obtain an in-plane orientation of the microdomains of the copolymer melt and an electric field was used to orient normal microdomains that were not 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 L0.6

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 and chemically modified PDMS elastomers 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 photoreactor, 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 L0.7

In this work, we explored the possibility of making monodisperse rigid polymer layered silicate nanocomposites via an electrophoretic process. The elastomeric, biocompatible/biodegradable polymer matrices with incorporation of organomodified, commercially available organoclay plates 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/diol or diol/ether with Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polyester, as the polymer matrix. We have shown that the development of viscosity of the polymer decreased the deposition of the system to exfoliate and randomly distribute the silicate layers throughout the matrix. Polarized light microscopy shows a high degree of birefringence suggesting that the polymer chains in m-scan fibers are well aligned. Conventional X-ray diffraction (XAXS) data revealed no crystalline peaks in m-scan fibers whereas annealed samples show extensive amount of crystallinity. While the polymer chains in spin fibers are not in perfect crystalline registry, annealing the samples above glass transition temperature for even 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 dispersions observed from WAXS Scanning Electron microscopy (SEM) 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 Silyloxane Particles and Liquid Crystalline Polymers.**
David A. Schirrali, Alaine P. Scamia 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 silyloxanes (POSSEs). Several liquid crystalline nanoparticles can be made by varying the alkyl spacer length of the cyanophenyl derivatives. A representative synthesis involves the reaction of n-alkylene bromide with 6-bromohexanol in the presence of sodium hydroxide and tetrabutylammonium. The resulting procducts is then reacted with 4-hydroxy-4'-diethylamino benzophenone in the presence of potassium carbonate and acetone. The cyanophenyl terminated alkene is then reacted with octaethyl POSS® via a hydroxilation reaction employing a Kinetred's catalyst. The LC POSS® nanoparticles were then compounded into thermotropic polyester liquid crystalline polymers (LCPs) as well as a "fibrilated" LCP based on 4,4'-dihydroxy aromatic acid and aliphatic diisocyanate. 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 LC nanoparticles into a 4-frustrated LCP. It is proposed that the LC nanoparticle will help to "unfrustrate" the LCP. The thermal stabilities, glass transition temperature, and the moduli of these LCP/LC nanoparticle composites will be reported.

1130 AM L0.11

**Nylon-6/Clay Nanocomposites Probed by Dielectric Relaxation Spectroscopy.**
Yi-Hsien Lai, Anthony J. Bur, Naoko Noda and Vivek M Prabhak; 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 occurrence of the liquid crystalline phases of the polymer blends. The two types of microstructure, namely, exfoliated and intercalated, are obtained by extruding Nylon-6 with Cloisite 15A and 30B, respectively. Time-domain spectrometer enables us to probe the low frequency relaxation (0.01 Hz to 100 Hz) and the network analyzer collects data in the high frequency domain (100 Hz to 1 MHz). The evolution of the characteristic frequency, relaxation strength, as well as the width of relaxation time distribution is carried out by fitting raw data with the modified Cole-Cole function in which the relaxation time distribution function is eliminated 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. A broadened 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.

1145 AM L0.12

**Glass Transition Temperature Behavior of Aluminum/Poly(methylmethacrylate) (PMMA) Nanocomposites.**
Benjamin J. Alsh, Linda L. Schaller* and Richard W. Siegel#
*Sandia National Laboratories, Albuquerque, New Mexico, Materials Science and Engineering Department, Remsizer Nanotechnology Center, Remsizer Polytechnic Institute, Troy, New York.

Aluminum/poly(methylmethacrylate) (PMMA) nanocomposites were synthesized by an in situ free-radical polymerization process using 38 nm and 17 nm diameter aluminum 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 additions of filler did not lead to additional Tg reductions. This novel thermal behavior is observed to vary with particle size, but this dependence disappears when normalized by specific surface area. The nanocomposite Tg phenomenon is thought to be due to non-adhering nanoparticles that act as well-dispersed internal void/polymer interfaces that break up the percolating structure of polymer domains recently hypothesized by researchers. The Tg reductions in polymer ultrathin films. The results also point to a dramatically increased scope of the so-called interaction zone (IZ) and its "far-field" effect on the entire matrix.

SESSION L1.0 Modeling and Theory

Chair: Rina Tannenbaum

Thursday Afternoon, December 4, 2003

Room 304 (Hynes)

1:30 PM L1.0.1

**Kinetics and Mechanism of Nuclear, Growth and Stabilization of Metal Oxide Nanoparticles.**
Rina 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 nanoparticles. 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 complex has been determined to be representative of the overall rate of the process. Moreover, it has implicitly been assumed that the formation kinetics of the metal nanoparticles directly mirror the decomposition kinetics of the precursors. In this present work, we attempt to decouple the kinetic characteristics of the various steps that constitute the overall nucleation and aggregation process of cobalt oxide nanoparticles stabilized by poly(methyl methacrylate) (PMMA). A combination of infrared and x-ray photoelectron spectroscopies, transmission electron microscopy and dynamic light scattering is used to identify the individual contributions of each step to the overall mechanism of metal nanoparticle formation. We have shown here that there are several crucial steps in the aggregation process of the nanoparticles, and that the traditional assumptions regarding the dynamics of the process are not correct. The formation of cobalt oxide nanoparticles with an average size above the detection threshold of dynamic light scattering (~3 nm) and TEM (~2-3 nm), does not mirror the decomposition of the precursor during the same time frame. Moreover, the stabilization process, i.e. the adsorption of the polymer chains onto the nanoparticle 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 later 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 L1.0.2

**Effect of Grain Growth on Grain-boundary Diffusion creep in Nanocrystalline Polycrystalline Pd by Molecular Dynamics Simulation.**

Molecular-dynamics simulations are used to elucidate the effects of grain growth on grain-boundary diffusion creep and grain-boundary sliding during high-temperature deformation of a nanocrystalline Pd model microstructure. The initial microstructure consists of a 25-grain polycrystal with an average grain size of about 1.5 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 in the initial growth phase enhance both the stress-induced grain boundary diffusive fluxes and grain-boundary sliding. Second, dislocations generated as a result of grain-rotation induced grain coalescence and grain-boundary demarcation in the vicinity of certain triple junctions also contribute to the deformation. *Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract Number W-31-109-Eng-38.
2:15 P.M. L10.3
On Molecular Dynamics Simulation of Metal Clusters and Their XRD and ELNES Spectra. Gregorio D’Agostino and Michiel Gioso, ENEA, Roma, Italy.

The present paper reports on classical molecular dynamics of close-compact metal nanoclusters. Attention will be focused 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 (100-1000 atoms) cannot be accounted for by molecular dynamics 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 trono-octahedra, truncated-decahedra and icosahedra) and cobalt (fcc and hcp based) of different sizes. Calorimetric curves have been evaluated than showing well known co-existence regions and lowering of melting temperatures (melting temperatures for Rh metal are about 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 via Bose statistics. X-rays diffraction patterns and near edge electron energy loss spectra have been simulated and compared. It is worth stressing that broadening of XRD peaks does not allow for direct recognition of the underlying lattice structure while the simulation provides clear interpretation of spectra. At very low temperature, spectra are dominated by finite-size effects and bond contraction at surfaces whereas at higher temperature Debye-Waller effects become relevant.

2:30 P.M. L10.4

A nanocomposite of multiwalled functionalized carbon nanotube and poly(3-methylthiophene) has been designed for selective sensing of halogenated methanes. TGA analysis of the composite showed two phase transitions at about 250 degrees and 700 degrees with a weight percent loss of about 38% at 250 degrees and 10% at 750 degrees. The multilayer functionalized carbon nanotube and poly(3-methylthiophene) showed phase transitions at about 250 degrees and 720 degrees. 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 CCl3. Similar experiments have been carried out with other halogenated methanes. The sensor has been constructed using two gold or two palladium microelectrodes on Si wafer or polymer substrates. The nanocomposite is cast between the electrodes for measuring either the resistance or voltage. For relevant comparison of the performance of the nanocomposites, sensors have been constructed with functionalized carbon nanotubes or poly(3-methylthiophene) or the blend. The nanocomposite showed high sensitivity for chloroform and very low sensitivity for carbon tetrachloride and methane. Other halogenated methanes have also been investigated to model the mechanism. Based on the results, a mechanism based on non-rigid charge transfer interaction between the nanocomposite and analyte is proposed. The nanocomposite requires analyses with ionization potentials less than 11.50 for the charge transfer interaction. The sensitivity of the nanocomposite appears to be governed by the activation energy of the non-rigid charge transfer complex. The selective sensing of CCl3, from a mixture of CHCl3 and CC4 suggests its potentialities for industrial applications.

2:45 P.M. L10.5
Molecular Modeling Computer Simulation of Organic Polymers: A Novel Computer Simulation Technique to Characterize Nanostructured Materials. Sarah G. Schae2, Hubert Kuhn2 and Guenter Schmidt1; 1Institute of Inorganic Chemistry, University of Essen, Essen, Germany; 2Aicon - Molecular Dynamics GmbH, Göttingen, Germany.

Complex nanostructured self-assemblies such as colloidal suspensions, micelles, immiscible mixtures, micromolecules, etc., represent a challenge for computational methods due to the presence of different time scales in their dynamics. We have recently successfully applied a novel computer simulation technique, Direct Potential of Trajectories (DPT), to model the behavior of diblock copolymers at the water/oil interface. With the use of a simple model we have performed simulations of polymer/water/oil systems at different concentrations. In this lecture we present the results of simulations of nanostructured polymer mixtures. Especially, DPT 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 C12H25 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 we are in remarkable agreement with the experiment. Even the so-called "breaking-effect", a concentration-dependent shift caused by the addition of water, 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 very useful for the interpretation of complicated experiments or even to obtain experimentally unattainable data. E. Rygkin, H. Kuhn, H. Rehage, R. Mueller, J. Peggau, Angew. Chem. Int. Ed., (2002), 41(6), 983.

3:00 P.M. L10.6
Predicting the Morphologies of Confined Copolymer/Particle Nanoparticle Mixtures. Anna C. Balse1, Jee Youn Lee and Zhenyu Zhou, 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 structures. This change in chemistry, in turn, affects the polymer-wall interactions and consequently, the structure of the films. We illustrate this point by considering the nature of the depletion interaction between diblock copolymers and nanoscale particles with symmetric diblock and show that the confining walls can be exploited to promote the self-assembly of the system into particle nanowires that extend throughout the films and are separated by nanoscale stripes of polymer domains. Such films constitute vital components in the fabrication of nanoscale devices. Furthermore, the results point to a novel technique for modifying the chemical nature of coatings and films entirely through self-assembly. Since this technique relies on entropic effects, it constitutes a fairly robust method that can be applied more generally than approaches that rely primarily on chemistry-specific enthalpic effects.

3:30 P.M. 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 2D Fibonacci lattice with a Fibonacci symmetry (8.9 gaps). 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 Wyckoff sites. Three of these fundamental geometries display complete band gaps -- including two: the F-RD with Fm3m symmetry and a group 21 frustrated with Fm3m symmetry that have not been reported previously. By using this systematic approach we were able to open gaps between 25, 5, 6, 8, and 9 bands in the FCC systems.

3:45 P.M. L10.8
Electronic structure calculations on ITQ-4 zeolite with guest alkali atoms. Hong Li and S. D. Mahanthi; Physics and Astronomy, Michigan State University, East Lansing, Michigan.

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

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than the experimental value, the c/a and b/a ratios are 0.23% and 0.02% larger than the corresponding experimental ones. The ITQ-4 system found with 12-atom models is in agreement with the previous calculations [1], where a C2/m space group symmetry was assumed. Experimentally Petkov et al. [2] find zigzag chains of Cs atoms along the channel. However, the plane containing the Cs atoms is found to be nearly perpendicular to that of the channel. We are reexamining their geometries by looking at other configurations and comparing directly the pdf [pair distribution function] [2] using the theoretical method with empirical potentials. Results with empirical potentials for different atom types (such as Na, K) and for different atom configurations are being investigated. [1] Z. Li et al., J. Am. Chem. Soc. 2003, 125, 6650.


4:00 PM L10.9
Atomic Modeling and Electronic Structure of Molecular Boxes. Ljubomir Miljkovic, Lev Sarkisov, Bin Deng, Donald E. Ellis, 1,2 and Randall Q Smrcka. 1,2 Physics and Astronomy, Northwestern University, Evanston, Illinois, 2Chemistry, Northwestern University, Evanston, Illinois.

Novel classes of nanoscale porous materials assembled from discrete building blocks offer possibilities for size- and shape-selected molecular separation, and control over chemical processes, with applications to catalysis and sensing. We describe "molecular boxes" built from six-connected molecule complexes of "core" aromatic rings which are interconnected by various organic linkers, such as pyridine, bipyrindidine, and metal porphyrins. We have performed first-principles density functional, and molecular dynamics analysis of Zn-porphyrin based cores, in which the characteristics for molecular recognition, 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
Modelling amorphous systems under high pressure at the nanoscale via molecular dynamics simulations. Li He1,2, Maria-Jose Caturia1,2, Alfonso Rubino2, Balakrishnan Sadagopan1,2, Teresa Diz de la Rubia1,2, James Shackleford1,2, Vishal J. Ravi1,2 and Stephen Garoffol1,2. 1Department of Chemical Engineering & Materials Science, UC Davis, Davis, California; 2Lawrence Livermore National Laboratory, Livermore, California, "Dept. Applied Physics, University of Alicante, Alicante, E-03607, Spain. 3Department of Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Transformations of the medium-range order and the dynamic behavior of amorphous 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 Reuson and Garofolini. In this article we present two different simulation schemes for studying the transformations in fused silica under high pressures, and show their equivalence. Both methods reproduce the equation of state (EOS) obtained from flyer plate experiments. We have centered our studies in the nanostructural changes occurring in the material with increasing pressure and the correlation between the medium-range order (~10 nm), through the structure factor, and the characteristic ring distribution of these amorphous glasses. An analysis of the ring distribution and structure factor reveals the changes occurring in this material in this regime and allows for an interpretation of the equation of state. The transition from elastic and plastic behavior is directly related to variations exhibited in the ring size distribution of this glass. During elastic compression, the ring distribution stays practically unchanged. However, this distribution varies continuously after the transition to the plastic regime takes place. This study can help understand the nanoscale nature of fused silica, influencing applications that depend on its structure under these conditions, such as 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

The synthesis, processing and characterization 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 developing a number of different computational approaches to tackling these problems and some selected examples will be described here. These include classical molecular dynamics simulations of single and multi-wall nanotube collapse under high pressures, Monte Carlo simulations of nanotube synthesis by chemical vapour deposition onto a metallic catalyst, and coarse-grained molecular mechanics calculations of nanotube persistence length. The overall aim will be to show that by constructing a modelling hierarchy spanning several orders of length and time scales, it is possible to build up a better understanding of effects at the nanoscale.

4:45 PM L10.12
Mesoscopic Modeling of Transport through Nanostructured Membranes. Mark A. Snyder and Dionisios G. 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 nanocaps. These systems challenge modeling approaches on several levels, including the strong energetic of the confined diffusion, the energetic anisotropy of the diffusion sites, the nanoscopic 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 novel mathematical framework for modeling diffusion of interacting species in nanostructured materials over larger length and time scales while retaining molecular scale information. In this work we explore a hierarchical approach, and develop a mesoscopic model for complex three-dimensional single crystal lattices. In particular, we focus on diffusion of aromatics in two practical zeolite systems, Faujasite and MFI. Comparison of gradient continuous time Monte Carlo simulations to the solutions of these new mesoscopic theories will be shown as validation of this approach in the limit of very thin membranes. Furthermore, this new theory allows us, for the first time, to perform quantitative comparisons of predicted macroscopic diffusion properties (e.g., molecular flux) to laboratory permeation experiments (e.g., benzene diffusion in Faujasite). In doing so, we assess the role that polycrystallinity (i.e., grain boundaries) plays in permeation and draw comparisons to the size and distribution of grain boundaries determined quantitatively via confocal imaging of realistic membranes saturated with fluorescent dyes.

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

L11.1 Solvent Effect on the Morphology of the Mesoporous TiO2
Jung-jun Chen1,2, Leiyu Wang1,2 and Wen-Yen Chin1,2. 1Department 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 morphology of as-synthesized TiO2 is determined by the sol-gel reaction rate is essential to prevent the formation of TiO2 particles in the solvent. The surface morphology of thus-prepared particles was examined by SEM and TEM. The surface pore size and its distribution of particles were investigated by BET and XRD techniques. The sol-gel effect on the shape and porosity of the TiO2 particles will be presented.
L1.1.2 Carbon nanotube deposition on the surface of metal wire by inductively coupled UHF plasma CVD

We have deposited carbon nanotubes (CNTs) on the surface of metal wires such as, and nickel, silver, and tungsten, using a high-frequency reactive UHF plasma CVD. At atmospheric pressure in ambient air, the plasma was generated in a quartz capillary of 750 micrometer inner diameter with Ar gas flowing, in which the metal wire of 100 micrometer diameter protrudes, by spinning the UHF plasma around the quartz capillary. In case of CNTs deposition on tungsten wire, methane gas and vaporized ferrocene were supplied in the plasma, while only methane gas was supplied in case of iron and nickel wires. Under the certain conditions of their gas flow rates and UHF power, CNTs were grown perpendicularly on the whole surface of the metal wires.

L1.1.3 HRTEM Characterization of Self-Assembled Manganese Oxide Thin Films

The formation of pure inorganic membranes is becoming increasingly important in the field of nanomaterials science. This work demonstrated the formation of inorganic free-standing thin films without the use of polymeric adhesive. These inorganic films have applications as selective oxidation catalysts, sensors, and in separation and ion-exchange processes. The free-standing films (15-150 mm thick) were fabricated by 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 a manganese oxide 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 chemical composition and microstructure of the films were determined by chemical testing of the films was performed. TEM was used to gain detailed morphological and structural data of the thin films. Novel approaches were applied for the preparation of TEM samples in order to retain morphological information. The microscopy data showed that the films are composed of OMS-2 (cryptomelane) fiber bundles, arranged in ordered layers. Synthesis of OMS-2 consists of mixed valent MnOOH octahedrons, sharing corners and edges to form tunnel structures. OMS-2 is a 2:2 structure with tunnel dimensions of 0.46x0.46 nm. The individual nanofibers aggregate together into bundles, which form the film matrix. The individual fibers and the corresponding bundles have an approximate diameter of 15 and 340 nm, respectively. Cross-sectional transmission electron microscopy (TEM) imaging along the long direction of the fibers. Additionally, EELS analysis provided data related to the electronic environment of the manganese species.

L1.1.4 Nanostructured Oxide Films for High Speed Sensors

We have engineered nanoscale porosity in oxide thin films using electron beam evaporation and substrate motion control of the Glancing Angle Deposition technique. The films consist of high aspect ratio (~10 to 30) columns separated by longitudinal pores of diameter ~100 nm or less, oriented perpendicular to the substrate. This anisotropic architecture comprises high surface area, high porosity films with remarkable sensitivity of the porous films to gases. To demonstrate sensor capability we have fabricated these nanostructured SO2, NO, 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.

L1.1.5 Nanostructured Ferrite Thin Films Prepared by Atmospheric MOCVD at room temperature

In this presentation, we will report synthesis of ferrite films with nanostructure by MOCVD. We also discuss the magnetic properties of films were closely related to film nanostructure. In this project, a MOCVD process has been successfully developed to deposit polycrystalline zinc iron ferrite, Cu₄Zn₆Fe₄O₁₄, films at temperatures of 300°C with zinc acetate, Cu(CH₃COO)₂, iron acetate, Fe(CH₃COO)₃, and oxygen as reactants, using a horizontal cold wall atmospheric reactor. AES and X-ray photoelectron spectroscopy (XPS) results showed that all films have a high stoichiometry of Zn₃Fe₂O₅ and CuO ferrite. X-ray diffraction (XRD) indicated that these CVD films were polycrystalline spinel ferrite, with grain orientations on [511], [400], [311], and [220] (pdf=16.1°, 21.0°, 25.2°, 29.7°, with [311] being the preferred grain orientation for Cu₄Zn₆Fe₄O₁₄ films. Most films were smooth, composed by clustered grains, as shown by FESEM. SEM. The small spherical particles, with size of 20-50 nm, clustered together to form a height shaped and diameter 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, (2-5-Oe), initial magnetic permeability (μi) 3.31×10⁵ H/m, saturation magnetization (Ms) 3.31×10⁵ emu/Oe, and remanence magnetization (Mr) 1.61×10⁴ emu/Oe. SQUID results also show that both μi and Ms are related to grain size, and temperature.

L1.1.6 Optical Properties of ZnO/Al₂O₃ Nanostructured Thin Films

Optical properties of ZnO/Al₂O₃ nanostructured thin films have been measured using a nanophotoluminescence setup. The films were deposited on glass substrates using MOCVD. The optical properties were characterized using nanophotoluminescence spectroscopy. The films were grown using a metalorganic chemical vapor deposition (MOCVD) technique. The films consist of ZnO nanocrystals embedded in Al₂O₃ matrices and the study of their optical properties. The excitation source used in our experiments was a nanophotoluminescence setup. The nanophotoluminescence technique enables the variation of nanoparticle diameter by the simple adjustment of an applied voltage. Using this method we have created layers of Al₂O₃ containing well-separated, size-selected ZnO nanoparticles with areal densities between 10⁵ and 10⁷ cm⁻². ZnO nanoparticles were deposited during the ablation of a ZnO target at 0.3-0.7 Torr in the NBPDL source using a KrF excimer laser (248 nm) at fluences of 1.5-5 J/cm². At a fluence of 1.5 J/cm², deposition of ZnO was achieved by ablation of alumin targets at 510 J/cm² in a 10⁻⁴ Torr atmosphere. ZnO nanoparticle diameter was tuned in the 5-15 nm range for different samples. We discuss the effects of the deposition conditions on the optical properties of these nanophotoluminescence measurements on these films will also be discussed in relation to the optical properties of these ZnO films. Our main focus is on the identification of size effects and interface phenomena in these nanostructured ZnO samples.
block copolymers have been examined. Our samples comprise stars containing a PS core and PEO corona (PS-P-(PEO)n), where n=3/4 and is the number of branches in each block polymer) as one
dendrimer-like star, PS-P(PEO)n. Both experiments demonstrated
the surface 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, pancake and brush regions were also observed in
the former depended on the amount of PEO while the later reflected PS
behavior. By continuously compressing and expanding the monolayer,
the structure of the polymer system was examined through
Grazing incidence X-ray scattering was observed with increasing pressure along with a
larger amount of PEO. Contact angle experiments showed that the
surface films readily flow at pressures below the pseudophase region.
Two stars containing the same PS core were chosen to
test 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 the PEO composition.

1.1.11
Self-Assembly of Telechelic, Pyrene-Labelled
Polydimethylsiloxane: Remarkable Melting Point Deposition
of Pyrenyl Nanocrystals and Novel Oxygen Sensing
Capabilities of an Associative Polymer. Bryce A. Jones¹, Sung
Dog Kim² and John M. Torokchian³, ², ³ Dept. of Chemical Engineering,
Northwestern University, Evanston, Illinois. ³ Dept. 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 pyrrole-polydimethylsiloxane
(Py-PDMS-Py). In contrast to most studies of organic nanocrystals
where an increase in control of glass transition temperature is
common, in this system an unexpected, strong depression in the
melting point is observed: in PMPS, for example, the melting point
of the pyrrole nanocrystals is 135 K lower than the bulk value.

1.1.9
Aerosol-Assisted Nanocomposite Materials.
John Eric Humprey¹, Jiheun Pung², Qiangjun Hu², Donghai Wang³,
Byron McCloy⁴, C. Jeffrey Brinker⁵ and Yunfeng Lu⁶
¹ Department of Chemical Engineering, Tulane University, New
Orleans, Louisiana; ² Direct Fabrication Department, Sandia National
Laboratories, Albuquerque, New Mexico.

Silica nanoparticles have been synthesized by an aerosol-assisted self-assembly process. Constituents such as
silica spheres, fluorescent dyes, organic ligands, catalyst particles, and metal oxide nanoparticles were added to the precursor sols
prepared by sol-gel technology (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, enriching the non-volatile components and results in the co-assembly of
dilute and surfactant into 3-dimensional mesostructures and in the
incorporation of the added constituents within the particle.

1.1.10
Novel Star Architectures of Polystyrene-block-Poly(ethylene oxide)
Copolymers as Surface Films at the Air/Water
Interface. Jennifer Lin Loom², Pascal Mass³, Brian Derve³,
Andrew Skolnik¹, Kaju Francis⁴,⁵, Daniel Ratch⁶, Yves Gravina⁴,⁵,⁶
¹ Department of Chemistry, University of Florida, Gainesville,
Florida; ² Chemistry, University of Bordeaux I, Bordeaux, France;
³ Chemistry, University of Calicut, Kerala, India.

The effect of star architecture and composition on the monolayer
behavior of polystyrene (PS) and poly(ethylene oxide) (PEO) diblock
copolymers at the air-water interface is examined and presented.
While numerous studies of linear PS-b-PEO systems exist in the
literature, our work is the first that branched structures of these
**L1.13**

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

**L1.14**

Dense Silica Dioxide Thin Films From Packed Silica Nanoparticles, Xinzhang "Jesse" Zhou, Sheng Wang, Kermit S. Kwa, 2 Zhongwei Li, 3,4 Gennan Kim, 2 David Q. Ha, 2 David L. Wyman 2 and Eric S. Moyer 2, 1 Electronics Science & Technology, Dow Corning Corporation, Midland, Michigan, 2 New Ventures: Inorganic R & D, Dow Corning Corporation, Midland, Michigan, 3, 4Analytical Science, Dow Corning Corporation, Midland, Michigan.

Compared to Chemical Vapor Deposition (CVD), Spin-On Dielectrics (SOD) can provide superior gap-fill capability, but tend to form comparatively low-density films in the 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 hydrophilic silica sol (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 tetramethyldisiloxane, and were subsequently modified with trimethylsilyl groups and dispersed in an organic solvent. The resultant silica nanoparticles were spherical with particle densities in the range of 2.00 – 2.16 g/cm³, mean particle diameters in the range of 10 – 16 nm and narrow particle size distributions. Low spin coating on patterned silicon wafers and a steam anneal at 700 °C, the silica nanoparticles were found to be tightly packed, even in small trenches with a base width of 80 nm and an aspect ratio of 9 (height/width). The films showed a porous texture. With a solution of silica nanogel and HSO 4 directly spin dispersed in a solvent, a dense silica dioxide film could be prepared. A minimal gap-fill limit of 32 nm (2x mean particle diameter) was observed for silica nanoparticles with a diameter of 16 nm. The film textures of the both the nanoparticle coating and the dense silica dioxide films have been examined by high-resolution scanning TEM using a specimen prepared with a focused ion beam (FIB).

**L1.15**

Development of Improved Routes towards Preparation and Surface Modification of Iron Oxide Nanoparticles, Lingfan Wang 1, 3, Jie Liu 1, 3, Li Hua 1, Minato Tomino 4 and Chun-Am Jim Zheng 1, 5 Suzan Binghamton, Binghamton, New York, 4Kumamoto 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. One approach is iron-storage ferritin, which was utilized for the preparation of iron oxide nanoparticles. The preparation involves thermal removal of the protein shell from ferritin. In the second approach, iron pentacarbonyl compounds are used for the preparation of iron oxide nanoparticles by thermal decomposition as controlled temperatures and under different capping agents. Iron oxide nanoparticles with a range of core sizes, different surface compositions, and high monodispersity have been prepared. The structure and morphology have been characterized using TEM, AFM, UV–Vis, and FTIR techniques. The implications of the findings to the design of advanced composite sensing materials will also be discussed.

**L1.16**

Probing nano scale dynamics in glassy polymers near glass transition temperature, konwarum sakamath and Nathan Iserloff, Dept of Physics, Northeastern University, Boston, Massachusetts.

The cooperativity concept of glassy dynamics has been investigated by nano scale probing of thermal noise fluctuations in a glassy polymer polyvinyl acetate (PVAc) near Tg. Using ultra high vacuum (UHV) capacitance scanning probe microscopy (SFM) techniques, nano scale probing of thermal noise fluctuations in a glassy polymer can be refined 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 variation and covariance, 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 (CHR) and energy landscape properties.

**L1.17**

Nanocomposites with Functionalized Carbon Nanotubes, Sheng K. Mestre, Yong K. Kim, Steven D. Warner, Prabir K. Patra, Philmanow Karagur and Autumn Dillmore, Textile Science, University of Massachusetts, North Dartmouth, Massachusetts.

Carbon nanotubes are known to have excellent mechanical, electrical and nonlinear optical properties because of their unique atomic geometries. These properties make carbon nanotubes potential candidates for high performance structural and high-response electrical and optical actuator applications. Despite their promises, no significant enhancement in the mechanical strength or modulus has been achieved in nanotube-polymer composites, presumably due to the weak interfacial bond between the CNTs surface and the polymer matrix. Also, most of these nanotube/polymer systems are poorly dispersed. One way of improving adhesion is to functionalize carbon nanotubes with chemical moieties that are compatible with the polymer substrate. Functionalization can give stronger adhesion (matrix to carbon nanotube) due to better interaction between the polymeric molecules and the chemical groups that are attached to the carbon nanotubes. Functionalization can also help in nanocomposite preparation giving additional advantages like easy solubility in solvents and better dispersion of nanosteepers 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 condensation, which is incompatible with polyester substrates. Two approaches for preparation of nanocomposites are under consideration, which consist of sandwiching functionalized carbon nanotubes between two ultrathin polyester films and other approach is multi-extending 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.

**L1.18**

Hydrothermal Synthesis of In203 Nanocubes, Bin Cheng 1, Lei Zhang 2 and Edward T. Samulski 1, 2, 3 Chemistry, University of North Carolina, Chapel Hill, North Carolina, 2Curriculum of Applied and Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

Bin Cheng 1, Lei Zhang 2, and Edward T. Samulski 1, 2, 3 Department of Chemistry, Curriculum of Applied and Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290. 1To whom correspondence should be addressed, etsamu@med.edu Forced hydrolysis of In3+ ions from different precursors was studied in detail. The composition of the final precipitates was identified as In(OH)3. In(OH), and In203. Small size (~ 40 nm) and regular shaped In203 nanocubes were successfully obtained for the first time by carefully controlled hydrothermal conditions. The composition, crystal structure and morphologies were characterized by XRD, SEM, TEM, and SAED. The photoluminescence of the mp-prepared novel nanostructure of In203 was also measured.

**L1.19**

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

Theoretical work by Bulm suggests that hard spherical nanoparticles included in block copolymers will undergo some form of self ordering. By modifying the particle species, size, and concentration, as well as the composition of the copolymer, order can be obtained. The work involves these possible systems as well as the efficiency of the method (modified by the inclusion of surfactants) and entropic needs of the system to obtain order.

**L1.20**

1Chemistry, University of Toronto, Ontario, Canada; 2Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

Non-siliceous mesoporous materials are of considerable interest, as they usually show excellent electronic, magnetic and catalytic properties compared with pure siliceous mesoporous materials. In particular, high surface area mesostructured titania (TiO$_2$) is a very interesting material with respect to its potential use in controlled delivery, chemical sensing, optical, catalytic, photochromic, or energy conversion applications. Recently, the synthetic approach based on the EISA (Evaporation Induced Self-Assembly) method, which makes use of ethanolic solutions of the precursors, has been used to develop mesoporous tri-block-copolymers as templates has been shown to be a general route for the preparation of many transition metal mesoporous materials. Additionally, this approach provides significantly more flexibility in processing, allowing for the preparation of 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 is based upon the well-documented EISA method using the nonionic amphiphilic tri-block-copolymer, Pluronic P123 (PEO$_34$PPO$_70$PEO$_34$) as the templating agent. Titania ethoxide [Ti(EO)$_4$] was chosen as the inorganic precursor. HCl is as the stabilizing agent and the absolute ethanol in the place of commonly used ethanol. The strategy employed here, which is the key to obtaining a robust, well-ordered mesoporous titania thin film, is based upon increasing the relative ratio of the Ti(IV) precursor (Pluronic P123 templating agent) and the absolute ethanol 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 m$^2$/g. Moreover, this structure composed of channel walls containing nanocrystalline titania was stable up to 400°C. Thin film samples are currently being used for the characterisation of optical microscopy. Characterisation of mesoporous titania thin layer samples were performed by Polarization Optical Microscopy (POM), powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), N$_2$ sorption analysis, Ramans spectroscopy, and Thermogravimetric analysis (TGA).

L11.23 Photoluminescence from the Silicon Surfaces Treated by Various Ionized Gases and Annealing Processes. Min-Chel Jung1, Young Ju Park2, Changhan Ko2, Moonsoo Han3, Chulyoung Ham1, Sung Ho Jun1 and Kyoungnam Park1.

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 characterization of nanocrystal silicon layer formed by two times of ionization/fusion and successive annealing processes on silicon surface. Cleaved surface was firstly ionized by the ionized N$_2$ gas at room temperature and low pressure. Atomic force microscopy and X-ray photoelectron spectroscopy analyses show that the nanometer-scale Si$_x$N$_y$ islands can be formed at the surface. After successive rapid thermal annealing, several ionized gases were exposed on the modified surfaces. Transmission electron micrograph shows that silicon nanoclusters are formed between the Si$_x$N$_y$ islands in the secondly formed oxide and for 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 conversion between the doping level and defect states on the ionized N$_2$ gas at room temperature and low pressure. Atomic force microscopy and X-ray photoelectron spectroscopy analyses show that the nanometer-scale Si$_x$N$_y$ islands can be formed at the surface. After successive rapid thermal annealing, several ionized gases were exposed on the modified surfaces. Transmission electron micrograph shows that silicon nanoclusters are formed between the Si$_x$N$_y$ islands in the secondly formed oxide and for 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 conversion between the doping level and defect states on the ionized N$_2$ gas at room temperature and low pressure. Atomic force microscopy and X-ray photoelectron spectroscopy analyses show that the nanometer-scale Si$_x$N$_y$ islands can be formed at the surface. After successive rapid thermal annealing, several ionized gases were exposed on the modified surfaces. Transmission electron micrograph shows that silicon nanoclusters are formed between the Si$_x$N$_y$ islands in the secondly formed oxide and for 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 conversion between the doping level and defect states on the ionized N$_2$ gas at room temperature and low pressure.
X-ray diffraction and transmission electron spectroscopy were used to determine the dispersion and compatibility of the montmorillonite with the polymer matrix, and the morphological properties were used to probe the structure and mechanical properties. 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 Ahn1, Amol Chandekar1, Bongwoo Kang2, Changwoo Song2 and James E. Whittem1; 1Department 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.

Organics-covered metal and semiconducting nanoparticles may have future applications for molecular electronics. In the present study, thiophene-terminated alkanethiols, T3H, (2-thiopheneethane thiolate) were synthesized and characterized by X-ray photoelectron spectroscopy (XPS), FT-IR, and UV-vis spectroscopy. Thiophene-functionalized gold nanoparticles (GNS) were subsequently synthesized by the addition of thiophene-terminated alkanethiol groups to gold nanoparticles. TEM images show the structure of gold nanoparticles in the range of 2-3 nm. Optical and spectroscopic properties of the gold nanoparticles dispersed in different solvents have been investigated using UV-vis spectroscopy. The band gap of the thiophene-functionalized gold nanoparticles is tunable over a range of 2-3 nm, and the structure of the gold nanoparticles is stable in different solvents.

L11.20 Dissipation in Polymer Films and Nanoparticles. Philip Smith Orderer1,2 and Nathan Isrealoff1,2; 1Physics Department, Northeastern University, Boston, Massachusetts; 2Nanomaterials Institute, Northeastern University, Boston, Massachusetts.

Using Ultrahigh Vacuum (UHV) Scanning Probe Microscopy (SPM) techniques, dissipation in polymer thin films and nanoparticles near the glass transition temperature has been investigated to study the effect of structure on glassy dynamics. Scanning Force Microscopy (SFM) has been used to map dissipation across a surface, yielding localized information on the dissipation in glassy polymer polyethylene-oxide (PEO). The implementation of scanning probe techniques including phase imaging and local force spectroscopy combined with Herzian dynamics allows local probing of dissipation, yielding insight into ideas of cooperatively rearranging regions (CHR). We also present analysis of methods of probing dissipation in glassy nanoparticles using SPM techniques, continued from previous studies of microparticles.


Recent advances in intrinsically conductive polymers have created new opportunities in a broad range of electrical and electronic applications. Through redox or, in some cases, protonic doping of the conjugated electrical structure, polymers can be prepared with metallic conductivities up to 10⁴ S/cm. They have found application in a broad range of technologies from batteries and light emitting diodes to computer electronics. Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), is widely used in the form of a film in a wide range of applications, (e.g. LED) because of its high conductivity (0.8 to 3000 S/cm). In this study, PEDOT in fiber form was explored. Successfully, PEDOT/PAN nanofibrous materials were produced using the electrospinning process. The electrical conductivity of the electrospun fibers was found to increase as the fiber diameter decreased. By using PEDOT polymer in fiber form, the application of PEDOT is expected to expand in the area of bioelectronics and medical electronics. In order to explore the functionality of producing multifunctional fibrous materials, SWNT was introduced into PEDOT matrix to enhance the structural performance and electrical conductivity. The SWNT/PEDOT blend was electrospun into nanocomposite yarn to facilitate the formation of higher order structures. The morphology of the conductive polymer and nanocomposites was examined by ESEM. The structure, electrical properties, and mechanical properties of the SWNT/PEDOT 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. Telulore Ohadigo Sahni and Scott S.R. Oliver; Chemistry, Binghamton University, Binghamton, New York.

Our efforts into the solvothermal (non aqueous synthesis) of new nano-materials will be discussed. Our long-term goal is to synthesize cationic materials for use in sensors, catalysts and sieves with tunable properties. We utilized the unique unplanned methodology of microstructure directing agents (SDA), focusing on nano-silica species that have the potential to act as SDA such as, BF4, PF6, and CF3SO3H. These SDAs are able to direct the structure as well as introduced specific charges on the synthesized materials. We also used a 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.


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 that the tool should wear very little, withstand high temperatures and the friction between the tool and the work piece should be minimised. An apparent approach to simultaneously satisfying such requirements is coating the tools with self-lubricating hard coatings. Quaternary TiAlCN is a rapidly developing hard coating suitable for a number of cutting applications. The well-known wear-resistant coating TiN has been demonstrated to have improved high-temperature oxidation resistance when 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, wear resistance and low friction coefficient of TiAlCN make it the ideal candidate for applications such as milling, hobbing, tapping, stamping and punching. MoS2 is a well-known solid lubricant widely used in tribological coatings, especially for applications working in vacuum or dry environment. Combining the wear resistance of the quaternary TiAlCN matrix with the lubricating properties of 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 diffraction and XTEM, electron diffraction and EDX. The tribological properties were examined in a Pin-on-Disk (P-on-D) tribometer. The adhesion was estimated by scratch test, and the hardness was measured by nanoindentation. All the coatings examined had a very low friction coefficient (typically below 0.05) and volumetric wear rates against 100Cr6 steel (AISI 5200) in the range of 10⁻⁷ mm³/Nm. The relation of deposition parameters to structure to properties is discussed. To the authors’ knowledge, this is the first paper describing quaternary TiAlCN matrix with inclusions of MoS2.


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 reinforcement for polymer matrix nanocomposite films has been studied. Barrier and mechanical properties of EGN/polymer nanocomposite films have been compared to similar nanocomposite films having either comparable filler morphology such as anionic clay or similar chemical composition such as conventional carbon black. The relationship between the
properties of the nanocomposites and the nanoparticle composition and morphology were examined. Barrier testing included permeation resistance to water, oxygen, and selected organic peroxides.

**L1.13 Structural Analysis of a (CoRe75, Re(5nm)/Co(2nm)/Re(0.6nm)) Superlattice Grown on Al2O3 (110), Wenjie Xu1, Timothy Cheriton2,3, Lance E. DeLong1 and David Lederer4; 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 (CoRe75, Re(5nm)/Co(2nm)/Re(0.6nm)) sample grown on a magnetron sputtering was thoroughly analyzed via x-ray diffraction (XRD), x-ray reflectivity (XRR) and transmission electron microscopy (TEM). Prior to the superlattice growth, a Re seed layer of 10 nm thick was deposited onto a 600°C Al2O3 substrate.

**L1.13 Effect of film composition and structure on the diffusion barrier properties of metal alloy layers formed by electrolytic deposition, Artur Kohl1, Nick Petrow1, Nishini Li1, Mariin Polynesina2, Jason Schier2 and Igor Izmov1; 1Blue29, Inc., Sunnyvale, California, 2KLA-Tencor, San Jose, California.**

Despite the numerous advantages of the use of copper as interconnect material in ultra large scale (ULS) microelectronic devices, the technology faces several problems such as metal corrosion, adhesion, high chemical reactivity, and considerable diffusion of copper in silicon. In particular, the poor adhesion of copper to SiN, SiC, SOIC 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 copper 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 electrolysis plating method. The corrosion protection and barrier properties of this layer depend largely on their micro and nanostructure as well as their composition. These properties can be altered by the deposition condition and composition of the electrolysis deposition bath. In the work presented, we focused on the deposition of Co-Re-Ni based alloy films. In this study, we examined the relationship between the deposition conditions and the resulting film properties. The films were characterized using x-ray diffraction and transmission electron microscopy. The results showed that the deposited films are suitable for use in microelectronic devices.

**L1.13.4 Oxidative Dehydrogenation of Ethylbenzene to Styrene Over Graphite Nanofibers, Xuejun Xu and R. Terry K. Baker; Catalytic Materials LLC, Holliston, Massachusetts.**

The industrial process is currently carried out at high temperatures (above 650°C) using promoted iron oxide catalysts in the presence of steam. The highly endothermic character imposes a thermodynamic limitation to the conversion of ethylbenzene that can be attained (about 50%), and requires a great deal of energy consumption. The oxidative dehydrogenation of ethylbenzene in the presence of oxygen is one of the 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 the formation of carbon. However, the surface areas of these materials are extremely low (about 0.5 m2/g), limiting their usefulness as practical catalytic 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 very similar to that of a commercial catalyst mainly composed of Fe5O3. Platelet GNF showed a selectivity of 34% and a conversion of 40% at 574°C. Tubular GNF exhibited a selectivity of 54% and a conversion of 53% at 545°C. No deactivation of GNF was observed during the experimental periods. Used GNF are very safe and easily recyclable.

**L1.13.5 Synthesis and Characterization of Thin-film Pt/AI2O3 Catalyst for Preferential Oxidation of CO in SI-based Microreactors, Huihong Chen, Xin Ouyang, Lucie Bednarova, Ronald S. Besser and Woon Young Lee; Chemical Biocatalysis and Microengineering, Stevens Institute of Technology, Hoboken, New Jersey.**

There has been a growing interest in the miniaturization of chemical reactors for portable uses such as fuel cells. High-performance microfluidic devices, however, are facing several challenges in the fabrication of microreactors is the incorporation of catalytic in the reaction channel. Thin-film is a preferred catalyst form for microreactors since it causes lower pressure drop in the microchannel and improves the application of catalyst 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 disordered micropores 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, $\text{H}_3\text{PtCl}_6$ 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 microreactors, followed by drying, calcination and reduction to form a porous catalyst layer. In the second method, the alumina sol was first infiltrated, deposited, and solidified. Subsequently, Pt was incorporated through the impregnation of the alumina layer. The surface and the fracture-section of the Pt/Al$_2$O$_3$ layer were observed by scanning electron microscopy. The thickness of the catalyst layer varied from 0.5 to 1.5 μm, being dependent on the volume of the injected liquid precursor and the geometry of the microchannel. The BET surface area of the amorphous Al$_2$O$_3$ support was 480 m$^2$/g, and the diameter of most pores was in the range of 3 to 4 nm. Particle size distribution of the Pt on Al$_2$O$_3$ was obtained by transmission electron microscopy. This 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/Al$_2$O$_3$ catalyst were tested for preferential oxidation of CO by $\text{O}_2$. This reaction is a critical part of fuel processing for proton exchange membrane fuel cell applications for removing CO from $\text{H}_2$-rich reformates. Simulated 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.


Mo doped vanadium oxides have found a wide range of applications because of their selective oxidation as well as the unique interaction between $\text{V}_2\text{O}_5$ and MoO$_3$ owing to the similarity of ionic radii and the structures in their highest oxidation state [1-3]. These similarities enable the formation of substitutional solid solutions with different oxidation states of cations. In the present work, Mo doped vanadium oxide nanotubes were prepared by modified sol-gel process from layered oxide precursor and organic molecules as structure-directing templates. The microstructures and structure 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 (0 0 1) facets 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 126 (2002) 10. [2]Najjar M., Applied Catalysis A: General 157 (1997) 223. [3]Chen W., Xu, Q., Mai L.O., Yu H.S., Zhu Q.Y., J Mater Chem 12 (2002) 1926. Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 50171016), the Teaching and Research Award Program for Outstanding Young Professors in Higher Education Institute, MOE, P.R. China and the Science Fund for Distinguished Young Scholars of Hubei Province (Grant No. 2002AC008).


Nanoporous structures composed of organic/inorganic nanoscopic building blocks hold much promise for providing innovative materials with superior properties. Recent experiments have demonstrated that polymer-mediated self-assembly of polyhedral oligomeric silsesquioxane (POSS) is a promising route for creating highly ordered and novel structures. These experiments suggest that control over the final assembly structure and ultimately the properties of the POSS-porous materials can be achieved by manipulating POSS-polymer topology and the conditions under which the assemblies are formed. We have performed molecular simulations to systematically explore the parameters, including solvent quality, volume fraction, temperature, tether length and edge length of the nano building block topology, that control the assembly process and influence the resulting equilibrium structures. In particular, we study mono- and multi-tethered POSS cubes and POSS/polymer "tekedelles" connected by two POSS micelles by a single silica-bonded tether, as neat materials and in selective solvents. We explore their phase diagrams, and present new results on novel nanostructures that result from microphase separation combined with the unique shape of these micellar building blocks. Our computational methodology provides insight to the assembly process, and facilitates the rational design of new nanoscale materials by enabling the exploration of various assemblies and the conditions under which these novel structures are formed. This research is supported by a collaboration between the University of Michigan, University of Virginia, Vanderbilt University, and Colorado School of Mines and is funded by the National Science Foundation under DMR-0102399.


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 a combustion synthesis. The synthesis process yielded ultra fine powders, which were subsequently annealed in a furnace to obtain particles of varying dimensions, from a few nanometers to 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 nanosynthesized state. However, upon heat treatment at 1273 K the powders showed an intense blue emission between 480 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.


Most practically important are many-particle-systems (MPS) such as nanocrystalline thin films, small domain-matter, particle-matrix-systems (metal-alloy-metal systems, imaging materials, granular superconductors, cluster tunnel junctions, cermets, dispersive optical compact disks), etc., from material science, even the simplest 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 properties of clusters, etc.) to large scale applications in imaging, analysis, record-keeping, etc. The functional properties of nanoparticle systems depend on a number of parameters that describe the single cluster (atomic and molecular structure, structural and morphological characteristics, size and shape), the nearneighbor and far-off effects of a given cluster. They all have to be considered in detailed multilevel microstructural and analytical characterization, and several can be manipulated to take advantage of their potential, e.g., by appropriate choice of the material properties. Such approach provides a logical synergism between engineering design (modeling) and characterization of MPS aimed for a better understanding of structure-property relationships. Within this concept, applications of a combination of imaging, diffraction and analytical electron microscopy (AEM) modes including (FE)-HRTEM, (cryo-)EFTEM/STEM/EDX/EDS, low-voltage FE-TEM/EDX and real-time EDX/STEM/EDX are included. The characterization of nanodisperse MPS will be discussed. Moreover, advanced AEM may give new insights into fundamental
structure-solid-state property relationships, local electronic and optical properties of mesostructured materials and dynamical structural and reactivity considerations. Traditional model materials include examples such as "giant clusters" of $\text{Pd}_{22}\text{La}_{3}\text{O}(\text{Ac})_{10}$ ($L=1.18\text{pm}$, benzene ring), $\text{Pd}_{22}[\text{PPh}_{3}]_{4}\text{La}_{3}$, and $\text{Pd}_{22}[\text{PPh}_{3}]_{4}\text{La}_{3}$ (benzene ring) (14), composite micromaterials used as AgX/NiCl, micromaterials with high effective characteristic size ranging from tens to over several hundreds nanometers. This presentation is focused on recent advances in fundamental statistical physics, statistical mechanics and computational methods to investigate properties of essentially three-dimensional synthesis of sub-10 nm structural nanomaterials such as silicon-based nanomaterials with prescribed physical properties. The discussed conceptually new approach and its applications allow the 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 are achieved by the chemical synthesis of such materials. This approach, called virtual manufacturing, is the first selfconsistent attempt to use fundamental theoretical predictions and computational manipulations of (1) a considered system structure, composition, chemistry, and (2) processing parameters (such as the average density, concentration, pressure, temperature) to control the desired transport properties of the processed sub-nanomaterials. Materials design and fabrication routes as predicted can be further utilized in and tuned to the corresponding experimental efforts.

**L1.14.41 Composites of Highly Ordered Polyethylene Filled with Aligned Carbon Nanotubes by Gelation Technique**
Yasutaka Inoue,1 Sei Imamura2 and Masaru Matsuo 3 1Graduate School of Human Culture, Nara Women’s University, Nara, Japan; 2Faculty of Human Life and Environment, Nara Women’s University, Nara, Japan. Electric conductive materials with high modulus and high strength were developed using multi-walled carbon nanotubes (MWNTs) and ultra-high molecular weight polyethylene (UHMWPE). The composites with 0.25 to 15 wt% of MWNTs were prepared by gelation/crystallization of decalin solutions and modified with iodine doping. The percolation field was found to be around 4 wt% of MWNTs in UHMWPE. The composite gel films could be elongated to more than 50%. The Young’s modulus was beyond 35 GPa while the draw ratio reached 50%. Scanning electron microscopes revealed that MWNTs with carbon networks are oriented closely parallel to the stretching direction. Such characteristic alignment of MWNTs plays an important role to form effective conductive paths in the high oriented composites. The co-orientation of MWNTs and UHMWPE in the stretching direction ensured that the composites possess high strength and high modulus and the electric conductivity of composites was hardly dependent upon the draw ratios. The ultra-drawn gel films were chemically modified with iodine doping. The electric conductivity of the composites increased from 10^{-9} S/cm to 10^{-6} S/cm. 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 electrical conductivity of polyethylene MWNTs composites, especially for the composites with low content of MWNTs.

**L1.14.42 Oxidation Resistance of Multi-Walled Carbon Nanotubes Coloured with SiC**
Yoshio Nakamura, Masakazu Matsuda, Toshiyuki Ishihara and Yoshinori Miyamoto, Jointing and Welding Research Institute, Osaka University, Higashi-Ibaraki, Japan.

MWCNTs have been used to reinforce various matrices. Such reinforcement can increase the overall thermal and mechanical properties and 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 nanosized SiC using SiO vapor. The growth mechanism of SiC and the oxidation resistance of the SiC-coated MWCNTs were investigated. The growth of the SiC coating was controlled using the partial pressure of CO using the carbon felt placed in an arc furnace for SiC coating. The nanoparticles SiC particles were deposited by the reaction between SiO(g) and CO(g). On the other hand, the thin surface of MWCNTs was converted to SiC with 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.

**L1.14.43 Synthesis of Mesoporous Titanium as a Filter for Nafion-Based Composite Membranes for Direct Methanol Fuel Cells**
Ursula Tekranakpip, Vincenzo Esposito, Silvia Lusco and Enrico Traverso, Dept. of Chem. Sci. Technol., University of Rome Tor Vergata, Roma, Italy.

The recent discovery of mesostructured materials has given new perspectives in a large number of environmental-friendly applications, such as sensors, catalysis, and energy production and storage. A very interesting materials for those applications is titanium. Liquid fuel cells are a promising alternative to hydrogen-fueled devices as portable and mobile electrochemical power sources. However, the power density and the efficiency of Direct Methanol Fuel Cells (DMFCs) are lower compared to Polymer Electroylyte Fuel Cells (PEMFCs), due to the slow chemical kinetics of methanol oxidation. The achievement of a fast and efficient 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 works we have proposed the synthesis of mesoporous titania based on Nafion containing finely dispersed nanocrystalline ceramic oxide powders 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 titania was studied, using micellar aggregates as templates. To avoid the high reactivity of Ti(IV) species towards hydrosilation and condensation, the precursor selected and synthesized was titania titrane complex (Dimethylaminoiminotitanate). The formation of the mesoporous oxide in fact depends upon the relative rates of the inorganic precursor hydrosilation 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 nafion-based composite membranes with Nafion. The dispersions of the mesoporous titania in the Nafion was very good, as shown by FE-SEM observations. Preliminary DMFC investigation of such membranes at high temperatures reveals a significant influence of the ceramic oxide surface area on the electrochemical behavior. At 140°C with about 230 mV recorded. These results are very promising and a better tailoring of mesoporous titania particles is now in progress.

**L1.14.44 Corrosion Protection of Materials Surfaces by Applying Nanotechnology Associated Studies**
Rajneesh Agarwal, FEITOC, Virginia Tech, Blacksburg, Virginia.

Corrosion - known as the destructive and unintentional attack on materials has been one of the most considered industrial problems in the world for several years. Corrosion mainly comes from corrosive ions and molecules (e.g., Cl-, O2, H2O) that are oxidized, accumulated, and reacted, creating alkaline and neutral environments, which are typical of industrial processes and industrial waste, as well as materials (UV and heat). It begins at the surface of materials and decreases the lifetime of materials used in construction, industry, and aerospace applications. Corrosion characteristics and behavior of materials in corrosion environments are commonly determined using non-destructive techniques such as optical microscopy, scanning electron microscopy, and X-ray diffraction. The effect of corrosion on the environment is significant, and it is estimated that more than 5% of the world’s gross national product (GNP) is spent on corrosion prevention, repair, and replacement. The cost of corrosion includes the cost of materials, labor, and equipment, as well as the cost of lost production time. The total cost of corrosion is estimated at $800 billion annually, which is about 3% of the US economy per year.
ways of decreasing corrosion to improve the lifetime of materials and devices. As recently determined, some of the corrosion results are directly related to nanotechnology studies. These include nanoscale film (potassium permanganate, zinc compounds, chromium, aluminum, phosphate, nickel, molybdenum, cadmium or zinc-rich layers) formation (or conversion coating) between substrate and film, nanoscale particles (SO2, Ar2O3 and ZrO2 carbon) addition to coating systems, interfacial controls, surface treatments and combination of them. The present results obtained using nanotechnology assisted methods show that materials performance are improved 10 to 1000 times. It is believed that the new protocols and methods outlined in 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 correlations and control systems.

L1.45
UV Curable Polymers With Organically Modified Clay As The Nanoinfillments. Fann M Uli1, Brian R Hinderliter2, Prashanth Dewaluri2, Stuart C Gerry2, Shing-Chang Wang3 and Dean C Webster2, 1 Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota; 2 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 curable such as rapid cure, solvent free systems, application versatility, low energy requirements, and low temperature operation. To be used in the electronics the film must possess the following attributes: high glass transition, barrier properties, low shrinkage, enhanced thermal, mechanical, and barrier properties were reported. Nanomodified nanocomposite containing clay or in situ polymerization. Little is understood on UV curable nanocomposites. This paper seeks to examine nanoclay-containing polymers using organomodified montmorillonite in UV curable systems and the effects of such clay inclinations on the properties of UV cured films. By x-ray diffraction it appeared that the intercalated structures were formed. In the case of an epoxy acrylic formulation an increase in glass transition temperature was observed for formulations containing clay.

L1.46
Boron Carbide Encapsulated by Nanocrystalline Ni Coating. Jianhong He1, Yuxiang Zhou1, Dean Baker2, Bill Har ENG1 and Enrique J Lemmon2, 1 Chemical 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 wettability with metal; therefore, a high temperature synthesis process for MMCs is necessary to improve the 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 CVD Fast Fluidized Bed process, patented by the Powdermet, Inc., enables a mass production capacity [500 lbs per lot] of ceramic powder encapsulated by metallic coating. Subsequent consolidation can be accomplished via metal/metal bonding, rather than through metal/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 1~5 µm. TEM examination shows the coating comprises single phase, nearly equiaxed grains with size from 10 to 100 nm, that is, synthesized coating is nanocrystalline Ni one. No apparent defects, such as pore, crack and dislocations are observed at the inter face between the coated particle and the Ni coating. The interface is relatively smooth and complete, thus, capsule processing is unique characteristics variability. Using the encapsulated boron carbide powder, a Ni/Na coated B4C coated composite was prepared by plasma arc methods. The results indicated that thin Ni capsule layer was persevered intact in the coating.

L1.47
Solution-phase synthesis of cubic and spherical nanostructures of Cu2O. Yuhang Wang, Yuxiang Sun and Younan Xia, Univ. of Washington, Seattle, Washington.

The preparation of two types of uniform and monodispersed Cu2O nanostructures - nanocubes (~50 nm in size) and nanospheres (~200 nm) will be reported in this presentation. Copper nitrate was used as the precursor in this synthesis, and the nanocrystalline 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. Electronic diffraction studies on both morphologically Cu2O indicated that the nanoparticles are polycrystalline in structure while the nanocubes are single crystals. Further investigation suggested that the mechanism of Cu2O nanocubes were the results of self-assembly of even smaller sized Cu2O particles (~10-20 nm) that could be served as the seeds for nanocube growth.

L1.48
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, Pochum-ku, 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 (1-10 micron) 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 12h showed the formation of plate-like clusters of crystals. Titania without PEO mixture and the formation of plate-like clusters of crystals with anatase volume fraction of 0.5. This difference in the morphological features and phase formation characteristics was considered from the perspective of activation energy for phase formation and bonding between PEO and chelated titania molecules.

L1.49

Mixture films between cobalt and C60 were prepared on MgO substrate by co-evaporation technique under UHV conditions. The compositions x, that is C60:xC60, were changed in the range of 0.5 - 700 by controlling the deposition rates of relevant materials. The films prepared were so sensitive to the exposure 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 downsink 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 transitions from cobalt atom to a C60 molecule. Although all the mixtures showed metallic character, conducting nature basically at ambient temperature, the evaluation of their temperature dependences reveals the details: 1) the mixtures with x > 60 corresponding to a metallic transition of cobalt particles are metallic but 2) the mixtures between x = 4 - 60 are thermally activated where the electron hopping process between the isolated cobalt particles is supposed to be operative. The mixtures with x < 4 are also thermally activated, however, their conductive nature might be attributed to the C60-based phase.

L1.50
On the development of the <111> fiber texture in nanocrystalline gold during growth and annealing. Klaus Pagh Andersen1, Thomas Jensen1, Jakob Hasler Petersen1, Martin Skov Jensen1, Jacques Chevallier3, Jorgen Bottiger1 and Norbert Schill2, 1Physics and Astronomy, University of Aarhus, Denmark; 2Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Dresden, Germany.

The evolution during growth and subsequent annealing of the <111> fiber texture in magneto-optically detected amorphous Ar films has studied experimentally using x-ray diffraction with synchrotron radiation. To quantitatively investigate this film texture, grain orientation distributions were recorded in situ during growth and during subsequent annealing using Bragg-Brentano geometry. The (111) diffraction intensity was measured as a function of the sample tilt χ, 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 nanocapillaries are important factors to determine the energy and intensity of the photoemission. Substrate temperature and oxygen content are main parameters to control the size and density of Si nanocapillaries. In this point, ion beam sputter deposition (IBSD) can be a good candidate for the growth of SiOx films. SiOx films can be prepared by IBSD, where the thin films grown at the deposition chamber could be transferred to a surface analysis chamber without exposing to the air. Therefore, the oxygen content (x) of the SiOx was directly analyzed by in-situ XPS. The variation of PL energy and intensity of SiOx and SiOx/SiO2 superlattices 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 nanocapillaries. The PL intensities of SiOx showed maximum values near x = 0.6. However, those of SiOx/SiO2 films showed maximum values near x = 1.2. This could be understood as a term of averaged concentration. The superlattices with very thin layers, PL exhibits similar tendency with those of single SiOx films where the x value is same with the average of the two layers. In the case of SiO1.2/2 nm SiO2/2 nm superlattices, the average composition is equivalent to x = 0.6. There is no evidence of any maximum PL intensity with the increase of deposition temperature.

L11.53
In-situ Control of Oxygen Content and the Effect on PL Intensity of SiOx/SiO2 Superlattices by Physical Deposition. Kyungsoo Kim1, Daewon Moon1, Moonseung Yang2, Jihong Jie2, Junghoon Shin2, Seungil Hong3, and Sukho Choi1,2
1Koren Research Institute of Standards and Science, Daejeon, South Korea; 2KAIST, Taejon, South Korea; 3Kyungho University, Seoul, South Korea.

The size and density of Si nanocapillaries are important factors to determine the energy and intensity of the photoemission. Substrate temperature and oxygen content are main parameters to control the size and density of Si nanocapillaries. In this point, ion beam sputter deposition (IBSD) can be a good candidate for the growth of SiOx films. SiOx films can be prepared by IBSD, where the thin films grown at the deposition chamber could be transferred to a surface analysis chamber without exposing to the air. Therefore, the oxygen content (x) of the SiOx was directly analyzed by in-situ XPS. The variation of PL energy and intensity of SiOx and SiOx/SiO2 superlattices 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 nanocapillaries. The PL intensities of SiOx showed maximum values near x = 0.6. However, those of SiOx/SiO2 films showed maximum values near x = 1.2. This could be understood as a term of averaged concentration. The superlattices with very thin layers, PL exhibits similar tendency with those of single SiOx films where the x value is same with the average of the two layers. In the case of SiO1.2/2 nm SiO2/2 nm superlattices, the average composition is equivalent to x = 0.6. There is no evidence of any 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 Frelun1,2, Vladimir Sadykov1,2, 3, Pavel Pavlov1, 3, Veniaminov1, 3, R. Bitin1, E. Burgina1, V. Kolomik1, T. Luria1, N. Mezentseva1,2, 3, F. Frelun1, 3, A. Vodolin1, 3, Henicke Institute of Catalysis, Novosibirsk, Russian Federation; Novosibirsk State University, Novosibirsk, Russian Federation; 3Penn State University, University Park, Pennsylvania.

Nonmesoporous 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 FTIR, SAXS, ESR, UV-Vis DRS, magnetic measurements and nitrogen adsorption-desorption isotherms. In applied routine, nanoparticles of Zr (Ce) phosphates of a layered structure with typical sizes in the range of 18-24 Å are formed at the mixing stage. Less basic Cu and Co cations are mainly co-ordinated with both phosphate groups of those nanoparticles and citric acid molecules. At subsequent thermal treatment, Cu and Co cations are incorporated within Zr (Ce) phosphate nanoparticles acquiring a low coordination approaching a tetrahedral one while restructuring into this of a framework type. Within this framework matrix, Cu and Co cations are isolated. Removal of citric acid by heating under air at 200 - 300°C preserves the size of nanoparticles while their ordered stacking forms mesoporous structure with a porous pore size distribution (PSD) with diameters ranging up to 200 m 2/g after calcination at 600°C. ESR of oxygen ion-radicals O generated by hydrogen peroxide adsorption revealed existence of covalently unsaturated surface sites for these materials. This feature is reflected in a high decease and NO adsorption capacity as well as ability to activate hydrocarbon molecules at heating. The binary phosphates promoted by a small amount of Pt were found to be effective catalysts of NO selective reduction by decene in the oxygen excess not subjected to coking with a high and stable performance at high space velocities in the presence of steam.

L11.55

Nanoporous polymeric materials are used as polymer electrolytes in fuel cells, separation membranes, templates for nanoparticle synthesis, and electroactive materials in biomedical applications. Design of nanoporous polymeric materials for these applications entailed controlling the permeability through the porous materials by tailoring the pore size and pore chemistry. Porous polymeric materials are usually synthesized using polymerization techniques. In these techniques, the final pore size and structural distribution of the material depends upon the thermodynamic pathway the system follows. Even a small deviation in processing conditions can lead to vastly different porous structures 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 nanoscopic polymeric materials that have better pore size control than the conventional methods is employed in this work. This technique involves the synthesis of nanoscopic polymeric materials by reactive encapsulation of an inert solvent using step-growth crosslinking polymerization reaction carried out until completion without phase separation. The condition of complete miscibility throughout polymerization suggests that for cross-linking systems, the network will encapsulate the solvent during reaction forming a porous superstructure. Theoretical pore dimensions can be controlled by the amount of solvent. So, potentially, better pore size control can be obtained by using a completely miscible system. The key structural parameters of these nanoscopic materials synthesized using the reactive encapsulation technique was investigated by means of supercritical extraction and SEM and small angle X-ray scattering. Micrographs of the materials synthesized using the reactive encapsulation technique showed that porous materials of pore size less than 100 nm are obtained. SAXS and WAXS showed that the reactive encapsulation technique can be employed, to synthesize nanoscopic polymeric materials of desired pore structure and size by changing the solvent content. The pore chemistry of the nanoscopic material synthesized by the reactive encapsulation technique was tailored by improving the hydrophilicity using a grafting technique based on Michael’s addition reaction. The equilibrium water uptake of the nanoscopic material, monitored by FTIR, showed a significant increase after grafting. A novel method for designing Interpenetrating Polymer Networks (IPNs) of hydrophilic and hydrophobic polymer networks is proposed. The steps involved in the design of IPNs were monitored using FTIR.

L1.56
Abstract Withdrawn

L1.57

Depending on deposition technique, thin films can exhibit an energetic state far from thermodynamic equilibrium. Due to energetic reasons, this is a general characteristic of nanometer multilayers. Energy supply can stimulate a transition of the film structure into other metastable states characterized by a translation closer to that of thermodynamic equilibrium. Besides of the sufficient quantity of activation energy significant contribution of interphases and stressed states to the free energy of the system and geometric constraints for transport processes can favour an unconventional metastable phase formation. It is of technical interest that a number of metastable phases can be stabilised at room temperature for characteristic times in the order of weeks. Examples of metastable phase formation are thermally stimulated solid state reactions in metallic nanometer multilayers of Al/Cu/Ni and phase formation and transition in metallic alloy films of the elemental system Fe/Cr exhibiting an extended miscibility gap at temperatures below ~720 K under equilibrium conditions. While in the case under appropriate conditions formation of a homogeneous textured layer of a decagonal quasicrystalline structure could be achieved, the second example illustrates a formation of unconventional phases during a pulsed laser co-deposition of restrictedly miscible elements and their transformation into other metastable phases by supplying of different kinds of activation/transport energy.

L1.58
Fabrication of the various oxide nanostructure materials by LDP methods. Takeshi Yamaguchi, Tadashi Hanaoka and Masanori Uno. Department of Nuclear Engineering, Osaka University, Suita, Osaka, Japan.

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

SESSION L12: Tubes, Rods and Dots
Chair: Sridhar Kommeni
Friday Morning, December 5, 2003
Room 304 (Hynes)

8:30 AM L12.1
Anomalous Magnetoresistance Behavior of Bismuth 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 nanocavities) 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 this 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<2K) and low magnetic fields (Bc1-T). These surprising observations are attributed to the semimetalsemiconductor transition and localization effects in low dimensional bismuth systems.

8:45 AM L12.2
Synthesis and Structural Characterization of Si Quantum Dots for Non Volatile Memories. Rosaria A. Pagliuca, G. Nicotra1, S. Lombardo1, C. Spinelli2, C. Gerardi2 and G. Ammodorci2. 1CNR-IMM, Catania, Italy; 2Central R&D, STMicroelectronics, Catania, Italy.

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

9:00 AM L12.3
Self-Assembled Nanostructures Through Spinodal Decomposition. Laldeep Mahohdes-Arockiel1, Haiwei Zheng1, Sarish B. Ogale1, Manfred Wittig1, Ramamoorthy Ramesh1, Beatrice Hirnsey2, Wei Tran3, Xiaoping Pan4 and Samuel E. Lofland4. 1Materials Science and Engineering, University of Maryland, College Park, Maryland; 2Institut des Materiaux, Universite 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 L-Si-Fe-O perovskite system as a function of oxygen pressure, using thin film heterogeneity in the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Growth in reducing environments (5E11O6/Torr of oxygen) leads to the formation of a nanostructure composite of α-Fe nano-pillars embedded in a matrix of a layered perovskite with a nominal composition of L-Si-Fe-O4. The height of the pillars is equal to film thickness. The lateral size, shape and density of these ferromagnetic nano-pillars depend systematically on growth.
conditions. This therefore affects the magnetic properties. High resolution Transmission Electron Microscopy results indicates that at high temperature, the ZnO nanofibers with uniform diameter and a square-sectioned shape are formed. As the deposition temperature is reduced, the shape evolves into octagonal and then circular section. Theoretical calculation on interface symmetry and interfacial energy is presented. We report in this paper these results as well as the result of our studies to induce a large-translational order among these ferromagnetic nanoparticles. This work is supported partly by NSF-MRSEC under contract No. DMR 00-80018 and by an ONR MURI program under contract No. N000140111701.

9:15 AM L124
Oriented Arrays of Single Crystal Titania Nanofibers Produced by Reaction With Hydrogen-Bearing Gas.
Szeun Yoo,2, Sheik A Akbar1 and Ken H Sandhage2,1. Dept. of Materials Science and Engineering, The Ohio State University, Columbus, Ohio, 2School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The processing conditions needed to achieve precise control of fine, nanoscale features in advanced materials is critical. In this paper, a simple, low-cost method for fabricating oriented arrays of single crystal titania nanofibers is reported: the reaction of dense TiO2 surfaces with H2-bearing gases at modest temperatures. Upon exposure to a flowing 5% H2/95% N2 gas mixture at 350 °C, polycrystalline titania surfaces were converted into arrays of discrete oxide nanofibers with diameters of 25-50 nm and lengths of 0.1-5 μm. The nanofibers that were formed from a given titania grain were oriented in the same direction. From time-resolved observations of the same grain, it was observed that the nanofibers formed by an etching process (not by a deposition process). During the initial stage of heat treatment, nanofibers formed on specific faces of the faceted rutile grains. The depth and interconnectivity of the nanoflament grid increased with time until the channels converged to yield indented, parallel nanofibers. Electron diffraction analysis revealed that each nanofiber was comprised of a single oxide crystal, with the fiber axis oriented parallel to the [001] crystallographic direction. Detailed characterization of the microstructure of the nanofibers, and the influence of various processing parameters (e.g., specimen pre-orientation conditions, H2/N2 gas flow rate, temperature) on the nanofiber formation process, will be discussed. The reaction-based process is readily scaled up (by continuous operation of controlled-atmosphere furnaces) to yield large quantities of low-cost, high-surface-area titania nanofibers arrays with photocatalytic, gas-sensing, electronic, and/or microbial functions for a wide variety of environmental, biomedical, transportation, and chemical manufacturing applications. 1S. Yoo, 2A. Akbar, K. H. Sandhage, U.S. Patent Application

9:30 AM L125
Zinc Oxide Nanotroops. Zheng Chen1,2, Zhwei Shann,3 Phillip Lee3,1, Olivier Mounsen2 and Scott T. Muns1. 1Department of Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, 2Department of Materials Science and Engineering, East China Shipbuilding Institute, Zhenjiang, China.

ZnO, a wide-gap (3.37 eV) semiconductor oxide, has attracted considerable attention due to its large exciton binding energy (≈60 meV) and band strength, which might make reliable high-efficiency photonic devices based on ZnO. Here we present our determinants' carothermal reduction synthesis of ZnO nanocrystals with different morphologies (dendrites, tripod-shaped, and wires) by carefully tuning the carrier gas (argon) flow rate at ambient pressure involving neither catalytic nor vacuum system. The synthesis of ZnO was carried out in a horizontal furnace. ZnO nanocrystals were directly grown in a quartz tube by heating ZnO and graphite powder mixture (1:1 mole ratio) under argon gas flow rate of 200 ml/min at a high purity argon carrier gas at a rate of 10-90 cm/s (standard cubic centimeter per minute). The growth time was typically 0.5-1 h. After evaporation and deposition, we found different products in different positions on the inner wall of the quartz tube. The crystal structures were analyzed using X-ray diffractometer (XRD-PHILIPS APD 3720). The morphology and size of the products were characterized using field-emission scanning electron microscope (FE-SEM, PHILIPS XL30) equipped with an energy-dispersive X-ray spectrometer (EDX). Transmission electron microscope (TEM, JEOL 2010F at 200 kV) was used to study the microstructure of the nanotroops. The energy dispersive X-ray spectroscopy (EDS) analysis shows that the atomic composition ratio of Zn/O is about 1:1. X-ray diffraction analysis reveals that all the products are hexagonal wurtzite structured ZnO with lattice parameters of a = 0.3249 nm and c = 0.5206 nm. Present results prove that the morphology and the composition of the ZnO products can be controlled by adjusting the carrier gas flow rate during the synthesis of ZnO via carothermal reduction process. We have shown that the carrier gas flow rate simultaneously affect the reaction rate between ZnO and carbon, the supersaturation of Zn vapor and oxygen, as well as the growth position and temperature. In addition to ZnO dendrites and nanowires, we have synthesized ZnO nanotroops by using a controlled carrier gas flow rate during synthesis. A seed-trapping mechanism has been proposed to explain the nucleation and growth of nanotroop ZnO. The special structure characters of the nanotroops may have interesting physical properties, and act as a candidate material for 3-D assembly of the nanodevices.

10:00 AM L126
Growth of Carbon Nanocone Using Three-nanometer Diameter Iron/platinum Nanoparticle-catalyst and Their Field Emission Properties. Hengtao Cui1, Xiaojing Yang2, Larry R. H. Hulsen1, Michael S. I. Simpson1,2, Walter L. Gardner1, Douglas L. Lowndes1, Lei An1 and Jie Liu1, National Radiological Protection Laboratory, Oak Ridge, Tennessee; 2Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 3Department of Chemistry, Duke University, Durham, North Carolina.

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

10:30 AM L127

Vanadium dioxide has found a wide range of applications in temperature sensing devices, optical switching devices, energetic and behavior controlling for fuel cells, because they undergo a phase transition at approximately 80°C from a semiconductive to a metal [1, 2]. Recently, one-dimensional nanostructure materials, such as nanotubes, nanowires and nanorods, have attracted much attention due to their unique properties different from their high surface area and low dimensionality [3]. In the present work, vanadium dioxide nanotroops have been synthesized, for the first time, using ethyltrimethoxysilane borotriazide (CTAB) as structure-directing template in hydrothermal condition. Morphology and structure of the sample were characterized by XRD, SEM, HRTEM, and TG-DTA. The results show that the products are monoclinic (C2/m) VO2 nanorods and they are 1-2 μm in length. HRTEM micrographs reveal that they indeed form bundles of agglomerated smaller filaments with diameters ranging from 20 to 40 nm besides single nanorod. This filament-like shape in the nanotroop dimension leads to the exposure of a large fraction of the atoms to the surface, these materials are promising candidates for the development of new functional materials. TG investigation shows that there are a weight loss of 22 % between 250-400°C corresponding to removal of the organic residue and a weight gain at about 400°C corresponding to oxidation of vanadium with low oxidation state. The simplicity of hydrothermal process, cheapness, and availability of raw materials are advantages favoring the scaling of nanorods. References [1] Hanlon TJ, Walker RE, Cotn JA. Thin Solid Films 410 (2002) 264; [2] Guisneton F, Jacques L, Valmante JC. J Phys Chem Soli 62 (2001) 1295; [3] Xiu Y, Yong P, Sun Y, et al Adv Mater 15 (2003) 3513. Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 50172160), the Teaching and Research Award Program for Outstanding Young Professors in Higher Education Institutions, MOE, P. R. China and the Science Fund for Distinguished Young Scholars of Hebei Province (Grant No. 2002CA068).

10:45 AM L128
Growth of Single Crystal Tungsten Nanorods by Oblique Angle Sputter Deposition. Tanaka, Kyoko,3 Goto, Hiroshi3,1,2, Gwo-Ching Wang1 and Tzou-Ming Lu1, Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York.

We report the creation of single crystal tungsten nanorods with unusual simple cubic β-phase. These novel nanostructures are grown by oblique angle deposition with substrate rotation [also known as glancing angle deposition (GAD)] through a physical assembly 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 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 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 atom mobility mechanisms. At the initial stages of growth, the β-phase W(100) islands grow taller due to the lower atom 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 shorter α-phase W(110) islands stop growing due to the shadowing effect.

11:00 A.M. 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 misorientation surface diffusion and atomic shadowing effects. Their shape, orientation, and arrangement can be controlled by ion-irradiation and deposition angles. CrN, TaN, SnN, and TiN layers were grown on MgO (100) at 600-1000 °C by ultra-high-vacuum magnetically-unbalanced magnetron sputter deposition in pure N2 and N2-Ar discharges at 5-20 mTorr. These deposition conditions result in a highly misoriented surface diffusion with hop-rates that are 7 orders of magnitude smaller on (111) versus (001) surfaces. This misorientation leads to kinetic surface roughening and the development of deep surface cavities which cause atomic shadowing and the formation of nanopipes that are elongated along the [001] growth direction. The nanopipes have rectangular cross-sections and form self-organized arrays aligned in orthogonal [100] and [010] directions, precisely replicating the in-plane correlation of the surface morphology. Non-normal deposition increases the level of atomic shadowing and introduces a controlled tilt to the nanopipes. Increasing the N2+ ion irradiation flux or decreasing the N2 partial pressure (and, hence, the steady-state N2 pressure) during growth provides a corresponding increase in cation surface mobilities leading to smoother surfaces, less atomic shadowing, and partial or full suppression of nanopipe formation.

11:15 A.M. L12.10
Polar surfaces induced growth of asymmetric nanocatalyzer arrays, Xiangrong Kong1, Zhong Lin Wang2, and J. M. Zuo3.
1 School of materials science and Engineering, Georgia Institute of Technology, Atlanta; 2 Materials Research Laboratory, University of Illinois, Urbana-Champaign, Urbana, IL 61801, Illinois.

Ionic crystals that consist of alternating layers of oppositely charged ions, stacked parallel to the polar surfaces, produce an accumulating normal dipole moment, resulting in divergence in surface energy. Crystals with polar surfaces generally have facets or edges having massive surface constructions to compensate the electrostatic charge on the surface, but ZnO(0001) is an exception, which is stable and without reconstruction. Structurally, the wurtzite structured ZnO crystal is described schematically as a repeating plane composed of fourfold tetrahedral-coordinated O and Zn+4 ions, stacked alternately along the c-axis. The oppositely charged ions produce positive charge [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 misoriented growth along [0001]. Longer and wider nanofinger arrays are grown from the [0001]-Zn surface, which is suggested to be a self-assembled process due to the enrichment of Zn at the growth front. This chemically active [0001]-surface typically does not grow nanobelt structure, but controlling experimental condition leads to the growth of nanobelt arrays of maximum and monolayer width, from the intersections between [0001]-Zn with (011)-O surfaces. The self-assembled process is likely a mechanism for the growth of nanobelts without the presence of foreign metallic catalysts. The nanocatalyst layers can be utilized as nanobelt arrays and tweezers arrays.

11:30 A.M. L12.11
Functionalized Carbon Nanotubes As Macromolecular Dops For Electrically Conducting Polymers, Mark Hughes1, Gwame A. Snaek3, George Z Chen2, Miao P Y Shaffer2, Derek J Fray3, and Alan H Winkle4.
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Electrically conducting polymers (ECPs), such as polypyrrole, polythiophene and polyaniline are frequently deposited as films via electrochemical oxidation of the relevant monomer. During deposition, an anionic dopant is typically incorporated into the ECP to balance the positive charge on the oxidized conducting polymer chains. The susceptibility of multiwalled carbon nanotube (MWNT) surfaces to functionalization makes them exciting candidates for a new class of dopant for ECPs. In this work, hydroxyl, carbonyl and carboxylic groups are attached to the surface of MWNTs via an acid-treatment process involving nitric and sulfuric acid. The functional groups give the acid-treated MWNTs a net negative charge, enabling them to provide charge balance for the oxidized ECPs. As do more conventional anionic dopants. Once deposited, the functionalized MWNTs are permanently embedded within the ECP, forming a continuous nanocomposite film. Previously, if there was insufficient anionic dopant available to ensure the deposited ECP was comprehensively oxidized, the electrical resistance of the neutral polymer prohibited further deposition. However, when using functionalized MWNTs, their electrical conductivity and high aspect ratio make it possible to grow MWNT doped ECPs in which the polymer is only partially oxidized. This phenomenon is attributed to the formation of an electrically conductive network comprising the MWNTs and the oxidized layer of ECP adjacent to the functionalized MWNT surface. The work described here relates to MWNT-polypyrrole nanocomposite films in which the MWNTs are the only dopant used during film deposition. Electrochemical impedance spectroscopy, cyclic voltammetry, scanning electron microscopy, Raman spectroscopy and a quartz crystal microbalance are used to characterize the doping behavior of the functionalized MWNTs. A comparison is made between pyrrole doped with embedded functionalized MWNTs and similarly prepared pyrrole films doped using large immobile anions such as dodecyl sulfate. Finally, the effect of growing MWNT-polypyrrole films in the presence of competing dopant anions is explored.

11:45 A.M. L12.12
Carbon Nanotubes and Nanofibers Grown by Microwave Plasma Enhanced Chemical Vapor Deposition on Nickel Substrate, Kaluji Gbemegboshi Bagay, Jeremy Jackson and Yan Xing.
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-etched with a 1.0μm 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 jotted 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 (MWNTs) 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.