SYMPOSIUM W
Nanoparticulate Materials
November 26 – 29, 2001

Chairs

Rajiv Kumar Singh
Dept of MS&E
Univ of Florida
217 MAE
Gainesville, FL 32611
352-392-1032

Heinrich Hofmann
Dept of MS&E
EPFL-Lausanne
MXD
Lausanne, CH-1015 SWITZERLAND
41-21-693-3607

Mamoun Muhammed
Dept of MS&E and Matls Chemistry Div
The Royal Inst of Technology (KTH)
2nd Floor
Stockholm, STHLM SE-100 44 SWEDEN
46-8-7908158

Richard Partch
Ctr for Advanced Matls Processing
Clarkson Univ
Box 5814
Potsdam, NY 13699-5814
315-268-2351

Mamoru Senna
Faculty of Sci & Tech
Keio Univ
Yokohama Kanagawa, 223-8522 JAPAN
81-45-566-1569

Symposium Support
EPFL, Switzerland
KTH, Sweden
University of Florida

Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 704
of the Materials Research Society
Symposium Proceedings Series

*Invited paper
8:30 AM *WL1.1 DISPERSING AND COAGGULATION AND STABILIZATION OF CONCENTRATED SUSPENSIONS. Lennart Bergström, YKI, Institute for Surface Chemistry, Stockholm, SWEDEN.

Nanoparticles are commonly processed as concentrated suspensions, e.g., in the production of structural and functional nanostructured materials. The utilization of the intrinsic properties of these materials requires thorough control of the microstructure and homogeneity, starting from the suspension preparation to the final material. This talk will discuss some of the inherent problems of deagglomeration and stabilization of nanoparticles. It will be shown how successful deagglomeration of the individual crystallites of a silicon nitride powder down to nanometer dimensions is achieved in a significant improvement of the suspension properties. The deagglomeration process was related to the nature of the interparticle bonds and the surface chemistry. It will be illustrated how successful deagglomeration could be achieved by optimization of the chemical conditions without the need of extensive mechanical treatment. The implication for other nanoparticulate systems will be discussed. Stabilization of nanoparticles requires fine tuning of the magnitude and range of the induced repulsive forces including diffusion-reduced repulsion of dispersed titania particles in ethanol will be presented and the results will be discussed in the context of DLVO theory.


Several emerging technologies such as chemical mechanical polishing (CMP), high speed coatings, inks, nanocomposites, and biomedical applications are increasingly relying on nanoparticulate dispersions to achieve optimum performance. Many of these technologies operate under extreme conditions such as high salinity (CMP, biosolids in medical applications), high shear rates (CMP, high speed coatings), and presence of complex additives (CMP, nanocomposites, bio applications). Under these extreme conditions, traditional dispersing methods such as electrostatics, inorganic dispersants, and polymers may not perform adequately. Surfactant solutions can provide a feasible alternative for stabilization of ultrafine particles under extreme conditions. The barrier to aggregation in presence of surfactants aggregates, measured using atomic force microscopy (AFM) was several orders of magnitude higher as compared to barrier expected from electrostatic interactions alone. The onset of this barrier was correlated to dispersion of nanoparticulate systems under extreme conditions. Further it was observed that the barrier strength increased with increasing chain length of the surfactant, addition of alcohol, addition of co-surfactant, and addition of electrolyte. The results indicate the presence of steric barrier due to the adsorbed micelles on the surface, the strength of the barrier increasing with increasing strength or compactness of the adsorbed micelles. These micelles absorb adsorption, neutralize potential, and polarized. Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATR-FTIR) were used to determine the transition in surfactant aggregate structure, in order to delineate the dispersion mechanism. The role of surface chemistry, surface structure, and surface crystallographic orientation on surfactant self-assembly was also investigated.

9:30 AM WL1.3 FACILE ROUTE TO NANOALLOY PARTICLE DOPED IN POROUS SILICAS. Bao-Hang Han, Markus Antonietti, Max-Plank Institute of Colloids and Interfaces, Potsdam, GERMANY.

We have reported a facile synthesis of metal-doped porous silica using cycloextrins as template for nanoparticle coating. The advantages lie on that cycloextrins not only act as template for microporous structures, but also introduce the organometallic (metal precursors) into the silica via inclusion complexation in their cavities. During calcinations, the pore wall could be enhanced in order to regulate the nucleation of metal particle, giving metal nanoparticles doped in porous silica. In this presentation, we will report the synthesis of nanoalloy particles doped in porous silica. Two and/or different organometallic [Pd, Pt, Ru, Ir, Mo, W, Ti, Zr, etc.]cycloextrin complexes can fully or partially be incorporated in a single step solution. After templating in solid-gel process, the metal precursors are homogeneously dispersed in the as-synthesized silica matrix. Upon calcinations, alloy particle in nanometer scale are formed and doped in the porous silica, which are characterized via TEM/EDX. The silica supported nanoalloy particle could find potential application in wide variety of fields, including catalysis and battery cell.

9:45 AM WL1.4 DISPERSION CHARACTERIZATION OF MECHANICALLY SYNTHESIZED NANO PARTICLES USING UV-VIS SPECTROSCOPY. Takuya Tsunzai, Paul G. McCormick, Advanced Nano Technologies Pty Ltd, Westfield, AUSTRALIA.

Nanoparticle melt-processed exhibit properties that substantially differ from those of bulk materials as a result of particle dispersion, surface area, quantum confinement and other effects. Many of these unique properties require not only the powder particles to be of nanometer size, but also that the powder particles be individual dispersed single crystals. Therefore, development of agglomeration free nanoparticles and characterization of dispersion/agglomeration states are of particular importance in nanoparticle systems. There are several techniques for the size/agglomeration characterization of nanoparticles, e.g., photo-correlation spectroscopy (PCS), electron microscopy (EM), BET specific surface area analysis (BET), and small angle x-ray scattering (SAXS). However, these methods have drawbacks: PCS requires extremely diluted particle suspensions, EM leads to selective measurements; BET and SAXS do not represent agglomeration states. Since scattering intensity of UV/Vis light by small particles is sensitive to the particle size, UV/Vis spectroscopy can be used for the characterization of dispersion/agglomeration states of nanoparticles. Light-scattering power of particles increases with the particle size, and high optical transmittance is possible only for the particles smaller than 40 nm with no agglomeration. The present paper discussed the dispersion characterization of nanopolystyrene polymers using UV-Vis spectroscopy. ZnO, CeO2, ZrO2 and Al2O3 nanoparticles of sizes ranging 10 - 250 nm were investigated for slurries having various concentrations. The particles were synthesized by mechanochemical processing, which enables building up nanoparticles through a solid-state chemical reaction, allowing the formation of separated nanoparticles embedded in a solid matrix, leading to agglomeration-free nanoparticles. The results show that UV/Vis spectroscopy is a highly promising technique for studying nanoparticle dispersions.

10:00 AM WL1.5 NANOPARTICLE AGGREGATION DURING DRYING STUDIED BY USAKS AND FESEM. Andrew Allen, NIST, Materiels Science and Engineering Laboratory, Gaithersburg, MD. Alejandro Vortmesser, Merrill Byroo, Pennsylvania State University, Department of Materials Science and Engineering, University Park, PA.

Aggregation during powder processing frequently prevents full densification of fabricated ceramics. It is known that drying of liquid-borne powders creates agglomerates, but not exactly how or why these agglomerates evolve. The problem is acute in the nanoparticle size regime, where powdered particle dissolution and dispersed electrostatic repulsion are strong dispersive forces, aggregation during drying. The aggregate shape and size evolution during the drying of different nanocrystalline zirconia powder suspensions has been studied by ultramicro-angle x-ray scattering (USAKS) and field emission scanning electron microscopy (FESEM) and dissolution varies by 4 orders of magnitude across the pH range, but no dramatic difference in the size or quantity of agglomerates is observed. However, shape changes are observed; these appear unrelated to dissolution but strongly related to particle surface change. Away from the inedcative point, large, fractally-rough agglomerates are observed by USAKS, likely produced by "reaction-limited" aggregation, and partly composed of short, entangled chains of primary particles. Near pH 8, where electrostatic regulation is minimal, aggregation is "diffusion-limited" and large mass-fractal aggregates are observed. Differences in the micrometer-scale morphology of fully-dried suspensions, observed by SEM, appear related to the nanometer-scale aggregation of primary particles, studied by USAKS. For example, for powders dried at high pH, micrometer-thick lamellae and grains with lamellar substructure may be associated with the presence of much finer nanometer-thick sheets in the originating suspension.

SESSION W2: NOVEL nanoparticle CHARACTERIZATION. Chair: C. Jeffrey Brinker.

Non-invasive techniques to study 'in situ' materials properties of advanced nanostructured materials are a necessity and of great interest for device development. In this presentation we exploit the capabilities of atomic force microscopy to investigate: 1) local magnetocrystallin and domain observations at atomic scales by measuring induced surface roughness of Co-magnetic dots (100-300 nm in diameter) patterned on Silicon substrates [1]. 2) The local sticking coefficient variations on a composite material consisting of TiN inclusions in an Alumininum matrix, 3) Domain configuration in pulsed laser deposited films of rhombohedral Fe3O4. This shows typical magnetocrystalline anisotropy with a rectangular shape of the Co magnetic dots is visible in the images. The Fe3O4 magnetic nanodots can be used in various technological applications such as magnetic storage devices and magnetic sensors. 4) The magnetic field induced flux-rotation phenomenon in biomineralized magnetotactic bacteria in which the chains of magnetic nanoparticles play an important functional role [3].

In order to understand the phenomena in these systems, we have studied their magnetic properties using external fields to control their orientation and studied their magnetic structure in these systems. Studies on novel model systems, with properties described above, using simulations and measurements, will be discussed. The results of these experiments will be presented.


SESSION W3: ELECTRONIC AND OPTICAL APPLICATIONS
M. Rajiv Kumar Singh and Heinrich Hofmann
Monday, December 20, 2011
Back Bay B (Sheraton)

1:00 PM W3.3
APPLICATION OF DISPERSIVE NANO PARTICLES
Masaki Okita
Tomoyuki Abe, Toshihiro Suzuki, Norimitsu Sato, Haruto Ishiwashi, Gihalp Kuthk, ULVAC Corporation, Nano-Particle Application Dept., Chiba-ken, JAPAN

Nano-particles can become one of the best materials for forming thin and fine pitch films at low temperature, if particles are individually dispersed densely in a solvent. Individually dispersed metal/nanoparticles (nano-particle) are formed as a state of suspension in an organic solvent by the modified gas evaporation method where formed particles are covered with an organic surfactant just after their formation. The particles formed by the gas evaporation method are metal impurity free and have a narrow size distribution. This suspension is condensed and used as film of solution or paste. Dielectric nanosphere or paste can be baked at 200°C to form metal thin films. These have been applied to PD electrode repairing, coating of car window glass, a filler of electric conductive resin paste and ULSI interconnection formation.

2:00 PM W3.2
EFFECT OF SURFACE TERMINATION ON THE BAND EDGES OF SEMICONDUCTOR NANO PARTICLES
T. van Buren, C. Booteit, N. Franco, J. Pluzko, L. Terrillen, Lawrence Livermore National Laboratory, University of California, Livermore, CA, USA.

A critical question in the area of nanometer-sized silicon is the effect of surface termination on the band edge structure. The use of ECP, ECQ, and AFM techniques allows the determination of the surface termination of nanometer-sized silicon. The ECP and ECQ techniques allow the determination of the band edge structure. The ECP and ECQ techniques allow the determination of the band edge structure. The ECP and ECQ techniques allow the determination of the band edge structure.
The scientific world is embracing all types of nanoscience and technology through the rapidly advancing work seen in the scientific communities. From molecular systems, knowledge of bond width, surface modification, and functionalization is rapidly evolving. For dry laser gap widening and band alignment as a function of particle size, and surface modification is critical to rational design and utilization of these novel materials. We use soft X-ray probes such as X-ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES), and Soft X-ray Fluorescence (SXF) experiments to determine the band gap shifts and surface effects on a variety of nanomaterials used in order to better understand the electronic properties. The reduced and enhanced band gap of these characterized include Si, Ge nanocrystals ranging in size from 1 - 5 nm. In particular we found that the quantum shifts in the conduction- and valence-band edges of hydrogen terminated silicon nanocrystals increase progressively with decreasing particle size. The ratio of the shift in the VB edge to the shift in the CB edge remains approximately constant and equal to 2, in agreement with various models for the quantum shifts. However, recent theoretical work suggests that this ratio is dependent on the type of surface termination. We report the results of our experiment in inert background gas, size classification using a low-pressure operating differential mobility analyzer, and deposition by nozzle jet onto a substrate. By using the sequential process system, we can classify the nanocrystals of nominal diameter between 3 and 7 nm with the geometrical standard deviation of 1.2. For the PL measurement, Si nanocrystals were deposited onto crystalline Si wafers. After exposing Si nanocrystals of 4 nm diameter to the air, broad PL spectrum (peak energy: 1.7 eV) was observed at room temperature. This spectrum could be decomposed into four Gaussian bands, whose peak positions are related to defects in silicon oxide. In order to measure the EL spectrum, we fabricated the light-emitting diodes (LEDs) in the active regions of the LEDs are Si nanocrystal films of 4 nm diameter exposed to the air. As transparent upper electrodes, indium oxide (In$_2$O$_3$) thin films were coated over the Si nanocrystal films. An EL spectrum had a nanosecond bandwidth of 0.15 eV. The peak energy was 1.17 eV, which is higher photon energy than the band gap energy of bulk Si of 1.1 eV at room temperature. This EL spectrum could originate from quantum confinement effects of the monodispersed Si nanocrystals. Thus, the EL mechanism differs from PL ones in our samples. Furthermore, we will discuss the luminescence mechanisms by analyzing the carrier dynamics in monodispersed Si nanocrystals.

**2:15 PM W3.3**

**ELECTRON-FIELD EMISSION FROM NON-DIAMOND FILMS.**
S.G. Wang, Q. Zhang, S.F. Yoon, J. Ahn, D.J. Yang, Q. Wang, Rusli, Nanyang Technological University, SINGAPORE.

Recently, CVD diamond with nanometer grain size (nano-diamond) has been regarded as an important new diamond material with special properties such as higher field emission efficiency and lower optical absorption coefficient due to its smaller grain size and smoother surface than common CVD diamond films. In this paper, the electron field emission from nano-diamond films with a grain size of 50 nm is studied. The nano-diamond films were prepared using a microwave plasma enhanced chemical vapor deposition system in a gaseous mixture of nitrogen, methane and hydrogen. The experimental results show that the grain size of nano-diamond films increases with increasing hydrogen gas flow ratio of [H]/[N$_2$+CH$_4$+H$_2$]. And the turn-on voltage for electron field emission increases following an increase in grain size of nanodiamond films. The nano-diamond films with small grain size have low turn-on voltage for electron field emission and large emission current.

**2:30 PM W3.4**

**THE COMBINED EFFECT OF QUANTUM CONFINEMENT AND SURFACE CHEMISTRY ON THE OPTICAL PROPERTIES OF STERICALLY STABILIZED INDIVIDUAL SILICON NANOCRYSTALS AND THEIR ENSEMBLES.**
Lindsey E. Poli, Douglas S. English, Kirk J. Ziegler, Paul F. Barbara, Keith P. Johnston, Brian A. Korgel, Brian A. Korgel, Department of Chemical Engineering, Texas Materials Institute, and Center for Nano and Molecular Science and Technology, University of Texas, Austin, TX.

We recently developed high temperature wet chemical approaches to synthesize silicon nanocrystals and their ensembles. The synthesis of silicon nanocrystals uses a supercritical organic solvent (500°C, >140 bar) with dissolved capping ligands that sterically stabilize the nanocrystals. A nanocrystal size can be tuned by changing precursor and capping ligand concentrations. Size separation methods, such as size selective precipitation and/or size exclusion chromatography, can isolate relatively monodisperse nanocrystals (>5%) with robust surface passivation. The particles are crystalline and luminescent with quantum efficiencies of over 20% in the blue and green for small (~20 nm) and large (~40 nm) particles, respectively. The 20 nm diameter nanocrystals exhibit size-dependent vibronic structure regardless of the capping molecules used, such as octadecyl, octanethiol, or octane. As the nanocrystal size increases, the intensity of the vibronic structure decreases and eventually the spectrum reduces to a single broad emission peak. At low temperatures (8 K), transverse and longitudinal optical (TO and LO) phonon transitions appear on the long wavelength side of the primary PL emission peak. The appearance of these phonon replicas confirms the narrow size distribution and high purity of the Si nanocrystals, as well as the strong coupling between phonons and excitons in nanocrystal silicon. Single particles that self-assemble into a polydispersed ensemble of thiol capped silicon nanoparticles using both 488 nm and 543 nm light from an Argon laser showed peak maxima that ranged over many wavelengths, from 555 780 nm. The single particle PL blinks on and off due to the ensemble of the single particle.
Particle size measurements and show the spherical shape of the particles. Final dopant concentrations were measured through inductively coupled plasma (ICP). ICP results show a dopant loss of 5% during processing for the europium-doped yttria and 8% for the manganese-doped zinc silicate. Green and red photoluminescence (PL) and cathodoluminescence (CL), at 523nm and 614nm respectively, were observed from these synthesized phosphor particles under UV excitation and electron bombardment. Results show that the non-doped samples with a mean diameter of 30nm displayed a significant increase in PL brightness over the seeded samples whose mean diameter was 215nm. Additional treatments such as annealing in a reducing atmosphere and surface etching of the phosphors on PL were positive.

4:15 PM W0.8
OPTICAL PROPERTIES METAL/OXIDE FILMS HAVING A TAYLORED NANOPARTICULATE DISTRIBUTION. B. Serna, J.C.G. De Sando, A. Suarez-Garcia, J. González, C. N. Alonso, Instituto de Optica, CSIC, Madrid, SPAIN. (to be confirmed). P.P.M., Madrid, SPAIN.

Metal nanoparticles (NPs) embedded in dielectric matrices exhibit special optical properties, which depend on the NP size, shape, and distribution. The fabrication of such materials in thin film configuration is sought both for its application to optical coatings and as base material for the development of integrated optoelectronic devices in waveguide configuration. Although the optical absorption of these nanoparticles is known to have the subject of detailed studies, the real part of the refractive index \( n \) has rarely been studied. The knowledge of \( n \) is however essential to achieve the needed refractive conditions in waveguide structures and has important implications in the overall response of the films. The aim of this work is to determine the optical properties (effective refractive index \( n \) and \( k \)) of specially tailored nanoparticulate thin films, and in particular for use in waveguide applications. The films are formed by metal \( Cu \) NPs embedded in an amorphous aluminium oxide \( (Al_2O_3) \) host prepared by alternate pulsed laser deposition. This technique has a high potential to produce materials with a mesoscopic control of their structure. The metal NPs are embedded in the matrix and are designed both by controlling the number of laser pulses on the Cu and \( Al_2O_3 \) targets respectively. The Cu NPs have average sizes from 3 to 6 nm and are distributed in a multilayer structure. Spectroscopic ellipsometry is used to determine the effective refractive index \( n \) for films with a Cu content in the range from 2 to 12 at% is found that the extinction coefficient is non-negligible and shows a maximum around 500 nm related to the surface plasmon resonance. In the neighborhood of this wavelength, the real part of the refractive index undergoes an anomalous dispersion, leading to a significant increase of the \( n \) value of the composite compared to that of the matrix. The specific optical response of the films having different NP size and distribution will be discussed within the framework of medium models.

SESSION W0/A4.4: JOINT SESSION SELF ASSEMBLY
Chairs: Mamaki Obtani and Mameze Sena
Tuesday afternoon, January 31, 2000
Back Bay B (Sheraton)

8:30 AM *W4.1/A4.4
NEW DIRECTIONS IN SOL- GEL PROCESSING: EVAPORATION-INDUCED SELF-ASSEMBLY OF POROUS AND COMPOSITE NANOSTRUCTURES. C. Jeffrey Brinker, Sandia National Laboratories and the University of New Mexico, Albuquerque, NM.

“Classical” sol-gel processing of oxides often results in highly disordered materials like aerogels characterized by a thus or surface fractal dimension. However recently, the combination of sol-gel processing with various self-assembly approaches has enabled the efficient formation of highly organized porous and composite materials in thin film and particulate forms. This talk will review recent work referred to as evaporation induced self-assembly. Starting with a homogeneous solution of inorganic and organic precursors plus amorphous structure directing agents like surfactants, we exploit evaporation accompanying coating, drying, or printing to promote the self-assembly of micelles that spatially separate and organize organic precursors (sequestered within the hydrophilic micelles) and inorganic precursors (sequestered around the hydrophobic micelles). This presentation will first provide a brief overview of our evaporation-induced self-assembly (EISA) approach and its extension to the preparation of hybrid, organic-functionalized silica frameworks and thin films. Other hybrid (organic)/polymer nanocomposite films will be discussed, as will a variety of mechanically and chemically defined patterns, where we utilize such homogeneous silsesquixitonic solutions as inks in rapid prototyping processes like micro-gel lithography, ink-jet printing, and selective de-wetting. Then I will discuss new work concerning the self-assembly of responsive nanocomposites. First by introduction of photochromic molecules into the inks, we can write arbitrary patterns of photosensitive mesophases. A subsequent lithographic patterning step then can be used to photo-define different structures and functionalities within the parent pattern, establishing a single-step process to hierarchical functionalized materials. Second, by using photoresponsive surfactants as both structure directing agents and monomers, we can self-assemble nanostructured architectures within which we topochemically polymerize the surfactant to form a conjugated polymer (polypyrrole)/silica nanocomposite.

9:00 AM W4.2/A4.4
ENGINEERING OF NANOPARTICLES FOR ADVANCED MATERIALS HETEROGENEOUS 3D AND 1D STRUCTURES. Muhannad Muhammad, Yi Zhang, Marin Mikhailov, Muhammad S. Toprak, German Silman-Blanco, Do-Kyung Kim, The Royal Institute of Technology, Dept of Materials Science and Engineering. Materials Chemistry Div, Stockholm, SWEDEN.

Nanoparticles are important building blocks in several applications of Nanotechnology. Beside the enormous increase of their surface area, the high surface to volume ratio of the nanoparticles results in extraordinary high reactivity and unusual physical properties (optical, magnetic, etc.). Dispersed nanoparticles are used in several important applications, e.g., catalysis, biomedical applications, etc. Nanostructured materials, prepared by consolidating nanoparticles with a very high density of grain boundary, have shown to have dramatically improved mechanical and physical properties. A recent promising development is the fabrication of nanometer features using self-assembly techniques and their use in the formation of high hierarchical artificial structures through self-assembly. The nanoparticles can be made of composites with controlled structure. Nanoparticles can be fabricated with different core-shell structures through the use of metallic core and oxide or reverse. The selection of the composition and structure of the shell layer allows different chemistry to be conducted at the surfaces, e.g., inducing bio-compatibility, enhanced electrical conductivity, or reactivity. By a proper combination of the chemistry at the surface of the particles and substrates, it is possible to achieve a spontaneous self-assembly of the particles on the substrate to form stable 2D and 3D structures. In this talk, a presentation of some of our recent development in the fabrication and self-assembly of composite nanoparticles will be presented together with some examples of applications.

9:15 AM W4.3/A4.4

Periodic mesoporous materials, discovered in 1992 by Mobil Oil Corporation researchers, are synthesized via the polymerization of organic species around a periodic organic template, which could be surfactant micelles, copolymers. After a thermal treatment, a porous material is obtained which porous-pores. In November of this year, the first truly periodic material was obtained which porous-pores. Thanks to their porous periodic network, these materials can act as template for the synthesis of periodic 2D or 3D arrays of nanoparticles.

Recently, we have reported the synthesis of fully organized mesoporous silica films by spin-coating on glass plates. They have a 3D hexagonal structure, consisting in an interconnected spherical pore network which is oriented with the 0 axis perpendicular to the film plane. These films are used as template for the synthesis of semiconductor and metal nanoparticles. Characterizations by X-ray diffraction, UV-visible spectroscopy and high resolution electron microscopy show that 300 nm thick films are totally filled with monodisperse and periodically distributed nanoparticles. The aggregates grow inside the pores without disturbing the structure, and their size (3 nm) and spatial arrangement are controlled by the silica porous matrix.

This is the first synthesis of 3D periodic arrays of nanoparticles inside mesoporous films. The use of such templates for the synthesis of periodic nanoparticle coatings opens new application opportunities, since large scale synthesis is possible.


9:30 AM W4.4/A4.4
SELF-ASSEMBLY AND GROWTH OF ORGANIC MOLECULAR
NANOCRYSTALS. Edward Van Keuren, Elena Georgiev, Michael Durst, Georgetown University, Dept. of Physics, Washington, D.C.

Nanoparticles of organic molecular crystals may be formed in binary solvents by changing the ratio of solvents, one in which the solubility of the solute is good, the other poor. This method is interesting both as a preparative method for nanoparticle suspensions as well as for studying aggregation and crystallization phenomena in model systems under well controlled conditions. We report on nanocrystals of antarhence formed in an acetone/water solution. The particle growth and crystal orientation were characterized using dynamic light scattering and UV-VIS absorption spectroscopy. A number of points in the ternary phase diagram below the critical size were also investigated for evidence of cluster formation.

9:45 AM W4.5/A44.5
FABRICATION OF TWO- AND THREE-DIMENSIONAL STRUCTURES OF NANOPARTICLES USING LB METHOD AND HYDROGEN CHLORIDE GAS. Kiyonori Takayama, Takayuki Takahashi, Satoru Sen, Tatsuya, Hiroyuki Sjukne and Shoko Shingubara, Hiroshima University, Graduate School of Advanced Science and Mitter, Hiroshi Hiroshima, JAPAN.

Recently, self-organization of nanoparticles has been object of researchers attention as powerful method to make nanostructures. We have carried out research to self-organization of two-dimensional array of gold nanoparticles. We successfully assembled highly regular and large area two-dimensional array of gold nanoparticles encapsulated by thiol chain molecular films. We used fabrication methods using Langmuir-Blodgett method and hydrogen chloride gas technique. We observed Cobalt electrodeposition on the Au-Co assembly, and moreover, to assemble material regularly containing much kind of particles, specific chemical reaction is considered to be useful. As the specific chemical reaction, we mention some kind bond reaction systems like sol-gel type reaction. One of most specific chemical reaction is hybridization reaction between complementary DNA sequences. Therefore, some workers tried to fabricate various nanostructures using DNA hybridization phenomenon. They demonstrated that gold nanoparticle coated DNA oligonucleotides capped with thiol group. DNA was confirmed to be useful for fabrication nanoparticle-structures. But they could not clearly show three-dimensional nanostructure fabrication using DNA. In the present study, we fabricated a structure of gold nanoparticles with two sizes using DNA oligonucleotides capped with thiol group. The high-resolution scanning electron microscopy observation confirmed that a three-dimensional structure in which two sizes gold nanoparticles alternately arranged was successfully assembled. The result indicates that the "DNA fabrication" is useful method for assembling the nanoparticles into the three-dimensional nanostructure we aimed. Furthermore, much more complex structure might be able to fabricate with electrical, optical functionality when the chemistry is well established to attach SAMS DNA to the surface of nanoparticles composed of other kind of elements.

10:30 AM W4.6/A44.6
MAGNETIC AND MECHANICAL PROPERTIES OF SELF-ASSEMBLED METAL NANO PARTICLES IN THIN FILM MATERIALS. John J. Wernick, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; J. Nayar; T.K. Nath; and Alex V. Kvit, Department of MSE, North Carolina State University, Raleigh, NC.

Nanocrystal magnetism currently provides a wealth of scientific interest and of potential applications. When the size of magnetic particles is reduced to a few tens of nanometers, they exhibit a number of outstanding physical properties such as giant magnetoresistance, superparamagnetism, large coercivities, high Curie temperature, and low saturation magnetization as compared to the corresponding bulk values. Due to the presence of these outstanding physical properties, under size reduction, magnetic nanoparticles are bringing revolutionary changes in a variety of applications. In view of the technological importance of producing magnetic nanocomposites, the synthesis of magnetic systems with characteristic nanoscale dimension has attracted a lot of research attention. In this context, we have developed a novel thin film processing method based upon pulsed laser deposition to process nanocrystalline magnetic materials with accurate size and interface control. Using this method, single domain nanocrystalline Fe and Ni particles in 5-20 nm size range were embedded in amorphous (Al2O3) and crystalline (TIN) matrices. For example, at room temperature the coercivity of Fe-Al2O3 sample decreases from 100 Oe to 15 Oe as the particle size decreases from 9 nm to 7 nm and finally the sample turns superparamagnetic when the Fe particle size becomes around 5 nm. The average volume (V) of magnetic particles, calculated from the expression: \( V_p = KV_0^2/k_B \), \( K_B \), \( V_0 \) being blocking temperature, magnetic anisotropy and the Boltzmann constant, respectively, is found to be in good agreement with the particle size measured using TEM studies.

11:00 AM W4.7/A44.7
STRUCTURAL AND MAGNETIC PROPERTIES OF SELF-ASSEMBLED Co NANO PARTICLES. H.R. Khan* and K. Perkinson, Physics Department, University of Tennessee, Knoxville, TN.

Arrays of magnetic nanoparticles have received considerable attention due to the interest in developing high density magnetic recording media (1,2). The magnetic properties such as coercivity (Hc), squareness (Mr/Ms) and magnetic energy product (BH) depend on the composition, diameter, and spacing of the nanoparticles. Cobalt nanoparticles of diameter in a wide range from 18 to 78 nanometer with spacing between 40 and 90 nanometer are electrodeposited into the self assembled pores of Al2O3-MgO substrates obtained by mask oxidation. Diffusion electrodes were used to obtain the various pore diameters. The anisotropic magnetic properties depend on the diameter and the length of the nanoparticles as shown by the hysteresis loops. A strong perpendicular magnetic anisotropy and maximum He and Mr/Ms values of 18500e and 0.9 are observed for the Co nanoparticle arrays of 18 nm diameter and 0.4 micro-meter length. The values decrease with increasing diameter. The magnetic properties of these arrays of nanoparticles in terms of the interactions between the nanoparticles and the possibility of their application as high density magnetic recording media will be discussed.

2. H.R. Khan and K. Perkinson, J. Magn. Magn. Mater. (in Press). This work is supported by Bundesministerium für Wirtschaft through Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. and grant no AIF 11429 N.

11:15 AM W4.8/A44.8
MATERIALS BASED ON ORDERED THIN FILM ASSEMBLIES OF NANOPARTICLES. Nicholas A. Koster, Oklahoma State Univ, OK.

Hybrid polyelectrolyte/nanoparticle thin films are made by the sequential adsorption of (nano)layers of oppositely charged inorganic colloids and polyelectrolytes also known as the layer-by-layer assembly (LBA). The major advantages of LBA are the nanometer scale controlled thickness of nanoparticle layers and high quality of the films combined with simplicity of the process. The LBA technique is a convenient method of processing of a variety of aqueous dispersions of nanoparticles into functional materials. The areas of applications currently considered for LBA assemblies include photovoltaics, light-emitting diodes, high-density magnetic memory, non-linear optical switches, nanoscale interconnects, resist layers, sensors, gas separation membranes, optical filters, and others. This presentation will be focused on the effect of ordering of the nanoparticle layers on the materials performance, which will include the control over optical, magnetic, electrical, and mechanical properties of thin films achieved by combining different nanocoatings deposited in predetermined order. The universality of LBA also affords the inclusion of biological entities in nanoparticle assemblies. The effect of stratification in biomimics prepared from layered protein/nanoparticle assemblies and molecularly engineered thin films will be discussed.

11:30 AM W4.9/A44.9
SELF-ASSEMBLING OF NANOPARTICLES IN THE FORM OF DOUBLE LINEAR CHAINS AND SUPERLATTICES ON THEIR BASIS. Rusnak Molchanowy, Robert Karshian, Mary Naparps, Scientific Production Enterprise "ATOL", Yerevan, ARMEIA; Changma Sung, University of Massachusetts, Lowell, MA.

The self-assembling systems in nanoscale powders of crystalline M-O3 particles are discussed. Particularly, in nanoscale powders of M-O3 treated by vibrationally excited molecules of hydrogen (1), for the first time the double linear chain aggregates of M-O3 nanoparticles were revealed. These chains are composed of two separate chains, which are closely disposed to each other. The transmission electron microscopic studies showed that these chain aggregates consist of spherical crystalline M-O3 nanoparticles with diameter of about 20nm. It is found that linear double chain aggregates form two sorts of superlattices. So the double linear chain aggregates form orthorhombic superlattice (with parameter of about 1 micronometers) from straight chains with length of about 30 micrometers that are parallel to each other. The double chain aggregates of nanoparticles in these superlattices have three-dimensional branches that in some places reach the neighboring chains. Moreover, the double linear chain aggregates form two sorts of superlattices. The following parameters: a = 200nm, b = 300nm. Both, double linear chain aggregates and formed on their basis linear and orthogonal superlattices, are considered in present.
work as self-assembling systems with building blocks of crystalline nanoparticles of MoO₃. In the first stage of self-assembling processes, the nanoparticles were suspended in a solution of dichloromethane, which then form a network. In the second stage of self-assembling processes, the nanoparticles were then exposed to microwave, which allowed the formation of nanostructured materials. Taking into account the fact that double linear chain aggregates and superstructures of nanoparticles were obtained only in case of the precursors, which were used to determine the phase, grain size, grain size distribution and crystallinity of the nanocomposites. These precursors are obtained through a process of pulsed wire discharge, PCD, and condensation by interaction with ambient gas. Since the electric energy is directly converted into thermal energy, the efficiency for a nanoparticle is very high in PCD. For the synthesis of AlN, the current is typically 180 kA/s, which is 50 times higher than that of conventional methods. Furthermore, industrial applications might be available due to advantages such as electrical resistance and mass productivity. AlN powders were prepared by the method of Al wire in NH₃/N₂ gas. Here, the stored energy in the capacitor of 10 μF was discharged to Al wire with 0.25 mm in diameter. Charging voltage was 4.6 kV. The particles were then condensed in the ambient gas to form a multilayer structure. The results were confirmed by X-ray diffraction. The diffraction methods were used to determine the phase, grain size, and crystallinity of the nanocomposites. We also confirmed that Al particles of nanocomposites were used in the synthesis. The particle size obeys log-normal distribution, and the geometric standard deviation was 1.29 which is close to that of nano-dispersed powders. The content of AlN in collected powders reaches 90 wt% by the discharge in 20% NH₃/N₂ gas at 750 Torr. In addition, the content was influenced by the inductance of the discharge circuit. The content increased with decreasing inductance, i.e., short pulse with high power was effective to enhance the reaction between alumina and nitrogen.

2:45 PM W5.5
LOW-COST MULTIMETALLIC SINGLE CRYSTALLINE OXIDE NANOPARTICLES FOR STRUCTURAL AND CATALYST APPLICATIONS. R.M. Laine, T. Hinklin, E. Gilani, E. Seker, Depts. of MSE and Chemical Engineering, University of Michigan, Ann Arbor, MI; A. Sutorik, S. Balint, Tal Materials Inc., Ann Arbor, MI.

We recently developed methods of producing oxide nanoparticles by flame spray pyrolysis (FSP) of ethanol solutions of low-cost metal alkoxide complexes as well as other soluble metal precursors. This scalable synthesis route provides reproducible, high-purity, self-dispersing nanoparticles. We have previously demonstrated the ease with which FSP can be used to prepare single crystal Al₂O₃, TiO₂, MgO, and partially crystalline Al₂O₃ powders with controllable mean particle sizes of 2-200 nm and surface area ~ 90-120 m²/g at production rates ~ 400 g/h. We focus on FSP processing of novel two-phase nanocomposites wherein segregation is desired and control is simultaneously generated catalytic support (e.g., CeO₂/ ZrO₂ solid solutions on d-Al₂O₃ nanoparticles), and other materials where two phases segregate at the nanoscale during processing of originally homogeneous nanoparticles.
and growth and crystal structure of the matrix, we can vary the
texture of nanocrystallites from random to epitaxial. The talk focuses on
syntheses of many-proven novel nanocrystal optical materials with a robust
matrix with excellent optical properties, nanocrystal characteristics, and correlations with optical properties.

Ferromagnetic FePt alloys with concentrations around the
stoichiometric composition are promising candidates for the magnetic
media in future high density magnetic data storage. We have prepared FePt nanoparticles with sizes in the range 3 nm ≤ dp ≤ 6 nm in the gas phase utilizing a DC sputtering process. Amorphous carbon films supported by copper grids are used as substrates. The particles are deposited either at a
position close to the sputtering gun or on a target prior to being deposited onto a target prior to being deposited. The sintering temperatures are in the range 200°C ≤ Ts < 600°C.

Morphology and structure of the particles are investigated by means of high resolution transmission electron microscopy (HRTEM).

Chemical information is obtained from electron energy loss spectroscopy (EELS) and energy dispersive X-ray analysis (EDX). As expected, the as-deposited FePt particles form large contiguous networks of individual particles already in the gas phase. On the other hand, particles which are sintered at Ts = 600°C are clearly separated from one another on the substrate. In addition, we observe a tendency of these sintered particles to form hexagonal superstructures on the amorphous carbon film via self-organization. Among them, as-deposited and sintered FePt nanoparticles we find nanohedral particles. Such multiply twinned particles (MTPs) are often observed in clusters or nanoparticles of FePt. However, there are only very few publications available, that report on the occurrence of multiply twinned alloyed particles. Particular attention is thus being paid to the question as to whether not the L10 order is favouring the formation of such FePt MTPs.

11:15 PM W5.8
C60 NANOCLUSTERS PRODUCED ON Au-Cu ALLOYS WITH AN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE
Stefan Maier, S. Dijkxhoorn, Patrick Schmidt, Department of Material Science, LJK, University of Erlangen-Nuremberg, Erlangen, Germany.

The electrochemical scanning tunneling microscope has been used to grow small C60 clusters on metallic substrates under electrochemical conditions. Clusters consist typically of 100-500 atoms and show an unexpected electrochemical stability to mild oxidation.

The C60 clusters in the gas phase are high enough to apply ex-situ methods like spectroscopic analysis. Therefore it is possible to generate small nanostructures under electrochemical conditions and investigate their functionality with, e.g., UV-techniques. As existing theory fails to explain this effect, our experimental efforts targeted the elucidation of various parameters influencing cluster stability. A key aspect was to create C60 clusters on binary alloy surfaces instead of pure metal surfaces. Using Au-Cu single-crystals of different composition and crystallographic orientation as substrates, we could modify the stability of the gas phase and the substrate interaction and other parameters in the system.

The experiments gave evidence that the stability of the metal clusters is not intrinsic (e.g., due to confinement effects), but more an effect of interfacial nano-alloying at the interface between cluster and substrate.

4:30 PM W5.9
HETEROGENEOUS NUCLEATION AND GROWTH ON NANOCHRISTALS--A SYNTHETIC APPROACH TO MONODISPERSE HOMO- AND HETEROATOMIC NANOPARTICLES
J.P. Wilcoxen, J.F. Martin and P.N. Provencio, Nanoparticles and Advanced Materials Chemistry Dept., Sandia National Labs, Albuquerque, NM

Using the inverse micelle method to grow monodisperse "seed" nanocrystals in a suitable reducing agent for the production of larger particles by slow deposition of atoms onto the surface of the seed crystals. The atom/ions to be deposited are slowly injected into the oil dispersion containing the seeds along with a suitable reducing agent. Important synthetic issues discussed are chemical purification and HPLC characterization of the monodisperse seeds which ensures a lack of alternative nucleation sites and the selection of the proper protecting agent which prevents cluster aggregation during growth but still allows access to the nanocrystal surface. The effect of injection rate is also discussed. We first demonstrate the shell-by-shell homonucleation of deposition of Au55 (d=1.5 nm) and Ag147 (d=2.0 nm) nanocrystals and then illustrate the versatility further production of polyhedral and spherical nanocrystals of various types. HPLC and TEM are used to analyze the size-distribution, optical, and chemical properties of the resulting particles. The presence of even a minority amount of one type of atom (e.g., Au) in the core of a predominantly Ag particle is shown to profoundly affect both the optical properties and chemical binding at the Ag surface compared to the homonucleated species of the same size. This work was supported by the Division of Materials Sciences, Office of Basic Energy Research, US Department of Energy under contract DE-AC04-94AL85000.

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

W5.10
NANOPARTICLES SYNTHESIS BY AHASSISTED ULTRASONIC SPRAY PYROLYSIS

Spray pyrolysis for synthesis of fine-grained powders has received considerable interest because it is a continuous process, chemically and physically operating at ambient pressure. However, the very broad size distribution and irregular shape of its production of particle size have often limited its use in advanced materials processing. This paper presents new findings on the effects of precursor drop sizes and size distributions generated by both the conventional ultrasonic atomization and a new spray technique, called air-assisted ultrasonic atomization or ultrasound-modulated two-fluid (UMTF) atomization. The UMTF atomization is capable of producing uniform precursor drops with a diameter determined by the third harmonic frequency of ultrasonic. Specifically, large precursor drops (peak diameter of 55 μm) generated by conventional ultrasonic atomization at 126kHz have yielded yttria stabilized zirconia (YSZ) particles with holes due to high solute evaporation rate in accordance with the conventional one particle per drop mechanism. In contrast, air-assisted ultrasonic or UMTF spray pyrolysis has yielded much smaller YSZ particles free from holes. In fact, despite the much larger drop sizes (peak diameter 30 μm) and broader size distribution (half width 40 μm), air-assisted ultrasonic (Umtf) spray pyrolysis at 126kHz and 2.3 W electrical drive power has yielded hole-free YSZ particles of which nearly half are <0.35 μm in diameter, while ultrasonic spray pyrolysis of 6.9 μm precursor drops (peak diameter 7 μm) has yielded YSZ particles with a mean diameter of 0.5 μm but only less than 10% are with a diameter >0.35 μm. Furthermore, the 6.9 μm precursor drops, generated using an ultrasonic nebulizer at 1.65 MHz and 33.5 W, under proper control of nebulizer rate and concentration, have yielded uniform spherical hole-free particles 150 nm in diameter via a vapor phase condensation mechanism. It may be concluded that through this new mechanism air-assisted ultrasonic (UMTF) spray pyrolysis can become a viable alternative to both these production of nanocrystals such as YSZ that are useful materials for application in thermal insulation and solid electrolyte fuel cells.


Support from the National Science Foundation, USA, the National Science Council and the Academia Sinica, Taiwan are acknowledged.
The luminescence intensity due to d-d transition of Mn$^{2+}$ for ZnS: Mn nanocrystals increases by ligand-exchange with polymerized acrylic acid (PAA). EPR measurements revealed two kinds of Mn$^{2+}$ sites, i.e., an isolated substitutional site corresponding to the signal I ($g=2.031; A=6.9$ mT) and a surface site corresponding to the signal II ($g=2.018, A=6.0$ mT). For a VIII element of X, the absolute value, [A], is linearly related with the conductivity of Mn-X bond. Therefore, the increase in [A] indicates the lower conductivity of Mn-X bonds for the signal II than that of signal I. According to inelastic transmission and X-ray absorption fine structure experiments, Mn$^{2+}$ in the Mn nanocrystals coated with PAA is oxidized by coordination of carboxyl group, and not simply by atmospheric oxygen. Consequently, the lower conductivity for signal II must be attributed to the existence of oxygen in the Mn nanocrystals. These results were discussed in terms of molecular orbital calculations by a DV-Xa method. The band gap of ZnS, Mn$^{2+}$ impurity level, the density of states, and the bond order were estimated by this method. From these results and calculations, we found that the exchange between Mn$^{2+}$ and its first neighbors is lowered when Mn$^{2+}$ is located in the vicinity of an oxygen atom. This reduction in the exchange between Mn$^{2+}$ and its first neighbors induces the change in the Mn$^{2+}$ impurity level. This could affect the enhanced photoluminescence due to the d-d transition of Mn$^{2+}$ for ZnS:Mn nanocrystals.

W6.5 GROUND AND EXCITED STATE ELECTRONIC STRUCTURE OF THE NANOCRYSTALLINE TITANIUM DIOXIDE SOLAR CELL SENSITIZER BIS[(4,4-DICARBOXY-2,2'-BIPYRIDINE)(ISOTHIOCYANATO)]RUTHENIUM(II).
Jeremy E. Monat, Jorge H. Rodriguez, James K. McOsker, Univ. of California at Berkeley, Dept. of Chemistry, Berkeley, CA.

The photosensitizer bis[(4,4-dicarboxy-2,2'-bipyridine)(isothiocyanato)]ruthenium(II) has been studied by density functional theory (DFT) to understand how the complex’s electronic structure relates to its effectiveness in nanocrystalline titanium dioxide-based photoelectrochemical cells. Time dependent density functional theory (TDDFT) calculations show that single and triplet excited states represent either metal to ligand charge transfers or nπ* (non-bonding to unoccupied) excitations. Comparisons between calculated and experimental electronic absorption spectra show good agreement, allowing us to provide spectral assignments. Notably, the first intense band is largely nπ* in character, while the second prominent band is dominated by metal to ligand charge transfer transitions. Implications for the rational selection of sensitizers for nanocrystalline titanium dioxide-based photoelectrochemical cells will be discussed.

W6.6 FABRICATION AND CHARACTERIZATION OF Si NANOCRYSTALS IN SiO$_2$ USING PULSED LASER DEPOSITION.
Ji Nian Zeng, Yee Yew What, Gong, Tong Wai, Chong Tow Chong, Department of Electrical and Computer Engineering, National University of Singapore, SINGAPORE.

Si nanocrystals embedded in SiO$_2$ have attracted extensive interest due to their potential application in Si-based optoelectronic devices. Silicon nanocrystal memory, silicon nanocrystal random access memory and silicon nanocrystal thin film transistors are all being considered for nonvolatile read write memories, as well as for use in electronic circuits. Nanocrystal memory devices are also of significance for compatibility with existing Si-based semiconductor manufacturing for ultrahigh scale integrated circuits. Besides wide application of Si nanocrystals, silicon nanocrystals also focused on quantum confinement of indirect bandgap semiconductors such as Si and Ge for enhancement of light emission efficiency, change of transition selection rule, as well as annealing and oxidation process of Si nanocrystals. We report that Si nanocrystals embedded in SiO$_2$ are fabricated using Pulsed Laser Deposition technique. A special deposition geometry is arranged to control size distribution of nanocrystals. Si nanocrystals generated by laser ablation are deposited on quartz or Si substrates simultaneously accompanied in ambient or using O$_2$ ion beam. The native oxides of Si are produced to isolate Si nanocrystals and form three dimensional confinement of nanocrystals. Parameters of laser ablation, ablation distance between target and substrate, deposition time on substrate (or intensity of ion beam) are optimized to control size and depth distribution of nanocrystals. Subsequent thermal annealing and laser annealing are utilized to improve quality of Si nanocrystals by recrystallization and oxidation process. Morphology of Si nanocrystals and size distribution are assessed by optical microscopy, AFM and TEM to provide evidence of Si nanocrystal formation and size distribution. Dimensions of visible microcrystals by optical microscopy are available in the range from 1nm to 300nm. Absorption/Transmission spectra from Si nanocrystal on quartz substrate show broad and blue-shifted absorption features spanning 800-3000nm due to quantum confinement, and quantum confinement of Si nanocrystals at st is expected to cause a broad redshift Raman peak with reduction of
particle size. Micro-Raman spectra are probed from various areas to make a comparison between Si nanocrystals with different sizes. The area with varying particle sizes present is dominant in the Si 520 cm^{-1} feature, while the areas with invisible particles give a broad peak at 467 cm^{-1} apart from the 520 cm^{-1} feature. The broad peak at 467 cm^{-1} is ascribed to Si nanocrystals of reduced size contribution. Quantum confinement size is considered to result in a weakening of the selection rule. Oxidation processes are also taken into account to affect the formation of Si nanocrystal and size distribution.

References

W6.7
Gd DOPED CdS NANOPOPARTICLES. Sheng-Ming Shih, Wei-Fang Su, Chi-Dong Chen, National Tsing Hua University, Institute of Materials Science and Engineering, Taipei, TAIWAN; National Taiwan University, Institute of Materials Science and Engineering, Taipei, TAIWAN; Academia Sinica, Institute of Physics, Taipei, TAIWAN.

Gd(III) (0.2-2 mol%) doped CdS nanoparticles were synthesized by reacting sodium sulfide with the mixture of cadmium acetate and gadolinium acetate. These nanoparticles were copped with p-hydroxythiophenol at the outer shell for stabilization. The diameters of these particles, ranging from 5 to 50 nm, were controlled by the molar ratio of p-hydroxythiophenol to CdS and organic molecules and a paramagnetic phase from CdGdS. Usually, the diamagnetic properties were disappeared when the extra magnetic field below 1000 gauss at 300 K. The paramagnetic property of nanoparticles was also observed by EPR (Electron Paramagnetic Resonance) experiments.

W6.8
SYNTHESIS AND CHARACTERIZATION OF BARIUM TITANATES WITH STRONG LUMINESCENCE. XIANG YAO, WANG JIAO, WU ZHAO, WANG XIANG, WANG CHEN, WANG XIN, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China.

Nano-sized barium titanate (BT) particles have been prepared at low temperature from various media, such as water, toluene and xylene. The particle size and morphology is significantly affected by the dielectric nature of solvents. Nucleation and growth during the early stage formation of BT particles has been studied and the dissolution precipitation mechanism is observed. The results from characterization and modification of BT nanoparticle surface will also be presented.

W6.9
THE CONSOLIDATION OF L12 PHASE Al2Zr3 and (Al12Zr12) powders with nanocrystalline structure has been studied to produce bulk intermetallic compounds which maintain metastable structures such as L12 and nanocrystalline structures. The powders were produced by 10 h mechanical alloying using planetary ball mill (PBM) grinding at 300 rpm. Full-density L12-Al (12.5 at% Zr) intermetallic was obtained by SPS at 600°C for 8 min. The specimens prepared with a longer holding time than 8 min at 600°C had a lightening size that was followed by the formation of micro-cracks. They had a lower relative density than the specimen at 600°C for 8 min. The smallest grain size was obtained in the specimen prepared at 600°C for 8 min, which was 200 nm as confirmed by TEM observation. This was the smallest grain size ever reported in the specimen prepared by other conventional methods of nanocrystalline powders. Accordingly, the highest micro-hardness, 985.6 H. V., was obtained in the specimen and this value was three times higher than those of the L12-Al (12.5 at% Zr) specimens with micro grain size. Full density Al2Zr3 intermetallics were prepared by SPS at 700°C for 8 min. However, the crystal structure was D12b and micro-hardness was 778.1 H. V. By using SPS, the sintering time can be reduced within 10 min, but the sintering temperature was not decreased. It was thought that the decrease in sintering temperature of 200-300°C of the PBF Al2Zr3 and (Al12Zr12) powders compared with the conventional sintering temperature was related to the refinement of microstructure to nanosize level. Keywords: Spark plasma sintering; Nanocrystalline material; Al2Zr3 intermetallics; Consolidation; Planetery ball milling.

W6.10
ALKYLATION AND COOH FUNCTIONALIZATION OF ULTRASMALE SILICON NAPROPARTICLES. Elena V. Rogozhina, Genevally A. Belomoin, Marnir H. Nayfeh, Paul V. Braun.

Coping of robust, electronically stable Si nanoparticles with functional organic molecules should result in material systems with enhanced properties and potential applications. Owing to interactions ranging from biological detection to inorganic/organic hybrid microelectronics. The functionalization of 1 nm, strongly luminescent H-terminated silicon nanocrystals with highly versatile organic molecules will be presented. The H-terminated nanocrystals were synthesized via a covalent etching of Si wafer as previously reported [1]. Treatment of the nanoparticles with chlorine gas, followed by reaction with alkyl amine resulted in alkyl functionalization of the silicon nanoparticles [2]. Alkylation of the nanoparticles was also accomplished through a thermally activated reaction between 1-alkene and the H-terminated silicon resulting in hydroxylation of the 1-alkenes terminal double bond. Thermal, and catalyzed room temperature hydroxylation of bi-functional compounds containing a terminal double bond and an ester group afforded ester functionalization of Si nanoparticles. The ester groups were then converted to COOH groups by hydration in basic or acidic media. The -COOH terminated nanoparticles obtained after functionalization and hydrolysis and the alkyalted nanoparticles retain their high luminescence. The maximum of the photoluminescence shifts from 400 nm to 445 nm when the nanoparticles are converted to the H-termination to the COOH-termination. Important for application, the functionalized particles are highly resistant to oxidation and aggregation.


W6.11
LARGE SCALE CONTINUOUS FLOW REACTOR FOR CdSe NANOCHYCLATES WITH STRONG LUMINESCENCE. S. S. Sain, T. Oshi, T. Kamiya, Mitsubishi Chemical Corporation MCC Group Science & Technology Research Center, JAPAN; K. Yoshih, MC Research & Innovation Center, CA.

Research on semiconductor nanoparticles is highly motivated by potential applications which include quantum dot lasers, high-speed nonlinear optical switches, or photovoltaic cells. Although the demand for production of high performance nanoparticles is increasing very rapidly, there has been very few report on industrial scale synthesis. Here, we report synthesis of CdSe nanoparticles in continuous flow aiming at large scale production, and discuss the size distribution and photoluminescence quantum yield. We designed a reactor to control the size distribution, which is capable of producing CdSe nanoparticles at a rate of up to 1 g/h at a production rate of 100 g/h. The reaction was carried out at 250 °C, and total feed rate of TOPO and the feed stock is between 5 and 20 ml/min as a result, we are able to produce 11 g/dy of CdSe whose mean size is controlled between 3nm and 6nm by adjusting the operating conditions. Size distribution was narrowed from 20% to 10% with the introduction of the static mixer. The photoluminescence quantum yield reached 10%, which is better than our typical batch synthesis products. Peng et al have suggested that impurities in TOPO play an important role on the formation of nanocrystals. In the present study, we attribute the high luminescence intensity of the CdSe particles to the impurities of low boiling point that remain in the reactor during the synthesis.


W6.12
FLAME SPRAY PYROLYTIC SYNTHESIS OF LOW-COST, DISPERSIBLE NANOPOWERS IN THE Al-20-5 mol% Y2O3 SYSTEM FOR USE IN PHOTONIC APPLICATIONS. Julian Machal, Tom Hindlin, Richard Lilie, University of Michigan, Dept. of MESE, Ann Arbor, MI.

Nanoized YAG and YAP powders can be produced by flame spray pyrolysis (FSP) by combustion of alcohol mixtures of very simple yttrium and aluminum precursors. These nanopowders can be doped with various rare earths [Nd, Yb, Er] in 0 to 11 mol% ratios. These powders provide the basis for forming fine grained YAG monoliths.
and novel photonic materials. This scalable synthesis route produces single crystal nanowires at > 100 g/h with surface areas of 5-80 m²/g depending on the precursor type, which strongly influences powder particle size and morphology. Typical powders consist of unaggregated partially amorphous particles with particle diameter ranging from 12 to 200 nm. The “in-situ” YAG powder composition is not crystallographically identical but converts to unaggregated YAG nanowires after annealing at 850°C. Green compacts sinter to essentially fully dense, crystalline YAG at 1400°C. Efforts to control the grain size and transparency of the resulting monoliths are described.


Lead(II) oxide exists in several structural polymorphs, with the phase being produced by previous synthetic techniques being dependent on experimental parameters such as temperature, pH, and concentration of the lead(II) starting solution. Additionally, microstructural phase changes—different from the two principal phases normally reported for the component compound as a result of the synthetic route used to prepare the material. The resulting phase is also partially dependent on contaminant species of various other elements present in the reaction solution in addition to the lead(II) ion itself. In the present work, nanoparticles of the red, tetragonal form of PbO, litharge, has been synthesized by an easy, quick, reaction sequence using water as the reaction medium by which, unlike previously reported syntheses, the litharge phase is reproducibly produced with no major side products or contaminating phases. The product was characterized by powder X-ray diffraction and compared to published data. Experimental parameters were discussed that lead to both other PbO forms being produced in wet syntheses and to microstructural alterations of litharge and other phases. This work was supported by the Center for Science and Engineering Education (CSEF) at Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098 for the U.S. Department of Energy.

W6.14 SYNTHESIS AND CHARACTERIZATION OF EUROPYIUM DOPED CADMUM Selenide Nanocrystals. Orlando E. Rojas, Geoffrey F. Streus, University of California Santa Barbara, Dept. of Chemistry and Biochemistry, Santa Barbara, CA.

Eu-doped cadmium selenide nanocrystals were prepared by a solvolithographic procedure using HDA as the coordinating solvent. The doped samples were characterized by IR, TEM, XRD, emission and absorption spectroscopy, solid state NMR and ICP-AES. The distribution of the dopant between the surface and the core was determined and a model for the interaction of the dopant with the nanocrystal is discussed.

W6.15 REACTIVE SUPERCRITICAL FLUID PROCESSING FOR THE PREPARATION OF METAL AND METAL-SULFIDE NANOPARTICLES. Harry W. Rollins, Chemistry Department, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

New methods are currently being developed for the size-controlled preparation of nanoscale metal and metal-sulfide particles due to their novel optical, electronic, and magnetic properties. Silver-containing nanoparticles have shown particular strong non-linear optical absorption properties. Silver and silver sulfide nanoparticles have been prepared by a new reactive supercritical fluid processing method and characterized using UV-Vis absorption spectroscopy, X-ray diffraction, and transmission electron microscopy. The effect of processing conditions on material properties will be presented.

W6.16 Abstract Withdrawn.

W6.17 Abstract Withdrawn.

W6.18 SYNTHESIS AND NOVEL PROPERTIES OF NANO-NaX ZEOLITIC MATERIALS. Bi-Zeng Zhou, Pasrion A Law, René Doucet and Mary Anne White, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, CANADA.

Framework zeolites are the most widely used catalysts in the petroleum industry. Synthesis of nanometerized faujasite-X and -Y zeolites has attracted much attention in the last decade. Until recently, nanometerized faujasite crystals could only be obtained in the presence of the organic template, tetramethoxysilane. We report here a novel and more efficient approach to synthesize faujasite NaX zeolite, free of organic additives. This method can tailor the size of NaX crystals from 20 nm to 1 µm by controlling the hydrothermal conditions and silicate sources. Powder X-ray diffraction, high-resolution SEM, FT-IR, N₂ adsorption, solid-state ²³Na NMR, and thermodynamic studies were employed to probe the novel properties of ultra-fine NaX (20-100 nm) and to compare them with the micrometerized NaX. Nanometerized NaX displays a very large external surface area and many interperticle voids, ranging from 20Å to 200Å. This micro- and mesoporous combination system could significantly improve the mass transport process, and therefore serve as a good support for various chemical processes such as catalysis and photochemical reactions. The incorporation of transition metals such as Ru and Co into nano-NaX (making nano-composites) is also discussed.

W6.19 SYNTHESIS OF SELECTIVE METAL-COMPLEXING NANOPARTICLES BY MICROEMULSION POLYMERIZATION. C. Lerpert, S. Amigoni-Gerber, University of Versailles St. Quentin, Versailles, FRANCE.

Ultrasound and monodispersed ligand-functionalized nanoparticles in the 12-18nm diameter range and containing high densities of tetraacyclohexyltrifluoride (cyclohexane) are readily prepared by a step microemulsion copolymerization procedure. The size and the amount of surface-end groups are controlled by the microemulsion composition and by the polymerization process. These nanoparticles exhibit high metalf-binding capacity and ligand accessibility as well as high selectivity for cupric ions.

W6.20 PRECIPITATION OF NANOSCALE ALUMINIUM TRIBROMIDE PARTICLES FROM SUPERSATURATED SODIUM ALUMINATE SOLUTIONS. Simon D.D. State University of New York College at Potsdam, Dept of Physics, Potsdam, NY; Don S. Ross and Emma P. Gagel, Clarkson University, Dept of Chemical Engineering, Potsdam, NY; Mass Grafe, Joel Rosenholm, Abo Akademi, Dept of Physical Chemistry, FINLAND; Albin Taccani, Dept of Chemical Engineering, Purdue University, IN.

Alumina particles used in industry must be manufactured in a cost-effective manner for a sufficient purity and have properties that are required by specific applications. The manufacturing processes should be highly reproducible and have proper size distribution with controlled surface properties. In this work, we have investigated the precipitation of nanoscale aluminium particles from sodium aluminate solutions by dilution and neutralization with water and oxalic acid in the presence of a polymer selected from sodium carboxymethylcellulose (NaCMC), polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA). This study is exploratory to the use of Bayer liquors as a source of nanoscale aluminium and provides some fundamental insights necessary for an understanding of the overall kinetics and mechanisms involved in the precipitation process. The polymers are surface active whereas the acid neutralization combines with hydrolysis to generate supersaturation of aluminum tribromide in a controlled fashion. We used scanning electron microscopy (SEM) to image the particles and to determine composition by energy dispersive analysis by X-rays (EDAX). We used transmission electron microscopy (TEM) to determine primary particle sizes. The results show that the aluminium particles precipitated in the presence of NaCMC had consistent diameters of 100 nm. The results from the EDAX studies do not correlate with increasing supersaturation. DLS of sols prepared using oxalic acid alone without polymer surfactant additive yielded particles average diameters of 175 nm, the TEM image of the sols trapped between microcellulose membranes shows the particles as nearly spherical and not pure aluminium tribromide as originally expected. These particles have a good structure and deform using stress. Oxalic acid aggregation of amorphous fibrous particles of aluminium tribromide contaminated with sodium. Continuing efforts focus on isolation of the primary precipitated and to achieve true nanoscale aluminium.

W6.21 Abstract Withdrawn.

W6.22 SYNTHESIS AND CHARACTERIZATION OF NOVEL Pd-Mn OXIDE. Heng Zhang, Jack Gromek, Mythe Augustine, G. Jananth Fernando, R. Samuel Boorse* and Harris L. Merdan*, Institute of Materials Science, University of Connecticut, Storrs, CT.

Novel Pd-Mn alloy and oxide have been synthesized using solgel and chemical processing. The composition, structure and surface features have been investigated using X-ray diffraction, SEM, EDS, TEM, AES
and XPS. The phase stability, thermal behavior and catalytic properties under methane atmosphere have been examined by using thermogravimetric analysis, differential scanning calorimetry, and $X$-ray diffraction $in$-$situ$ experiments and $X$-ray phase microspectroscopy. The study indicated that the $Pd-Mn$ alloy and oxide powders have nano-meter structure. The alloying of Mn improves the thermal stability and modifies the hysteresis characteristic of the phase transition between palladium and palladium oxides during the thermal cycle.

**W6.23**

**NUCLEATION AND GROWTH OF METAL OXIDE NANOPARTICLES FROM HOMOGENEOUS SOLUTION.**

Peter G. Scowen, Gerlof Oskam, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD.

Solution phase methods have become widely used for the synthesis of crystalline semiconductor nanoparticles. In most cases these techniques involve nucleation and growth from homogeneous solution. This approach has been used to synthesize nanoparticles of $III-VI$ compounds, $IV$ compounds, and a wide range of metal oxides. In order to tailor the optical, electrical, chemical, and magnetic properties of nanoparticles for specific applications, it is essential to develop a fundamental understanding of the nucleation and growth processes. In this paper we describe the growth kinetics of metal oxide nanoparticles and show that under a wide range of conditions growth is dominated by coarsening. In this case the growth kinetics follow the LS&W rate law where the cube of the particle radius is proportional to time. We also show where growth occurs by oriented attachment.

**W6.24**

Abstract Withdrawn.

**W6.25**

**FUNDA MENTAL STUDIES ON NANO CAPSULED PULMONARY DRUG DELIVERY SYSTEM.**


By encapsulating drug particles with a thin layer (nanometric dimensions) of biodegradable polymer, significant sustained release characteristics for pulmonary drug delivery system can be obtained. Earlier studies have shown that the release characteristics of inorganic drugs can be suitably modified by this method. The biodegradable coatings are formed by the pulsed laser ablation process. The coating composition, architecture and bonding of the nanocapsulated layer is quite important in controlling the drug delivery characteristics. This study will focus on various material characterization studies (XPS, FTIR, GPC, NMR) to study the composition and architecture of the coatings.

**W6.26**

**MICROSTRUCTURE OF CARBON ENCAPSULATED SUPERPARAMAGNETIC Co NANO PARTICLES.**

Xiang-Cheng Sun, Prog. Simulation Molecular, Instituto de Tecnologia del Petroleo (IMP), D.F., MEXICO; X.L. Dong, Shenyang Polytechnic University, Shenyang, P.R. CHINA; R. Reyes-Gaona, Instituto de Fisica, National University of Mexico, D.F., MEXICO; J.A. Toledo, Prog. Simulation Molecular, Instituto de Tecnologia del Petroleo (IMP), D.F., MEXICO.

Carbon encapsulated superparamagnetic Co nanoparticles had been synthesized by modified arc-discharge method. Both high resolution transmission electron microscopy (HR-TEM) and powder x-ray diffraction (XRD) profiles revealed the presence of 8-10nm diameter crystallites coated with 1-2nm graphite layers. Specially, HR-TEM images indicated that the interplane and contiguous carbon fringe around those Co nanoparticles was good evidence for complete encapsulation by carbon shell layers. The encapsulated nanoparticles were identified as hcp [(a)Co and fcc [(b)Co by electron nano-diffraction (ED) and energy dispersive x-ray analysis (EDX). No evidence was found by XRD for metastable cobalt carbide phases. However, some fcc [(b)Co particles with a significant fraction of stacking faults were observed by HR-TEM and confirmed using Fast Fourier transform (FFT) spectra of HR-TEM lattice images. All the simulated HRTEM images are found to match well with those two hcp and fcc phase HRTEM lattice images taken along different crystal axes.

It is expected that such carbon encapsulated nano-domain Co nanoparticles system offer us good candidate to study the superparamagnetic properties and the relation with their novel encapsulation structure.

**W6.27**

**TEMPLATED SYNTHESIS OF HOLLOW POLYMERIC NANOCAPSULES CONTAINING BETA CYCLODEXTRIN.**

Jason J. Hsu, Alex D.Q. Li, Washington State University, Dept. of Chemistry, Pullman, WA.

Submicron surfactant-dibenzyl siloxane colloids were used as templates around which beta-cyclodextrin was polymerized in a polyurethane matrix. Hollow capsules were harvested after etching out the silicic core with hydrofluoric acid. Permeability of the polymer shell to two model compounds, Rhodamine B and p-nitrophenol, was studied in aqueous solutions. Transmission Electron Microscopy showed that the two compounds did enter the hollow cavities by permeating the polymer shells, while UV-VIS spectroscopy yielded quantitative information about the nanocapsules absorption capacity in aqueous solutions of model compounds.

**W6.28**

**IN SITU GOLD COATING OF SUPERPARAMAGNETIC NANOPARTICLES BY MICROEMULSION METHOD.**

Do-Kyung Kim, Maria Mikhalkova, Muhammed S. Toprak, German Salazar-Ahumez, Mansour Muhammad, Materials Chemistry Division, Royal Institute of Technology, Stockholm, SWEDEN.

Colloidal processing of magnetic nanoparticles has been extensively studied, with emphasis on the characteristics of dispersion of superparamagnetic nanoparticles as ferrofluid. Suspensions of superparamagnetic nanoparticles have been developed as ferrofluids and magnetic dipole-dipole interaction generated from residual remanence magnetic force that tends to stick particles together. To stabilize the ferrofluid, the dispersion force due to thermal motion, repulsion, etc. in ferrofluid must be stronger than attraction force. To prevent agglomeration of superparamagnetic nanoparticles, a sequential microemulsion-based synthesis is introduced to fabricate nanoparticles with core-shell structure. The reverse micelle microemulsion is formed using CTAH, cetyl and varying the water to surfactant ratio (w). The superparamagnetic nanoparticles are formed inside the reverse micelle by alkanizing an aqueous iron source with NH$_4$OH. After alkanization, the micelle containing HAuCl$_4$ as surrounding solution is used to form a shell on nanoparticle core, by in situ reduction of HAuCl$_4$ with NaBH$_4$. The superparamagnetic nanoparticles are isolated by applying an external magnetic field, and the supernatant is removed by decantation and are dried under vacuum. Detailed characterization of core-shell structured nanoparticles is carried out using EDS attached to TEM. Optical, chemical and physical properties are also investigated.

**W6.29**

**ENCAPSULATION OF MAGNETIC PARTICLES IN METALLIC HOLLOW NANOSPHERES.**

Muhammed S. Toprak, German Salazar-Ahumez, Do-Kyung Kim, Maria Mikhalkova, Mansour Muhammad, Royal Institute of Technology, Dept. of Materials Science and Engineering, Materials Chemistry Division, Stockholm, SWEDEN.

The fabrication of micro- and nanosized capsules (or shells) which enable the encapsulation of various materials are of both scientific and technological interest. In recent years, the increased interest in fabrication of composite micro- and nanoscale capsules with shells of different chemical composition. Composite (or core-shell) particles, produced by controlled coating with inorganic or organic layers, are exploited in separation, catalysis, and electronic fields. The fabrication of hollow particles using the template-based approach offers a high degree of flexibility with regard to size of particles as well as composition of materials used. In this study, a novel type of metallic hollow particles with a fixed size in the sub-micron range containing magnetic material have been produced. These capsules are prepared in several steps by employing a solution chemistry approach. First, size-selected SiO$_2$ nanospheres were coated by electronless deposition with gold to form a porous layer of gold shell around silica and the core was then removed by chemical etching to obtain gold capsules. As the final step, the inclusion of nanoparticles inside these hollow capsules was carried out using a suitable chemical method. In this study we report on the filling of the gold hollow particles with magnetic materials (Fe$_3$O$_4$).

The composite particles are characterized by several techniques. Effect of the thickness of the metallic layer on the magnetic properties is reported. The characterization of prepared structures by SEM, TEM, EDS, and c-potential is presented.

**W6.30**

**SELF-ASSEMBLED ARRAYS FROM GOLD AND SULFUR CONTAINING FULLERENE NANOPARTICLES.**

Sheng-Ming Shih, Wei-Feng Su, Yuh-Jiun Lin, C.-S. Wu, Chi-Dong Chen, National...
Two-dimensional (2D) arrays of gold nanoparticles with sulfur containing fullerene nanoparticles were self-assembled through the formation of Au-S covalent bonds. Dithiol functional groups were introduced into C60 molecule by reacting propyl 2-aminoethyl dithiol with C60. The 2D arrays were formed at the interface of aqueous phase of gold particles and organic phase of fullerene particles as a blue transparent film. TEM images showed that the fullerene spacing between adjacent Au (~10 nm) particles was about 2.1 ± 0.4 nm which is consistent with the expected 2.1 nm estimated by molecular modeling calculations (MM). The UV-visible spectrum of this film showed a red shift and increased bandwidth due to the small spacing between gold nanoparticles. These arrays were deposited on the top of patterned silicon wafers to form 2D nanostructured electronic devices. The electrode pairs were made by electron beam lithography techniques, and the separation between tips of the two electrodes in a pair was about 50 nm. Transport measurements at low temperatures exhibited Coulomb blockade type current-voltage characteristics, the lower the temperature the pronounced the Coulomb gap. The assembled arrays have potential applications as nano-electronics due to the expected charge effects.

**W6.31**

ASSEMBLY OF QUANTUM DOTS WITH CONJUGATED MOLECULES. M. SCOUTELLES, Steven Xiao, Alireza Sajjadi, and Geoffrey F. Strouse, University of California, Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

Metallic and semi-conducting nanocrystals present a new venue of opportunities for the fields of electronics and sensing due to their intrinsic electrical and optical properties. The connectivity to and spatial arrangement of these materials are important if they are to be employed in the aforementioned scientific sectors. The employment of organic molecules to assembly nanomaterials into higher ordered three-dimensional constructs has been well examined. Another facet in the use of organic molecules with quantum dots is the blending of conjugated polymers with the nanomaterials to create photonics and optoelectronic devices. The combination of the two systems, an organic polymeric molecule possessing functionalities to bind to the surface of the quantum dots, would be advantageous in this field of research. In this presentation the assembly of IL61 quantum dots with poly-dipropoxyphenylene ethylene dibenzylidithials will be shown. The selected use of organic functionality allows not only for assembly of the nanomaterials but preservation of the photo-luminescence of the crystals and energy transfer from the organic polymer to the quantum dots.

**W6.32**

SELF-ASSEMBLY EFFECT OF Ni NANOPARTICLES GROWN ON SAPPHIRE AND Si/IN SUBSTRATES BY PULSE LASER DEPOSITION. Alexander Kvit, Honghui Zhou and Jagdish N. Narayan, NSF Center for Advanced Materials and Smart Structures, Department of Materials Science and Engineering, NC State, Raleigh, NC.

Pulse laser deposition is fast-developed technique for formation of semiconductor and metallic nanoparticles in various matrices. The size, shape, distribution and epitaxial relationship were determined by transmission electron microscopy (TEM) in lateral direction and by cross-sectional transmission electron microscopy (XTEM) in vertical direction. The Strasheim-Krasnov crystal growth mode leads to the self-assembly of small-scale islands driven by lattice mismatch between the nanoparticles and the underlying substrate. It was found that the nucleation process of Ni nanoparticles is determined by several epitaxial relationships between nanostructures and matrix, which disturb ordering. High-resolution Z-contrast (STEM) mode is used for investigation initial stages of nucleation process and type of chemical bonding between nanoparticles and substrate corresponding to the different epitaxial orientation. By varying growth parameters it is possible to control undesirable orientations of metallic islands.

**W6.33**

Abstract Withdrawn.

**W6.34**

NANOFIBER FORMATION BY ELECTRODEPOSITION IN MODIFIED NANOPOROUS POLYCRYSTALLINE ANODIC ALUMINA TEMPLATES. Marin Miklukov, Muhammet S. Tograk, German Salerno-Alvarez, De-Kying Kim, Memoun Mohamed, Mark Chemistry Dept., Royal Inst. of Tech., Stockholm, SWEDEN.

There are several approaches to prepare large arrays of nanostructures, for example, by lithographic technique such as electron beam lithography and ion beam lithography. Compared with these techniques, electrodeposition method is a very popular and cost-effective method to fabricate large array of nanostructures with a very large aspect ratio, which is not possible with standard lithographic techniques. The matrix can be easily formed by modifying oxalate in an acidic solution. The structural features of porous anodic alumina like thickness, pore surface concentration, pore base diameter and structural shape were significantly related with the preparation conditions. High purity alumina template was used and cleaned in HF/HNO3 mixture solution. Subsequently, the foil was annealed under nitrogen ambient at 510°C for 30 min, and electropolished to decrease the roughness of the surface.

Deposition consistent with sulfide electrolyte (H2SO4, H3PO4, oxalic acid) and its concentration on the pores formation were studied. One side of the porous anodic alumina template was coated with a gold layer for further electrodeposition process. Several different nanowires were grown by electrodeposition from sulfide electrolyte solutions. Detailed characterization of the structural arrangement of porous anodic alumina template and morphology of the nanowires were done with SEM, TEM and AFM.

**W6.35**

NANOSTRUCTURING OF MULTILAYERS BY A THERMALLY DRIVEN SELF-ASSEMBLY PROCESS. Carsten Hepp, P. Troche, S. Dreyer, C. Lang, H.C. Freyhardt, Institut für Materialphysik, Universität Göttingen, GERMANY; J. Hoffmann, Zentrum für Funktionswerkstoffe gGmbH Göttingen, GERMANY.

Multilayers consisting of two immiscible elements (e.g. a thin layer of a magnetic component like iron and a thicker layer of a noble metal like silver) are promising in view of a thermally induced nanomachining accompanied by a self assembling process. After deposition in UV an appropriate heat treatment causes a disintegration of the layered structure leading to isolated magnetic particles with a size of 53 nm in a surrounding noble metal matrix. The particles are mostly arranged along the triple points of the growth columns of the multilayered structure. Therefore, the disintegrated multilayer consists of spherical chains of particles perpendicular to the substrate, separated by a distance of the order of the growth column size. Previous investigations revealed that the interfacet stress, the different diffusion coefficients and the local curvature at the interface are relevant physical parameters determining the disintegration process, but the interpretation remains still somewhat controversial. Therefore, in addition to the microstructural characterization by x-ray diffraction and TEM, the disintegration was investigated in situ by measuring the resistance during film growth on during the following heat treatment, i.e. the following disintegration. At low temperatures detailed investigations of the GMR have been performed. Decreases in resistance of up to 6% at 4.2K have been obtained, although the noble metal layers separate the magnetic layers with 10 nm which is far beyond the regime of magnetic exchange coupling. The variation of this technology of the coercive field has been used to keep the film thin before the disintegration. First attempts have been undertaken to introduce the disintegration by prepatterned substrates, i.e. substrates with a well-defined wavy or terraced surface like vicinal cut crystals.

Proof of this work was supported by the German Research Society DFG, project No. FR 452/4-2.

**W6.36**

SELF-ASSEMBLING NANOPARTICLE AT THE AIR/WATER INTERFACE. Ivy Wang, K. Yoon, Y-S. Seo, V.A. Sushkov, J. Sokolov, M. Rafailovich, SUNY at Stony Brook, Department of Materials Science and Engineering, Stony Brook, NY; K.W. Shin, NCNR, NIST, A. Ulman, Polytechnic University, Dept. of Chemical Engineering Chemistry and Materials Science, NY.

We report on X-ray reflectivity and TEM studies of nanoparticle self-assembly at the air/water interface. Thin films of functionalized magnetic colloids (20 nm diameter) were formed by evaporation of the toluene. The phase diagram showed a large plateau region where the self-assembly is shown to occur. A nanochemocatalysis method was used for functionalization of the nanoparticles (WS2). The sonication procedure provides uniform tubular approximately 9 nm in diameter and 100 nm in length. The surface pressure-area diagram also shows a strong plateau which is interpreted as being due to self-assembly. The electric properties of these films were correlated to the structure of the films, to be discussed.

This work is supported by NSF-MSEC program.

**W6.37**

CHEMICAL NANOTECHNOLOGY. E.P. Smirnov, V.K. Gromov, The Kire Institute of Technology, St. Petersburg, RUSSIA.

A cross-discipline attack on the starting material aimed at object miniaturization is one of the modern determining traits of creating a
new technology. Chemical approaches are playing an increasingly larger role among these processes. Principles of precision synthesis, collectively termed "chemical assembly", allowing to form atomic and molecular scale structures, precisely both dimensionally and compositionally, on the surface of the solid phase substrate were theoretically formulated and experimentally conformed in the seventies in Saint Petersburg Technological Institute under the leadership of Academician Alexesovsky and his research specialist. It consists in the realization of the non-equilibrium conditions of chemical reactions on the surface of the solid between the external reagents and the surface functional groups. The fundamental elements of the method guarantee the strict reproducibility of the structure formation on the solid surface with a monolayer precision. Depending on the synthetic program, creation of the practically any surface atomic-molecular structures with the defined structure and composition, among them the artificial ones, not found in nature, is possible. The fundamental and the experimental results of obtaining "chemically assembled" solids with a modified surface will be presented in the report. These results are the elements of the chemical synthesis nanotechnology have been analyzed. Highly dispersed, porous, fibrous and flat substrates of varying chemical nature have been used as experimental substrates. Employing a variety of physical-chemical methodologies (electron X-ray spectroscopy, AFM, TEM, ellipsometry and others) it was determined that the thickness of the forming structures grows with the precision of 0.2-0.3 nm.

**W6.38**

**Transferred to W7.1**

SESSION W7: THIN-FILM-BASED NANOSTRUCTURES

**Chairs:** Horst Blum and Heinrich Hofmann

**Wednesday, Morning, November 28, 2001**

**Back Bay B (Sheraton)**

**8:45 AM W7.1**

**FABRICATION AND PROPERTIES OF SELF-ASSEMBLED NANOROD PARTICLES**


The preparation of nanoparticle arrays with defined periodic structures is a key point in nanotechnology due to their specific optical, chemical, and physical properties. Such substrates are under study to determine their use in novel applications, e.g., soft-lithography preparation technique, magnetic storage devices, etc. Property-tunable systems can be fabricated by controlling the hierarchical structure of assembled materials through self-organization. In this work, we report on the synthesis of nano-sized copper, nickel, and cobalt composite particles. The nanoparticles consist of a metal core covered by an oxide layer shell with varying thickness were prepared by reducing or oxidizing the metal ions in solution by using a seeded growth/seedless solution method in microemulsion systems as microreactors. The metallic nanocrystals were used as nucleation sites for the formation of the metal oxide coating. The self-assembly of prepared nanoparticles on flat substrates was achieved by functionalizing the substrate surface with polymeric ligands, resulting in the formation of a layer of nanoparticles that can be dispersed in a number of solvents. Examination of the dispersed and assembled particle systems by X-ray diffraction (XRD), infrared spectroscopy (FTIR), transmission electron microscopy (TEM), Auger spectroscopy (AES), and atomic force microscopy (AFM) will be reported.

**9:00 AM W7.2**

**NOVEL METHOD FOR SELECTIVE DEPOSITION OF METALLIC COATING SURFACES**


The ability to fabricate and position magnets on a nanometer scale offers unique scientific and technological opportunities in magnetic microtechnology. Increasing the storage capacity of magnetic media requires reducing the size of the magnetic elements. Combination of nanomagnets with present semiconductor technology may lead to a new class of magnetically active devices. In this paper, we investigate an unique method for selective deposition of metallic nanoparticles on silicon surface. This method is based on preferential nucleation of metallic clusters on silicon surface in presence of dilute HBF solution. Silicon wafer covered with a small array of dots is dipped in a solution containing the metallic ions. A 25 W Leiss incandescent lamp was used to illuminate the wafer in order to increase metal outgassing. Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Atomic Force Microscope (AFM) were used to characterize metal deposition on silicon surface. Superconducting quantum interference device (SQUID) magnetometers were used to characterize the magnetic properties of these particles. It was found that metallic particles preferentially deposited on structurally modified regions. Studies on the nucleation and deposition of these particles will be presented.

**9:15 AM W7.3**

**MULTIFUNCTIONALITY BY NANOCRYSTALLINE COMPOSITE COATINGS**

Elian Kraussmann, Gerhard Duhm, Eduard Arts, Max-Planck-Institute for Metals Research, Stuttgart, Germany; Veit Schier, Walter AG, Tübingen, Germany; Sascha Henke, Alexander Schütte, Thomas Beck, Robert Bosch GmbH, Stuttgart, Germany.

Coatings are a vital part of many components and tools. They fulfill various functions, mainly protection against wear, corrosion and friction. The development of new coating materials, with which different properties such as extreme high hardness, high-temperature stability, toughness and a low friction coefficient can be embodied, is a major task. The aim of the presented work is to develop a multilayer nanocrystalline titanium nitride particles in an amorphous silicon nitride matrix. The outstanding mechanical properties will be investigated by adjusting the microstructure of the layer system. The TiN and TiSiN coatings are grown at low temperatures by physical vapour deposition techniques which are applicable to industrial production equipment. The microstructure of the deposited coatings is visualized by means of focused ion beam and transmission electron microscopy. The mechanical properties are investigated by nanoindentation experiments. Our results indicate, that a columnar grain structure to spherical grains at about 4.5 GPa, which is almost twice the value of standard TiN coatings. High resolution TEM has been used to confirm a grain size of TiN below 10 nm in coating with a silicon content of about 10%.

This work is supported by the federal ministry of education and research (Bundesministerium für Bildung und Forschung) [contract number MSTech 6SN081]. The authors are responsible for the content of this publication.

**9:30 AM W7.4**

**PHOTOCATALYTIC DECOMPOSITION OF FATTY STAINS BY TiO2 THIN FILMS**


Anatase TiO2 nanoparticles have been prepared as aqueous colloidal solutions by a conventional sol-gel process. Thin films have been deposited onto glass substrates by dip-coating and eventually further crystallized by heat treatment up to 600°C. Such transparent coatings have been evaluated regarding their catalytic activity under UV exposure. The photocatalytic activity of the prepared anatase TiO2 thin films was determined by decomposition of artificial pollutants formed by fatty acids deposited onto the TiO2 layer (adipic or stearic acid). The kinetic of stain photodecomposition has been followed by in-situ infrared spectroscopy absorption studies. UV-visible absorption and electron microscopy were also used to study the change in the thickness and morphology. The effect of the TiO2 film thickness, porosity and particle size on the reaction kinetics have been studied as well as the staining thickness of the fatty acid layers. This allows to discuss the role of UV light absorption and the interdiffusion of radicals and oxygen. The mechanism for stain decomposition is shown to be associated to a shrinkage of the solid film at the surface of the porous oxide film after a diffusion of the excited radicals from the oxide. The TiO2 nanocrystals have been modified during synthesis of the nanoparticles by various doping cations deeply increasing the catalytic activity. These results on the decomposition of a wide variety of materials are compared with the photocatalytic properties of the same nanoparticles in solution and with the literature data.

**9:45 AM W7.5**

**SPONTANEOUS NANOPARTICLE FORMATION IN INSULATORS USING INTENSE ION IMPLANTATION**

K. Kihelmoto, Y. Takeda, Nanomaterials Laboratory, NIMS, Tsukuba, Ibaraki, Japan; N. Umeda, University of Tsukuba, Ibaraki, Japan.

Metal nanoparticles embedded in insulators are one of the candidates for photonic materials, since electrons in a metallic particle yield nonlinear and fast optical response with the surface phonon resonance. Employment of ion implantation provides merits to widen material selection for both metal and matrix species, since the non-equilibrium nature of ion implantation enables us to inject immiscible elements. In this paper, we discuss effects of ion annealing on metallic microparticle fabrication, particularly those embedded with ion fluxes. Negative Cu ions of 60 keV are implanted into amorphous (w)
SiO₂, MgO₃Al₂O₃ and LiNbO₃ at high doses. Kinetic behaviors of the in-beam precipitation are studied by changing the dose rate, up to 100 μA/cm², on a fixed total dose of 3 x 10¹⁵ ions/cm². Nanoparticle morphology is studied by cross-sectional TEM. Optical absorption is measured in a photon energy range from 0.5 to 6.5 eV, and nonlinear optical properties are evaluated around the photon energy of 2.2 eV. Metal precipitation behaviors strongly depend on the substrate species for a fixed implant of Cu, although spontaneous precipitation occurred more or less. For SiO₂, the particle size increased with increasing dose rate, up to 10 μA/cm². At high dose rates of 50 μA/cm², the SiO₂ nanocrystals were spontaneously formed and the size was suitable for nonlinear optical properties. Further increase in dose rate led to shrinkage of nanoparticle size, due to peculiar mass transport. The in-beam metallic substrates of SiO₂ showed pronounced precipitation. On the other hand, the Mg-Al spinel exhibited particle coarsening even at high dose rates up to 50 μA/cm², maintaining crystallinity of the lattice. The nanoparticles in the spinel remained less than 5 nm. The different material behaviors under intense ion implantation are unable to control nanoparticle structures and resultant optical properties.

10:30 AM W7.6
SHOCK-WAVE SYNTHESIS OF NANOPARTICLES DURING ION SPUTTERING. LE. Rehn, R.C. Birtcher, S.E. Denne, P.M. Baldos and L. Funk, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Previous studies have shown that the size distributions of smaller (n<40) where n is the number of atoms in a given cluster) nanoparticles generated by low-energy ion sputtering obey an inverse power-law, with an exponent varying between 2 and 4 depending upon the total sputtering yield. Such large sputtered clusters have not been explained by simple physical mechanisms. Here we report electron microscopy studies of the site-distributions of the larger nanoparticles (n>500) that are emitted from the surface by high-energy ion impacts. These nanoparticles also yield an inverse power-law, but with one exponent of -2, and one that is independent of total sputtering yield. This inverse-square dependence indicates that the clusters are produced when shock waves, generated by surface displacement cascades, impact and ablate the surface. Any smaller clusters can result from fragmentation of the larger clusters, which helps explain the large negative exponents that have been reported previously. An important corollary: on the smaller clusters, that synthesized nanoparticles have zero surface fraction of the original surface, that is, that have not undergone any large thermal excursions. Experiments are in progress to demonstrate that laser-implanted nanoparticles can be produced in this manner.

This work is supported by DOE-Office of Science under Contract W-31-109-Eng.38.

10:45 AM W7.7

We have used sequential ion implantation of Fe and Pt, followed by thermal annealing to form ferromagnetic Fe₃Pt nanoparticles with extremely high magnetic coercivity (greater than 2 Tesla) embedded in both crystalline Al₂O₃ and amorphous SiO₂ matrices. The Al₂O₃ matrix has been synthesized by optical, high temperature, and particle size varies from a few nm to ~100 nm depending on the implantation and annealing conditions. Nano-composites with both single and multiple orientations of nanoparticles have been produced. By changing the relative doses of Fe and Pt, we have varied the Pt atomic fraction [Pt/(Fe+Pt)] from 25% to 75%. In the Pt-atomic fraction range from 35% to 55%, x-ray diffraction measurements show that the chemically ordered Li₂ structure phase of Fe₃Pt is produced. These nanoparticles are ferromagnetic with a coercivity that maximizes at a Pt concentration of ~55%. In this case, the coercivity can exceed 2 Tesla (at 30 K). At lower (25%) and higher (75%) Pt concentrations, the x-ray diffraction results are close to those expected from the Li₂ structures of Fe₃Pt and Fe₃Pt₁₃, respectively. In SiO₂, the Fe₃Pt nanoparticles are randomly oriented, and the particle size varies from a few nm to ~70 nm depending on the implant and annealing conditions. For Fe₃Pt nanoparticles in SiO₂, the coercivity can exceed 2 Tesla (for a Pt atomic fraction of 45%). The application of these techniques to form Fe₃Pt nanoparticles in other matrices is under investigation.

Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

11:00 AM W7.8
MAGNETIC PROPERTIES AND INTERACTIONS OF CLUSTER-ASSEMBLED FILMS. Y. Qiang, Z.G. Sun and D.J. Sellmyer, Center for Materials Research and Analysis and Benthin Laboratory of Physics, University of Nebraska, Lincoln, NE.

We have developed a universal cluster deposition system, which combines a new kind of sputter-gas-aggregation cluster beam source, with two atom beams from magnetron sputtering. This system is used to deposit simultaneously or alternatively, very thin films or multilayers, and offers the possibility to control independently the incident cluster size and concentration, and thereby the interaction between clusters and cluster-matrix material which is of interest for fundamental research and industrial applications. The properties and interactions of Co cluster-assembled materials have been measured with a SQUID magnetometer. Co clusters are embedded in various matrices (Cu, Ag or SiO₂) in which the volumetric concentration of Co clusters can be varied from 5% to 95% and the cluster mean size from 200 to 10,000 atoms (2 to 9 nm) with the size distribution (delta d/lambda) of about 0.2. The magnetization (Ms) of the film is clustersize and concentration dependent, and always significantly less than that of bulk cobalt. For the bulk of clusters (9000 atoms), the Ms for the SiO₂ matrix is close to Co bulk value and much larger than those for the metal matrices. This could be expected if there are some alloying effects at the surfaces of clusters which reduce the magnetization. The peak temperature (Tπ), for which we have a maximum value of the magnetization in the zero-field-cooled curves, increases with the concentration and the cluster size, which indicates the intercluster interactions between clusters. Theoretical explanations will be discussed.

Research supported by NSF, DARPA through ARO, and CMRA.

11:15 AM W7.9

Deposition of clusters from the gas phase has been proposed as an interesting technique for the synthesis of nanoeolnterface materials. Among different experimental approaches, supersonic clusters beam deposition has been shown as a viable route for the production of films ranging from organized nanoislands to nanostructured thin films. From the point of view of practical applications, the development of high- intensity cluster source is a necessary requisite together with the capability of size selecting the aggregates prior to deposition, while maintaining high particle fluxes. By using a pulsed microplasma cluster source (PMCS) and by exploiting nanodisruptive effects of supersonic beams it is possible to obtain very high deposition rates with a control on neutral cluster mass distribution, allowing the deposition of films with controlled nanostructure over large area. Due to high deposition rates, high lateral resolution, low temperature processing, supersonic cluster beams can be used in conjunction with other film deposition techniques for the efficient production of nanocomposite materials. As an example we will discuss the case of carbon cluster assembling. The nano and mesostructure of films obtained by carbon cluster assembling can be controlled by selecting in the beam the elemental building blocks, moreover functional and structural properties can be controlled and tailored. The use of PMCS allows also the production of nanostructured films with useful physico-chemical and topographical properties such as mesocavous carbon foams and nanostructured carbon materials containing carbide and/or transition metal particles. [1] P. Mibani, S. Innoccu, Cluster Beam Synthesis of Nanostructured Materials, Springer-Verlag, Berlin (1999).

11:30 AM W7.10
CONTROLLED AND SELECTIVE AGGREGATION OF SUBMICROMETER Cu-CRYSTALITES ON FIB SENSTITIZED p-Si. Adrian Spiegel, Swiss Federal Institute of Technology, Lausanne (EPFL), Dept. of Materials Science, LTP, Lausanne, SWITZERLAND, Patrick Leben, University of Erlangen-Nuremberg, Dept. of Material Science, LKO, Erlangen, GERMANY.

Electrochemical deposition of metals and alloys onto metallic substrates plays an important role in many modern technologies. In the electronics industry, electrochemical and electodesposition are widely used for applications, such as copper printed circuit boards, through-hole plating, multilayer read/write heads, and thin film magnetic recording media. Usually, a photolithographic patterning process is used to produce the desired feature on the surface of the substrate. An alternative method to patterned metal deposition on semiconductors is based on changing the electrochemical properties of the semiconductor surface by a chemical modification. Using focused ion beam (FIB) implantation to introduce defects into a p-Si followed by a selective metal deposition is a very promising method to produce structures in the submicrometer range in this work, we study the selective deposition behavior of different metals (Cu, Au, Pt) on FIB sensitized surface locations and show that
crystallite growth follows a three dimensional growth law. Crystals grow very rapidly in a first phase and reach a size of roughly 200nm after 0.6s. Usually we investigate in-situ factors such as FIB dose and electrochemical parameters that determine nucleation, growth, and coalescence of metal clusters as well as limiting factors of the FIB sensitization process.

SESSION W8: NOVEL APPLICATIONS
Chaitu K. Sharma and Rajiv R. Singh
Wednesday Afternoon, November 28, 2001
Back Bay B (Sheraton)

1:30 P.M. W8.1
PROCESSING COMPLEX & UNIFORM NANOPARTICLES FOR MICROELECTRONIC & PHOTONIC APPLICATIONS
Nobuyuki Kusumi, NanoGram Corporation, Fremont, CA.

Nanoparticles are a new class of material building blocks for microelectronic and photonic applications because of their size and unique physical properties. However, two major challenges must be overcome for such industrial applications. The first challenge is how to make uniform nanoparticles in industrial-scale, as multi-component materials must be synthesized to meet very diversified device performance goals. The second challenge is how to convert these nano-building blocks to application forms such as device structures or coatings. NanoGram has developed a novel chemical reaction process to generate an entirely new class of nanomaterials having extremely narrow size distributions. In this paper, NanoGram's production process and examples of complex multi-component materials are outlined as well as scalability issues. In addition, high levels of dispersion can be achieved for many of these nanomaterials, especially in organic solvents. Chemical bonding of metal oxide nanoparticles to organic materials has been found to enable control of the refractive index in nanocomposites through a broad range, over 50%. Industrial applications are discussed based on these observations, with emphasis on phosphor lightwave devices, photonic nanocomposites for index engineering, and plasma etching processes for electronic chips.

2:00 P.M. W8.2
HYDROGEL-MEDIATED SYNTHESIS OF NANOPARTICULATE METAL CHALCOGENIDES
Paul J. Nguyen and Ronald A. Guidotti, Sandia National Laboratories, Power Sources Engineering and Development Department, Albuquerque, NM.

We present results for the synthesis and characterization of novel iron, cobalt, nickel, and manganese-containing dilsulfides using hydrothermal conditions [up to 250°C and up to 3.6 MPa (525 psi)]. The discussion emphasizes the preparation of metal chalcoengides that represent potential candidates as alternative battery-active materials for use in lithium thermal batteries as well as lithium-ambient-temperature batteries. The metal dilsulfides were prepared by the reaction of metal sulfides with sodium tetrasulfide in aqueous media. The reactions occur at temperatures of 140°C and 345 kPa (50 psi) over 24 hours. The reactivity of the reaction mixture, metal monosulfides or metal dilsulfides can be obtained. Subsequent work has shown that pressure as low as 48 kPa (7 psi) also yield nanoparticulate samples. Scanning electron microscopy and X-ray powder diffraction examinations have confirmed that 1:3:1 iron, cobalt, and nickel dilsulfide having a pyrite structure is produced. Solid solutions of iron, cobalt, and nickel dilsulfide were easily obtained using mixed metal sulfides in the reaction. Materials such as Fe₉₋ₓCoₓS₂, CoₓNiₓS₂, and Fe₉₋ₓNiₓS₂ exhibit similar size and structural properties as the previously described parent metal dilsulfides. When prepared as previously described, single-phase materials were always obtained.

Electrochemical characterization tests in high-temperature thermal cells are currently in progress. The initial results are very promising.

SNI is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States DOE under contract DE-AC-94-AL85000. This work was supported in part by CRADA SC001549 with Engle-Picher Technologies, LLC, Joplin, MO.

2:15 P.M. W8.3
COLLOIDAL COATING OF OXIDE NANOPARTICLES FOR ANTIDEGRADATION OF ZnS-BASED PHOSPHORS
Takahiro Inagaki, Tetsuo Kato, and Kazutoshi Ohno, Sony Corporation, Home Network Company, Atsugi, JAPAN; Tetsuhiho Ito, Masatosu Sato, Keio University, Faculty of Science and Technology, Yokohama, JAPAN.

ZnS-based phosphor particles, notably ZnS:Ag:C1 with their average particle size 4.2 μm, were coated with a variety of nano-particles via a colloidal chemical route. Degradation of their cathode luminescence (CL) intensity after electron beam (EB) irradiation at 7kV for several hours was monitored and the effects of coating for anti-degradation properties were evaluated. The degradation of ZnS:Ag:C1 modified with ZnO nanocrystalline particles was reduced by 40% after 9h exposure to EB. Comparison with similar coating by Y₂O₃ revealed that the electrical conduction of the coating particles play a significant role for degradation prevention, particularly the prevention of local oxidation of ZnS. Detailed evaluation of coating was further made by using thermal glow or thermo luminescence (TL) properties under programmed heating. After EB irradiation, TL intensity decreased and the TL peak shifted to the lower temperature side. By comparing TL thermograms of mechanically damaged ZnS:Ag:C1 ZnS:C1 with varying C1 concentration as well as ZnS:Ag:Al after EB irradiation, it was concluded that decrease in the effective concentration of C1 serving as an excitonic luminescence center, is also responsible for the CL degradation of ZnS:Ag:C1 by EB irradiation.

2:30 P.M. W8.4
NANO-ENCAPSULATED ZnS:Ag PHOSPHORS FOR FIELD EMISION FLAT PANEL DISPLAY APPLICATIONS

For more than 30 years, the display industry has attempted to create a thin flat low power version of the highly successful cathode ray tube (CRT). The present market leader in flat panel displays (FPDs) is the active matrix liquid crystal display (AMLCD), which has made a significant improvement in the last decade, but still meet all the needs for reduced power consumption, brightness, efficiency, video response, viewing angle, operating temperature, full color gamut and scalability. In contrast, field emission displays (FEDs) which are based on field emission, as in CRTs, can meet all these requirements, but they have been plagued by some technological challenges. One of the challenges is the loss of brightness of the surface-bonded phosphors (ZnS:Ag) upon continuous irradiation with the e-beam. Additionally, the sulfide ions, which out-gas from the phosphor during degradation, poison the cathode emitter tips and thus significantly reduce their lifetime. To overcome these challenges, the ZnS:Ag phosphor particles were encapsulated with nanometer thick films of indium tin oxide (ITO) in order to slow the degradation process of the phosphor as well as to reduce the amount of sulfur species out-gassing from the phosphor. By conformally depositing the deposition conditions using a modified pulsed laser deposition system, the optical transmission properties, electrical conductivity, and thickness of the coatings were optimized to provide the best combination of reduced degradation while maintaining the maximum brightness. Optical properties, electrical properties, and thickness measurements of the ITO are shown for the different thicknesses as well as the corresponding degradation curves. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical changes on the coated and uncoated particle surface. Scanning Electron Microscopy (SEM) was used to show the changes of the surface morphology due to the cathodoluminescent degradation.

2:45 P.M. W8.5
HYDROGEN STORAGE CAPACITY IMPROVEMENT OF NANOSTRUCTURED MATERIALS
Jeremy Lawrence, Liang Zhang, Gu Xu, McMaster University, Hamilton, Ontario, CANADA.

Safe, lightweight, and cost-effective materials are required to practically store hydrogen for use in portable fuel cell applications. Compressed hydrogen and on-board hydrocarbon reforming present certain advantages, but their limitations must ultimately render them insufficient. Storage in hydrides and adsorption systems show promise in models and experimentation, but a practical medium remains unavailable. To study hydrogen storage properties a new volumetric temperaturat apparatus was designed. Nanomaterial properties as the previously described were evaluated over a range of pressure from 0 to 4000 psi and range of temperature from 0 to 100°C. A new approach to the preparation of nanostructures aimed at improving interaction with hydrogen has been developed. These new materials show promising results that may be due to their special surface and interface properties.

3:30 P.M. W8.6
TAILOR NANO-MATERIALS FOR STRUCTURAL AND FUNCTIONAL APPLICATIONS

Nano powders and nano-powder-derived products are being actively pursued for use in a wide range of applications, including electrochemical energy storage and generation, chemical sensors, optoelectronics, semiconductors, wear and scratch resistant coatings, and heat transfer. The interest stems from the fact that researchers...
see immense potential for improving functional properties of components and devices by nanostructuring. In some cases, the use of nanoparticles as the reactive material can lead to benefits in a number of applications, it is crucial to tailor the structure and composition of the starting powder in order to maximize the property enhancements and performance, thereby realizing the true potential of nanomaterials. We are developing an array of vapor phase and solution synthesis methods for the production of nanomaterials. Progress has been made in developing (i) kinetically stabilized nanoparticles of vanadium oxide for use in rechargeable Li-ion batteries, (ii) alumina powders for use as second phase in heat transfer fluids and transparent parent ceramics on polymer substrates, (iii) metallic tungsten-carbide powders for thermal sprayed coatings, and (iv) oxide lithium titanate for next generation rechargeable energy storage hybrid devices. Specific synthesis approaches for each of these materials will be outlined. The physical characteristics of the nanoparticles, and the corresponding functional or structural properties in each of these applications will be described.

4:00 PM WE.7
FePt NANOPARTICLES WITH HIGH COERCIVITY, Yunhe Huang, H. Okumura, G.C. Huijpenwyn, Department of Physics and Astronomy, University of Delaware, Newark, DE; Dieter Weller, Seagate Technology, Pittsburgh, PA.

In this study, we have fabricated high coercivity FePt nanoparticles embedded in a C matrix by depositing the films onto heated substrates. The FePt/C films were prepared by sputtering from solid FePt and C targets onto Si [111] substrates using the tandem mode. At ambient substrate temperature, FePt and C form a multilayered structure with the desired ferrostructure which is magnetically soft. Post annealing at temperature in the range of 500 to 850°C is required to form the ordered FePt particles. As the substrate temperature increases, the microstructure of FePt films changes to a mixture of, at least, the ordered [001] and disordered [100] nanoparticles. When the substrate temperature increases to higher than 500°C, the FePt particles become elongated and start orienting in a direction perpendicular to the film. By varying the temperature of the substrates, the different degrees of [001] texture were obtained. TEM study showed well-separated FePt particles with uniform size distribution. Prolonged annealing at 850°C leads to spherical particles with particle size in the range from 5 to 15 nm and a coercivity as high as 34 kOe at room temperature when measured in the perpendicular direction and 31 kOe parallel to the field. A magnetic field perpendicular to film plane during sputtering is designed in order to enhance the perpendicular coercivity at lower temperatures.

Work supported by NSF-DMR 0972235 and Seagate Technology.

4:15 PM WE.8
CONTROLLING PERCOLATION IN FIELD-STRUCTURED PARTICLE COMPOSITES: OBSERVATIONS OF GIANT THERMOELECTRICITY, AND CHEMORESISTANCE, James E. Martin, Robert A. Anderson, Judy Odinke, Douglas Addle, Sandia National Laboratories, Albuquerque, NM.

When conducting-particle composites are prepared very near the percolation threshold, their resistivity is highly sensitive to small fluctuations in volume changes. Such nanocomposite materials have potential as simple temperature, pressure, or chemical sensors, but in practice it is difficult to prepare compositions close to the percolation threshold. We have shown that conducting field-structured composites, consisting of gold-coated magnetic particle chains in a polymeric resin, can reproducibly be brought to the percolation threshold, regardless of particle concentration. The low dimensionality conducting chains form a dense population of critical current paths with extreme sensitivity to specific volatile components of the resin. These compositions exhibit giant thermoelectric power factors, high temperature coefficient of resistivity, and high TCE and thus appear to have great potential for sensor applications.

4:30 PM WE.9
FIRST-PRINCIPLES SIMULATIONS OF ATOMIC STRUCTURE AND MAGNETISM IN Fe NANOPARTICLES, A.Y. Postnikov and P. Enzel, Theoretical Low Temperature Physics, Gerhard Mercator University Duisburg-Germany, Pablo Ordejon, Instituto de Ciencia de Materiales de Barcelona (CSIC), Bellaterra, SPAIN.

The properties of small Fe nanoparticles, consisting of 62 atoms on the largest, are studied from first principles making use of density functional theory, norm-conserving pseudopotential and numerical local orbitals method, implemented in the SIESTA code. 1 In the development of previous simulation of Fe-related nanosystems done earlier with the GEA theory, 2 we concentrated now on the interplay of lattice relaxation, this is the most pronounced near the surface of particles, and the magnetic characteristics of the latter. We confirm the previously obtained theoretical findings (see, e.g., Ref [3]) of enhanced magnetic moments in the outer shells of nanoparticles. These results are refined by taking structure relaxation into account and by considering more representative bead- and force-related calculations. Moreover, we allowed antiferromagnetic ordering along with ferromagnetic interactions and discuss interplay of magnetic ordering and structure relaxation. The comparison with all-electron calculation results is done for some crucial cases.


4:45 PM WE.10
Gd AND Tb NANOPARTICLES OBTAINED BY "THE PARTICLE-GUN" TECHNIQUE. V. Skumryev, S. Stepansky, Y. Huang, Y. Zhang, Z. Yan, and G.C. Huijpenwyn, Univ. of Delaware, Dept. Physics, Newark, DE.

Gd and Tb nanoparticles have been obtained by "gas-condensation" using the particle gun technique and embedded in non-magnetic matrix (BN) produced by conventional sputtering. The role of particle-gun parameters including the sputtering power and pressure, temperature of the gun, and the target-to-substrate distance, on the particle growth is discussed. Depending on the particles size, different magnetic behavior were observed. Particles with a size below 5 nm are paramagnetic while the larger particles are ferromagnetic. This unexpected behavior is presently being examined and the results will be reported along with the structural and microstructural data. Work supported by NSF under NSF-DMR 9972925.

SESSION WE.9: POSTER SESSION NANOPARTICULATE MATERIALS CHARACTERIZATION AND NOVEL APPLICATIONS

Chair: Heinrich Hofmann, Mamoun Mohammed and Shanmugum Kumar
Wednesday, November 29, 2001
8:00 PM
Exhibition Hall D (Hynes)

WE.9 HIGHLY ENHANCED ELECTRICAL AND MECHANICAL PROPERTIES OF THE MULTILAYER PIEZOELECTRIC TRANSFORMER BY FABRICATING THE RAW MATERIAL OF PZT USING SCALED POWDER WITH A BALL SIZE OF 300 µm. Haiqiong L. Chen Material Research Center, Applied Physics Department, Hong Kong Polytechnic University, Kowloon, Hong Kong, CHINA.

High-energy wet millng technique was successfully applied to a commercial lead zirconate titanate (PZT) powder to fabricate the fine nano-scaled powder, and the surface treatment technique by introducing the PVA gel covering on the surface of each PZT particle and then dry the powder and ball milling again for another 6 hours. Through this process, a fine and uniform nano-scaled PZT powder with a ball size of about 300 µm in size can be obtained and due to the surface treatment, the aggregate effect of the nano-scaled powder will be prevented. This fine PZT nano-scaled powder was then used to fabricate the PZT ceramic thick green sheet, and finally for producing the multilayer piezoelectric transformer. Compared with the multilayer piezoelectric transformer fabricated by non-treated PZT powder, several advantages can be easily seen. First, smaller amount of organic contents used as plastic in the PZT ceramic green sheet can be expected, which means a higher density of the PZT ceramic can be gain after sintered. Second, more uniform PZT ceramic can be expected, which will highly increase the mechanical and electrical properties of the final piezoelectric device. For example: the mechanical quality factor Qm can increase for about 300 and reach to 1300 by using the same hard doped raw PZT powder, piezoelectric charge constant d33 can increase for about 70 and reach to 320, the ceramic density can increase about 10% and from the SEM photograph we can see, a more uniform PZT ceramic grain structure has been obtained. Third, due to the nano-effect, the PZT ceramic device's sintering temperature can reduce from 1280 Celsius degree to 1200 Celsius degree, so that low temperature sintering process can be expected. Besides that, due to the nano-effect, the PZT ceramic device's sintering temperature can reduce from 1280 Celsius degree to 1200 Celsius degree, so that low temperature sintering process can be expected. Besides that, due to the nano-effect, the PZT ceramic device's sintering temperature can reduce from 1280 Celsius degree to 1200 Celsius degree, so that low temperature sintering process can be expected.
be clearly reduced; secondly, the output power of the multilayer transformer can be easily increased due to the reason of higher power density. To transmit power through the device, thirdly, the final power transmission efficiency can also increase and maintaining at a high value at a much wider range of working frequency. From all the above reasons it can be concluded that the fabrication of the PZT nanoscaled powders and its surface treatments is a very effective way for improving the PZT ceramic's physical property. Further more it can also serves as a very important step in the whole fabrication process of the multilayer piezoelectric transformers to increase its electrical and mechanical quality.

W9.2 EFFECT OF PARTICLE SIZE ON CHEMICAL MECHANICAL POLISHING OF METALS AND DIELECTRICS. Kyoko Sato, Seung-Min Lee, Jiyoung Park and Rajiv K. Singh, Department of Materials Science and Engineering and R&D Center for Particle Science and Technology, University of Florida, Gainesville, FL.

Particle size plays a critical role in controlling the performance of chemical mechanical polishing (CMP) slurries. The surface finish as well as the deflection of the surface depends on the size of the particles used for CMP. It is assumed that the higher the surface to volume ratio of the nanoparticles, the higher the material removal rate of CMP. Also the small size of the particles is expected to lead to a low density of surface defects. We have conducted extensive studies on the effect of the primary particle size (30-150 nm) of silicon and alumina on the polishing characteristics of silicon, copper and tantalum blanket films. The primary as well as the secondary particle size was measured using standard particle instrumentation techniques. SEM and X-ray analysis were done to evaluate the effects of the polishing rates as well as the surface finish of the wafers were determined and correlated with processing parameters. Based on these measurements, a preliminary model to understand the particle size effects on the polishing characteristics has been developed and will be discussed in detail.

W9.3 GROWTH AND CHARACTERIZATION OF SILVER NANO-PARTICLES. C. Baker, S. Ismat Shah, Univ. of Delaware, DE; J. Atkins, Pramanik Dr., DE.

An inert gas condensation (IGC) technique has been used to obtain nanometer size silver particles. The technique is based on evaporation under a high partial pressure of an inert gas. The particle size was varied from 25 to 100 nm by changing process conditions such as inert gas pressure, flow rate, and evaporation boat temperature. Particles were characterized by X-ray diffraction (XRD). Particle size was calculated by Scherrer's formula for peak broadening. Other complimentary techniques used for particle size distribution included transmission electron microscopy (TEM) and dynamic light scattering (DLS). The morphology of the particles was studied using atomic force microscopy (AFM). The dispersibility of silver nanoparticles is problematic, thus inhibiting their use in solid and liquid media. We will present results of the use of silver nanoparticles in nanofluids for thermal conductivity enhancement. Another important application of these particles is as antibacterial agents. Results on antibacterial properties of Ag nanoparticles dispersed in polymeric fibers will also be presented.

W9.4 SYNTHESIS, CHARACTERIZATION OF InS$_2$ NANO-COLLOIDS AND THEIR SURFACE MODIFICATION BY RuBipy$_2$N$_2$. Davendar K. Negah, Xiorong Liang, Arif Anamedou, Margaret A. Frommert, Tong Ni, Nicholas A. Kotev, Oklahoma State University, Dept of Chemistry, Stillwater, OK; Gordon Gainer, Jin-Joo Song, Oklahoma State University, Center for Laser and Photonics Research, Stillwater, OK; Michael G. Hahm, Hein-Meier-Institut, Abt. Physikalische Chemie, Berlin, GERMANY.

Stable aqueous colloids of 2.8 nm InS$_2$ nanocrystals have been prepared by using the classical method of nanoparticle stabilization by low molecular weight thiols. The analysis of the nanoparticles, Surface Enhanced Raman Scattering (SERS), X-ray diffraction, EDAX data, and electron diffraction indicate that the nanocrystals are predominantly In$_x$S$_y$$_2$. They exhibit relatively strong excitonic emission at 363±150 nm with a quantum yield of 1.2%. The calculated radiative lifetime of the excitonic emission is 350 ns and indicates that a direct allowed electronic transition is responsible for this emission. The NMR lines of the stabilizer are strongly broadened and shifted as a result of deshielding induced by positively charged metal ions. This effect quickly wears off as the carbon chain becomes longer and the separation between the hydrogen atoms of the stabilizer and the semiconductor surface increases. Broadening is attributed to the reduced mobility of the stabilizer in the nanoparticle shell. It is demonstrated that for InS$_2$ nanocrystals of the same size this effect is substantially stronger than for InS$_3$. Lower density of metal centers in InS$_3$ than in InS$_2$, which serves as anchor points for the stabilizer, promotes greater mobility of the stabilizer molecules. Surface modification of these nanoparticles can be achieved by utilizing the chalcogen atoms to bind the modifier. This is significantly different since the chalcogen atoms are electronically conjugated to the ground state of the nanoparticles. Surface modification was achieved by utilizing a mixed metal complex of Ru with hydridine moieties. The UV-Vis absorption, emission and excitation spectra suggest the relaxation of the electron confinement and partial mixing of semiconductor nanoparticle and the Ru systems of the aromatic ligands. This type of surface modification via Saites tends to new routes to building nanoparticle supramolecules.

W9.5 MICROSTRUCTURE AND MAGNETIC PROPERTIES OF Fe(C) AND Fe(O) NANO PARTICLES. Xian-Cheng Sun, N. Nawa, V.G. Fehlau, Prog. Molecular Simulation, Instituto Mexico del Petroleo, D.F., Mexico, GIMEX, Instituto de Fisica, National University of Mexico (UNAM), D.F., Mexico; X.L. Dong, Shanghai Tech University, Shanghai, P.R. CHINA.

Two types of iron (Fe) nanoparticles—carbon-coated Fe nanoparticles (FeC) and pure α-Fe nanoparticles that coated with oxide layers (FeO)—were successfully synthesized using modified graphite arc-discharge method. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), nanowire-x-ray energy dispersive spectroscopy (XEDS) and selected area electron diffraction (SAED) analysis had been used to characterize these distinct structural morphologies of this two kinds of Fe nanoparticles (FeC and FeO). It was indicated that those two Fe nanoparticles have an average grain size of 15±3 nm. The presence of carbon encapsulated α-Fe, γ-Fe and FeC phases were clearly identified by X-ray diffraction in those FeC particles, and further confirmed by Fast Fourier Transform (FFT). The evidence for good α-Fe nanocrystal coated with oxide layer was also revealed by using HRTEM images and SAED patterns in those Fe(O) particles. Mössbauer spectra at room temperature for the as-prepared FeC and FeO nanoparticles confirmed their distinct nanostructures, which examined by XRD analysis and HRTEM observation. On the other hand, FeC nanoparticles exhibited ferromagnetic properties at room temperature due to the interaction between ferromagnetic α-Fe core and antiferromagnetic oxide (α-Fe)$_2$O$_3$ shell. However, superparamagnetic relaxation was observed in the assembly of FeC nanoparticles, which was attributed to the nanocrystalline nature of the carbon-coated nanoparticles.


Composite metal powders for use as negative electrode materials in lithium ion batteries have been prepared by electroless plating methods. Electroless plating allows a conducting or non-conducting substrate to be coated with a metallic film whose thickness is dependent only on conditions used during the plating process. Iron, nickel and copper non-alloying powder substrates were coated with metallic tin. Results of coin cell tests have been evaluated.

W9.7 PREPARATION AND CHARACTERIZATION OF NANO-STRUCTURED PARTICULATE CATALYTIC MATERIALS. Baiyun Tong$^{1,2}$, Yue Gu$^{3}$, Yuji Sato$^{1}$, Seohun Y. Naido$^{2}$, Akumi N. Moriy$^{2}$ and Zhencong Zhong$^{1,2}$. $^{1}$Institute for Microengineering, Louisiana Tech University, Ruston, LA. $^{2}$Department of Physics, Grambling State University, Grambling, LA. $^{3}$Institute of Metal Research, Chinese Academy of Sciences, Shenyang, CHINA.

Novel nanoparticle catalysts Fe/Cu and Co/Cu will provide a promising alternative to conventional catalysts for the efficient conversion of CO/CO$_2$/H$_2$ gases to useful fuels. We have prepared g-Al$_2$O$_3$ granular support (80-120 mesh) by three steps: (i) boehmite sol (g-AOOH) preparation, sol gelatinization and shaping (oil dropping), and dry and calcinations. Laser induced solution deposition (LISD) is a novel method for preparing proposed catalysts Fe/Cu and Co/Cu on g-Al$_2$O$_3$ granular support. In the initial experiments, we have deposited nanostructured pure Co/Cu oxide and Fe/Cu oxide nanoparticles. We have studied the microstructure and composition of deposited nanoparticles by scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and transmission electron microscope (TEM). We have investigated the magnetic and electronic structural characteristics of the deposited nanoparticle catalysts by XPS, magnetization measurements, Mossbauer study and zero field nuclear
magneto resonance (ZFN.MR). This project supported by DOE under the grant no. DE-FG26-
00NT41856.

W9.8 STRUCTURAL AND SPECTROSCOPIC STUDY OF Mn AND Ir SILICIDE ISLANDS ON Si. Miyoko Tanaka, Masaki Takeguchi, Qi Zhang, Junling Liu, Karuatsu Masanori, Kaste Furuya, Nanomaterials Laboratory, National Institute for Material Science, Tsukuba, JAPAN.

In order to achieve nanometrized devices, the study of nano-silicides is becoming increasingly important. Direct band-gap silicides attract much attention because of its potential application to optical devices. For this purpose, it is quite effective to evaluate silicide materials multiply in-situ under UVH condition. We report our observation and analysis results on Mn and Ir metal silicide islands on Si substrate with UVH-TEM and UVH-STM. Si (111) substrate was used as UHV-TEM/STM characterization system (UTS-4CS) with Ar ion sputtering and direct heating. Deposition of Mn and Ir were performed at RT with an electron beam evaporator. Samples were then annealed at 573 - 873 K and transferred to each apparatus. Besides structural and morphological observation, EELS measurement was performed in UVH-TEM and cathodoluminescence measurement in UVH-STM. TEM observation of Mn deposited sample showed islands formation with the size order of 100 nm. The analysis of SED pattern taken from one of these islands suggested that this island consist of MnSi type silicide. TEM image also showed more fringes between Si and MnSi island. Because its periodicity is pretty long, it is considered that the fringe width in high resolution TEM substrate Si. HRTEM analysis revealed that the silicide islands grew epitaxially but that the interface is incommensurate. The result of exact structural and spectroscopic analysis will also be reported.

W9.9 PARTICLE SHAPE AND PORE DIAMETER EFFECTS IN GEL PERMEATION CHROMATOGRAPHY USING NANOPOROUS SILICA. Andrew G. Elkind and Christopher C. Landry, Dept. of Chemistry, University of Vermont, Burlington, VT.

Gel permeation chromatography (GPC), also known as size exclusion chromatography, is a technique commonly used to determine the molecular weights of organic polymers and polyesters. The most commonly used commercial materials consist of derivatized organic polymers with a specific distribution of pore diameters and particle diameters. Silica can also be employed in GPC and is particularly useful in high pressure environments due to its rigidity and resistance to pore collapse. Mesoporous silica, with surface area 3 to 4 times higher than commercial silica, is a superior chromatographic substrate. The higher surface area results in longer retention times, larger analyte capacity factors, and much better analyte resolution.

Mesoporous silica also has an unusually narrow pore size distribution, an important feature in GPC where size restriction is a significant effect. It can be used in normal phase, reverse phase, and normal high pressure liquid chromatography (HPLC). However, mesoporous silica has not been used in GPC. In this study, the mesoporous silica APMS-30 and MCM-41 are compared to a commercial silica, Nucleosil. APMS-30 consists of particles 4.10 microns in diameter, while MCM-41 is comprised of particles that are highly irregular and variable in size. Polyurethanes of various molecular weights were passed through these column solutions of the silicas in the GPC with injection volume of 10 microliters. The molecular weight cutoff (a calculation of the molecular weight of the largest polyurethane still showing a size exclusion effect) proved to be a remarkably accurate method of determining pore diameters in the silicas themselves. Finally, APMS-30 showed a lower slope than MCM-41, most likely due to the spherical morphology of the former material.

W9.10 THE NATURE AND BEHAVIOUR OF NANOSCALE PARTICLES OF NOBLE AND TRANSITION METALS. Jitendra Kumar, Indian Institute of Technology, Materials Science Programme, Krieger, INDIA.

Nanoparticles of noble and transition metals, such as gold, platinum, palladium, nickel and iron, dispersed over aluminia-thin films by thermal evaporation under vacuum have been studied by TEM with regard to their shape, morphology, phase, etc., and changes that occur when held under vacuum and on exposure to oxygen and hydrogen atmospheres at elevated temperatures. These particles are shown to exhibit phases which either correspond to respective bulk metal or a distorted cubic or hexagonal phase. TEM studies of the same particles taken at different temperatures revealed that these particles retain their metallic character under conditions where they would otherwise oxidize or disproportionate. Also, they assume spherical or irregular shapes with varying size distributions depending upon the metal, substrate temperature and mass taken for dispersion. A number of phenomena observed namely, coarsening of particles, foaming with well-defined shapes, e.g., cubic, hexagonal, rhombohedral, pentagonal, wetting of substrate, formation of oxides or hydrides and emergence of core-shell or torna shape particles have been described at length. Evidence is advanced to support the Ostwald ripening mechanism for growth of particles. Accordingly, coarsening results not particle migration, collision and subsequent coalescence but by transfer of species/atoms from smaller to larger particles via substrate and for jump process, irrespective of whether particles retain their metallic character or undergo transformation to form respective oxide or hydride. The implications of these findings are discussed in light of industrial applications such as catalysts in various reactions, e.g., oxidation, hydrogenation, dehydrogenation, petroleum cracking, etc.

W9.11 MONITORING OF SILICON NANO-CRYSTAL DOT'S FORMATION ON SiO2 AND ON SnS4 IN A UVH-CVD SYSTEM. Takayuki Kawashima, Supika Mashiro, Junro Sakai, ANELVA Corporation, Tokyo, JAPAN; Rajesh Rao, R. Muradalher, Bich-Yen Nguyen, Bruce White, Motorola Material and Structures Laboratories, Austin, TX.

Recently, a lot of research has been made for application of the Si nano-crystals dots to flash memories. In such flash memories, density and size of Si dots closely relate to device characteristics and hence precise control of Si nucleation and growth process should be achieved. To ensure repeatability of the Si dots' size and density, in-situ monitoring method of Si dot formation is required. We had reported that Si dot formation process on SiO2 can be monitored by using optical pyrometer. However, pyrometer is not optimal for an in-situ monitoring method of Si dots' formation because of two reasons. One is that the change of pyrometer readout is determined by radiation from parts behind wafer. Another is that the sensitivity of pyrometer readout to the change of surface morphology is influenced by emissivity of the under layer. In this work, we have examined applicability of SPA (Surface Photo-Absorption) as an in-situ monitor of Si dot formation, and we examined applicability of SPA to an in-situ monitor by comparisons between pyrometer measurement and SPA performed on both oxide wafer and nitride surfaces.

We have found that SPA provides a signature of the Si dot nucleation and growth process as a function of irradiation time, as the pyrometer measurement did. SPA is more sensitive than pyrometer so that read-out curve can be used to provide the optimum gas irradiation time on SiO2 and SnS4 surfaces and obtain better process repeatability for device applications. By using SPA as an in-situ monitor of the optimum gas irradiation time, good repeatability of both dot density and size was obtained on both oxide and nitride surfaces.


Tungsten trioxide has been studied for gas sensing application towards NO and NO2 gases. In this work WO3 polycrystalline nanoparticles obtained by precipitation from a methanol/water (3:1 mol:mol) solution of tungstic acid, H2WO4 and successive thermal treatment in air (400-700 °C). Thick films (3 μm) of the nanopowdered WO3 showed a good electrical sensitivity to NO2 (SeHxWO3/HxWO3) with low interference of CO and CH4. The range of atmosphere composition was 0.5-5.0 ppm of NO2 in dry and moistened air. The oxide sensitivity was influenced by crystallinity, particle size and surface area of WO3, which strongly depended on the preparation method and thermal treatment temperature. In the present work was the study of the surface reactivity of WO3 towards NO, NO2 and air, in order to understand the mechanism of sensing properties. We tested and monitored the formation of defect centers and surface species involved in the reactions between the oxide and the gases. In this context Electron Paramagnetic Resonance (EPR) spectroscopy was a good tool to detect the interaction of chemisorbed NO and NO2 groups. The relations between the surface paramagnetic species and the structural and morphological properties were also investigated. In fact WO3 samples prepared from tungstic acid were compared with samples prepared by a sol-gel process from a tungsten ethoxide/ethanol/water solution.

W9.13 PHOTON ANNihilation IN CdSe QUANTUM DOTS. Christian Hinterberger, Northeastern University, Boston, MA; Marc Bawyer, Kelvin Lynn, Washington State University, Pullman, WA; Phil Sterne, Lawrence Livermore National Laboratory, Livermore, CA.
Arthur Denison, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Position annihilation measurements in CdSe quantum dots are reported. Results from four different quantum sizes are compared to a single crystal sample of CdSe using the coincident Doppler-broadening position annihilation technique. Analysis of the spectra shows progressive changes in annihilation line shape as the quantum size decreases below 6 nm. Evidence is provided that the position is entrained within the quantum dot. A model is presented in which electron tunneling is taken into account. This model leads to the prediction that the band gap $E_g$ and this band gap increases as $1/R^2$ of the quantum sphere.

W9.14 ROLE OF CLAY SOLVENT INTER AND INTRAPARTICLE INTERACTIONS ON SWELLING CHARACTERISTICS OF MONTMORILLONITE NANO-MESO MICRO SCALE PARTICULATE SYSTEMS. Dinesh R. Katti, Kalyana S. Katti, V. Venkataraman, Srinivasa Murthy, North Dakota State University, Department of Civil Engineering, Fargo, ND.

This paper deals with fundamental molecular issues related to macroscopic mechanical properties of nano-meso-microscale montmorillonite clay particulate systems. Molecular interaction of high aspect montmorillonite particles with solvents has large influence on resulting swelling characteristics in clays consisting of montmorillonite. A new controlled uniaxial swelling (CUS) cell is designed which allows simultaneous measurement of swelling and swelling pressure in addition to ease of removal of undisturbed samples for microscopy and transmission electron microscopic and X-ray diffraction investigations. Our work shows that the swelling behavior of montmorillonite directly results from breakdown of large particles to smaller nano and meso scale particles with increased water incorporation in the interlayers. The vibrational bands and regions of the montmorillonite spectra obtained at controlled amounts of swelling by 100% (where 0% swelling is defined as fully saturated samples under no volume change) show changes in band shape, intensity, and position resulting from increased hydrogen bonding in the interlayers and surface of montmorillonite particles. In addition, orientation dependent micro strong reflection (ATR) spectroscopic investigations are also conducted on the controlled swelling samples. Results indicate that such reduced particle size with increased swelling is related to increased misorientation of the montmorillonite platelets. The relationship between molecular interactions microstructure and macroscopic response (swelling and swelling pressure) is the key to development of novel nanocomposite systems based on montmorillonite with tailored properties.

W9.15 STUDY OF DYNAMIC PROPERTIES OF CO NANOPARTICLE SYSTEMS. Leonard Spini, Le Duc Tong, Jiey Fang, Charles J. O’Connor, ARIE, University of New Orleans, New Orleans, LA; Srikrishna Hariharan, University of South Florida; Dept. of Physics, FL, Al. Stancu, “AIL, Censi” University of Physics, Iasi, ROMANIA.

The dynamics of magnetic nanoparticle systems is a subject of considerable interest due to their fundamental and technological importance. The magnetic property of such systems is strongly modified compared to the bulk, due to greater texture and the small size of the grains. Important issues like superparamagnetic relaxation and inter-particle interactions can be best probed in particles dispersed in a medium where the magnetic concentration can be systemically varied. In this paper we present a study of the magnetic properties of different samples of Co nanoparticles dispersed in different volume fractions in a wax matrix. The degree of dilution in the wax controls the average particle distance and therefore the strength of interactions between Co nanoparticles. The synthesis of cobalt nanocrystals were carried out using standard organometallic reaction procedures with airless/moisture-less devices and commercially available reagents. The dispersions of nanoparticles in the wax matrix were carried out by ultrasonically mixing the concentrated cobalt nanocrystals in hexane with wax-hexane solution, followed by increasing temperature of the system to remove the solvent. Structural and morphological analysis of the Co nanoparticle systems were performed by TEM and X-ray scattering experiments. TFreen transverse susceptibility experiments at various temperatures, susceptibility in the frequency range (10 Hz, 10^5 Hz) and various field and temperature dependent magnetization processes were used in order to investigate dynamics in Co nanoparticle systems. The frequency variation of the blocking temperature has been analyzed for a series of samples with the same volume distribution of inter-particle interactions of different strength. Thermodynamic and thermal spectroscopic properties of magnetic nanoparticles in different concentrations were investigated. The study of inter-particle interactions is fundamental in defining the overall magnetic properties of magnetic nanoparticles. Work at ARIE supported by DARPA Grant No. MDA-972-97-1-0003.

W9.16 PREPARATION OF NANOPARTICULATE METAL OXIDE THIN FILM SURFACED AND PARTICLE SIZE CONTROL OF METAL OXIDE COLLOIDS. S.C. Pang, Faculty of Resource Sciences & Technology, Universiti Malaya Sarawak, Sarawak, MALAYSIA; S.F. Chin, Marc A. Anderson, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, WI.

Nanostructured materials of tailored microstructure have numerous potential applications in areas such as microelectronics, optics and chemically-stored devices. There are many nanosized particles of various metal oxides, e.g., cobalt dioxide, iron oxide, manganese dioxide, titanium dioxide, and iron(III) oxide. The surface area of such nanoparticles is very large, which can lead to high catalytic activity. Understanding the properties of these particulate systems of defined particle sizes in the nanometric regime have been shown to exhibit properties that are dramatically different from those of bulk phases. Our recent studies have shown that nanomaterials such as titanium dioxide, zinc oxide, and iron(III) oxide exhibit large change in storage capacity or capacitance. In this study, we have synthesized nickel manganese oxide and iron oxide colloidal suspensions of varying particle sizes. In the case of manganese oxide, particle size control was achieved by utilizing various organic templates of large and less electropositive organic cations, whereas for iron oxide (magnetite), particle size control was achieved through controlling the pH and ionic strength of the reaction medium. Thin films of nanostructured materials were formed on supporting substrates through controlled gelation and subsequent thermal treatments. Such films were formed from colloids of various monodispersed particle sizes, as well as from homogenous mixtures of colloids with varying proportion of particle sizes. Nanostructured materials derived from the self-assembly of functionalized nanoparticles were also investigated. Various material characterization methods such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Nitrogen Absorption-desorption (BET) were employed to elucidate the effect of particle size and surface functionality on the microstructural evolution of these thin films.

W9.17 MICROSTRUCTURAL INVESTIGATION OF GRAIN GROWTH IN CRYOMILLED INCONELO 625 POWDER. Kyung H. Chang, Jongsung Lee, Rodolfo Rodriguez and Enrique J. Llewellyn, Department of Chemical, Bioengineering and Materials Science, University of California at Irvine, Irvine, CA.

The grain growth behavior of cryomilled nanocrystalline Inconel 625 powders was investigated during isothermal heat treatment at 600 - 900 °C for 1 - 4 hours. The grain size of cryomilled Inconel 625 remained under 250 nm following heat treatment in the temperature range of 600 - 900 °C up to 4 hours, which represents an improved grain stability compared to that of conventional Inconel 625 and cryomilled pure Ni. Microstructural studies, using TEM, revealed the existence of oxides, rhombohedral structure NiO, particles after cryomilling; moreover, the particles remained essentially unchanged following isothermal heat treatment. This observation is consistent with the suggestion that a Zener-Drag mechanism is responsible for the observed thermal stability. The pinning effects on grain size stability by cryomilled particles was quantitatively analyzed and compared with other possible stabilizing mechanisms. The grain stability of cryomilled Inconel 625 powders at 900°C was noted to be greater than that at lower temperatures. This behavior was attributed to the presence of two types of precipitates found at this temperature, which were identified as spherical M23C6 carbides and rod shaped sulfide inclusions of varying precipitate. The grain growth resistance at this particular temperature via grain boundary pinning mechanism. The preferred nucleation sites of these precipitates was noted to be grain boundaries, thereby augmenting the grain boundary pinning effect. This research funded by ONR Grants Numbers N0014-94-1-0017, N0014-95-1-0569, N0014-94-1-0018.


Uniform multi-walled carbon nanotubes were produced by the vapor-phase decomposition of xylene with a ferrocene catalyst in a flow reactor. The nanotubes contain a few percent residual iron catalyst. A Mossbauer spectrum of the nanotubes indicates that the iron is present as about 60% solid iron (Fe3C). When pyridine is used as the feed during the synthesis, the residual iron is present in 1% elemental iron, 79% Fe3C and 4% of an unidentified divalent iron component. It is noteworthy that no iron oxide is observed in either sample. Effects of subsequent nanotube reactions with bromine and other electrophilic reagents will be reported.
SEMICONDUCTOR NANOCRYSTALS have the potential for making contributions to electronics and photonics applications such as sensors, switches, light-emitting diodes, data storage and manipulation, and photovoltaic devices. We have been involved in developing luminescent CdSe/ZnS quantum dot (QD) and CdTe/ZnS quantum dot (QD) systems for use as fluorescent reporters in immunomodulatory-based sensors. As part of our efforts to bind semiconductor CdSe/ZnS quantum dots to antibody proteins for this work, we functionalized the quantum crystals with a variety of organic acid salts to impart water solubility to the nanocrystals. During the course of working with these derivatized, water-soluble quantum dots, we observed significant differences in their chemical reactivities and physical characteristics compared to those of undervinylated CdSe/ZnS nanocrystals. One of the most striking differences observed is the reactivity of the derivatized and undervinylized nanocrystals with stainless steel surfaces. The fluorescence of aqueous mixtures of our water-soluble nanocrystals is immediately quenched upon exposure of the mixtures to stainless steel surfaces or to other transition metal oxides, whereas undervinylized quantum dots exhibit little or no reactivity at all. As has been reported by several other laboratories, the water-soluble nanocrystals also exhibit a significantly lower quantum yield compared to the undervinylized nanocrystals. We have also found that both the water-soluble quantum dots and the undervinylized quantum dots can lose fluorescence upon exposure to certain amine compounds. We will discuss the unusual reactivity exhibited by these nanocrystals, and suggest possible explanations for their interesting chemical behavior. We will also describe methods to prevent the quenching of water-soluble derivatized quantum dots by stainless steel and metal oxides.

Study of the optical characteristics of Bi2O5-doped ZnO powder by cathodoluminescence microscopy. X.L. Sun 
*1, J.I. Brakkee 
*1, 2, 3.

1Department of Electrical Engineering, 2Center for Materials Research, 3Department of Physics, The Ohio State University, Columbus, OH, USA.

ZnO ceramics doped with a small amount of Bi2O5 show strongly nonlinear current-voltage (IV) characteristics and are thereby used as varistors in various electronic devices. In this paper, we have used low temperature (10 K) cathodoluminescence (CL) spectroscopy to investigate optical characteristics of Bi2O5-doped ZnO powders prepared under different processing conditions. Our 29 keV ultrahigh vacuum (UHV) Auger microprobe and Scanning Electron Microscopy (SEM) enabled us to collect spectra from submicron ZnO grains and to distinguish clearly between volumes in the grain centers versus the boundaries of the grains. The data for three sets of samples show strong deep level defect emission at 2.5 eV, characteristic of either O vacancies or Zn interstitials. Normalized to the near band edge emission of ZnO, this defect emission varies considerably from grain bulk to grain boundary. In general, the emission is much stronger in the grain bulk than at the grain boundary. The low temperature CL spectra display a number of excitonic, donor-acceptor pair (DAP) and its phonon replica features that agree in energy with those reported previously for crystalline ZnO. These CL spectra also show the appearance of a new feature located at ~40 meV below the near band edge excitation line at grain boundaries. Its energy is ~7 meV higher than a well-known DAP transition line. The energy and intensity of this line appear to vary between samples. The changing behavior of this feature suggests a correlation with processing, more pronounced with higher doping concentration and annealing above the eutectic temperature. Presumably, this is associated with Bi phase segregation or the formation of new electrically-active defects.


Silica glasses with different nano-size pores are characterized by atomic force microscopy (AFM). The AFM images visualize the hierarchical structure of silica porous glasses, which is similar to that of silica aerogels. The boundary regions between grains and between clusters consist of pores for the glass with 20 nm pores. The cylinder shaped nano-size pores with 2-3.0 nm in diameter are revealed by AFM in the glass with 2.5 nm pores, and also the grain boundary network consist of the large pores. CdSe is well dispersed in glasses with 2.5, 5.0, and 7.5 nm pores by diffusion, and aggregated in the glass with 2.0 nm pores. An irregular shaped aggregated CdSe structures with sharp edges at micron scale are observed by AFM in the glass with 2.0 nm pores. Doping CdSe into nano-size pores in silica glasses shows good optical limiting properties and the relationship between the structural features and optical limiting performance is correlated.

SYNTHESIS AND REACTIVITY OF POROUS SILICA DOPED WITH NANOPARTICLES OF Fe, Co, AND Cu. Joseph G. Moore, Jennifer Eggerlein, Kevin Schneider, and Christopher Landry, University of Vermont, Dept. of Chemistry, Burlington, VT.

Metal-doped porous silica has been shown to be useful in a variety of catalytic applications, from synthesis of hydrocarbons by the Fischer-Tropsch method to the degradation of nitric oxides. This material is typically produced by post-synthetic treatments such as ion exchange with a metal salt. In situ, one-pot methods of synthesizing the metal-doped material are needed due to the propensity of metals to form oxides or hydroxides at the high pH conditions required for the formation of the porous silica. In this study, we report the use of cationic organometallic complexes that are stable at high pH as metal dopant agents used during the assembly of the porous silica. The material produced by this method can be doped at high levels due to the electrostatic attraction between the metal complexes and the growing anionic silica framework under basic conditions. The metal complexes do not interfere with the silica growth process and nitric oxide photolysis measurements that indicate retention of pore ordering. Calcination to remove the organic ligands leaves a porous silica doped with metal ions, which can be reversibly reduced under hydrogen to give metal clusters with diameters in the nanometer range (from TEM measurements). The resulting metal-doped materials are highly active in a variety of catalytic applications as determined by gas chromatography.

HARD POLYMER NANOCOMPOSITE COATINGS FOR OPTICAL APPLICATIONS. Amit Singhal and Genshe Skundur, Nanopowder Enterprises, Inc., Pittsburgh, PA.

There is an immediate need to develop high abrasion and chemical resistant coatings for plastic substrates, enabling them to become attractive alternatives to inorganic glasses in applications, such as automobile windows and headlamps, high index ophthalmic lenses, and transparencies for aircraft cockpits. We are developing a new class of hard, high refractive index and optically transparent coatings that are composed of relatively large aluminum oxide particles dispersed in a polymer-methoxide oxide matrix. Large ceramic particles impart excellent wear and scratch resistance due to their large size and surface. We have engineered the surface of these large particles so that they are durable against the polymer's swelling process and nitrogen pyrolysis oxide matrix. For the first time, transparent films with relatively large ceramic particles have been developed. Structural and optical properties of these films will be discussed in this paper. We would like to acknowledge Prof. G.L. Wilkes of Virginia Polytechnic Institute and State University for his technical input.

LIGHT SCATTERING BY ISOLATED AND SUPPORTED NANOPARTICLES USING DDA. Iwao O. Sao, Cecilia Noguez and Ralph G. Barrera Instituto de Fisica, UNAM, MEXICO.

Optical spectroscopies have shown to be useful tools to characterize nanostructures, due to their in situ potentialities and non-destructive character. Nanoparticles have been accurately described using a variety of optical measurements like Differential Reflectance (DR), Anisotropy Reflectance Spectroscopy (ARS), Surface-Enhanced Raman Spectroscopy (SERS). Recently, the DR spectra of supported nanoparticles have been theoretically described in terms of substrate-induced multipolar modes [1]. However, the theoretical calculations are limited to nanoparticles with spherical geometries. In this work, we use the Discrete Dipole Approximation (DDA) to calculate the optical response of isolated and supported nanoparticles. This method allows to study nanoparticles of any shape. Here, we present results of the optical response of different nanoparticles having at different distances over a substrate. To perform the calculations, we have adapted the DDA code to include the image dipoles due to the presence of the substrate. The results are compared and discussed with other theoretical methods and with experimental measurements.

ENERGY AND ELECTRON TRANSPORT IN METAL/SEMICONDUCTOR NANOCRYSTAL SOLIDS. Arjey Javier, G.F. Stroscio, Univ. of California at Santa Barbara, Dept. of Chemistry, Santa Barbara, CA.

Size-tunable excitonic luminescence of semiconductor quantum dots (CdSe, ZnSe) and composition-tunable surface plasmon resonances of metal nanocrystal alloys (Au/Ag) are exploited to study energy and electron transport in drop-cast and spin-cast solids. Solution phase Synthesis as well as controlled nanocrystal doping to form electronically coupled layers within the mechanism of transport of electrons and electronic excitation energy from nanocrystal to nanocrystal as a function of increasing nanocrystal quencher concentration. Continuous wave and time-resolved photoluminescence and electroluminescence techniques are used to probe these phenomena.

SYNTHESIS OF ENGINEERED MICROPOROUS NANO-PARTICULATES FOR CHEMICAL MECHANICAL POLISHING. K.S. Choi, J.D. Park, N. Basim and R.K. Singh, Department of Materials Science and Engineering, University of Florida, Gainesville, FL.

This experiment is to investigate the microporosity in spherical silicon particles with a very narrow particle size and size distribution by the hydrolysis reaction of tetraethylortho-silane in ethanol containing water and ammonia and to synthesize the engineered nanoparticulate suspensions (microporous silica particles) for Chemical Mechanical Polishing. Spherical microporous silica powders with a narrow size distribution have been prepared by a precipitation technique involving the hydrolysis reaction of silicon alkoxide in ethanol. The intraparticle microporosity has been created by adsorption of an organic compound (glycerol) as the pore-growth agent. The presence of glycerol during the synthesis is of considerable importance to the mechanism and its effect on the particle size will be discussed. The synthesis of silicon microporous spheres of narrow size distribution yielded the preparation, by varying particle size and porosity, of a wide range of porous silicon slurries. The influence of particle size, particle size distribution, porosity and particle concentration will be discussed in chemical mechanical polishing applications. Although silica particles show larger plastic deformation than the bulk material, very good glass polishing rate are obtained due to the plastic deformation of the silica layer during CMP. Silicon particles are suitable candidates for application in CMP because silica can be directly precipitated as monodispersed spheres, their narrow size distribution being an important requirement for CMP applications.

CHROMIUM DOPED LiMn\textsubscript{2}O\textsubscript{4} NANO-PARTICLES PREPARED BY THE SOL-GEL PROCESS FOR LITHIUM SECONDARY BATTERIES. Ching-Hsin Lu, You Lin, Hsien-Cheng Wang and Wen-Jeng Huang. Department of Chemical Engineering, Nat'l Taiwan Univ., Taipei, TAIWAN ROC.

Lithium manganese oxides with spinel structure are of great interest as insertion electrode for use in 4.0 V lithium ion rechargeable batteries. It presents advantages in economy, ecology and safety. The major disadvantage of lithium manganese oxides is the low capacity during cycling and during storage in the electrolyte, especially at elevated temperatures. The reason for the capacity loss is the electrolyte decomposition. In this study (i) double decation (Na\textsuperscript+ and Ca\textsuperscript2+) which is an important factor in the capacity retention during cycling, (b) random ionization reaction, (c) increase of lattice constant at cycling, and (d) site change between Li and Mn. It has been recently reported that the capacity retention during cycling can be improved by partial substitution of manganese ions by trivalent or divalent cations like Co, Cr, Al, and Mg. Certain literature reported that a chromium substitution (Cr\textsubscript2O\textsubscript3) was beneficial to the specific capacity and energy of the spinel. The purpose of this study was to optimize the composition of the new manganese oxide by synthesizing a new Li\textsubscript1-xMn\textsubscriptxO\textsubscript4 powders which have nanosize, narrow size distribution and high crystallinity. Chromium-doped LiMn\textsubscript2O\textsubscript4 powders have been synthesized by the sol-gel method using PVA in this study, and evaluated as a cathode electrode material for Li-ion batteries. Polyvinyl alcohol was found to maintain the homogeneity of the system in the precursors. Once the precursors were calcined at high temperature, single spinel phase was formed in all of the precursors. The parameters are found to depend on the calcination conditions and the dopant amount of chromium species. The cyclability of the cathode materials was demonstrated to be improved by the doping of chromium species in the spinel phase.

A STUDY OF THE GROWTH CURVES OF C XEROSIS AND E. COLI BACTERIA IN MEDIUMS CONTAINING NANOMICRO AND NANO-DIAMOND POWDERS. Daniel M. Thompson, Le Blanc, Javier Aviles, Metropolitan University, Dept of Science and Technology, San Juan, PR; Lidiah San Miguel, Oscar Resto, Luis Fonseca, Dept. of Physics, University of Puerto Rico, San Juan, PR.

In this research, we have elaborated nanometric and micrometric particles from luminescent (red, in approximately 625nm) porous silicon film to be inoculated in C xerosis and E. coli bacterial strains. Recent studies indicates the selectivity of different types of bacteria to particle size. This thought take us to a bacteriological sensor, furthermore, we got that luminescence was an optical factor (it depended on the size of the electronic dopant) for the electron transport curve of C. xerosis as well as E. coli bacteria with silicon particles present changes compared to the standard curve. The growth curves of E. coli and C. xerosis with nanometric silicon are above their respective standard curve. For the C. xerosis curve with nanometric particles, this present alsas oscillations of intervals of almost 1 hour. This could be caused by its slow growth. The oscillations are repeated at higher times when the solution is diluted. Similar studies have been made with micrometric particles. There is a possible tendency of the E. coli bacteria to incorporate nanometric particles inside of it; a tendency that C. xerosis has with micrometric particles.

ELECTROCHEMICAL QUARTZ CRYSTAL NANO-BALANCE AND SCANNING FORCE MICROSCOPY INVESTIGATIONS OF NANOPARTICLE CATALYSTS. Jin Luo, Mathew M. M. Yang, Yongying Lou, Chew-Joo Zheng, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY; Marin Hepel, Dept of Chemistry, State University of New York at Potsdam, Potsdam, NY.

Gold and alloy particles in the nanometer-sized range are explored as candidates for highly effective catalysts. A key challenge is the effective isolation of the nanosized properties while retaining the nanoscale catalytic properties. Core-shell nanoparticles provide an intriguing pathway because the encapsulating structure enables tailoring of core size and enhancement of stability of nanosized catalysts against aggregation propensity. This presentation reports the recent findings of electrochemical quartz crystal microbalance (EQCM) and atomic force microscopy (AFM) investigations. The EQCM studies the mass transport associated with catalytic activation and methanol oxidation at nanostructured Au and alloy nanocrystals. It is demonstrated that the catalytic activation and oxidation of methanol are accompanied by mass fluxes across the nanostructured film. The mass transport involves oxidation-reduction of surface oxygenated species, methanol adsorption and oxidation, solvent breath and product release. The AFM probes the morphological changes of the nanostructures under the catalytic conditions. The implication of the results to the understanding of the core-shell nanostructured catalytic mechanism and tailoring strategies via interfacial nanoscale manipulation will also be discussed.

XP S AND MAGNETIZATION STUDIES OF CrMn NANO-PARTICLES. W. Amulski-Krajzewicz, West Virginia University, Physics Department, Morgantown, WV; U. Lee, U.S. Army Research Laboratory, Adelphi, MD.

Cr\textsubscript{1-x}Mn\textsubscript{x} (x \leq 6.3 %) alloy in the bulk form is an interesting complex system that behaves in many but not all respects like a spin-glass system. In this study, 14 nm-size CrMn nanoparticles with 5% Mn were synthesized by ball milling of Cr and Mn powder in Ar atmosphere. After 50 hours of milling, the x-ray diffraction pattern indicated alloying of the two metals Cr and Mn. However XPS data proved the formation of MnO\textsubscript2 and Cr\textsubscript2O\textsubscript3 oxides on the surface of the chromium core in the nanoparticle. These oxides on the surface, like the Cr core, are antiferromagnets. Magnetization (M) measurement at 200 G as a function of temperature (T), after zero-field-cooling, showed that M increased as T increased from 5 K to 330 K, which is a Neel temperature for the Cr and the oxides. Even though the magnetization value is in the range of typical antiferromagnet at all temperatures from 5 K to 330 K, the shape of M versus T curve is neither that of an antiferromagnet nor that of a spin-glass. It appears that the behavior of the magnetization curve is due to the frustration of the spins by weak fields associated with spin-density-wave. This frustration should be different from the frustration of the spins due to the ferromagnetic-antiferromagnetic competition in spin-glass systems.

IRON DOPED TIN OXIDE NANO-PARTICLES SYNTHESIZED BY MECHANO-CHEMICAL PROCESSING. Lina Gao, Paul G. transcripts, Research Center for Advanced High-Speed Processing, The University of Western Australia, AUSTRALIA;
The use of nanoparticulate or nanocrystalline materials in the preparation of gas sensors is a well-established method to enhance sensor sensitivity. Advantages and benefits of using these materials include higher sensitivity and stability. The size effects of the particles have been recognized through extensive studies, with particular emphasis on the photoelectric effect. In addition, the introduction of dopants has been recognized as a means to further increase the sensitivity. It is also believed that the doping elements may change the morphology by inhibiting particle growth. In conjunction, the dopant is also believed to alter the conductivity of the base material, with the direction of change dependent on the charge of the dopant.

Recent studies have shown that when carriers are added to the material, it can act as a suitable pathway for the production of oxide nanoparticles for gas sensing applications. The nanocrystalline process involves milling suitable precursor powders to form a nanocomposite structure of the starting materials. The mixture reacts during milling or subsequent heat treatment to form separated nanoparticles of the desired phase in a solid matrix. The nature of the process means that the desired oxide can be made during the milling stage, leading to the production of doped nanoparticles. The synthesis of FeO-doped SnO2 nanoparticles was investigated using the mechanoochemical process, forming SnO2, TiO2, and NiO2O3 precursor powders in an agglomerated precursor with the desired particle size, with XRD crystallite sizes less than 10 nm measured. The nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, BET surface area analysis, and X-ray photoelectron spectroscopy. Gas sensing measurements of the FeO-doped SnO2 nanoparticles revealed a 10-fold increase in the sensor response, in comparison to pure SnO2.


Porous micrometric aluminum oxide (AAO) template-based technique for carbon nanotube (CNT) fabrication has an advantage in growing two-dimensional (2D) CNT arrays with perfect alignment of templates with the same diameter and uniform distribution. So, the technique can be one of the alternative methods for what is called CNT-nano-device. There had been results about electrical properties of CNT-Al2O3/Al produced by the AAO template-based technique. In the previous works, Coulomb blockade was observed in the interface at low temperature. However, for the applications of CNT-nano-devices, this phenomenon must be occurred at room temperature. For this purpose, we changed the interfacial structure by neloxal treatment and investigated the electrical property by measuring current voltage (I-V) characteristics. It is shown that the I-V characteristic is linear for the as-grown sample over the whole range of voltages from 0 to 1.7V at room temperature. However, the I-V curve of the annealed sample is nonlinear and the resistivity becomes larger than as-grown sample. From the comparison with the I-V behavior of interface removed sample, we found that the electron tunnel junction is formed in the annealed CNT/Al2O3/Al interface. Transmission electron microscope image of the annealed interfaces shows that Crystallized aluminum layer is newly formed between CNT and aluminum substrate during annealing treatment. In this presentation, an electron tunneling behavior of CNT/Al2O3/Al and its system mechanism will be discussed.

**W9.33** Fabrication of Nano-Hydroxyapatite Particles Doped with Transition Metal Ions. Hyoung-Suk Oh, Jee-Young Choe, Hyoung-Kyu Choi, Young-Keun Jeong, Korea Institute of Ceramic Engineering and Technology, Seoul, KOREA

Some of the transition metals such as Cu, Zn and Ag are known to possess antibacterial effects in ionic states. By substituting such ions into the solid ion carrier materials, the antimicrobial effects can be integrated into the solid state, thus extending the field of applications due to its convenience. The release of the antimicrobial metal ions from the carriers is strongly influenced by the states of carriers. The interest of the research was to explore the antimicrobial effects for the carrier particles. Nano-sized particles were reduced to nano-range. Hydroxyapatite was selected as a carrier and by properly controlling the experimental parameters such as aging time, temperature, and stirring speed during the precipitation, nano-sized particles similar in size to 50nm could be synthesized. The antimicrobial effect was developed either by co-precipitation or direct ion exchanges. Antimicrobial effects against E. Coli were observed and discussed in terms of the size of particles and doped ion concentrations.

**W9.34** Nanostructured Thin Films of Titanium Oxide, Nickel Oxide and Complex Titanates Using Cathodic Electrodeposition. Igor Zhidomirsky, McMaster University, Hamilton, Ontario, CANADA

Cathodic electrodeposition has been utilized for preparation of nanostructured thin films of titanium oxide, nickel oxide, zirconium titanate, ZrO2 and composites titanium oxide - ruthenium oxide, titanium oxide-aluminium oxide. Peracetic acid was used in order to solve problems connected with formation of oxide compound. The important finding was that complex oxide compounds such as zirconium titanate and ZrO2 can be deposited in a corresponding peracetic precursors. In contrast, ruthenium and titania-silicate precursors produced only independent compounds. The composition of the deposited material can be controlled by variation of the concentration of Ru and Ti species in the solutions. Oxide films were obtained by thermal dehydration of these precursors. Obtained using peracetic acid, composed of Ti, RuO2, SEM, and Auger methods. Crystalline sizes were derived at different temperatures from X-ray broadening data. Nanostructured films were obtained as monolayers or multilayer on various conductive substrates. The amount of the deposited material was controlled by variation of deposition time and current density. Applications of thin films prepared using electrodeposition are discussed.

**W9.35** Sensing Characteristics of Cubic and Rhombohedral Nanostructured ITO Thin Films Jeung-Soo Hah, Dong-Chul Kim, Kyungpook National University, Daegu, KOREA, Jeong-Ock Lim, Medical Research Institute, Kyungpook National University, KOREA

In nanostructured materials, the surface-to-volume ratio is much greater than that of coarse materials, surface properties tend to become paramount. Despite the nanostructured thin film gas sensors are widely investigated, however, fundamental understanding on the gas sensing materials is still insufficient. In particular, the effect of crystal structures on sensing characteristics of nanostructured gas sensors has not been reported. Therefore, the purpose of this study is to investigate the gas sensing characteristics of two nanostructured gas sensors and to attempt to correlate the performance of these sensor materials with their respective crystal structure. We selected the different crystal structures nanostructured ITO powders with different particle sizes. Their crystalline structures are cubic and rhombohedral, respectively and particle sizes of both powders are identical, at 15nm in diameter. Nanostructured thick films for gas sensors are prepared by screen printing with 20µm thickness. Gas sensing properties are examined depending on the operating temperature and gas concentration. Gaseous ethyl sensitivity is higher in rhombohedral thicker film than in cubic thicker film at all operating temperatures.

**W9.36** Dyes and ROP of Metal Containing Norbornene Derivatives. J. Healy, C. Coates, D. Gobin, D. E. M. Pollach, J. B. Liu, Robert Coates, Naval Research Laboratory, Chemistry and Materials, Washington, DC

We report the synthesis of a series of highly functional metal chelated silyl-protected dimethylaminoborane derivatives. Subsequent alterations to the previously synthesized norbornene adducts likewise afford many other derivatives containing such functionalities as silyl, cyano, esters, and ethers. These derivatives are then subjected to ROP to afford polymer or block polymers. The block polymers formed serve as a unique template for the formation of size controlled metal nanoparticles having a narrow dispersion. These metal nanoparticles containing a block polymers are evaluated as unique electroluminescent and optical materials.

**W9.37** Separation and Magnetic Properties of Fe Nanoparticles by Chemical Vapor Condensation Process. C.J. Choi, B.K. Kim, Korea Institute of Machinery and Materials, Changwon, KOREA, X.L. Dong, Laboratory of Ultrathin Particles, Shenyang Polytechnic University, Shenyang, CHINA

Nano-sized Fe particles were synthesized by Chemical Vapor Condensation (CVC) process using the precursor of iron carbonyl (Fe(CO)5) as the source. We investigated the microstructures, magnetic properties of the Fe nanoparticles and their oxidation behavior during annealing systemically by means of HRTEM, DTA-TGA, Mössbauer spectroscopy and magnetic measurement. The prepared particle was nearly spherical shaped and core-shell type structure with 2±10nm in mean size. Oxidation heat treatment leads to the successive appearance of oxide phases. The magnetic states of Fe nanoparticles changed from super.
**W9.38**

**ELECTRICAL TRANSPORT PROPERTIES OF NANO-STRUCTURED METAL-CARBON FILMS.** M. Brunz, S. Miglio, INFN, Dipartimento di Energetica, Firenze, ITALY; P. Pineri, G. Bongiorno, I. Kholmanov, P. Milani, INFN, Dipartimento di Fisica, Milano, ITALY.

We present a study on electrical conduction in nanostructured carbon (r-cc) films produced by deposition of a supersolid beam of neutral carbon clusters. By introducing small amounts of metallic precursors containing Mo and Co in the buffer gas (Helium) of the Pulsed Microplasma Cluster Source it has been possible to control the nanostructure of the cluster-assembled films. Compared to the material grown without catalyst particles, the carbon-metal films show higher p-orbital regions mixed with a more compact nanostructured carbon phase. The use of different catalysts influence significantly the pore diameters. Electrical properties of these films have been studied as a function of temperature, gas (H₂, N₂, CH₄, He) pressure and relative humidity. Conductivity vs. temperature measured in vacuum in the range 300-400 K is characterized by a constant activation energy of ~0.3 eV in nanostructured carbon films without catalysts. In samples grown with metallic precursors the conductivity presents a lower value at room temperature, but higher activation energy. The electrical conductivity of samples produced with molybdenum is sensitive to changes in gas pressure and relative humidity, showing reversible behavior. This sample is characterized by conductivity in vacuum at high temperature definitely higher than in gas atmosphere. The current response does not change significantly in the presence of different gases, suggesting a gas-surface interaction dominated by physisorption. The dependence of the resistivity on gas composition indicates an intimate chemical behavior, with a strongly dependent on the relative humidity.

**W9.30**

**SURFACE CHARACTERIZATION OF CARBON NANO MATERIALS VIA ADSORPTION MEASUREMENTS.** S.K. Talapatra, A.D. Migeon, Southern Illinois Univ at Carbondale, Dept of Physics, Carbondale, IL.

We present the adsorption isotherm results of various gases on single wall carbon nanotube bundles and recently discovered carbon nanohorns. The surface to adsorbate binding energy and specific surface area were calculated and compared for both these samples. In light of the results obtained we discuss the potential use of these materials in differential gas separation techniques and as hydrogen storage materials.

**W9.40**

**PHOTOLUMINESCENCE STUDY OF THIOL-CAPPED GOLD NANO PARTICLES.** A. Okano, H. Nagashima, Y. Kuriyama, S. Sumida, T. Sato, Tokodai Univ, Dept of Physics, Sendai, JAPAN; T. Sekine, Tokodai Univ, Dept of Chemistry, Sendai, JAPAN.

A photoluminescence study of thiol-capped gold nanoparticles has been carried out in order to investigate in detail the electronic structures of metallic nanoparticles. We have prepared the dodecanethiol-capped gold nanoparticles with a diameter of 3.5 nm by using the two-phase (water-nonaqueous) reduction of AuCl₄⁻ by sodium borohydride in the presence of thiol [1]. The thiol-stabilized gold nanoparticles were deposited on the highly oriented pyrolytic graphite substrates and loaded into ultrahigh vacuum chamber. From the ultraviolet photoluminescence measurements, it is found that the spectral intensity at the Fermi energy is vanished. On the other hand, the optical absorption spectra of such prepared gold nanoparticles exhibit a distinct plasmon resonance for all sizes. The existence of a plasmon resonance indicates the occurrence of the valence electrons in the metal. We have analyzed the observed photoluminescence spectra with a simple model that takes into account the finite lifetime of the photobold remaining in the gold nanoparticle during the photoluminescence process and interaction between the nanoparticle and substrate [2]. It is found that the observed spectra were well reproduced by this model. From these results, we discuss the interaction between the gold nanoparticle and substrate on a femtosecond time scale. Additionally, we have carried out the X-ray photoelectron measurements for the dodecanethiol-capped gold nanoparticles. We discuss the chemical states of the present gold nanoparticles from detailed analyses of spectra.


---

**SESSION W10: NOVEL STRUCTURES**

**W10.1**

**THE EFFECT OF INTERFACIAL VISCOSITY ON THE KINETICS OF FORMATION OF SILVER NANO PARTICLES IN WATER-OIL MICROEMULSIONS AS NANOREACTORS.** D.O. Shah, R.P. Bagwe and B.S. Purohit, Center for Surface Science and Engineering, Research Engineering Center for Particle Science and Technology, Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, FL.

Silver nanoparticles were prepared by the method of mixing of two microemulsions having similar chemical composition but different reactants in their respective aqueous core. One microemulsion contains silver nitrate in the aqueous core and other contains sodium hydroxide. The silver nanoparticles formed were characterized using UV-visible absorption spectra and TEM micrographs. The effect of addition of Arched-20 to the AOT/HpgEnv microemulsion (keeping total molar concentration of surfactant fixed) on particle size and absorption spectra of silver nanoparticles was studied. TEM photographs showed agglomerated and bigger particles increase of pure AOT whereas addition of Arched-20 showed dispersed and smaller particles. Reaction kinetics was observed for silver nanoparticles using UV-visible spectrophotometer. Silver nanoparticles show characteristic absorption band near 400 nm region. Silver nanoparticles prepared using pure AOT surfactant showed plasmon band (416 nm) immediately after preparation and the intensity of the band decreases with time due to agglomeration of particles. No absorption band of silver nanoparticles was observed for mixed surfactant microemulsion of AOT and Arched-20 for few hours indicating the reaction kinetics is slowed down upon addition of Arched-20. This observation can be explained using the concept of rigidity of surfactant film at the air/water interface. It is proposed that higher the interfacial viscosity, slower is the coalescence rate of nanodroplets in the microemulsion system. Higher rigidity of the mixed film of AOT and Arched-20 is further supported by the QELS studies on the diffusion measurements of droplets as a function of concentration of water. Keywords: silver nanoparticles, AOT, Arched-20, microemulsion, plasmon band, interfacial fluidity, molecular packing in mixed surfactant film, reaction kinetics.

---

**W10.2**

**TIN OXIDE \(\text{SnO}_2\) NANO WIRES, NANO DISKETTES, NANO TUBES, AND NANO STRUCTURES SUPPORTED ON SILICA NANO SPHERES.** J. L. Gole,† Z. Rong Da,† J. D. Stout,‖ and Z.L. Wang.‡ George Institute of Technology, Athens, GA.

Two unique syntheses have been used to generate \(\text{SnO}_2\) nanowires, nanotubes, and nanodiskettes. Crystalline nanowires which display both a rutile and orthorhombic structure are formed from high temperature synthesis with \(\text{SnO} + \text{SnO}_2\) and \(\text{Sn} + \text{SnO}_2\) mixtures. Several of the wires display phase transformations between the rutile and orthorhombic crystal structures. Similarly, under somewhat different experimental conditions nanotubular structures also displaying contained rutile and orthorhombic structures are obtained. With additional modification, it has been possible to synthesize larger \((\sim 200 \text{ nm})\) nanodiskettes and channelled nanotubes which appear to display a crystalllographic structure. The latter tubes with their near cubic cross sections may contain \(\text{SnO}_2\) diskettes and thus might be used as nanoreactors. A single step mixed \(\text{SnO}/\text{SiO}_2\) synthesis has been used to form silica nanospheres decorated with \(\text{SnO}_2\) nanocrystals. Partially agglomerated \(\text{SiO}_2\) nanospheres of diameter \(\sim 45 \text{ nm}\) have been used as nanosupports (substrates) for \(\text{SnO}_2\) crystallites of diameter \(3-6 \text{ nm}\). The ability to disperse these extremely small \(\text{SnO}_2\) nanocrystallites on a nanostructured silica substrate can have important consequences for future sensor technology. In addition, they might play an important role in advanced acid catalysis and in the detection of algicines.

---

**W10.3**

**3D HIGHLY ORIENTED ARRAY OF METAL OXIDE NANO- TO MICROPARTICULATE MATERIALS.** L. Nogues, J.C. Guo, J. Nordgren, Univ. of Physical Chemistry, Uppsala, SWEDEN.

A novel concept has been developed in order to create a new generation of smart and functional materials [i.e. purpose-built nanomaterials], modeled, designed and engineered to match the physical and structural requirements of their applications. This concept, well-sustained by a thermodynamic model, monitoring the nucleation, growth and aging process through the control of the interfacial free energy of the system allows to control the particle size.
and its surface morphology as well as the ability to thermo-
dynamically stabilized metastable crystal phases. The experimental
collection of such concept for the thin film processing of metal oxide
materials is of great interest both for fundamental and applied
research purposes since the influence of parameters such as particle
size, shape and orientation as well as the overall film texture and
crystallinity of various transition metal oxides on their physical properties
may be probed and demonstrated. Moreover, designing well-controlled
materials allows tuning and optimizing the physical properties of
current devices as well as the ability to create novel and improved
devices. The synthesis and surface growth synthesis allows to generate, at large scale and low-cost, novel
design and well-ordered metal oxides to micro- and nanoparticulate thin
film materials with a complex architecture such as, for instance, 3D
crystallization of various oriented nanocrystals on ferroelectric oxide films (hematite and akaganite), 3D crystalline arrays of highly oriented nanocrystals,
nanocrystals and microstructures of ZnO (zinc) grown on various
substrates such as glass, conducting glass (TCO), single crystalline
sapphire as well as silicon and silicon dioxide wafers.

9:30 AM W10.4
CHEMICAL APPROACHES TO THE LARGE-SCALE SYNTHESIS OF MONODISPERSED NANORODS
Brian Myers, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA

We have demonstrated solution phase approaches based on
homogeneous nucleation and controlled growth to the synthesis of
monodisperse nanorods from a variety of materials (such as Si, Te,
Se,Sn alloys, and metals). The internal dimensions of these nanorods
could be tightly controlled between 50-300 nm, with their lengths
ranging from 100 nm to several micrometers. These spherical
nanoparticles are ideal components for fabricating composite materials
that may exhibit photoconductive and piezoelectric properties. In this
presentation, we will discuss the mechanism (as revealed by our SEM
and TEM data) and the formation of monodisperse nanorods, as well as some preliminary measurements on their properties.

10:45 AM W10.5
FORMATION OF FERROMAGNETIC Ni/SiO2 NANOSPHERES
S.M. Prokes, W.E. Carlos, Naval Research Lab, Washington, DC; Toward Siah, Stephen Lewis, and James L. Gole, Georgia Institute of Technology, Atlanta, GA

Recently, it has been demonstrated that the formation of
semiconductor nanorods and oxide-based nanocrystals can be achieved by
crystallization in solution, which, as a function of experimental
conditions, can be made to produce a variety of nanospheres and
nanowires. We have produced SiO2 nanospheres, having an average 30
nanometer diameter, which have then been nickel plated using an electrowet plating solution consisting of Nickel chloride, Ethylene diamine, Sodium hydroxide and Sodium borohydride. Magnetic Resonance
(MR) experiments performed on these samples indicate the presence of Ni(II)
paramagnetic centers, which are most easily seen below 40K, and the formation a ferromagnetic metallic Ni coating, which can be
readily seen above 100K and at room temperature. These MR results indicate only the presence of paramagnetic Ni in the spin
plagging solution that does not contain any SiO2 nanospheres. Using the
AFM technique, the presence of Ni has also been confirmed by
August-Elbert Electron Spectroscopy. Substantial amounts of oxygen
drawn from the KI transition) have also been detected, due to the
SiO2 and the organic present in the electrowet plating solution. These
results suggest that an interfacial reaction at the surface of the
SiO2 nanospheres leads to the formation of ferromagnetic Ni, which
then deposits onto the SiO2 spheres and forms a room temperature
ferromagnetic Ni/SiO2 nanosphere composite.

10:15 AM W10.6
NANOCONTAINERS FOR NANOPARTICLES
D.M. Speckman, T.L. Jennings, and N. Presser, The Aerospace Corporation, Los Angeles, CA

Derivation of semiconductor nanocrystal surfaces with organic
functional groups can impart unique physical and chemical properties
to the nanocrystals. For example, semiconductor nanocrystals can be
made water-soluble by the condensation of these molecules onto the
nanocrystal surfaces. Furthermore, surface passivation by organic
ligands can significantly enhance the quantum yield of luminescent
nanocrystals. Accurate characterization of the organic functional
moieties on these self-assembled nanocrystals is important to
understanding the chemical techniques such as infrared spectroscopy is often not possible however,
since it is difficult to obtain purified samples of the derivatized
nanocrystals. We have shown that organic functionalized nanocrystals are
typically dispersed in solvent mixtures containing excess quantities
of these organic reactants used to functionalize and/or passivate the
surface, and hence the unbound organic layers interfere with signals due
to nanocrystalline organics. In order to accurately characterize
organic-functionalized nanocrystals, methods must be developed to

10:30 AM W10.7
NANOCOATING ON POWDERS FOR COLLOIDAL CERAMIC PROPERTIES
EXPERIMENTS AND SIMULATIONS
W.Y. Shih, C.-Y. Yang, H. Gu, and W.-H. Shih, Drexel University, Dept.
Materials Engineering, Philadelphia, PA

Surface modification on ceramic powders can lead to better rheological and consolidation behavior of aqueous suspensions. It is also a tool to control the reactions between different components in a powder mixture. We examined the sol-gel nanocoating on ceramic powders and its effects on colloidal processing. Examples including boehmite coating on SiC for improved rheological and consolidation properties and Mg(OH)2 coating on Nb2O5 for pyrophosphate precursor PMN will be shown. The coating process was also studied using Monte Carlo simulations. Under conditions where precipitated particles of the coating species exhibited repulsive interactions, we identified an important ratio, Ew, where Ew is the ratio of the energy between the coating species and -Ew the attraction energy between the coating species and the core particle surface. Three different regimes were categorized with respect to E/Ew. With E/Ew > 1, the coating was patchy and the coverage decreased with increasing E/Ew. With E/Ew ~ 1, coating could be patchy or continuous and the coverage increased with decreasing E. With E/Ew < 1, the core particle surface was fully covered with a continuous shell-like coating. These results will be compared with experiments.

10:45 AM W10.8
SIZE AND COMPOSITION EFFECTS IN THE STRUCTURE AND PROPERTIES OF POLYMER-PROTECTED BI-METALLIC NANO PARTICLES
Marie-Jose Castano, Pierre Lecante, Marie-Claire Fromen, CEMES, CNRS, Toulouse, FRANCE, Fabrice Desanvoy, Fritz Haber Institute, Berlin, GERMANY, Marc Reugnet, LITMC, Toulouse, FRANCE, David Zitoun, Catherine Amiens, Bruno Chaudret, LCC, CNRS, Toulouse, FRANCE

Nanometer size metal particles, well-known to exhibit unique physical
and chemical properties, are playing an more and more important role in
catalysis, magnetism and micro-electronics. Bimetallic particles present a particular interest both from a technological and a fundamental points of view. Indeed, the combination of size reduction and alloying with a 3d element like cobalt can induce a spin
polarization in 4d metals. Addition of a second element can also improve the activity and/or selectivity of metal catalysts. Besides, bimetallic particles may offer the opportunity to study combined size, composition and segregation effects in binary alloys, as well as to investigate modified phase diagrams. Addressing the chemical and/or
physical properties of bimetallic clusters requires an accurate control of size, dispersion and composition, which means a reliable synthesis,
as well as a precise determination of the corresponding structure, which in turn implies the use of appropriate structural techniques. We
investigate the structural evolution of Pt-Ru, CoRh and CoRu ultrasmall bimetallic particles as a function of the composition in the whole range of stoichiometry. The particles are synthesized by simultaneous deposition of organometallic precursors in the presence of a stabilizing polymer. Their size, dispersion and structure are analyzed using high-resolution transmission electron microscopy, wide angle x-ray scattering and extended x-ray absorption fine structure techniques. Well-dispersed particles with narrow size distribution ranging from 1.5 to 2.5 nm were obtained in the different alloys. The size of Ru on the surface of the CoRh nanoparticles is evidenced. In the Pt-Ru alloys, we demonstrate the role of composition in the structural transition from the face
centered cubic to the hexagonal close packed structure in nanoscaled particles and we detail the mechanism of this transition. We point the effect of size reduction and alloying in the structure and enhanced magnetization in CoRh particles.
Gold nanorods are prototype wires for nanoelectronics. Particularly interesting is the fact that the surface plasmon resonance of the conduction electrons can provide information on the rod aspect ratio and mechanical properties. We demonstrate that laser heating induces bending of the rods, with a characteristic frequency, lower than that of the breathing mode. We also show how electric charge can direct rod growth, which opens up the possibility to grow designer nanowires.

11:15 AM W10.10
CONTROL OF INJECTION TO REALIZE HIGH-DENSITY SI QUANTUM DOTS ON SiO2 THIN FILMS Jiansong Zhai, W. Thomas Lench and John G. Ekerdt, Dept of Chemical Engineering, The University of Texas at Austin, TX

Predeposition of amorphous Si by hot-wire CVD is found to facilitate the nucleation of Si quantum dots on SiO2 thin films, which were subsequently grown by conventional UHV-CVD using disilane. Growth without predeposition, the density of the Si quantum dots is considerably increased and their size distribution is narrowed. The dot density and size can be controlled by the amount of predeposition. High density ($9.5 \times 10^{10} \text{cm}^{-2}$) and small size (5.5 nm) Si quantum dots were realized. The mechanism for dot nucleation by this method will be discussed. Results on dot growth and dot coalescence in the subsequent UHV-CVD step will also be presented.

11:30 AM W10.11
SYNTHESIS AND APPLICATION OF NANOPOROUS DAM-1 MATERIALS. Kenneth J. Balkus, Jr., Decio Coutinho, Sudhin Madanagari, Claudia Meek and Paul Fantone, University of Texas at Dallas, Department of Chemistry, Richardson, TX.

Vitamin E TPGS has been used to template the synthesis of mesoporous silica, alumina and other metal oxides which we refer to as Dallas Amorphous Materials (DAM-1). By controlling the synthesis variables, the DAM-1 particles can be prepared in several geometries and sizes including hexagons, gyroids, discoids, spheres and fibers. Novel applications that exploit the unique shapes of these particles will be described. In one case, a noncovalent drug delivery system based on a microwell array etched or the distal face of an optical fiber bundle was developed. DAM-1 particles have been deposited into the microwell, where each individual particle can be optically addressed. A pH sensor based on this array will be described. DAM-1 has also been prepared as patterned thin films using a combination of pulsed laser ablation and novel line patterning process. Additionally, a new process for the spinning of DAM-1 and related molecular siee nanofibers will be presented.

11:45 AM W10.12
THE EFFECT OF NANOCRYSTALLINE GRAIN SIZES IN [82 MOE. %] YTTRIA STABILIZED ZIRCONIA ON THE TETRAGONAL PHASE STABILITY. Arav Suresh, Merril J. Mayo, The Pennsylvania State University, Dept. of Mat&Eng, University Park, PA; Wallace D. Porter, Claudia J. Raven, High Temperature Materials Lab, Oak Ridge National Lab, Oak Ridge, TN.

It has long been observed that the melting points of metals change with particle size. This can be attributed to the interfacial energy of the solid, which contributes to the total free energy of the system, thereby changing the thermodynamics of melting (phase transformation) and leading to a "size effect". Similar effects of interfacial energy are expected and seen in solid-state transformations. High temperature phases below a critical size can be stabilized to room temperature if the surface energy difference between the high temperature phase and the room temperature phase is negative. Surface tension effects have been invoked to explain the room-temperature stabilization of the high temperature phase in some other systems, e.g., TiO$_2$, ZnSe, rutile, Bi$_2$Ti$_3$O$_9$, cubic tetragonal, Al$_2$O$_3$, Al$_2$O$_3$, $\alpha$-Al$_2$O$_3$, etc. In the present study, the effect of particle size on the tetragonal $\rightarrow$ monoclinic phase transformation in yttria-doped zirconia was examined. The monoclinic stability was important in the zirconia system, as the tetragonal phase has to be retained as service temperature for increased fracture toughness by transformation toughening. By varying the grain size and the yttria content of nanocrystalline zirconia samples and carrying out dilatometry, high temperature DSC and HTXRD we were able to determine the phase stability region of the tetragonal phase. The T-M phase transformation temperature was seen to vary linearly with inverse particle size. The shift of the yttrium oxide phase diagram with particle size is also predicted by thermodynamic analysis. Transformation temperatures were calculated from the change in chemical free energy, interfacial energy and strain energy of the T-M transformation. Critical grain sizes below which the tetragonal phase is stable at room temperature were determined to be 7nm, 100nm, 177nm for 0.5, 1.0, 1.5 mol% Y$_2$O$_3$, ZrO$_2$, respectively.

SESSION W11: MEDICAL APPLICATIONS
Chair: Dimitri O. Shahe and Nobuyuki Krume
Thursday Afternoon, November 29, 2010
Back Bay B (Sheraton)

1:30 PM W11.1
ULTRATHIN COATINGS FOR PULMONARY DRUG DELIVERY. Gianluca Hochstanger, Jiwoon Ko, Wook Seok Kim, Valentina Crociu, Rajeev Singh, Departments of Pharmaceutics and Materials Science and Engineering, University of Florida, Gainesville, FL; James Talton, Nanosphere Inc. Alachua, FL.

Pulmonary drug delivery is gaining therapeutic importance for systemic and topical drug delivery. Previous theoretical work has shown that the therapeutic performance of such formulations can be improved if the drug is released in the lung with slow release characteristics. We have evaluated the use of pulsed laser deposition (PLD) of biodegradable polymers as a means of introducing ultrathin coatings on drug particles with slow release properties. Rationale for developing this PLD technology is to modulate the biopharmaceutical characteristics of inhalation dry powders (such as the pulmonary residence time and the degree of pulmonary selectivity) with minimal polymer load, the absence of wet chemistry and minor changes in the inhaled efficiency of these powders. Work will be presented that describes the suitability of pulsed laser deposition of biodegradable polymers for drug delivery and evaluates the relationships between laser ablation conditions and their resulting biopharmaceutical properties.

2:00 PM W11.2
SURFACE MODIFICATION OF SUPERPARAMAGNETIC NANO PARTICLES FOR IN VIVO BIO-MEDICAL APPLICATIONS. Do-Kyung Kim, Muhammet S. Toprak, German Salazar-Alvarez, Mauro Michielon, Mahmoun Muhammed, Materials Chemistry Division, Royal Institute of Technology, Stockholm, SWEDEN.

Recently, there is a growing interest in colloidal superparamagnetic nanoparticles for many important bio-medical applications including MRI, MR imaging is especially used to increase compuacity of adjacent internal organ and tissue. Also, superparamagnetic nanoparticles can be used to monitor extracellular macromolecules both at single cell level (genes and proteins) and network level (intercellular communication), by in vivo monitoring of particle movement in the living brain tissue. For this kind of bio-medical applications, narrow size distribution and surface modification with biocompatible material are demanded. Based on computer-assisted chemical equilibrium calculations, several optimum operation conditions for coprecipitation process were predicted and magnetic nanoparticles have been prepared under N2 flow to protect the chemical oxidation. In this way, monocrystalline nanoparticles of Fe$_3$O$_4$ with size of few nanometers have been synthesized. These particles were further coated by ultra-thin films of PVA, Dextrin, Dextrin, PEG and MPEG to obtain a biocompatible particle surface for further functionalization purposes. The effect of surface modification of the superparamagnetic nanoparticles in terms of chemical and physical properties of the samples were investigated with several techniques including microelectrophoresis measurement. The feasibility of using superparamagnetic nanoparticles was investigated by in vivo treatment in rat brain.

2:15 PM W11.3
DEVELOPMENT OF NANOFORMULATIONS: BULK CHARACTERISTICS OF DRUG NANO PARTICLES. Janghui Lee and SanjibParti Pramanik, Department of Pharmaceutical Research and Development, Meek Sharp and Dolame Research Laboratories, West Point, PA.

The particle size of a drug is one of the important parameters that needs to be controlled for proper drug delivery. The preparation of nanoparticles of active ingredients is a convenient method to increase their dissolution rate when they have limited solubility. In this study, nanoparticles of a relatively hydrophilic drug were prepared by wet milling (mean particle size < 200 nm), and three-point bending (3PB) specimens were prepared by wet compaction. Their physical properties were compared with two types of microparticulate (mean particle size = 10-100 micron) systems, one from direct compaction and the other from wet compaction. The 3PB test data show that nanoparticulate systems have significantly higher modulus and stress to break than the other two systems. Linear elastic and brittle failure behavior could be observed in all three systems. However, the differences in scanning electron microscopy and X-ray diffraction data revealed that there is significant difference to the crystallinity of drugs by milling.

2:30 PM W11.4
NEW POSSIBILITIES FOR CHEMICAL SEPARATIONS USING MAGNETIC nanoparticles WITH TAILORABLE SURFACES. Seyda Bucak, Geoff Aitcheson, Lifen Shen, T. Alan Hatton, 466
Magnetic nanoparticles consisting of stable colloidal suspensions of magnetite nanoparticles with tailored surfaces provide opportunities in chemical separations. Chemical precipitation to form magnetic nanoparticles with diameters of 8 to 12 nm provides a flexible approach for designing dispersive and readily recoverable nanoparticles that are coated by a molecular or polymeric layer. The composition of this layer affords a high surface area colloid suspension, essential for the separation of a wide range of magnetic nanoparticles exposing charged surfaces with tunable charge densities, polymeric films of varying hydrophobicities, and molecular films expressing chiral surfaces. The particles have been characterized using a range of techniques including SANS, TEM, HR-TEM, DSC and used for separating proteins, hydrophobic compounds, and chiral species. Magnetic filtration provides an efficient means for removing the nanoparticles and any adsorbed species present in their suspension medium.

3:15 PM W11.5
CELLULAR RESPONSE TO NANOPARTICLES. Sonya Shortkroff, Mary Beth Turell, Karen Rice, Thomas Thornhill, Dept. of Orthopedic Surgery, Brigham and Women’s Hospital, Harvard Medical School, Boston, MA.

Recent developments in nanotechnology have the potential to significantly impact the biomedical field. Nano-structures are being investigated as coatings and as composites for implantable materials. Because of their nanometer size, these structures have unique mechanical properties that may revolutionize ophthalmic, cardiac, orthopedic and dental implant materials, drug delivery systems and the field of tissue engineering. One such nanocomposite utilizes nanometer sized BaSO₄ particles to optimize the properties of polymethyl methacrylate (PMMA), a cement used for orthopedic implants. BaSO₄, a relatively insoluble salt, is a radiopaque agent that permits radiographic assessment of the stability of the implant over time. By decreasing the average size of the particles from 1-2 μm to 0.1 μm and applying sodium citrate coating, the nanoparticles increase the fatigue characteristics of PMMA and are more uniformly dispersed throughout the PMMA. While studies have found the micron sized particles to be inert and biocompatible, the effects of highly charged nanoparticles on cells has not been addressed. The unique properties conferred on these nanometer-sized particles and constructs may affect the cellular and tissue biocompatibility of the materials. The response of three cell types, fibroblasts, macrophages and osteoblasts, were investigated. Cells were incubated for 24 h in the presence of various concentrations of micro- and micron sized particles of BaSO₄. To determine the effects of the coating, nanoparticles with and without sodium citrate were evaluated. The cell culture media was analyzed for induction of an inflammatory response by release of cytokines, IL-1, IL-6 and TNFα. The effects of nanomaterials on viability and proliferation and induction of apoptosis also were investigated. Particle size, volume and number were considered for these studies and will be discussed.

3:30 PM W11.6
MECHANISM OF CRACK PROPAGATION AND FRACTURE TOUGHNESS OF PMMA-BARIUM SULFATE NANOCOMPOSITE BONE CEMENT. Mary Beth Turell, Heino Schmalzrieder, Wolfgang Fütz, Richard D. Scott, Thomas S. Thornhill, Anna Beller, Department of Orthopedic Surgery, Brigham & Women’s Hospital, Harvard Medical School, Boston, MA.

Polyethylene methacrylate (PMMA) based orthopedic bone cement contains 8-10 weight % barium sulfate particles of approximately 1 micrometer diameter to enable orthopedic surgeons to monitor cement fracture using x-ray radiographs. Incomplete dispersion of barium sulfate particles in the PMMA matrix leads to the presence of large agglomerates, which reduce its toughness, thereby leading to loosening of cemented joint replacement prostheses. In this study, the 1 micrometer size barium sulfate was replaced using 100nm and 50nm size barium sulfate. To determine the effects of the coating, nanoparticles with and without sodium citrate were evaluated. The cell culture media was analyzed for induction of an inflammatory response by release of cytokines, IL-1, IL-6 and TNFα. The effects of nanomaterials on viability and proliferation and induction of apoptosis also were investigated. Particle size, volume and number were considered for these studies and will be discussed.

3:45 PM W11.7
QUANTITATIVE AND REVERSIBLE LECTIN-INDUCED ASSOCIATION OF GOLD NANOPARTICLES MODIFIED WITH α-LACTOSYL-α-MERCAPTOPOLY(ETHYLENE GLYCOL). Hidemori Otsukawa, Nanomaterials Research Center [NARC], National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, JAPAN; Yukio Nagai, Department of Materials Science and Technology, Science University of Tokyo, Nofta, Chiba, JAPAN; Yoshitaka Akiyama, Kansui Kozuka, Department of Materials Science, Graduate School of Engineering, The University of Tokyo, Tokyo, JAPAN.

Our strategy to synthesize various types of hetero-bifunctional poly(ethylene glycol) (PEG) is based on the ring-opening polymerization of ethylene oxide using a metal alkoxide initiator with a protected functional group. Specifically, synthesis of heterofunctional PEG containing both mercapto and acetal terminal groups (α-acetals-mercapto-PEG; acet-PEG-SH) was recently reported. The acetal moiety can readily be transformed into a reactive aldehyde group by simple treatment with dilute acid. Gold nanoparticles (1-10 nm size range) were prepared with an appreciably narrow size distribution by in situ reduction of HAuCl₄ in the presence of α-acetals-mercapto-PEG. The α-acetals-PEG layers formed on gold nanoparticles impart appreciable stability to the nanoparticles in aqueous solutions with elevated ionic strength and also in serum-containing medium. The PEG acetal terminal group was converted to aldehyde by gentle acid treatment, followed by the reaction with p-aminophenyl-β-D-glucopyranoside (Lac) in the presence of CuCl₂/NH₄OH. Lac-conjugated gold nanoparticles exhibited selective aggregation when exposed to recombinant agglutinin (RCA120), a bivalent lectin specifically recognizing the β-D-glucoside residue, inducing significant changes in the absorption spectrum with concomitant visible color change from pinkish red to purple. Aggregation of the Las-functionalized gold nanoparticles by the RCA120 lectin was reversible, recovering the original dispersed phase and color by addition of excess galactose. Further, the degree of aggregation was proportional to lectin concentration, allowing the system to be utilized to quantitatively link concentration with nearly the same sensitivity as ELISA. This simple yet highly effective derivatization of gold nanoparticles with heterofunctional PEG provides a convenient method to construct various colloidal sensor systems currently applied in bioscans and biocollection.

4:00 PM W11.8
BIOMIMETIC FABRICATION OF SILVER NANOCRYSTALS. Sarah J. Stringer, Rakesh R. Naik, Sharon E. Jones, and Morley O. Stone, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

Biomimetic approaches for material synthesis is an alternative design route for nanoscale materials. Many biological systems are capable of synthesizing nanoparticles from inorganic materials such as silica, silver, and ferric oxide. Isolation of the organic molecules involved in these processes may provide a route to the creation of hybrid materials. Proteins that recognize inorganic surfaces could be used as templating or enzymatic agents for controlled material synthesis. Using a commercial phase peptide display system, we were able to isolate peptide sequences that specifically bind to silver particles. Both the phase particles displaying the silver-specific peptide as well as a synthetic peptide based on phase-displayed peptide sequence are able to catalyze the formation of silver nanocrystals from a dilute solution of silver nitrate. Here we will present results on the selection of silver-specific peptides and characterization of the silver nanocrystals. Currently, we are investigating ways of patterning the peptides for possible future applications in bottom-up fabrication approaches.

References: