

**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

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\* Invited paper

SESSION W1: WET PROCESSING  
Chair: Brij M. Moudgil  
Monday Morning, November 26, 2001  
Back Bay B (Sheraton)

**8:30 AM \*W1.1**

**DISPERSING NANOPARTICLES: DEAGGLOMERATION AND STABILISATION OF CONCENTRATED SUSPENSIONS.**  
Lennart Bergstrom, 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 require a 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 deagglomerating and stabilizing nanoparticles. It will be shown how successful deagglomeration of the individual crystallites of a silicon nitride powder down to nanosized dimensions result 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 optimisation 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. Stabilization of nanosized titania particles in ethanol will be presented and the results will be discussed in the context of DLVO theory.

**9:00 AM \*W1.2**

**DISPERSION OF NANOPARTICULATE SYSTEMS USING SELF-ASSEMBLED SURFACTANT AGGREGATES.**  
Brij M. Moudgil, Pankaj K. Singh, Madhavan Esayanur, Joshua J. Adler, Yakov I. Rabinovich, Engineering Research Center for Particle Science and Technology, University of Florida, Gainesville, FL.

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 salt (CMP, biofluids in medical applications), high pressure (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 nanoparticles 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 micelle. Techniques such as adsorption, contact angle, zeta potential, and polarized Attenuated Total Reflection Fourier-Transform Infra-Red 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 W1.3**

**FACILE ROUTINE TO NANOALLOY PARTICLE DOPED IN POROUS SILICAS.** Bao-Hang Han, Markus Antonietti, Max-Planck Institute of Colloids and Interfaces, Potsdam, GERMANY.

We have reported a facile synthesis of metal-doped porous silica using cyclodextrins as template for nanocasting procedure. The advantages lie on that cyclodextrins not only act as template for microporous structures, but also introduce the organometallics (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 silicas. In this presentation, we will report the synthesis of nanoalloy particles doped in porous silicas. Two and/or more different organometallic (Pd, Pt, Ru, Ir, Mo, W, Ti, Zr, etc.)-cyclodextrin complexes can fully mix at molecular level in aqueous solution. After templating in sol-gel process, the metal precursors are homogeneous dispersed in the as-synthesized silica materials. Upon calcinations, alloy particle in nanometer scale are formed and doped in the porous silicas, 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 W1.4**

**DISPERSION CHARACTERIZATION OF MECHANOCHEMICALLY SYNTHESIZED NANOPARTICLES USING UV-VIS SPECTROSCOPY.** Takuya Tsuzuki, Paul G. McCormick, Advanced Nano Technologies Pty Ltd, Welshpool, AUSTRALIA.

Nanoparticulate materials exhibit properties that substantially differ from those of bulk materials as a result of particle dimension, surface area, quantum confinement and other effects. Many of these unique properties require not only the powder particles to be of nanometre 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 nanoparticulate systems. There are several techniques for the size/agglomeration characterization of nanoparticles smaller than 50 nm, e.g., photo correlation spectroscopy (PCS), electron microscopy (EM), BET specific surface area analysis (BET), and small angle X-ray scattering (SAXRS). However, these methods have drawbacks: PCS requires extremely diluted particle suspension; EM leads to selective measurements; BET and SAXRS 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 discusses the dispersion characterization of nanoparticles using UV-Vis spectroscopy. ZnO, CeO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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 W1.5**

**NANOPARTICLE AGGLOMERATION DURING DRYING STUDIED BY USAXS AND FESEM.** Andrew Allen, NIST, Materials Science and Engineering Laboratory, Gaithersburg, MD; Alejandro Vertanessian, Merrilea Mayo, Pennsylvania State University, Department of Materials Science and Engineering, University Park, PA.

Agglomeration 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 those agglomerates evolve. The problem is acute in the nanoparticle size regime, where heightened powder dissolution and diminished electrostatic repulsion are strong drivers for agglomeration during drying. The agglomerate shape and size evolution during the drying of different nanocrystalline zirconia powder suspensions has been studied by ultrasmall-angle x-ray scattering (USAXS) and field emission scanning electron microscopy (FESEM). 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 charge. Away from the isoelectric point, large, fractally-rough agglomerates are observed by USAXS, likely produced by "reaction-limited" aggregation, and partly composed of short, entangled chains of primary particles. Near pH 8, where electrostatic repulsion is minimized, 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 USAXS. For example, for powders dried at high pH, micrometer-thick lamellae and grains with lamellar sub-structure 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  
Monday Morning, November 26, 2001  
Back Bay B (Sheraton)

**10:30 AM \*W2.1**

**LOCAL MAGNETIC MEASUREMENTS AT A NANOSCALE ON MAGNETIC, MECHANICAL, AND BIOLOGICAL SYSTEMS USING MODIFIED AFM.** K.V. Rao, Dept of Matls Sci-Tmfy-MSE, The Royal Inst of Tech, Stockholm, SWEDEN.

Non-invasive techniques to study 'in-situ' materials properties of advanced nanostructured materials are a necessity and of great interest for the emerging technologies of the next decade. In this presentation we exploit the capabilities of atomic force microscopy to investigate: 1) local magnetostriction and domain observations at atomic scales by measuring induced surface roughness of Co-magnetic dots (150-350 nm range diameter) patterned on Silicon substrates [1], 2) The local sticking coefficient variations on a composite material consisting of TiN inclusions in an Alumina matrix, 3) Domain configuration in pulsed laser deposited films of rhombohedral  $\text{PbZr}_{0.65}\text{Ti}_{0.35}\text{O}_3$ , [2], and 4) magnetic flux reversal phenomenon in biomineralized magnetotactic bacteria in which the chains of magnetic nanoparticles play an important functional role [3] In order to understand the above we have suitably modified our atomic force microscopy wherein the samples are appropriately activated by using external fields in order to monitor its response at the fundamental and harmonic frequencies of excitation. Some of the highlights of our studies are: 1) Rather large values are observed for the magnetostriction in Co-dots which is sensitive to the position in the dots as well as the dot size. 2) The size and the separation distance among the dots, in the range 150 to 350nm, provide information on the domains, domain wall widths, and possible interactions among the neighbouring dots in the matrix. 3) In the case of the ferroelectric films the domains were detected registering the electromechanical response of the films in the presence of a low ac field. A direct correlation between the unexpected polydomain configuration and the microstructural feature in the as deposited films has been established. 4) In biomineralized magnetotactic bacteria the chains of magnetic nanoparticles are found to play an important functional role. The size and the Fe-content of these nano-entities give rise to domain structures in them and thus effect the flux reversal process. Studies on novel model systems, with properties described above, using simultaneously information available from magnetic force-, and modified atomic force microscopies on the same material will also be presented.

In cooperation with J. Wittborn, Josep Nogués, Ivan K. Schuller, and Dan Dahlberg and his group at Univ of Minnesota.

[1] to appear in Applied Physics Letters, Vol 76 May 15 issue 2000.

[2] Applied Physics Letters 74, 3191 (1999).

[3] NANOSTRUCTURED MATERIALS 12, 1149 (1999) -Proc NANO98.

#### 11:00 AM W2.2

PHASE TRANSFORMATION, COALESCENCE AND TWINNING OF MAGNETIC FePt NANOCRYSTALS. Z.R. Dai, Z.L. Wang, Center for Nanoscience and Nanotechnology, School of MS&E, Georgia Institute of Technology, Atlanta, GA; Shouheng Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Depending on the Fe to Pt elemental ratio, the Fe-Pt alloys can display chemically disordered face centered cubic (fcc) phase (A1 Fm -3 m) or chemically ordered phases. The structural variation has dramatic effect on the magnetic properties of the alloys. Recently, monodisperse FePt nanocrystals with good control on particle size and composition were produced by a solution phase chemical procedure. We report detailed microscopic studies on phase transformation, coalescence and twin structure formation of thermally annealed 6 nm FePt nanocrystals under high vacuum on an amorphous carbon surface. Our high-resolution transmission electron microscopy (HRTEM) studies show that A1 to L10 phase transformation occurs at 530°C. The multilayered nanocrystal assemblies coalesce to form larger grains at 600°C. We notice that the coalescent temperature of the nanocrystal monolayer assembly depends on the substrate used. On  $\text{SiO}_2$  surface, the FePt nanocrystal monolayer can stand up to 700°C without any obvious aggregation. The coalescent nanocrystals show dominant {111} twin defect inside, while their surface and coalescent grain boundary consist of both {111} and {001} facets.

#### 11:15 AM W2.3

NANOSTRUCTURED GOLD AND ALLOY NANOPARTICLE CATALYSTS. Chuan-Jian Zhong, Mathew M. Maye, Jin Luo, Yongbing Lou, Scott Kowaleski, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY; Maria 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 nanobalance (EQCN) and atomic force microscopy (AFM) investigations. The EQCN 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.

#### 11:30 AM \*W2.4

ON THE MECHANICAL STABILITY OF NANOSTRUCTURED COATINGS BY SYNCHROTRON RADIATION. Thomas Tsakalakos, I. Zakharchenko, Y. Gulak, Dept. of Ceramics and Materials Engineering, Rutgers Univ, Piscataway, NJ; M. Croft, Physics Dept., Rutgers University, Piscataway; Z. Zhong, J. Hestings and J.Z. Hu, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; R. Holtz, K. Sadananda, NRL, Washington, DC; R. Rigney, R. Brunhouse, Jr., R. Shroshire, A&A Company Inc., So. Plainfield, NJ.

We have been successful in the development of two new powerful techniques, the Scattered Intensity Tomographic Profiling (SITP) and the Energy Dispersive X-ray Diffraction (EDXRD), to probe internal stresses in inhomogeneous solids. This represents a major breakthrough in the field of nondestructive evaluation of localized and global strains in nano/polycrystalline materials for depths from a few micrometers to a few centimeters. We measured triaxial residual stress depth profiles, directly and accurately, using synchrotron light source methods. We performed control experiments using cantilever beam specimens, which verified the accuracy of our method. Examples of residual stresses profiles will be presented which include: blank steel specimens, grit blasted steels, the effects of Nanostructured Coatings on steel substrates. The results on WC/Co and  $\text{Al}_2\text{O}_3/\text{TiO}_2$  nanocoatings confirm the expectation of large distributions of compressive and tensile stresses. The correlation of the residual stress profiling to fatigue deformation processes will be also discussed. These findings might explain the different types of failure (crack modes) and the effect of fatigue strain tolerance recently reported for same type of Nanostructured Coatings. A critical comparison of internal stress distributions between nano and micro size grain coatings will be presented on specimens undergone a number of different deformation processes such as elastic, plastic, wear and fatigue. The great importance of this stress field profiling method lies in its ability to conveniently bridge a crucial gap in the lexicon of direct/non-destructive strain profilometry.

We gratefully acknowledge the support of the Office of Naval Research under grant #N000149910424. The authors wish to express their gratitude to Dr. A.K. Vasudevan for his meaningful suggestions, continuous support and encouragement. We gratefully acknowledge also the support of the Office of Naval Research under grant DURINT -MIT #N00014-01-1-0808.

#### SESSION W3: ELECTRONIC AND OPTICAL APPLICATIONS

Chairs: Rajiv Kumar Singh and Heinrich Hofmann  
Monday Afternoon, November 26, 2001  
Back Bay B (Sheraton)

#### 1:30 PM \*W3.1

APPLICATION OF DISPERSED NANO PARTICLES. Masaaki Oda, Tomoyuki Abe, Toshihiro Suzuki, Norimichi Saito, Hisashi Iwashige, Ghalip Kutluk, ULVAC Corporation, Nano-Particle Application Dept., Chiba-pref., 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 (gold, silver, copper) nano-particles (d-nano particle) are formed at 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 a form of solution or paste. D-nano-particles solution or paste can be baked at 200-300° to form metal thin films. These has been applied to PDP electrode repairing, coloring 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 NANOPARTICLES. T. van Buuren, C. Bostedt, N. Franco, J. Pitzko, L. Terminello, Lawrence Livermore National Laboratory, University of California, Livermore, CA; T.A. Callcott, Department of Physics, University of Tennessee, Dept of Physics, Knoxville, TN; D.E. Ederer, Tulane University, New Orleans, LA.

The scientific world is embracing all types of nanoscience and technology through the rapidly advancing work seen in the scientific community. For many of these material systems, knowledge of band gap widening and band alignment as a function of particle size, and surface termination 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 edge shifts and surface effects on a variety of nanostructured materials in order to better understand the electronic properties. The reduced dimensional materials characterized include diamond, Si<sub>1</sub>(1) and Ge nanoclusters 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 nanoparticles 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 passivation. We report on how the change in surface passivation effects the ratio of VB shift to CB shift in silicon nanoclusters and other systems and compare to recent theory. This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, and performed under the auspices of the U. S. DOE by LLNL under contract No. W-7405-ENG-48, and at the ALS, LBNL under Contract No. DE-AC03-76SF00098. C. Bostedt is supported by the German Academic Exchange Service DAAD. 1. T. van Buuren, L. Dinh, L.L. Chase, L.J. Terminello, Phys. Rev. Lett. 80, 3803 (1998).

#### 2:15 PM W3.3

ELECTRON FIELD EMISSION FROM NANO-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 several special properties such as higher field emission efficiency and lower optical absorption coefficient due to its smaller grain size and smoother as-grown surface than common CVD diamond films. In this paper, the electron field emission from nano-diamond films with a grain size of 5-60nm is studied. The nano-diamond films were prepared using a microwave plasma enhanced chemical vapor deposition system from 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<sub>2</sub>]/[N<sub>2</sub>+CH<sub>4</sub>+H<sub>2</sub>]. And the turn-on voltage for electron field emission increases following an increase in grain size of nano-diamond 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. Lindsay E. Pell, 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 nanowires [1,2]. The silicon nanocrystal synthesis uses a supercritical organic solvent (500°C, >140 bar) with dissolved capping ligands that sterically stabilize the nanocrystals; 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 size-monodisperse nanocrystals (<±10%) with robust surface passivation. The particles are crystalline and luminesce with quantum efficiencies on the order of 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 octanol, octanethiol or octene. As the nanocrystal size increases, the intensity of the vibronic structure decreases and eventually the spectra 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 nanoscale silicon. Single particle spectroscopy performed on a polydisperse sample 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 550-700 nm. The single particle PL blinks on and off before permanent photobleaching.

[1] J.D. Holmes, K.P. Johnston, R.C. Doty, B.A. Korgel, Science, 281,

1471-1473 (2000). [2] J.D. Holmes, K.J. Ziegler, R.C. Doty, L.E. Pell, K.P. Johnston, B.A. Korgel, J. Am. Chem. Soc., 123, 3743-3748 (2001).

#### 2:45 PM W3.5

LUMINESCENCE PROPERTIES OF MONODISPERSED SILICON NANOPARTICLES PREPARED BY PULSED LASER ABLATION IN INERT BACKGROUND GAS. Toshiharu Makino, Yuka Yamada, Nobuyasu Suzuki, Takehito Yoshida, Matsushita Electric Industrial Co., Ltd., Advanced Technology Research Lab, Kawasaki, JAPAN; Ikuro Umezu, Akira Sugimura, Konan Univ, Dept of Physics, Kobe, JAPAN.

We have observed both photoluminescence (PL) and electroluminescence (EL) of monodispersed silicon (Si) nanoparticles. It was clarified that the luminescence centers of PL were different from those of EL. Monodispersed Si nanoparticles have been synthesized using the sequential process system which has the ability for carrying out formation of nanoparticles by pulsed laser ablation 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 nanoparticles of nominal diameter between 3 and 7 nm with the geometrical standard deviation of 1.2. For the PL measurement, Si nanoparticles were deposited onto crystalline Si wafers. After exposing Si nanoparticles 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 spectra, we fabricated the light emitting diodes (LEDs). The active regions of the LEDs are Si nanoparticles of 4 nm diameter exposed to the air. As transparent upper electrodes, indium oxide (In<sub>2</sub>O<sub>3</sub>) thin films were covered onto the Si nanoparticles. An EL spectrum had a narrow bandwidth of 0.15 eV in near infrared region. The peak energy was 1.17 eV, which is higher photon energy than the band gap energy of bulk Si of 1.10 eV at room temperature. This EL spectrum should originate from quantum confinement effects of the monodispersed Si nanoparticles. 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 nanoparticles.

#### 3:30 PM \*W3.6

LASER CLEANING OF NANOPARTICLES FROM SOLID SURFACES. Y.F. Lu, L. Zhang, B. Luk'yanchuk, W.D. Song, W.J. Wang, M.H. Hong, W.Y. Zheng, and T.C. Chong, Laser Microprocessing Lab, Dept of Elect and Computer Eng and Data Storage Institute, National Univ of Singapore, Singapore, SINGAPORE.

Laser cleaning of micro- and nano-particles from solid surfaces has been extensively investigated as an alternative of liquid-based cleaning methods. Two types of laser cleaning techniques have been developed recently, relying on pulsed laser heating of the surface without or with the presence of a thin liquid coating. For dry laser cleaning, two cleaning models were established for removal of particles from substrate surfaces from the viewpoint of energy and force. For steam laser cleaning, a cleaning model was established for removal of particles from substrate surfaces with a thin liquid layer by taking Van der Waals force, capillary force, cleaning force, and chemical bonding into account. The models not only explain the influence of incident direction, wavelength, fluence on cleaning efficiency, but also predict the cleaning thresholds. The experimental results show that the laser cleaning efficiency increases with increasing fluence and pulse number, but does not depend on the repetition rate. Under laser irradiation, it is also observed that nanoparticles behave as spherical microcavities which support optical resonance. The optical resonance can lead to near-field emission of strongly-enhanced laser light in nanometer range. This near-field emission can reduce the laser fluence required to remove the particles, but tends to cause nanometer-size damages on the solid surfaces.

#### 4:00 PM W3.7

SYNTHESIS AND LUMINESCENT PROPERTIES OF NANO-PHOSPHORS. Thomas S. Copeland, Burt I. Lee, and Jason Qi, Clemson Univ, School of Materials Science & Engineering, Clemson, SC; S.A. Bukesov, A.V. Strel'tsov Saratov State University, Saratov, RUSSIA.

Green light emitting Mn<sup>2+</sup> doped Zn<sub>2</sub>SiO<sub>4</sub> and red light emitting Eu<sup>3+</sup> doped Y<sub>2</sub>O<sub>3</sub> phosphor nano-particles were synthesized by a hydrothermal method and by a sol-gel method combined with a furnace firing. All samples were prepared at various temperatures and times both with and without a polymeric surfactant in order to determine if the particle size is tailorable over a significant range. The particle size, measured using dynamic light scattering, was between 30 nm and 1 micron depending on conditions. The microstructure of the phosphor crystals by scanning electron microscopy confirm previous

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 58% during processing for the europium-doped yttria and 89% for the manganese-doped zinc silicate. Green and red photoluminescence (PL) and cathodoluminescence (CL), at 522nm and 614nm respectively, were observed from the synthesized phosphor particles under UV excitation and electron bombardment. Results show that the non-seeded 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 W3.8

**OPTICAL PROPERTIES METAL/OXIDE FILMS HAVING A TAYLORED NANOPARTICULATE DISTRIBUTION.** R. Serna, J.C.G. De Sande\*, A. Suarez-García, J. Gonzalo, C. N. Afonso, Instituto de Optica, CSIC, Madrid, SPAIN. \*E.U.I.T.T., U.P.M., Madrid, SPAIN.

Metal nanocrystals (NCs) embedded in dielectric matrixes exhibit special optical properties, which depend on the NC 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 these nanoparticulate materials has been 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 index-matching conditions in waveguide devices 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  $n = n_i k$ ) of specially tailored nanoparticulate thin films, and in particular to analyze the  $n$  behaviour. The films are formed by metal (Cu) NCs 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 average dimensions and distribution of the metal NCs are designed both by controlling the number of laser pulses on the Cu and  $Al_2O_3$  targets respectively. The Cu NCs 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% it is found that the extinction coefficient is non-negligible and shows a maximum around 590 nm related to the surface plasmon resonance. In the neighbourhood 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 NC size and distribution and will be discussed within the frame effective medium models.

#### SESSION W4/AA4: JOINT SESSION SELF ASSEMBLY

Chairs: Masaaki Oda and Mamoru Senna  
Tuesday Morning, November 27, 2001  
Back Bay B (Sheraton)

#### 8:30 AM \*W4.1/AA4.1

**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 mass 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 amphiphilic structure directing agents like detergents, we exploit evaporation accompanying coating, spraying, or printing to promote the self-assembly of micelles that spatially separate and organize organic precursors (sequestered within the hydrophobic micellar interiors) and inorganic precursors (organized around the hydrophilic micellar exteriors). 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 as well as (organic) polymer-silica nanocomposite films, particles and a variety of physically and chemically defined patterns, where we utilize such homogeneous silica/surfactant solutions as inks in rapid prototyping processes like micro-pen 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 photosensitive 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 simple route to hierarchically organized functional materials. Second, by using polymerizable 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 (polydiacetylene)/silica nanocomposite.

#### 9:00 AM W4.2/AA4.2

**ENGINEERING OF NANOPARTICLES FOR ADVANCED ARTIFICIAL HETEROGENEOUS 2D AND 3D STRUCTURES.** Mamoun Muhammed, Yu Zhang, Maria Mikhailova, Muhammet S. Toprak, German Salazar-Alvarez, 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 systems with nanometer features using self-assembly. Nanoparticles can be used for the fabrication 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 and shell structures, e.g., metallic core and oxide shell or the reverse. The selection of the composition and structure of the shell layer allows different chemistry to be conducted at the surfaces, e.g., inducing biocompatibility, enhanced electrical conductivity, or reactivity. By a proper combination of the chemistry at the surface of the particles and substrate, it is possible to achieve a spontaneous self-positional organisation of the particles on the substrate to form stable 2D and 3D structures. In this talk, a presentation of some of our recent results on the fabrication and self-assembly of composite nanoparticles will be presented together with some examples of applications.

#### 9:15 AM W4.3/AA4.3

**3D PERIODIC ARRAYS OF NANOPARTICLES INSIDE MESOPOROUS SILICA FILMS.** Sophie Besson, Thierry Gacoin, Jean-Pierre Boilot, LPMC, Ecole Polytechnique, Palaiseau, FRANCE; Catherine Jacquiod, Laboratoire CNRS/Saint-Gobain, Aubervilliers, FRANCE; Christian Ricolleau, LMCP, Universités Paris VI et Paris VII, FRANCE.

Periodic mesoporous materials, discovered in 1992 by Mobil Oil Corporation researchers, are synthesized via the polymerization of inorganic species around a periodic organic template, which could be surfactant micelles, copolymers. After a thermal treatment, a porous material is obtained which pores are the perfect replica of the organic species. 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.<sup>1,2,3</sup> They have a 3D hexagonal structure, consisting in an interconnected spherical pore network which is oriented with the c-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 nanoparticulate coatings opens new application opportunities, since large scale synthesis is possible.

<sup>1</sup> S. Besson, T. Gacoin, C. Jacquiod, C. Ricolleau, D. Babonneau, J.-P. Boilot, J. Mater. Chem. 2000, 10, 1331.

<sup>2</sup> S. Besson, C. Ricolleau, T. Gacoin, C. Jacquiod, J.-P. Boilot, J. Phys. Chem. B, 2000, 104, 51, 12095.

<sup>3</sup> S. Besson, C. Jacquiod, T. Gacoin, A. Naudon, C. Ricolleau, J.-P. Boilot, MRS Symp. Proc. 2000, 628.

#### 9:30 AM W4.4/AA4.4

**SELF-ASSEMBLY AND GROWTH OF ORGANIC MOLECULAR**

NANOCRYSTALS. Edward Van Keuren, Elena Georgieva, Michael Durst, Georgetown University, Dept. of Physics, Washington, DC.

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 preparation method for nanoparticle dispersions as well as for studying aggregation and crystallization phenomena in model systems under well-controlled conditions. We report on nanocrystals of anthracene formed in an acetone/water solution. The particle growth above the critical nucleation size was 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/AA4.5

FABRICATION OF TWO- AND THREE-DIMENSIONAL STRUCTURES OF NANOPARTICLES USING LB METHOD AND DNA HYBRIDIZATION. Takayuki Takahagi, Shujuan Huang, Gen Tsutsui, Hiroyuki Sakaue and Shoso Shingubara, Hiroshima University, Graduate School of Advanced Science and Matter, Higashi-Hiroshima, JAPAN.

Recently, self-organization of nanoparticles has been object of researchers attention as powerful method to make nanostructures. We have also carried out research to self-organization of two-dimensional array of gold nanoparticle. We successfully assembled highly regular and large area two-dimensional array of gold nanoparticles encapsulated by alkanethiol molecule films. We used fabrication methods using Langmuir-Blodgett method. And we observed Coulomb blockade phenomenon at room temperature using this array. 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 covalent bond reaction systems like esterification 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 using gold nanoparticle colloid and 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 work, we tried to fabricate three-dimensional 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 of DNA to the surface of nanoparticles composed of other kind of elements.

#### 10:30 AM \*W4.6/AA4.6

MAGNETIC AND MECHANICAL PROPERTIES OF SELF-ASSEMBLED METAL NANO PARTICLES IN THIN FILM MATRICES. D. Kumar and J. Sankar, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; J. Narayan, T.K. Nath, and Alex V. Kvit, Department of MS&E, North Carolina State University, Raleigh, NC.

Nanoscale 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 realization of these outstanding physical properties upon 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 ( $Al_2O_3$ ) and crystalline (TiN) matrices. For example, at room temperature the coercivity of Fe- $Al_2O_3$  sample decreases from 100 to 50 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:  $T_B = KV/25k_B$ , ( $T_B$ ,  $K$ ,  $k_B$  are 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/AA4.7

STRUCTURAL AND MAGNETIC PROPERTIES OF SELF-ASSEMBLED Co NANOPARTICLES. H.R. Khan<sup>a,b</sup> and K. Petrikowski<sup>a</sup>, <sup>a</sup>FEM, Materials Physics Department, Schwaebisch Gmuend, GERMANY; <sup>b</sup>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 ( $H_c$ ), squareness ( $Mr/Ms$ ) and magnetic energy product ( $B.H$ ) depend on the composition, diameter, length and spacing of the nanoparticles. Cobalt nanoparticles of diameter in a wide range from 18 to 78 nm with spacing between 40 and 90 nm are electrodeposited into the self assembled pores of Al-1%Mg substrates obtained by anodic oxidation. Different electrolytes were used to obtain the various pore diameters. The anisotropic magnetic properties depend on the diameter and length of the nanoparticles as shown by the hysteresis loops. A strong perpendicular magnetic anisotropy and maximum  $H_c$  and  $Mr/Ms$  values of 1850 Oe 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.

1. H.R. Khan, O. Loebich and G. Rauscher, Thin Solid Films 275 (1996)207-209.

2. H.R. Khan and K. Petrikowski, 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/AA4.8

MATERIALS BASED ON ORDERED THIN FILM ASSEMBLIES OF NANOPARTICLES. Nicholas A. Kotov, Oklahoma State Univ, OK.

Hybrid polyelectrolyte/nanoparticle thin films are made by the sequential adsorption of (mono)layers of oppositely charged inorganic colloids and polyelectrolytes - the technique also known as the layer-by-layer assembly (LBL). The major advantages of LBL are the nanometer scale controlled thickness of nanoparticle layers and high quality of the films combined with simplicity of the process. The LBL technique can be a convenient method of processing of a variety of aqueous dispersions of nanoparticles into functional materials. The areas of applications currently considered for LBL assemblies include photovoltaics, light-emitting diodes, high-density magnetic memory, non-linear optical switches, nanoscale interconnects, resist layer, 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 nanocolloids deposited in predetermined order. The universality of LBL also affords the inclusion of biological entities in nanoparticle assemblies. The effect of stratification in biomaterials prepared from layered protein/nanoparticle assemblies and molecularly engineered thin films will be discussed.

#### 11:30 AM W4.9/AA4.9

SELF-ASSEMBLING OF NANOPARTICLES IN THE FORM OF DOUBLE LINEAR CHAINS AND SUPERLATTICES ON THEIR BASIS. Razmik Malkhasyan, Robert Karakhanyan, Mary Nazaryan, Scientific-Production Enterprise 'ATOM', Yerevan, ARMENIA; Changmo Sung, University of Massachusetts, Lowell, MA.

The self-assembling systems in nanoscale powders of crystalline  $MoO_3$  are disclosed. Particularly, in nanoscale powders of  $MoO_3$ , treated by vibrationally excited molecules of hydrogen (1), for the first time the double linear chain aggregates of  $MoO_3$  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 arbitrary oriented crystalline  $MoO_3$  nanoparticles with diameter of about 20nm. It is found that linear double chain aggregates form two sorts of superlattice. So the double chain aggregates form a linear superlattice (with parameter of about 1 micrometers) 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 transversal branches that in some places reach the neighboring chains. Moreover, the double linear chain aggregates form orthogonal superlattice with the following parameters:  $a = 200nm$  and  $b = 300nm$ . 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  $\text{MoO}_3$ . In the first stage of self-assembling processes the spontaneous generation of double linear chain aggregates take place, which then form (again owing to self-assembling processes) linear and orthogonal superlattices. Taking into account the fact that double linear chain aggregates and superlattices of nanoparticles were obtained only in case of powders, which are treated with molecules of hydrogen we can conclude that the mentioned treatment of nanoscale powders can be a possible method of obtainment of long self-assembling chains of inorganic materials with controlled properties.

References:

1. R.T. Malkhasyan. Metastable Phase and Microstructures. Material Research Society. Symposium Proceeding, Boston, Massachusetts, USA, 1995, v. 400, p. 77.

#### SESSION W5: NOVEL SYNTHESIS AND CHARACTERIZATION

Chairs: Mamoun Muhammed and Richard Partch  
Tuesday Afternoon, November 27, 2001  
Back Bay B (Sheraton)

##### 1:30 PM \*W5.1

RANDOM ASSEMBLING AND COALESCENCE OF MONO-DISPERSED SIZE  $\text{Co}$  CLUSTERS. K. Sumiyama, D.L. Peng, S. Yamamuro and T. Hihara, Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya, JAPAN.

Cluster assembling, in which nanometer-size clusters are directly deposited on a substrate, is a promising alternative to fabricate nano-scale-structure-controlled materials. Recently, we have constructed a plasma-gas-condensation (PGC)-type cluster-deposition system based upon plasma-glow-discharge vaporization and inert gas cooling, and succeeded in producing a large amount of transition metal clusters whose size range between 5 and 15 nm in diameter with the standard deviation less than 10% of the mean cluster sizes. In order to understand how these clusters evolve to random networks and continuous assemblies we have carried out the transmission electron micrograph observation, in situ electrical conductivity and ex situ magnetization measurements for the deposition processes of monodispersed size  $\text{Co}$  clusters on substrates. We monitored the deposited quantity of clusters by a quartz oscillation type thickness meter and analyze the cluster assembling processes from the discontinuous to continuous networks in terms of the 2 dimensional percolation. The magnetic percolation is detected a little earlier than the geometrical percolation by TEM observation and the electrical percolation by resistivity measurement. The detailed scaling analysis of the electrical conductivity reveals that the critical percolation index depends on the cluster size and deposition rate, while the critical percolation thickness on the deposition rate and substrate temperature. We discuss these features in regard to the soft percolation. We also mention the magnetic characteristics of  $\text{Co}$  clusters whose mean diameters are between 6 and 13 nm: the critical size of superparamagnetic to ferromagnetic transition and the magnetic coercivity.

##### 2:00 PM W5.2

PROCESSING OF ENGINEERED MATERIALS WITH THE CIRCULATION TYPE MECHANOFUSION SYSTEM. C.C. Huang, M. Sadakane, Hosokawa Micron Powder Systems, Summit, NJ.

Mechanofusion is a dry powder processing technique of creating materials with new properties by mechano-chemical surface fusion mechanism. In the Mechanofusion Process, the powders are intensively mixed and subjected to compression, attrition, frictional shearing and rolling. Therefore, mechanical thermal energies are generated, resulting in a variety of distinct effects on powder materials. This technique has proven its uniqueness in developing various multi-layer particles and composite materials in the past few years. In this study, a new Mechanofusion design will be discussed. The new Mechanofusion system enables the circulation of processing material in the system. This improvement not only produces powders with high uniformity but also greatly enhances its capacity and energy utilization efficiency. Examples of new applications, such as particle shape control, particle coating, nano-phase mixing etc., with the circulation type Mechanofusion system will also be elucidated.

##### 2:15 PM W5.3

INDIUM OXIDE AND TIN OXIDE NANOPARTICLES PREPARED BY CHEMICAL VAPOR SYNTHESIS. Joachim Brehm, Markus Winterer, Horst Hahn Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERMANY.

Nanoparticles of indium oxide, tin oxide and indium/tin oxide (ITO) have been prepared by CVS (a modified CVD process) starting with

In-(thd) as a precursor. A modification of the CVS process using a new radio-frequency reaction zone has been developed in order to avoid the rapid decomposition of the nanocrystalline oxide particles. These oxides are candidates for applications as transparent conducting oxides, catalysts and gas sensors. Structural characterization by high resolution scanning and transmission electron microscopy and X-ray-diffraction has been used to determine the phase, grain size, grain size distribution and crystallinity of the nanoparticles. Nitrogen adsorption and photon correlation spectroscopy have been performed to determine the specific surface area, grain or agglomerate size of the powders and of aqueous dispersions. In addition, Zeta-potential measurements were carried out. It was found that the CVS powders exhibited a narrow size distribution with an average size of approx. 5 nm. Compared to commercial nanopowders, the dispersability in water was improved. Results of property measurements will be presented.

##### 2:30 PM W5.4

NANO-PARTICULATE OF ALUMINUM NITRIDE PREPARED BY PULSED WIRE DISCHARGE. Yoshiaki Kinemuchi, Channarong Sangurai, Tsuneo Suzuki, Hisayuki Suematsu, Weihua Jiang and Kiyoshi Yatsui, Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata, JAPAN.

Nano-particulates of aluminum nitride,  $\text{AlN}$ , have been successfully synthesized by pulsed wire discharge, PWD. The principle of PWD is categorized in three processes: a) joule heating of thin conductive wire by pulse current, b) vaporization and ionization of wire material, and c) condensing vapor by interaction with ambient gas. Since the electric energy is directly converted into thermal energy, the efficiency for a synthesizing nano-particulate is very high in PWD. For the synthesis of  $\text{AlN}$ , we have typically 180 g/(kW·h), which is 50 times higher than that of arc discharge method. Furthermore, industrial applications might be available due to advantages such as simple apparatus and mass productivity. Aluminum nitride was prepared by the discharge of Al wire in  $\text{NH}_3/\text{N}_2$  gas. Here, the stored energy in the capacitor of 10  $\mu\text{F}$  was discharged to Al wire with 0.25 mm in diameter. Charging voltage was 4-6 kV. The particulates floating in the ambient gas were collected by pumping the gas through a membrane filter, and subjected to further analysis. The analysis of the particulates was conducted by X-ray diffraction, Brunauer-Emmet-Teller method, transmission electron microscopy, electron diffraction, and energy dispersive spectroscopy. Median diameter was found to be 28 nm. It was also found that Al particles of submicron were included in the particulates synthesized. The particle size obeys log-normal distribution, and geometric standard deviation was 1.29 which is close to that of mono-dispersed powders. The content of  $\text{AlN}$  in collected powders reaches 90 wt% by the discharge in 20% $\text{NH}_3/\text{N}_2$  gas of 750 Torr. In addition, the content was influenced by the inductance of the discharge circuit. The content increased with decrease in inductance, i.e., short pulse with high power was effective to enhance the reaction between aluminum and nitrogen.

##### 2:45 PM W5.5

LOW-COST, MULTIMETALLIC, SINGLE CRYSTAL, OXIDE NANOPARTICLES FOR STRUCTURAL AND CATALYST APPLICATIONS. R.M. Laine, T. Hinklin, E. Gulari, E. Seker, Depts. of MS&E and Chemical Engineering, University of Michigan, Ann Arbor, MI; A. Sutorik, S. Baliai, Tal Materials Inc., Ann Arbor, MI.

We recently described methods of producing oxide nanopowders by flame spray pyrolysis (FSP) of ethanol solutions of low-cost metal alkoxide complexes as well as other soluble metal complexes. This scaleable synthesis route provides reproducible, high purity, self-dispersing nanopowders. We have previously demonstrated the ease with which FSP can be used to make single crystal  $\text{d-Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) and partially crystalline mullite ( $3 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) powders with controllable average particle sizes of 2-200 nm and surface areas = 40-120  $\text{m}^2/\text{g}$  at production rates \* 400 g/h. We focus here on FSP processing of novel two phase nanoparticles wherein segregation is desired and effected to simultaneously generate catalyst and support (e.g  $\text{CeO}_2/\text{ZrO}_2$  solid solutions on d-alumina nanoparticles), and other materials where two phases segregate at the nanoscale during processing of originally homogeneous nanopowders.

##### 3:30 PM \*W5.6

NANOSCALE PHOTONICS-FUNCTIONALITY BY DESIGN. John Muth, Jagdish Narayan, Dept of Electrical and Computer Engineering and Dept of MS&E, NSF Center for Advanced Materials and Smart Structures, North Carolina State University, Raleigh, NC.

Nanocrystalline photonic materials possess unique optical properties such as wavelength tunability of emission and absorption, significant enhancement of nonlinear optical effects, and increased radiative efficiency. We have used a pulsed laser deposition technique to control the size, uniformity, and number density of nanocrystallites which can be embedded in a matrix of our choice. By controlling the nucleation

and growth and crystal structure of the matrix, we can vary the texture of nanocrystallites from random to epitaxial. The talk focuses on synthesis and self assembly processing of novel nanocrystalline optical materials within a robust matrix with excellent optical properties, nanoscale characterization and correlations with optical properties. The systems to be covered include Ge and metallic nanoparticles in oxide and nitride matrices, and III-nitrides and ZnO based nanomaterials in the above matrices. The quantum confinement effects as a function of size, interface structure, and crystal structure of nanocrystals are investigated and correlations with optical properties discussed.

#### 4:00 PM W5.7

**MULTIPLY TWINNED STRUCTURES IN GAS-PHASE SINTERED STOICHIOMETRIC Fe-Pt NANOPARTICLES.** Bernd Rellinghaus, Sonja Stappert, Mehmet Acet, Eberhard F. Wassermann, Experimentelle Tieftemperaturphysik, Gerhard-Mercator-Universität, Duisburg, GERMANY.

Ferromagnetic FePt alloys with concentrations around the stoichiometric composition are promising candidates for the magnetic media in future high density magnetic data storage. The thermodynamic equilibrium structure of FePt is a chemically ordered tetragonal phase ( $L1_0$ ), which exhibits a large magnetocrystalline anisotropy and thus allows for the preparation of particularly small and thermally stable magnets. We have prepared FePt nanoparticles with sizes in the range  $3 \text{ nm} \leq d_p \leq 6 \text{ nm}$  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 (*as-deposited* particles) or pass a sintering tube prior to being deposited (*sintered* particles). The sintering temperatures are in the range  $20^\circ \text{C} \leq T_s \leq 700^\circ \text{C}$ . 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 Fe-Pt particles form large contiguous networks (*agglomerates*) of individual particles already in the gas-phase. On the other hand, particles which are sintered at  $T_s = 600^\circ \text{C}$  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-organisation. Among both, as-deposited and sintered Fe-Pt nanoparticles we find icosahedral particles. Such multiply twinned particles (MTPs) are often observed in clusters or nanoparticles of fcc metals. However, there are only very few publications available, that report on the occurrence of multiply twinned alloy particles. Particular attention is thus being paid to the question as to whether or not the  $L1_0$  order is favouring the formation of such Fe-Pt MTPs.

#### 4:15 PM W5.8

**Cu NANOCLEUSTERS PRODUCED ON AuCu-ALLOYS WITH AN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE.** Stefan Maupai, Andrea S. Dakkouri, Martin Stratmann, Patrik Schmuki, Dept. of Material Science, LKO, University of Erlangen-Nuremberg, Erlangen, GERMANY.

The electrochemical scanning tunneling microscope has been used to generate small Cu clusters on metallic substrates under electrochemical conditions. Clusters consist typically of 100-500 atoms and show an unexpected electrochemical stability to anodic oxidation. The stability of the clusters is 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. UHV-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 Cu clusters on binary alloy surfaces instead of pure metal surfaces. Using AuCu single-crystals of different composition and crystallographic orientation as substrates opened the possibility to vary the tip-substrate interaction and other parameters in the system. The experiments give 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 NANOCRYSTALS-A SYNTHETIC APPROACH TO MONODISPERSE HOMO- AND HETEROATOMIC NANOPARTICLES.** J.P. Wilcoxon, J.E. Martin and P.N. Provencio, Nanostructures and Advanced Materials Chemistry Dept., Sandia National Labs, Albuquerque, NM.

Using the inverse micelle method to grow monodisperse "seed" nanocrystals dispersed in oils provides a starting point for the production of larger particles by slow deposition of atoms onto the

surface of the seed crystals. The atoms/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 nanocrystalline seeds which ensures a lack of alternative nucleation sites and the selection of the proper passivating 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 homoatomic deposition of atoms onto Au55 ( $d \sim 1.5 \text{ nm}$ ) and Ag147 ( $d \sim 2.0$ ) nanocrystals and then illustrate the versatility further by production of core-shell nanocrystals of various types. HPLC and TEM are used to analyze the size-dispersion, 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 homoatomic 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-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

#### 4:45 PM W5.10

**NANOPARTICLES SYNTHESIS BY AIR-ASSISTED ULTRASONIC SPRAY PYROLYSIS.** Shirley C. Tsai, California State Univ, Dept of Chemical Engineering, Long Beach, CA; Y.L. Song, C.Y. Chen, T.K. Tseng, C.S. Tsai, Academia Sinica, Institute for Applied Science and Engineering Research, Taipei, TAIWAN; H.M. Lin, Tatung Univ, Dept of Materials Engineering, Taipei, TAIWAN.

Spray pyrolysis for synthesis of fine-grained powders has received considerable interests because it is a continuous process, chemically flexible and operating at ambient pressure. However, the very broad size distribution and irregular shape of its product particles 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 [1]. The UMTF atomization is capable of producing uniform precursor drops with a diameter determined by the third harmonic frequency of ultrasound. Specifically, large precursor drops (peak diameter of  $55 \mu\text{m}$ ) generated by conventional ultrasonic atomization at 120kHz have yielded yttria stabilized zirconia (YSZ) particles with holes due to high solvent 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  $30 \mu\text{m}$ ) and broader size distribution (half width  $40 \mu\text{m}$ ), air-assisted ultrasonic (UMTF) spray pyrolysis at 120kHz and 2.3 W electrical drive power has yielded hole-free YSZ particles of which nearly half are  $< 0.35 \mu\text{m}$  in diameter, while ultrasonic spray pyrolysis of  $6-9 \mu\text{m}$  precursor drops (peak diameter  $7 \mu\text{m}$ ) has yielded YSZ particles with a mean diameter of  $0.5 \mu\text{m}$  but only less than 10% are with a diameter  $> 0.35 \mu\text{m}$ . Furthermore, the  $6-9 \mu\text{m}$  precursor drops, generated using an ultrasonic nebulizer at 1.65 MHz and 23.5 W, under proper control of heating rate and concentration resulted in uniform spherical hole-free particles  $150 \text{ nm}$  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 process for mass production of nanoparticles such as YSZ that are useful materials for application in thermal insulation and solid electrolyte fuel cells.

[1] S.C. Tsai, P. Childs, and P. Luu, "Ultrasound-Modulated Two-Fluid Atomization of a Water Jet," *AIChE J.*, 42, 3340-3350, 1996.

Support from the National Science Foundation, USA, the National Science Council and the Academia Sinica, Taiwan are acknowledged.

### SESSION W6: POSTER SESSION NANOPARTICULATE MATERIALS: SIMULATION AND MODELING, SYNTHESIS AND NOVEL STRUCTURES

Chairs: Mamoru Senna, Richard Partch and Lennart Bergstrom

Tuesday Evening, November 27, 2001  
8:00 PM

Exhibition Hall D (Hynes)

#### W6.1

**NANO-STRUCTURAL ANALYSIS OF HIGH-CAPACITY EDLC USING IMAGE-PROCESSING AND MOLECULAR ORBITAL**



CALCULATION. K. Katayama, H. Hara, M. Endo, T. Hayashi, K. Ishii, Shinshu University, Nagano, JAPAN; K. Oshida, T. Miyazaki Nagano, Nagano National College of Technology, JAPAN.

In this study, we will evaluate the capacity characteristics of nano-structured carbon material based aqueous electric-double-layer capacitor in order to find the optimum condition to meet the demand from the market. We first start from the capacity measurement and then move to the image analysis using the image of the nano-structured PVdC carbon material obtained using TEM, SEM and STM. We have successfully applied the FFT and fractal dimension analysis to the TEM image to obtain the information on the nano-structured pores. Combining this result with the gas-adsorption analysis, we are able to analyze the pore structure with high accuracy.

**W6.2**  
SMALL TIN CLUSTERS: AN *AB-INITIO* THEORETICAL STUDY FOR NEUTRAL AND CHARGED CLUSTERS. C. Majumder, V. Kumar, H. Mizuseki and Y. Kawazoe, Institute For Materials Research, Tohoku University, Sendai, JAPAN.

The present work is motivated by the recent experimental results of Jarrold and his co-workers, which predicted that tin clusters between 15 and 30 atoms have melting points at least 50 K higher than the bulk tin [A.A. Shvartsburg and M.F. Jarrold, Phys. Rev. Lett. 85 (2000) 2530]. It is assumed that the different structures and a consequence of different chemical bonding of small clusters compared to the bulk could be the reason for such unusual high melting behavior of tin clusters. Tin clusters are also interesting as their position in the periodic table is below germanium (semiconductor) and above lead (metal). Therefore understanding the atomic and electronic structure of tin is very important as there could be various isomers having different nature of bonding from covalent to metallic. In the present work we have carried out an *ab-initio* study of small tin clusters ( $n = 2-20$ ) using the ultrasoft pseudopotentials and generalized gradient approximation for the exchange and correlation energy. The lowest energy isomers upto 8 atoms have the same structures as Si clusters but larger clusters seem to favor a different structure. Interestingly the binding energies of clusters with  $n > 10$  are found to be only about 10% less than the calculated bulk value. The higher binding energies of small tin clusters are predicted to be responsible for the higher melting temperatures of these clusters. The adiabatic ionization potentials of tin clusters have been calculated using the optimized geometries of neutral clusters as the initial configuration. The fragmentation behavior and ionization potentials calculated in this work shows an excellent agreement with the experimental results and suggest that the lowest energy structures, obtained here, are close to the global minima.

**W6.3**  
AB INITIO MOLECULAR DYNAMICS AND ELASTIC PROPERTIES OF TiC AND TiN NANOPARTICLES. A.V. Postnikov and P. Entel, Univ of Duisburg, Duisburg, GERMANY.

TiC and TiN prepared as nanoparticles find many different applications. Among their peculiar properties different from those in the bulk phase, a considerable softness could be expected. In order to check this assumption and understand its possible microscopical origins, we studied the electronic structure and simulated Born–Oppenheimer dynamics in stoichiometric or nearly stoichiometric clusters of different size, with 64 atoms on the largest. The simulations have been done with the SIESTA code<sup>1</sup> using norm-conserving pseudopotentials, numerical local orbitals as basis functions, and local density approximation for exchange-correlation. The results give insight into electronic structure of (relaxed) nanoparticles; the comparison with bulk systems is facilitated by the fact that the latter was simulated by the same method, only under imposing periodic boundary conditions. Vibration frequencies for the bulk have been estimated by both frozen phonon scheme and time-step dynamical simulation using the Nosé–Hoover thermostat, in very good agreement with experiment and with all-electron calculation results. For nanoparticles, only the latter approach was used in order to extract vibration frequencies and corresponding displacement patterns. From the latter, the impact on the elastic characteristics of nanoparticle could be elucidated.

<sup>1</sup>D. Sánchez-Portal, P. Ordejón, E. Artacho and J. Soler, Int.J.Quant.Chem. **65**, 453 (1997); E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García and J.M. Soler, Phys.Stat.Sol. (b) **215**, 809 (1999).

**W6.4**  
ELECTRONIC STATES OF  $Mn^{2+}$  IN  $ZnS:Mn$  NANOPARTICLE EXAMINED BY EPR MEASUREMENTS AND MOLECULAR ORBITAL CALCULATION. Sanshiro Nagare, Tetsuhiko Isobe, Mamoru Senna, Keio Univ, Faculty of Sci & Tech, Yokohama, JAPAN; Takahiro Igarashi, Sony Corp, Luminescent Matl Engr Dept, Atsugi, JAPAN.

The luminescence intensity due to d-d transition of  $Mn^{2+}$  for  $ZnS:Mn$  nanoparticle increases by hybridizing with polymerized acrylic acid (PAA). EPR measurements revealed two kinds of  $Mn^{2+}$  sites, i.e., a isolated substitutional site corresponding to the signal I ( $g=2.0024, |A|=6.9mT$ ) and a surface site corresponding to the signal II ( $g=2.0013, |A|=9.0mT$ ). For a VIB element of X, the absolute value,  $|A|$ , is linearly related with the covalency of Mn-X bond. Therefore, the increase in  $|A|$  indicates the lower covalency of Mn-X bonds for the signal II than that of signal I. According to infrared absorption and X-ray photoelectron spectroscopies,  $ZnS:Mn$  nanoparticles coated with PAA is oxidized by coordination of carboxyl group, and not simply by atmospheric oxygen. Consequently, the lower covalency for signal II must be attributed to the existence of oxygen near  $Mn^{2+}$  sites. These results were discussed in terms of molecular orbital calculations by a DV-X $\alpha$  method. The band gap of ZnS, the  $Mn^{2+}$  impurity levels, the density of states, and the bond order were estimated by this method. From the bond order calculations, we found that the covalency between  $Mn^{2+}$  and its first neighbors is lowered when  $Mn^{2+}$  ion is located in the vicinity of an oxygen atom. This reduction in the covalency between  $Mn^{2+}$  and its first neighbors induces the change in the  $Mn^{2+}$  impurity levels. This could affect the enhanced photoluminescence due to the d-d transition of  $Mn^{2+}$  for  $ZnS:Mn$  nanoparticles.

**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. McCusker, Univ of California at Berkeley, Dept of Chemistry, Berkeley, CA.

The photosensitizer bis[(4,4'-dicarboxylate-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 (TD-DFT) calculations show that singlet and triplet excited states represent either metal to ligand charge transfers or  $n-\pi^*$  (non-bonding to antibonding) 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  $n-\pi^*$  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 NANO-CRYSTALS IN  $SiO_2$  USING PULSED LASER DEPOSITION. Ji Nan Zeng, Yeow Whatt Goh, Yong Feng Lu, 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 its potential application in Si-based optoelectronic devices, Si-nanocrystal memory and single electron transistors. It is of significance for compatibility with existing Si-based semiconductor manufacturing for ultralarge scale integrated circuits. Besides wide application of Si nanocrystals, active fields of basic research are 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 PLD technique. A special deposition geometry is arranged to control size distribution of nanocrystals. Si particles generated by laser ablation are deposited on quartz or Si substrates simultaneously accompanying oxidation process in oxygen ambient or using O ion beam. The native oxides of Si are produced to isolate Si nanoparticles and form three dimensional confinement of nanoparticles. Parameters of laser ablation, ablation distance between target and substrate, deposition temperature, and ambient pressure (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 microparticles by optical microscopy are available in the range from 10um to 300nm. Absorption/transmission spectra from Si nanocrystal on quartz substrate show broad and blue-shifted absorption features spanning 800-300nm due to quantum confinement compared with indirect bandgap of 1060nm. Influence of quantum confinement on phonon states causes a broadening and 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 areas with visible Si particles present a dominant Si vibration mode at  $520\text{cm}^{-1}$  while the areas with invisible particles give a broad peak at  $467\text{cm}^{-1}$  apart from the  $520\text{cm}^{-1}$  feature. The broad peak at  $467\text{cm}^{-1}$  is ascribed to Si nanocrystals of reduced size contribution. Quantum confinement of Si nanocrystals is considered to result in a weakening of the k-selection rule. Oxidation processes are also taken into account to affect the formation of Si nanocrystal and size distribution.

References:

L. Patrone, D. Nelson, V. I. Safarov, M. Sentis, W. Marine and S. Giorgio, J. Appl. Phys. 87 (3829) 2000.

#### **W6.7**

**Gd DOPPED CdS NANOPARTICLES.** Sheng-Ming Shih, Wei-Fang Su, Chii-Dong Chen, National Taiwan 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% molar) doped CdS nanoparticles were synthesized by reacting sodium sulfide with the mixture of cadmium acetate and gadolinium acetate. These nanoparticles were capped with p-hydroxythiophenol at the outer shells for stabilization. The diameters of these particles, ranging from 5 to 50 nm, were controlled by the molar ratio of p-hydroxythiophenol to sodium sulfide. SQUID (Superconducting Quantum Interference Device) measurements showed a sign change in the magnetic susceptibility when the temperature was raised from 5 to 300 K, with the zero crossing at temperatures between 25K and 35 K. The crossing temperature was depended on the amount of Gd in the nanoparticles. This sign-change can be described by a two-phases model, namely, a diamagnetic phase from CdS and organic molecules and a paramagnetic phase from  $\text{Gd}^{2+}\text{S}_3$ . Unusually, 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 TITANATE NANOPARTICLES FROM VARIOUS MEDIA.** Xinyu Wang, Dang-Hyok Yoon, Burtrand I. Lee, Clemson University, School of Materials Science and Engineering, Clemson, SC; Michael Z-C. Hu, Oak Ridge National Laboratory, Oak Ridge, TN.

Nano-sized barium titanate (BT) particles have been prepared at low temperature from various media, such as water, toluene and alcohol. 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  $\text{L}_{12}$  PHASE  $\text{Al}_3\text{Zr}$  AND (Al 12.5 AT% Cu) $_3\text{Zr}$  POWDERS WITH NANOCRYSTALLINE STRUCTURE DURING SPARK PLASMA SINTERING.** Kyoung Il Moon, Seung Chul Kim, Kyung Sub Lee, Div. of MS&E, Hanyang Univ, Seoul, KOREA.

The Spark plasma sintering (SPS) processes of  $\text{L}_{12}$  phase  $\text{Al}_3\text{Zr}$  and (Al 12.5at.%Cu) $_3\text{Zr}$  powders with nanocrystalline structure has been studied to produce bulk intermetallic compounds which maintain metastable structures such as  $\text{L}_{12}$  and nanocrystalline structures. The powders were produced by 10 h mechanical alloying using planetary ball mill (PBM) rotating at 300 rpm. Full-density  $\text{L}_{12}$  (Al 12.5at.%Cu) $_3\text{Zr}$  intermetallic was obtained by SPS at  $600^\circ$  for 0 min. The specimens prepared with a longer holding time than 0 min. at  $600^\circ$  or a higher temperature than  $600^\circ$  had a local melting areas that was followed by the formation of micro-cracks. They had a lower relative density than the specimen at  $600^\circ$  for 0 min. The smallest grain size was obtained in the specimen prepared at  $600^\circ$  for 0 min., which was 20-30 nm as confirmed by TEM observation. This was the smallest grain size ever reported in the specimens processed by various consolidations of nanocrystalline powders. Accordingly, the highest micro-hardness, 989.5  $\text{H}_V$ , was obtained in the specimen and this value was three times higher than those of the  $\text{L}_{12}$  (Al 12.5at.%Cu) $_3\text{Zr}$  specimens with micro grain sizes. Full density  $\text{Al}_3\text{Zr}$  intermetallics were prepared by SPS at  $700^\circ$  for 0 min. However, the crystal structure was  $\text{D}_{023}$  and micro-hardness was 778.1  $\text{H}_V$ . 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 $^\circ$  of the PBM  $\text{Al}_3\text{Zr}$  and (Al 12.5at.%Cu) $_3\text{Zr}$  powders compared with the conventional sintering temperature was related to the refinement of microstructure

to nano-size level. Keywords: Spark plasma sintering; Nanocrystalline material;  $\text{Al}_3\text{Zr}$  intermetallics; Consolidation; Planetary ball milling.

#### **W6.10**

**ALKYLATION AND -COOH FUNCTIONALIZATION OF ULTRASMALL SILICON NANOPARTICLES.** Elena V. Rogozhina, Gennadiy A. Belomoin, Munir H. Nayfeh, Paul V. Braun.

Coupling of robust, electronically stable Si nanoparticles with functional organic molecules should result in material systems with enhanced properties and processing opportunities with applications ranging from biological detection to inorganic-organic hybrid microelectronics. The functionalization of 1 nm, strongly luminescent H-terminated silicon nanocrystallites with highly versatile organic molecules will be presented. The H-terminated nanoparticles were synthesized via anodic 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]. Alkyl functionalized particles were also obtained through a thermally activated reaction between 1-alkene and the H-terminated silicon resulting in hydrosilylation of the 1-alkenes terminal double bond. Thermal, and catalyzed room temperature hydrosilylation 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 hydrolysis in basic or acidic media. The -COOH terminated nanoparticles obtained after functionalization and hydrolysis and the alkylated nanoparticles retain their high luminescence. The maximum of the photoluminescence shifts from 400 nm to 445 nm when the nanoparticles are converted from the H-termination to the N-termination, while it shifts very little in the case of C-termination. Important for application, the functionalized particles are highly resistant to oxidation and aggregation.

1. G. Belomoin, J. Therrien, and M.H. Nayfeh, Appl. Phys. Lett. 77, 779 (2000); L. Mitas, J. Therrien, R. Twisten, M.H. Nayfeh, Appl.Phys.Lett. 78, 1918 (2001).  
2. E. Rogozhina, G. Belomoin, A. Smith, L. Abuhassan, N. Barry, O. Akcikir, P.V. Braun, M.H. Nayfeh, Appl.Phys.Lett. 78, 3711 (2001).

#### **W6.11**

**LARGE SCALE CONTINUOUS FLOW REACTOR FOR CdSe NANOCRYSTALS WITH STRONG LUMINESCENCE.** S. Saita, T. Ohtsu, I. Kamiya, Mitsubishi Chemical Corporation MCC-Group Science & Technology Research Center, JAPAN; K. Yoshie, 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 made of stainless steel tube typically 4mm in diameter. Nanoparticle formation is very rapid once precursors are mixed at elevated temperatures, indicating that the reaction is diffusion controlled. Hence, we set a small static mixer in the reactor to enhance the mixing. Feed stock was prepared by mixing dimethyl-cadmium, selenium, tri-butyl-phosphine and hexane. TOPO (tri-n-octylphosphine oxide) melt and the feed stock are pumped into the reactor and then mixed to start reaction. The operating temperature is typically  $350^\circ\text{C}$ , 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 10g/day of CdSe whose mean size is controlled between 3nm and 6nm by adjusting the operating conditions. Size distribution was narrowed from 23% to 19% 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 nanoparticles[1]. 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.

[1] X. Peng et al.; Nature 404,59-61 (2000).

#### **W6.12**

**FLAME SPRAY PYROLYTIC SYNTHESIS OF LOW-COST, DISPERSIBLE NANOPOWDERS IN THE  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  SYSTEM FOR USE IN PHOTONIC APPLICATION.** Julien Marchal, Tom Hinklin, Richard Laine, University of Michigan, Dept. of MS&E, Ann Arbor, MI.

Nanosized YAG and YAP powders can be produced by flame spray pyrolysis (FSP) by combustion of alcohol mixtures of very simple yttria and alumina precursors. These nanopowders can be doped with various rare earths (Nd, Yb, Er, Pr at 0.1 to 2.5 mol%). These powders provide the basis for forming fine grained YAG monoliths,

and novel photonic materials. This scaleable synthesis route produces single crystal nanopowders at > 100 g/h with surface areas of 5-80 m<sup>2</sup>/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 "as-shot" YAG composition powder is not crystalline YAG, but converts to unaggregated YAG nanopowder 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.

#### **W6.13**

**A FACILE WET SYNTHESIS OF NANOPARTICLES OF LITHARGE, THE TETRAGONAL FORM OF PbO.** D.L. Perry, E. Spiller, T.J. Wilkinson, S.E. Derenzo, P. Berdahl, and M.J. Weber, Lawrence Berkeley National Laboratory, Berkeley, CA.

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 compound—can result 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 repeatably 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 are discussed that lead to both other PbO forms being produced in wet syntheses and to microstructural alterations of both the litharge and other phases.

This work was supported by the Center for Science and Engineering Education (CSEE) at Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098 for the U.S. Department of Energy.

#### **W6.14**

**SYNTHESIS AND CHARACTERIZATION OF EUROPIUM-DOPED CADMIUM SELENIDE NANOCRYSTALS.** Orlando E. Raola, Geoffrey F. Strouse, University of California Santa Barbara, Dept. of Chemistry and Biochemistry, Santa Barbara, CA.

Eu-doped cadmium selenide nanocrystals were prepared by a solvothermal procedure using HDA as the coordinating solvent. The doped samples were characterized by HRTEM, XRD, emission and absorption spectroscopies, 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 nano-scale metal and metal-sulfide particles due to their novel optical, electronic, and magnetic properties. Silver-containing nanoparticles have shown particularly 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 Zhan, Patricia A Laws, René Doucet and Mary Anne White, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, CANADA.

Faujasite zeolites are the most widely used catalysts in the petroleum industry. Synthesis of nanometer-sized faujasite-X and -Y zeolites has attracted much attention in the last decade. Until recently, nanometer-sized faujasite crystals could only be obtained in the presence of the organic template, tetramethylammonium. 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  $\mu$ m by controlling the synthesis conditions and silicate sources. Powder X-ray diffraction, high-resolution SEM, FT-IR, N<sub>2</sub> adsorption, solid-state <sup>29</sup>Si NMR, and thermodynamic studies were employed to probe the novel properties of ultra-fine NaX (20-100 nm) and to compare them with the micrometer-sized material. Nanometer-sized NaX displays a very large external surface area and many interparticle voids, ranging from 20 Å to 200 Å. This micro- and mesoporous combination system could significantly improve the mass-transfer process, and therefore could serve as a good support for various chemical processes such as catalysis and photochemical reactions. The incorporation of transition metals such as Ru and Ce into nano-NaX (making nano-composites) is also discussed.

#### **W6.19**

**SYNTHESIS OF SELECTIVE METAL-COMPLEXING NANOPARTICLES BY MICROEMULSION POLYMERIZATION.** C. Larpent, S. Amigoni-Gerbier, University of Versailles St. Quentin, Versailles, FRANCE.

Ultrafine and monodispersed ligand-functionalized nanoparticles in the 12-13nm diameter range and containing high densities of tetrazacyclotetradecane (cyclam) are readily prepared by a one 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 metal-binding capacity and ligand accessibility as well as huge selectivity for cupric ions.

#### **W6.20**

**PRECIPITATION OF NANOSCALE ALUMINIUM TRIHYDROXIDE PARTICLES FROM SUPERSATURATED SODIUM ALUMINATE SOLUTIONS.** Biman Das, State University of New York College at Potsdam, Dept of Physics, Potsdam, NY; Don Rasmussen, Chris Brancewicz, Clarkson University, Dept of Chemical Engineering, Potsdam, NY; Mats Graffe, Jarl Rosenholm, Abo Akademi, Dept of Physical Chemistry, FINLAND; Alicia Toscano, Dept of Chemical Engineering, Purdue University, IN.

Alumina particles used in industry must be manufactured in a cost-effective manner, be of 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 alumina 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 as to the use of Bayer liquors as a source of nanoscale alumina 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 trihydroxide 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 alumina particles precipitated in the presence of NaCMC had consistent aggregate diameters of 600 to 700 nm, those precipitated with PVP had diameters of 80 to 250 nm. The sizings from DLS experiments 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 nitrocellulose membranes shows the particles as nearly spherical and not pure aluminum trihydroxide as originally expected. These particles have a gel like structure and deform under stress. Dehydration leads to aggregation of amorphous fibrous particles of aluminous trihydroxide contaminated with sodium. Continuing efforts focus on isolation of the primary precipitated and to achieve true nanoscale alumina.

#### **W6.21**

Abstract Withdrawn.

#### **W6.22**

**SYNTHESIS AND CHARACTERIZATION OF NOVEL Pd-Mn OXIDE.** Heng Zhang<sup>1</sup>, Jack Gromek<sup>1</sup>, Matthew Augustine<sup>1</sup>, Gayanath Fernando<sup>1</sup>, R. Samuel Boorse<sup>2</sup> and Harris L. Marcus<sup>1</sup>.  
<sup>1</sup>Institute of Materials Science, University of Connecticut, Storrs, CT.  
<sup>2</sup>Precision Combustion Inc., North Haven, CT.

Novel Pd-Mn alloy and oxide have been synthesized using sol-gel 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, gas environment high temperature X-ray diffraction in-situ experiments and gas phase mass spectroscopy. 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 C. Searson, Gerko Oskam, Department of Materials Science and Engineering; Noshir Pesika and Kate Stebe, Department of Chemical 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 II-VI compounds, III-V 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 LSW rate law where the cube of the particle radius is proportional to time. We also show cases where growth occurs by oriented attachment.

**W6.24**  
Abstract Withdrawn.

**W6.25**  
FUNDAMENTAL STUDIES ON NANOCAPSULATED  
PULMONARY DRUG DELIVERY SYSTEM. W-S. Kim<sup>1</sup>, M. Ollinger<sup>1</sup>, V. Craciun<sup>1</sup>, R.K. Singh<sup>1</sup>, I. Coowantiwong<sup>2</sup>, G. Hochhaus<sup>2</sup>, H. Hofmann<sup>3</sup>, R. Houriet<sup>3</sup>, N. Koshizaki<sup>4</sup>. <sup>1</sup>Dept of Materials Science & Engineering, <sup>2</sup>Dept of Pharmaceutics, <sup>3</sup>Engineering Research Center for Particle Science and Technology, University of Florida, Gainesville, FL, <sup>4</sup>Powder Technology Laboratory, Dept of Materials Science, Swiss Federal Institute of Technology (EPFL), Lausanne, SWITZERLAND. <sup>4</sup>Dept of Composite Materials, National Institute of Materials & Chemical Research (NIMC), Ibaraki, JAPAN.

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 antiasthmatic drugs can be suitably modified by this method. The biodegradable coatings are formed by the pulsed laser ablation process. The chemical composition, architecture and bonding of the nanoencapsulated 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 NANOPARTICLES. Xiang-Cheng Sun, Prog. Simulacion Molecular, Instituto Mexican del Petroleo (IMP), D.F., MEXICO; X.L. Dong, Shenyang Polytechnic University, Shenyang, P.R. CHINA; R. Reyes-Gasga, Institute of Physics, National University of Mexico, D.F., MEXICO; J.A. Toledo, Prog. Simulacion Molecular, Instituto Mexican 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 8-15nm diameter crystallites coated with 1-3 graphitic layers. Specially, HR-TEM images indicated that the intimate and contiguous carbon fringe around those Co nanoparticles was good evidence for complete encapsulation by carbon shell layers. The encapsulated nanophases were identified as hcp ( $\alpha$ )-Co and fcc ( $\beta$ )-Co by electron nano-diffraction (ED) and energy dispersive x-ray analysis (XEDS). No evidence was found by XRD for metastable cobalt carbides phases. However, some fcc ( $\beta$ )-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 HREM images are found to match well with those two hcp and fcc phase HRTEM lattice image taken along different crystal planes. It is expected that such carbon encapsulated mono-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. Han, Alex D.Q. Li, Washington State University, Dept. of Chemistry, Pullman, WA.

Submicron surface-functionalized silica colloids were used as templates around which beta-cyclodextrin was polymerized in a polyurethane matrix. Hollow capsules were harvested after etching out the silica 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 Mikhailova, Muhammet S. Toprak, German Salazar-Alvarez, Mamoun Muhammed. 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 van der Waals' force 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 microreactor is formed using CTAB, octane and varying the water to surfactant ratio ( $\omega$ ). The superparamagnetic nanoparticles are formed inside the reverse micelle by alkalizing an aqueous iron source with  $\text{NH}_4\text{OH}$ . After alkalization, the micelle containing  $\text{HAuCl}_4$  as surrounding solution is used to form a shell on nanoparticle core, by *in-situ* reduction of  $\text{HAuCl}_4$  with  $\text{NaBH}_4$ . 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. Muhammet S. Toprak, German Salazar-Alvarez, Do-Kyung Kim, Maria Mikhailova, Mamoun Muhammed, Royal Institute of Technology, Dept of Materials Science and Engineering, Materials Chemistry Division, Stockholm, SWEDEN.

The fabrication of micro- and nano-sized 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 nanoparticles that consist of either organic or inorganic cores coated 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 given 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  $\text{SiO}_2$  nanospheres were coated by electroless 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 particles was carried out using a suitable chemical method. In this study we report on the filling of the gold hollow particles with magnetic materials ( $\text{Fe}_3\text{O}_4$ ). 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, EDX, and  $\zeta$ -potential is presented.

**W6.30**  
SELF-ASSEMBLED ARRAYS FROM GOLD AND SULFUR  
CONTAINING FULLERENE NANOPARTICLES. Sheng-Ming Shih, Wei-Fang Su, Yuh-Juan Lin, C.-S. Wu, Chii-Dong Chen, National

Taiwan University, Institute of Materials Science and Engineering, Taipei, TAIWAN; National Taiwan University, Institute of Materials Science and Engineering, Taipei, TAIWAN; Biomedical Engineering Center, Industrial Technology Research Institute, Hsinchu, TAIWAN; Academia Sinica, Institute of Physics, Taipei, TAIWAN.

Two-dimensional (2D) arrays of gold nanoparticles with sulfur containing fullerene nanoparticles were self-assembled through the formation of Au-S covalent bonds. Disulfide functional groups were introduced into C60 molecule by reacting propyl 2-aminoethyl disulfide 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 was consistent with the result of 2.18 nm 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. The arrays were deposited on the top of pairs of gold electrodes to form 2D colloidal single electron 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.

#### **WG.31**

**ASSEMBLY OF QUANTUM DOTS WITH CONJUGATED MOLECULAR WIRES.** C. Steven Yun, Artjay Javier, 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 avenue of opportunities for the fields of electronics and sensing due 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 have 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 photovoltaic 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 II-VI quantum dots with poly-dipropoxyphenylene ethynylene dibenzylthiols will be shown. The selected use of organic functionality allows not only for assembly of the nanomaterials but preservation of the photoluminescence of the crystals and energy transfer from the organic polymer to the quantum dots.

#### **WG.32**

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

Pulse laser deposition is fast-developed technique for formation semiconductor and metallic nanoparticles in various matrixes. 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 Stranski-Krastanov 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 nucleation process of Ni nanoparticles is determined by several epitaxial relationships between nanoclusters 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 Ni islands and substrates corresponding to the different epitaxial orientation. By varying growth parameters it is possible to control undesirable orientations of metallic islands.

#### **WG.33**

Abstract Withdrawn.

#### **WG.34**

**NANOWIRE FORMATION BY ELECTRODEPOSITION IN MODIFIED NANOPOROUS POLYCRYSTALLINE ANODIC ALUMINA TEMPLATES.** Maria Mikhailova, Muhammet S. Toprak, German Salazar-Alvarez, Do-Kyung Kim, Mamoun Muhammed. Mats Chemistry Div, 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 of nanoscale materials in the pores of self-ordered nanochannel matrix is relatively low cost and fast processing time 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 anodization of Al 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 aluminum foils were degreased in acetone and cleaned in HF:HNO<sub>3</sub>:HCl:H<sub>2</sub>O mixture solution. Subsequently, the foil was annealed under nitrogen ambient at 500°C for 30 min, and electropolished to decrease the roughness of the ample surface. Dependence of anodic voltage, electrolyte (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, 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 of different ions from suitable 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.

#### **WG.35**

**NANOSTRUCTURING OF MULTILAYERS BY A THERMALLY DRIVEN SELF ASSEMBLING PROCESS.** Carsten Herweg, 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 nanostructuring accompanied by a self assembling process. After deposition in UHV an appropriate heat treatment causes a disintegration of the layered structure leading to isolated magnetic particles with a size of 5-30nm in a surrounding noble metal matrix. The particles are mostly arranged along the triple points of the initial growth columns of the multilayered structure. Therefore, the disintegrated multilayer consists of pearl chains of particles perpendicular to the substrate, separated by a distance of the order of the growth-column size. Previous investigations revealed that the interface 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 resistivity during film growth an 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 10nm which is far beyond the regime of magnetic exchange coupling. The variation of the anisotropy of the coercive field has been used to keep track of the desintegration. First attempts have been undertaken to introduce the disintegration by prepatterned substrates, i.e. substrates with a well-defined wavy or terraced surface like vicinally cut crystals. Part of this work was supported by the German Research Society DFG, project No. FR 452/4-2.

#### **WG.36**

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

We report on X-ray reflectivity and TEM studies of nano-particle self-assembly at the air/water interface. Thiol functionalized spherical Pd particles (~3 nm in diameter) were found to form highly ordered lattices. The phase diagram showed a large plateau region where the self assembly is shown to occur. A novel sonochemistry method was used functionalized nanotube (WS2). The sonication procedure provides uniform tubes 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 film which correlate to their structure will be discussed.

This work is supported by NSF-MRSEC program.

#### **WG.37**

**CHEMICAL NANOTECHNOLOGY.** E.P. Smirnov, V.K. Gromov, The State 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, precise both dimensionally and compositionally, on the surface of the solid phase substrate were theoretically formulated and experimentally confirmed in the seventies in Saint Petersburg Technological Institute under the leadership of Academician Aleskovsky 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 fundamentals 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 dialed in structure and composition, among them the artificial ones, not found in nature, is possible. The fundamentals and the experimental results of obtaining "chemically assembled" solids with a modified surface will be presented in the report. Their relationship to the fundamentals of the chemical 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 physico-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 Hahn and Heinrich Hofmann  
Wednesday Morning, November 28, 2001  
Back Bay B (Sheraton)

#### **8:45 AM W7.1**

**FABRICATION AND PROPERTIES OF SELF-ASSEMBLED NANOSIZED PARTICLES.** German Salazar-Alvarez, Do-Kyung Kim, Maria Mikhailova, Muhammet S. Toprak, Mamoun Muhammed, The Royal Institute of Technology, Dept of Materials Science and Engineering, Materials Chemistry Division, Stockholm, SWEDEN.

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-organisation. In this work, we report on the synthesis of nanosized copper, nickel, and cobalt composite particles. The nanoparticles consisting of a metal core covered by an oxide layer shell with varying thickness were prepared by reducing or oxidising the metal ions in solution by using water/oil/water 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 functionalising the substrate and particle surfaces with bifunctional organic molecules that attaches to both particles and substrates. Examination of the dispersed and assembled particle systems by a number of characterisation techniques including dynamic light scattering (DSL), transmission electron microscopy (TEM), X-ray diffraction (XRD), infrared spectroscopy (FTIR),  $\zeta$ -potential, Auger spectroscopy (AS), and atomic force microscopy (AFM) will be reported.

#### **9:00 AM W7.2**

**NOVEL METHOD FOR SELECTIVE DEPOSITION OF METALLIC NANOPARTICLES ON SILICON SURFACES.** Jaeyoung Choi, Srinivas Pietambaram, Rajiv K. Singh, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL.

The ability to fabricate and position magnets on a nanometer scale offers unique scientific and technological opportunities in magnetic miniaturization. Increasing the storage capacity of magnetic media requires reducing the size of the magnetized domains. 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 HF solution. Silicon wafer containing an array of dots is dipped in a solution containing the metallic ions. A 25 W Leica incandescent lamp was used to illuminate the wafer in order to increase metal outplating. 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) magnetometer was 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.** Florian Kauffmann, Gerhard Dehm, Eduard Arzt, Max-Planck-Institute for Metals Research, Stuttgart, GERMANY; Veit Schier, Walter AG, Tübingen, GERMANY; Sascha Henke, Alexander Schattke, Thomas Beck, Robert Bosch GmbH, Stuttgart, GERMANY.

Coatings are a vital part of many components and tools. They fulfill very different goals, mainly protection against wear, oxidation and heat. It is the aim of this project to develop single layer coatings which combine different properties such as extremely high hardness, high-temperature stability, toughness and a low friction coefficient thru the embedding of nanocrystalline titanium nitride particles in an amorphous silicon nitride matrix. The outstanding mechanical properties will be tailored by adjusting the microstructure of the coatings. 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 analyzed by means of focused ion beam and transmission electron microscopy. The mechanical properties are investigated by nanoindentation experiments. Our results indicate a transition from a columnar grain structure to spherical grains at about 4.5 at% Si. The hardness of the coatings reaches values of about 45 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 at%. This work is supported by the federal ministry of education and research (Bundesministerium für Bildung und Forschung) (contract number MaTech 03N3081). The authors are responsible for the content of this publication.

#### **9:30 AM W7.4**

**PHOTOCATALYTIC DECOMPOSITION OF FATTY STAINS BY TiO<sub>2</sub> THIN FILMS.** Juan Peris Vicente, Clarisse Durand, Thierry Gacoin, Philippe Barboux, Jean-Pierre Boilot, Physique de la Matière Condensée, Ecole Polytechnique, Palaiseau Cedex, FRANCE; Mauricette Rondet, Lethicia Guéneau, Saint-Gobain Recherche, Aubervilliers, FRANCE.

Anatase TiO<sub>2</sub> 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 crystallised by heat-treatment up to 600°C. Such transparent coatings have been evaluated regarding their catalytic activity under UV exposure. The photocatalytic activity has been measured by decomposition of artificial pollutants formed by fatty acids deposited onto the TiO<sub>2</sub> layer (adipic or stearic acid). The kinetics 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 stain thickness and morphology. The effect of the TiO<sub>2</sub> film thickness, porosity and particle size on the reaction kinetics have been studied as well as the starting thickness of the fatty acid layer. This allows to discuss the role of UV light absorption and the interdiffusion of radicals and oxygen across the interfaces. 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 TiO<sub>2</sub> anatase has been modified during synthesis of the nanoparticles by various doping cations doping increase the catalytic activity. These results on the decomposition of a solid state materials are compared with the photocatalytic activity 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.** N. Kishimoto, Y. Takeda, Nanomaterials Laboratory, NIMS, Tsukuba, Ibaraki, JAPAN; N. Umeda, University of Tsukuba, IMS, Tsukuba, Ibaraki, JAPAN.

Metal nanoparticles embedded in insulators are one of candidates for photonic materials, since electrons in a metal particle yield nonlinear and fast optical response with the surface plasmon 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 in-beam annealing on metal nanoparticle fabrication, particularly those caused by intense ion fluxes. Negative Cu ions of 60 keV are implanted into amorphous (a-)

SiO<sub>2</sub>, MgO on Al<sub>2</sub>O<sub>3</sub> and LiNbO<sub>3</sub> at high doses. Kinetic behaviors of the in-beam precipitation are studied by changing the dose rate, up to 100 μ% A/cm<sup>2</sup>, at a fixed total dose of 3 × 10<sup>16</sup> ions/cm<sup>2</sup>. 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 property is evaluated around the plasmon energy of 2.2 eV. Metal precipitation behaviors strongly depended on the substrate species for a fixed implant of Cu, although spontaneous precipitation occurred more or less. For a-SiO<sub>2</sub>, the particle size increased with increasing dose rate, up to 10 μA/cm<sup>2</sup>. At high dose rates < 50 μ% A/cm<sup>2</sup>, Cu nanocrystals with a diameter of 10 nm 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 metastable nature of a-SiO<sub>2</sub> favors pronounced precipitation. On the other hand, the Mg-Al spinel prohibited particle coarsening even at high dose rates up to 30 μA/cm<sup>2</sup>, sustaining crystallinity of the lattice. The nanoparticles in the spinel remained less than 5 nm. The different material behaviors under intense ion implantation are usable to control nanoparticle structures and resultant optical properties.

#### 10:30 AM W7.6

SHOCK-WAVE SYNTHESIS OF NANOPARTICLES DURING ION SPUTTERING. L.E. Rehn, R.C. Birtcher, S.E. Donnelly, P.M. Baldo 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 ion sputtering obey an inverse power law, with an exponent varying between 8 and 4 depending upon the total sputtering yield. Such large negative exponents have not been explained by any simple physical mechanism. Here we report electron microscopy studies of the size-distributions of the larger nanoparticles ( $n > 500$ ) that are sputtered from the surface by high-energy ion impacts. These new measurements also yield an inverse power-law, but one with an 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 sub-surface displacement cascades, impact and ablate the surface. Many smaller clusters can result from fragmentation of these larger ones, which helps explain the large negative exponents that have been reported previously. An important corollary from these results is that the synthesized nanoparticles consist of simple fragments of the original surface, that is ones that have not undergone any large thermal excursions. Experiments are in progress to demonstrate that layered 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

FORMATION OF FERROMAGNETIC FePt NANOPARTICLES BY ION IMPLANTATION. C.W. White, S.P. Withrow, J.D. Budai, L.A. Boatner, K.D. Sorge, J.R. Thompson, Oak Ridge National Laboratory, Oak Ridge, TN; K.S. Beaty, A. Meldrum, The University of Alberta, Alberta, CANADA.

We have used sequential ion implantation of Fe and Pt, followed by thermal annealing to form ferromagnetic FePt nanoparticles with extremely high magnetic coercivity (greater than 2 Tesla) embedded in both crystalline Al<sub>2</sub>O<sub>3</sub> and amorphous SiO<sub>2</sub> matrices. In Al<sub>2</sub>O<sub>3</sub>, the nanoparticles are crystallographically oriented and particle size varies from a few nm to ~100 nm depending on the implantation and annealing conditions. Nanocomposites 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 73%. In the Pt-atomic-fraction range from 35% to 53%, x-ray diffraction measurements show that the chemically ordered L1<sub>0</sub> tetragonal phase of FePt is produced. These nanoparticles are ferromagnetic with a coercivity that maximizes at a Pt concentration of ~45%. In this case, the coercivity can exceed 2 Tesla (at 30K). At lower (25%) and higher (73%) Pt concentrations, the x-ray diffraction results are close to those expected from the L1<sub>2</sub> structures of Fe<sub>3</sub>Pt and FePt<sub>3</sub>, respectively. In SiO<sub>2</sub>, the FePt nanoparticles are randomly oriented, and the particle size varies from a few nm to ~70 nm depending on the implant and annealing conditions. For FePt nanoparticles in SiO<sub>2</sub>, the coercivity can exceed 2 Tesla (for a Pt atomic fraction of 45%). The application of these techniques to form FePt 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 Behlen Laboratory of Physics, University of Nebraska, Lincoln, NE.

We have developed a universal cluster deposition system, which combines a new kind of sputtering-gas-aggregation cluster beam source, with two atom beams from magnetron sputtering. This system is used to deposit simultaneously or alternately mesoscopic 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 industry applications. Magnetic 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 SiO<sub>2</sub>) in which the volumetric concentrations of Co clusters can be varied from 5% to 50% and the cluster mean size from 200 to 10,000 atoms (2 to 9 nm) with the size distribution ( $\Delta d/d$ ) of about 0.2. The magnetization (Ms) of the films is cluster-size and concentration dependent, and always significantly less than that of bulk cobalt. For the same size of clusters (9000 atoms), the Ms for the SiO<sub>2</sub> 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 (Tp), 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

SUPERSONIC CLUSTER BEAMS: A POWERFUL METHOD FOR THE MANIPULATION OF CLUSTERS AND THE SYNTHESIS OF NANOSTRUCTURED MATERIALS. P. Milani, P. Piseri, E. Barborini, C. Lenardi, S. Vinati, G. Bongiorno, INFN-Dipartimento di Fisica, Universita' di Milano, Milano, ITALY.

Deposition of clusters from the gas phase has been proposed as an interesting technique for the synthesis of nanoparticulate materials. Among different experimental approaches, supersonic clusters beam deposition has been shown as a viable route for the production of systems ranging from organized nanoislands to nanostructured thin films [1]. In view of practical applications the development of highly intense 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 aerodynamical effects typical 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 novel physico-chemical and topological properties such as mesoscopic carbon foams and nanostructured carbon matrices containing carbide and/or transition metal particles.

[1] P. Milani, S. Iannotta, Cluster Beam Synthesis of Nanostructured Materials, Springer-Verlag, Berlin (1999).

#### 11:30 AM W7.10

CONTROLLED AND SELECTIVE AGGREGATION OF SUBMICROMETER Cu-CRYSTALLITES ON FIB SENSITIZED p-Si. Adrian Spiegel, Swiss Federal Institute of Technology, Lausanne (EPFL), Dept. of Materials Science, LTP, Lausanne, SWITZERLAND; Patrik Schmuki, 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 electrodeless deposition 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 altering its surface in a controlled way. Using focussed ion beam (FIB) implantation to introduce defects into 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 behaviour of different metals (Cu, Au, Pd) on FIB sensitized surface locations and show that

crystallite growth follows a three dimensional growth law. Crystallites grow very rapidly in a first phase and reach a size of roughly 200nm after 0.5s. In the present study we investigate a variety of 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  
Chairs: Kenji Sumiyama and Rajiv Kumar Singh  
Wednesday Afternoon, November 28, 2001  
Back Bay B (Sheraton)

#### 1:30 PM \*W8.1

PROCESSING COMPLEX & UNIFORM NANOPARTICLES FOR MICROELECTRONIC & PHOTONIC APPLICATIONS. Nobuyuki Kambe, 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 performances goals. The second challenge is how to convert these nano-building blocks to application forms such as device structures or coatings. NanoGram has developed laser-driven chemical reaction processes to generate a versatile range of nanoparticles 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 nanoparticles, especially in organic solutions. 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, even over 50%. Industrial applications are discussed based on these observations, with some emphasis on planar lightwave devices, photonic nanocomposites for index engineering, and planarization processes for electronic chips.

#### 2:00 PM W8.2

HYDROTHERMAL SYNTHESIS OF NANOPARTICULATE METAL CHALCOGENIDES. Paul J. Nigrey 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 disulfides using hydrothermal conditions [up to 250°C and up to 3.6 MPa (525 psig)]. The discussion emphasizes the preparation of metal chalcogenides that represent potential candidates as alternative battery-active materials for use in lithium thermal batteries as well as lithium ambient-temperature batteries. The metal disulfides were prepared by the reaction of metal sulfates with sodium tetrasulfide in aqueous media. The growth process for the metal sulfides consists of initial rapid nucleation induced by the sulfidizing agent followed by aggregation to form nanoparticulate metal sulfides. The syntheses were carried out in either a stainless steel commercial autoclave or a glass pressure reactor. Initial experiments performed in the steel autoclave at 140°C and 345 kPa (50 psig) yielded nearly quantitative amounts of metal disulfide. Depending on the pressure and pH of the reaction mixture, metal monosulfides or metal disulfides can be obtained. Subsequent work has shown that pressure as low as 48 kPa (7 psig) also yield nanoparticulate samples. Scanning electron microscopy and X-ray powder diffraction examinations have confirmed that 10-30 nm iron, cobalt, and nickel disulfide having a pyrite structure are formed. Solid solutions of iron, cobalt, and nickel disulfide were easily obtained using mixed metal salts in the reaction. Materials such as  $\text{Fe}_{0.2}\text{Co}_{0.8}\text{S}_2$ ,  $\text{Co}_{0.5}\text{Ni}_{0.5}\text{S}_2$ , and  $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{S}_2$ , exhibit similar size and structural properties as the previously described parent metal disulfides. 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. SNL 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 SC991549 with Eagle-Picher Technologies, LLC, Joplin, MO.

#### 2:15 PM W8.3

COLLOID CHEMICAL COATING OF OXIDE NANOPARTICLES FOR ANTIDegradation OF ZnS-BASED PHOSPHORS. Takahiro Igarashi, Tsuneo Kusunoki, Katsutoshi Ohno, Sony Corporation, Home Network Company, Atsugi, JAPAN; Tetsuhiko Isobe, Mamoru Senna, Keio University, Faculty of Science and Technology, Yokohama, JAPAN.

ZnS-based phosphor particles, notably ZnS:Ag,Cl with their average particle size 4.3 $\mu\text{m}$ , were coated either with ZnO or  $\text{Y}_2\text{O}_3$  nano particles via a colloid 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,Cl modified with ZnO nanosized particles was reduced by 40% after 9h exposure to EB. Comparison with similar coating by  $\text{Y}_2\text{O}_3$  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,Cl, ZnS:Cl with varying Cl concentration as well as ZnS:Ag,Al after EB irradiation, it was concluded that decrease in the effective concentration of Cl, serving as active luminescence center, is also responsible for the CL degradation of ZnS:Ag,Cl by EB irradiation.

#### 2:30 PM W8.4

NANO-ENCAPSULATED ZnS:Ag PHOSPHORS FOR FIELD EMISSION FLAT PANEL DISPLAY APPLICATIONS. Michael Ollinger, Valentin Craciun, Rajiv K. Singh, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL.

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 although has made a significant improvement in the last decade, has not met 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 sulfide based 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 nano-meter 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 controlling 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 coating 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 degraded particle surfaces. Scanning Electron Microscopy (SEM) was used to show the changes of the surface morphology due to the cathodoluminescent degradation.

#### 2:45 PM 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 testing apparatus was designed and constructed. Absorption conditions are evaluated over a range of pressure from 0 to 4000 psig and range of temperature from 0 to 100°C. A new approach to 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 PM \*W8.6

TAILORED NANOMATERIALS FOR STRUCTURAL AND FUNCTIONAL APPLICATIONS. Ganesh Skandan, Amit Singhal, Nanopowder Enterprises Inc., NJ.

Nanopowders and nanopowder-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 feedstock material can facilitate processing of an improved end-product at a lower cost. However, it is becoming increasingly clear that while the use of nanoparticles as starting 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 tailored nanopowders. In particular, 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 coatings on polymer substrates, (iii) multimodal tungsten-carbide powders for thermal sprayed coatings, and (iv) ultrafine 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 nanopowders, and the corresponding functional or structural properties in each of these application areas will be described.

#### 4:00 PM W8.7

**FePt NANOPARTICLES WITH HIGH COERCIVITY.** Yunhe Huang, H. Okumura, G.C. Hadjipanayis, 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 disordered fcc structure which is magnetically soft. Post annealing at temperature in the range of 550 to 850°C is required to form the ordered fct FePt particles. As the substrate temperature increases, the microstructure of FePt films changes to a mixture of disordered fcc and ordered fct FePt 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 substrate 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 rather 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 in the parallel direction. A magnetic field perpendicular to film plane during sputtering is designed in order to enhance the perpendicular texture at lower temperatures. Work supported by NSF-DMR 9972035 and Seagate Technology.

#### 4:15 PM W8.8

**CONTROLLING PERCOLATION IN FIELD-STRUCTURED PARTICLE COMPOSITES: OBSERVATIONS OF GIANT THERMORESISTANCE, PIEZORESISTANCE, AND CHEMIRESISTANCE.** James E. Martin, Robert A. Anderson, Judy Odinek, Douglas Adolf, Sandia National Laboratories, Albuquerque, NM.

When conducting-particle composites are prepared very near the percolation threshold their resistivity is highly sensitive to small specific volume changes. Such near-threshold materials have potential as simple temperature, pressure, or chemical sensors, but in practice it is difficult to prepare composites 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 volume changes of the resin. These composites exhibit giant (11 decade) thermoresistance, piezoresistance, and chemiresistance, and thus appear to have great potential for sensor applications.

#### 4:30 PM W8.9

**FIRST-PRINCIPLES SIMULATIONS OF ATOMIC STRUCTURE AND MAGNETISM IN Fe NANOPARTICLES.** A.V. Postnikov and P. Entel, Theoretical Low-Temperature Physics, Gerhard Mercator University Duisburg, GERMANY; Pablo Ordejón, Institut de Ciència de Materials 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, as implemented in the SIESTA code.<sup>1</sup> In the development of previous simulation of Fe-related nanosystems done earlier with this approach in fixed (perfect) geometry,<sup>2</sup> we concentrate now on the interplay of lattice relaxation, that 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 outer shells of nanoparticles. These results are refined by taking structure relaxation into account and by considering more representative bcc- and fcc-related particles. Moreover, we allowed antiferromagnetic ordering along with ferromagnetic one and discuss interplay between magnetic ordering and structure relaxation. The comparison with all-electron calculation results is done for some crucial cases.

<sup>1</sup>D. Sánchez-Portal, P. Ordejón, E. Artacho and J. Soler, Int.J.Quant.Chem. **65**, 453 (1997); E. Artacho, D. Sánchez-Portal, P. Ordejón, A. Garcia and J.M. Soler, Phys.Stat.Sol. (b) **215**, 809 (1999).  
<sup>2</sup>J. Izquierdo, A. Vega, L.C. Balbás, D. Sánchez-Portal, J. Junquera and E. Artacho, Phys.Rev.B **61**, 13639 (2000).  
<sup>3</sup>N. Fujima and T. Yamaguchi, Mater.Sci.Engin. **A217/218**, 295 (1996).

#### 4:45 PM W8.10

**Gd AND Tb NANOPARTICLES OBTAINED BY "THE PARTICLE-GUN" TECHNIQUE.** V. Skumryev, S. Stoyanov, Y. Huang, Y. Zhang, Z. Yan, and G.C. Hadjipanayis, 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/orifice 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 9972035.

#### SESSION W9: POSTER SESSION NANOPARTICULATE MATERIALS: CHARACTERIZATION AND NOVEL APPLICATIONS

Chairs: Heinrich Hofmann, Mamoun Muhammed and  
Dhananjay Kumar

Wednesday Evening, November 28, 2001  
8:00 PM

Exhibition Hall D (Hynes)

#### W9.1

**HIGHLY ENHANCED ELECTRICAL AND MECHANICAL PROPERTIES OF THE MULTILAYER PIEZOELECTRIC TRANSFORMER BY FABRICATING THE RAW MATERIAL OF PZT NANO-SCALED POWDER AND ITS SURFACE TREATMENT.** Yu Zhang, Jian Sun, Helen L.W. Chan, Choong L. Choy Material Research Center, Applied Physics Department, Hong Kong Polytechnic University, Kowloon, HungHum, Hong Kong, CHINA.

High-energy wet milling 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 side 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 shape of about 200 nm 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. Compare 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 plastics 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 16% 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 1050 Celsius degree, so that low temperature sintering process can be expected. Besides that, due to the improvement of the PZT ceramic by using the nano-scaled PZT powder, more advantage can be gain by putting the multilayer device into practice. From the experiment result we can see: firstly, the thermal-electrical loss of the device will

be clearly reduced; secondly, the output power of the multilayer transformer can be easily increased due to the reason of higher power density can be permitted to transmit 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 nano-scaled powder with its surface treatment is a very effective way for improving the PZT ceramic's physical property. Further more it can also serve 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.** Kyo-Se Choi, Seung-Mahn Lee, Joodong Park and Rajiv K. Singh, Department of Materials Science and Engineering and Engineering, Research 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 defectivity 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 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 silica and alumina on the polishing characteristics of silica, copper and tantalum blanket films. The primary as well as the secondary particle size was measured using standard particle instrumentation techniques. Standard slurry formulations were designed to polish each of these materials. 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 NANOPARTICLES.** C. Baker, S. Ismat Shah, Univ of Delaware, DE; J. Adkins, Fraunhofer Ctr, 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) in the tapping mode. The dispersion 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  $\text{In}_2\text{S}_3$  NANOCOLLOIDS AND THEIR SURFACE MODIFICATION BY  $\text{RuBIPY}_2$ .** Dattatri K. Nagesha, Xiaorong Liang, Arif A Mamedov, Margaret A. Eastman, Tong Ni, Nicholas A Kotov, 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 Giersig, Hahn-Meitner-Institut, Abt. Physikalische Chemie, Berlin, GERMANY.

Stable aqueous colloids of 2-3 nm  $\text{In}_2\text{S}_3$  nanocrystals have been prepared by using the classical method of nanoparticle stabilization by low molecular weight thiols. The analysis of TEM crystal lattice spacing, X-ray diffraction, EDAX data, and electron diffraction indicate that the nanoparticles are predominantly in the  $\beta$   $\text{In}_2\text{S}_3$  form. They exhibit relatively strong excitonic emission at 360-380 nm with a quantum yield of 1.5 %. 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 electron withdrawing 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 CdS nanoparticles of the same size

this effect is substantially stronger than for  $\text{In}_2\text{S}_3$ . Lower density of metal centers in  $\text{In}_2\text{S}_3$  than in CdS, which serves as anchor points for the stabilizer, promotes greater mobility of the stabilizer moieties. Surface modification of these nanoparticles can be achieved by utilizing the chalcogen atoms to bind the modifier. This is significantly different as 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 bipyridine moieties. The UV-Vis absorption, emission and excitation spectra suggest the relaxation of the electron confinement and partial mixing of semiconductor nanoparticle and the  $\pi$  systems of the aromatic ligands. This type of surface modification via S-sites leads to new routes to building nanoparticle supramolecules.

#### **W9.5**

**MICROSTRUCTURE AND MAGNETIC PROPERTIES OF  $\text{Fe}(\text{C})$  AND  $\text{Fe}(\text{O})$  NANOPARTICLES.** Xiang-Cheng Sun, N. Nava, V.G. Febles, Prog. Molecular Simulation, Instituto Mexicano del Petroleo (IMP), D.F., MEXICO; J. Reyes-Gasca, Institute of Physics, National University of Mexico (UNAM), D.F., MEXICO; X.L. Dong, Shenyang Polytechnic University, Shenyang, P.R. CHINA.

Two types of iron (Fe) nanoparticles-carbon-coated Fe nanoparticles ( $\text{Fe}(\text{C})$ ) and pure  $\alpha$ -Fe nanoparticles that coated with oxide layers ( $\text{Fe}(\text{O})$ ), were successfully synthesized using modified graphite arc-discharge method. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), nano-area 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 ( $\text{Fe}(\text{C})$  and  $\text{Fe}(\text{O})$ ). It was indicated that those two Fe nanoparticles have an average grain size of 15-30nm. The presence of carbon encapsulated  $\alpha$ -Fe,  $\gamma$ -Fe and  $\text{Fe}_3\text{C}$  phases were clearly identified by X-ray diffraction in those  $\text{Fe}(\text{C})$  particles, and further confirmed by Fast Fourier Transform (FFT) spectra. Whereas, the evidence of pure  $\alpha$ -Fe nanocrystal coated with oxide layer was also revealed by using HRETM images and SAED patterns in those  $\text{Fe}(\text{O})$  particles. Mossbauer spectra at room temperature for the assembly of  $\text{Fe}(\text{C})$  and  $\text{Fe}(\text{O})$  nanoparticles confirmed their distinct nanophases which examined by XRD analysis and HRTEM observation. On the other hand,  $\text{Fe}(\text{O})$  nanoparticles exhibited ferromagnetic properties at room temperature due to the interaction between ferromagnetic  $\alpha$ -Fe core and antiferromagnetic oxide ( $\text{Fe}_3\text{O}_4$ ) shell layers. However, superparamagnetic relaxation was observed in the assembly of  $\text{Fe}(\text{C})$  nanoparticles, which was attributed to the nanocrystalline nature of the carbon-coated nanoparticles.

#### **W9.6**

**PLATED METALS: NEGATIVE ELECTRODE MATERIALS FOR LI-ION BATTERIES?** T.A. Hugener, M.M. Desko, N.G. Jones, F. Galasso, S.L. Suib, Univ Connecticut, Dept Chemistry, Storrs, CT; S. Iaconetti, P.G. Russell, J.F. DiCarlo, Yardney Technical Products, Pawcatuck, CT.

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 on bath conditions and the total plating duration. 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 NANOSTRUCTURED PARTICULATE CATALYTIC MATERIALS.** Baiyun Tong<sup>1,3</sup>, Qun Gu<sup>1</sup>, Upali Siriwardane<sup>1</sup>, Seetala V. Naidu<sup>2</sup>, Akundi N. Murty<sup>2</sup> and Zhenchen Zhong<sup>1,2</sup>. <sup>1</sup>Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA. <sup>2</sup>Department of Physics, Grambling State University, Grambling, LA. <sup>3</sup>Institute of Metal Research, Chinese Academy of Sciences, Shenyang, CHINA.

Novel nano-particle catalysts  $\text{Fe}/\text{Cu}$  and  $\text{Co}/\text{Cu}$  will provide a promising alternative to conventional catalysts for the efficient conversion of  $\text{CO}/\text{CO}_2/\text{H}_2$  gases to useful fuels. We have prepared  $\text{g-Al}_2\text{O}_3$  granular support particles by sol-gel method through three steps: boehmite sol ( $\text{g-AlOOH}$ ) preparation, sol gelatinization and shaping (oil drooping), and dry and calcinations. Laser induced solution deposition (LISD) is a novel method for preparing proposed nanoparticle  $\text{Fe}/\text{Cu}$  and  $\text{Co}/\text{Cu}$  catalysts, which impinged on the  $\text{Al}_2\text{O}_3$  granular support. In the initial experiments, we have deposited nanostructured pure  $\text{Co}/\text{Co}$  oxide and  $\text{Fe}/\text{Fe}$  oxide nanoparticles. We have studied the microstructure and composition of deposited nanoparticles by scanning electron microscope (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 (ZFNMR).

This project supported by DOE under the grant no: DE-FG26-00NT40836.

#### **W9.8**

**STRUCTURAL AND SPECTROSCOPIC STUDY OF Mn AND Ir SILICIDE ISLANDS ON Si.** Miyoko Tanaka, Masaki Takeguchi, Qi Zhang, Junliang Liu, Kazutaka Mitsuishi, Kazuo Furuya, Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, JAPAN.

In order to achieve nanometric-sized 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 UHV condition. We report our observation and analysis results on Mn and Ir metal silicide islands on Si substrate with UHV-TEM and UHV-STM. Si (111) substrates were cleaned in UHV-TEM/STM integrated characterization system (UTSICS) 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 UHV-TEM and cathodoluminescence measurement in UHV-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 Moire fringes between Si and Mn silicide island. Because its periodicity is pretty long, it is considered that Mn silicide grew in good coordination with substrate Si. HRTEM analysis revealed that the silicide islands grew epitaxially but that the interface is of 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. Eklund 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 polypeptides. 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 areas 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 chiral high pressure liquid chromatography (HPLC). However, mesoporous silica has not been used in GPC. In this study, the mesoporous silicas 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. Polystyrenes of various molecular weights were passed through HPLC columns of the silicas and retention times were plotted as a function of molecular weight. APMS-30 and MCM-41 were more effective than Nucleosil at identifying the molecular weights of very short polystyrene oligomers due to their smaller pore sizes. The molecular weight cutoff (a calculation of the molecular weight of the largest polystyrene still showing a size exclusion effect) proved to be a reasonably 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**

**ON THE NATURE AND BEHAVIOUR OF NANOSCALE PARTICLES OF NOBLE AND TRANSITION METALS.** Jitendra Kumar, Indian Institute of Technology, Materials Science Programme, Kanpur, INDIA.

Nanoscale particles of noble and transition metals, such as gold, platinum, palladium, nickel and iron, dispersed over alumina thin films by thermal evaporation under vacuum have been studied by TEM with regard to their 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 phase in case of gold and platinum in some situations. 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, faceting with well defined shapes, e.g., cubic, hexagonal, rhombohedral, pentagonal, wetting of substrate, formation of oxides or hydrides and emergence of core-and-ring or torus shape particles have been described at length. Evidence is advanced to support the Ostwald ripening mechanism for growth of particles. Accordingly, coarsening results not by particle migration, collision and subsequent coalescence but by transfer of species/atoms from smaller to larger particles via substrate and/or jump process, irrespective of whether particles retain their metallic character or undergo reaction to form respective oxide or hydride. The implications of these findings are discussed in light of industrial applications of such systems as catalysts in various reactions, e.g., oxidation, hydrogenation, dehydrogenation, petroleum cracking, etc.

#### **W9.11**

**MONITORING OF SILICON NANO-CRYSTAL DOTS FORMATION ON SiO<sub>2</sub> AND ON Si<sub>3</sub>N<sub>4</sub> IN A UHV-CVD SYSTEM.** Takayuki Kawashima, Supika Mashiro, Junro Sakai, ANELVA Corporation, Tokyo, JAPAN; Rajesh Rao, R. Muralidhar, 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 dots formation process on SiO<sub>2</sub> 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 read-out is obscured by radiation from parts below wafer. Another is that the sensitivity of pyrometer read-out 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 the 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 SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> 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.

#### **W9.12**

**SURFACE CHEMISTRY OF NANOPOWDERED WO<sub>3</sub> IN GAS SENSING REACTIONS WITH NO AND NO<sub>2</sub>.** C. Canevali, F. Morazzoni, R. Scotti, Univ di Milano-Bicocca, Dept Scienza dei Materiali, Milano, ITALY; J. Arbial, A. Cornet, I. Jimenez, J.R. Morante, Univ. de Barcelona, Dept Electronica, Barcelona, SPAIN.

Tungsten trioxide has been studied for gas sensing application towards NO and NO<sub>2</sub> gases. In this work WO<sub>3</sub> polycrystalline nanopowders (30-70 nm) were obtained by precipitation from a methanol/water (3:1 mol:mol) solution of tungstic acid, H<sub>2</sub>WO<sub>4</sub> and successive thermal treatment in air (400 -700 °C). Thick films (3 μm) of the nanopowdered WO<sub>3</sub> showed a good electrical sensitivity to NO<sub>2</sub> ( $S = R_{NO_2}/R_{air}$ ) with low interference of CO and CH<sub>4</sub>. The range of atmosphere composition was 0.5-5.0 ppm of NO<sub>2</sub> in dry and moistened air. The oxide sensitivity was influenced by crystallinity, particle size and surface area of WO<sub>3</sub>, which strongly depended on the preparation method and thermal treatment temperature. Aim of this work was the study of the surface reactivity of WO<sub>3</sub> towards NO, NO<sub>2</sub> 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 NO<sub>2</sub> groups. The relations between the surface paramagnetic species and the structural and morphological properties were also investigated; in fact WO<sub>3</sub> samples prepared from tungstic acid were compared with samples prepared by a sol-gel process from a tungsten ethoxide/ethanol/water solution.

#### **W9.13**

**POSITRON ANNIHILATION IN Cd-Se QUANTUM DOTS.** Bernardo Barbiellini, Northeastern University, Boston, MA; Marc Weber, 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.

Positron 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 positron 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 positron is entrained within the quantum dot. A model is presented in which electron momentum "smearing" is proportional to the change in 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, Kalpana S. Katti, Vijayakumar Shanmugasundaram, 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 a simultaneous measurement of swelling and swelling pressure in addition to ease of removal of undisturbed samples for electron microscopic and fourier transform infrared spectroscopic 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 Si-O vibration band regions of the montmorillonite spectra obtained at controlled amounts of swelling from 0-100% (where 0% swelling is defined as fully saturated samples under no volume change) show changes in band shape, intensity, and positions resulting from increased H-bonding in the interlayers and surface of montmorillonite particles. In addition, orientation dependant micro-attenuated total reflectance (ATR) spectroscopic investigations are also conducted on the controlled swelled samples. Our results indicate that the 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 Spinu, Le Duc Tung, Jiye Fang, Charles J. O'Connor, AMRI, Univ. of New Orleans, New Orleans, LA; Srikanth Hariharan, Univ. of South Florida, Dept. of Physics, FL; Al. Stancu, "A.I. Cuza" Univ., Faculty of Physics, Iasi, ROMANIA.

The dynamics of magnetic nanoparticle systems is a subject of considerable interest due to their fundamental and technological interest. The properties of such systems are strongly modified compared to the bulk, due to granular 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 matrix where the volume concentration can be systematically 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 syntheses of cobalt nanocrystallites were carried out using standard organometallic reaction procedures with airless/moisture-less devices and commercially available reagents. The dispersion of Co nanoparticles in the wax matrix was carried out by ultrasonically mixing the concentrated cobalt nanocrystallites 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 light scattering experiments. RF transverse susceptibility experiments at various temperatures, ac susceptibility in the frequency range (10 Hz,  $10^4$  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 and inter-particle interactions of different strengths. It is shown that the combined effect of magnetic relaxation and interactions is fundamental in defining the overall magnetic properties of magnetic nanoparticle systems.

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**W9.16**  
PREPARATION OF NANOPARTICULATE METAL OXIDE THIN FILMS: SYNTHESIS AND PARTICLE SIZE CONTROL OF METAL OXIDE COLLOIDS. S.C. Pang, Faculty of Resource Sciences & Technology, Universiti Malaysia 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 charge-storage devices. Nanostructured materials prepared from nanoparticles 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 nanoparticulate  $MnO_x$  and  $NiO_x$  thin films exhibit large charge storage capacity or capacitance. In this study, we have synthesized stable 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 used 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 INCONEL 625 POWDER. Kyung H. Chung, Jongsang Lee, Rodolfo Rodriguez and Enrique J. Lavernia, Department of Chemical, Biochemical Engineering 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 stability by oxide 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 better 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 MC carbides and rod shaped  $\delta$ -phase intermetallic precipitates. These precipitates promote grain growth resistance at this particular temperature via a grain boundary pinning mechanism. The preferred nucleation sites of those precipitates was noted to be at grain boundaries, thereby augmenting the grain boundary pinning effect.

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**W9.18**  
MOSSBAUER ANALYSIS OF THE IRON CATALYST RESIDUE IN MULTI-WALLED CARBON NANOTUBES. John P. Selegue, John E. Anthony, Grant J. Palmer, Department of Chemistry; Rodney Andrews, David Jacques, Center for Applied Energy Research; Frank E. Huggins, Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, Lexington, KY.

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 66% elemental iron and 34% cementite ( $Fe_3C$ ). When pyridine is used as the feed during the synthesis, the residual iron is present as 17% elemental iron, 79%  $Fe_3C$  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.

### W9.19

#### QUENCHING PHENOMENA IN WATER-SOLUBLE CdSe/ZnS QUANTUM DOTS. D.M. Speckman, T.L. Jennings, S.D.

LaLumondiere, and S.C. Moss, The Aerospace Corporation, Los Angeles, CA.

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 core-shell nanocrystals (quantum dots) for use as fluorescent reporters in immunoassay-based biological sensors. As part of our efforts to bind semiconductor CdSe/ZnS quantum dots to antibody proteins for this work, we functionalized the nanocrystal surfaces 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 underivatized CdSe/ZnS nanocrystals. One of the most striking differences observed is the reactivity of the derivatized and underivatized 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 underivatized 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 yields compared to the underivatized nanocrystals. We have also found that both the water-soluble quantum dots and the underivatized 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.

### W9.20

#### STUDY OF THE OPTICAL CHARACTERISTICS OF Bi<sub>2</sub>O<sub>3</sub>-DOPED ZnO POWDER BY CATHODOLUMINESCENCE MICROSCOPY. X.L. Sun<sup>a</sup>, L.J. Brillson<sup>a,b,c</sup>.

<sup>a</sup>Department of Electrical Engineering, <sup>b</sup>Center for Materials Research, <sup>c</sup>Department of Physics, The Ohio State University, Columbus, OH. Y.-M. Chiang, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

ZnO ceramics doped with a small amount of Bi<sub>2</sub>O<sub>3</sub> show strongly nonlinear current-voltage (I-V) characteristics and are thereby used as varistors in various electric devices. In this paper, we used low temperature (10 K) cathodoluminescence (CL) spectroscopy to investigate optical characteristics of Bi<sub>2</sub>O<sub>3</sub>-doped ZnO powders prepared under different processing conditions. Our 25 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, this 'Green' 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 bound exciton line at grain boundaries. Its energy is ~ 6 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, becoming 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.

### W9.21

#### MICROSTRUCTURES AND C60 DIFFUSION BEHAVIOR IN NANO-SIZE PORES OF SILICA GLASSES. Weijie Lu,

Melvin Hunt, III, W. Eugene Collins, Department of Physics, Fisk University, Nashville, TN; Benjamin G. Penn, Space Science Laboratory, NASA Marshall Space Flight Center, Huntsville, AL; Hari B. Sunkara, Laurent Sibille, and Hossin Abdeldayem, Universities Space Research Association, Huntsville, AL.

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 xerogels. The boundary regions between grains and between clusters consist of pores for the glass with 20nm pores. The cylinder

shaped nano-size pores with 2.0-3.0 nm in diameter are revealed by AFM in the glass with 2.5nm pores, and also the grain boundary areas consist of the large pores. C60 is well dispersed in the glasses with 2.5, 5.0, and 7.5nm pores by diffusion, and aggregated in the glass with 20nm pores. An irregular shaped aggregated C60 structures with sharp edges at micron scale are observed by AFM in the glass with 20nm pores. Doping C60 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.

### W9.22

#### SYNTHESIS AND REACTIVITY OF POROUS SILICA DOPED WITH NANOPARTICLES OF Fe, Co, AND CU. Joseph G. Moore,

Jennifer Epperlein, Kevin Schneider, and Christopher Landry, Univ 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 avoided 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 doping 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, as shown by XRD and nitrogen physisorption 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.

### W9.23

#### HARD POLYMER NANOCOMPOSITE COATINGS FOR OPTICAL APPLICATIONS. Amit Singhal and Ganesh Skandan, Nanopowder

Enterprises, Inc., Piscataway, NJ.

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 head lamps, 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-nanophase oxide matrix. Large ceramic particles impart excellent wear and scratch resistance due to their large wear surface. We have engineered the surface of these large particles so they are compatible with the polymer-nanophase 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.

### W9.24

#### LIGHT SCATTERING BY ISOLATED AND SUPPORTED

NANOPARTICLES USING DDA. Iván O. Sosa, Cecilia Noguez and Rubén G. Barrera Instituto de Física, UNAM, MEXICO.

Optical spectroscopies have shown to be useful tools to characterize nanostructures, due to their in situ potentiality 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 spheroidal 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 lying 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. [1] C.E. Roman-Velazquez, C. Noguez, and R.G. Barrera, Phys. Rev. B61, 10427 (2000).

#### **W9.25**

**ENERGY AND ELECTRON TRANSPORT IN METAL/ SEMICONDUCTOR NANOCRYSTAL SOLIDS.** Artjay Javier, G.F. Strouse, 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 spun-cast solids. Solution phase Stern-Volmer studies as well as nanocrystal film doping elucidate 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.

#### **W9.26**

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

This experiment is to investigate the microporosity in spherical silica particles with a very narrow particle size and size distribution by the hydrolysis reaction of tetraethoxysilane 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 a silicon alkoxide in ethanol. The intraparticle microporosity has been created by adsorption of an organic compound (glycerol) as the progen. The presence of glycerol during the synthesis affects considerably the precipitation mechanism and its effect on the particle size will be discussed. The synthesis of silica microporous spheres of narrow size distribution yielded the preparation, by varying particle size and porosity, of a wide range of aqueous silica 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. Silica 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 in CMP applications.

#### **W9.27**

**CHROMIUM DOPED  $\text{LiMn}_2\text{O}_4$  NANOPARTICLES PREPARED BY THE SOL-GEL PROCESS FOR LITHIUM-ION SECONDARY BATTERIES.** Chung-Hsin Lu, Yueh Lin, Hsien-Cheng Wang and Wen-Jeng Hwang, Department of Chemical Engineering, Natl Taiwan Univ, Taipei, TAIWAN ROC.

Lithium manganese oxides with spinel structure are of great interest as insertion electrode for use in 4-volt lithium ion rechargeable batteries. It presents advantages in economy, ecology and safety. The main disadvantage in application of this material is the loss of capacity during cycling and during storage in the electrolyte, especially at elevated temperatures. The reasons for the capacity loss are totally clear yet, but many models are proposed: (a) Jahn-Teller distortion, (b) disproportionation reaction, (c) change of lattice constant at cycling, and (d) site exchange 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 ( $\text{Cr}_2\text{O}_3$ ) was beneficial to the specific capacity and energy of the spinel. The purpose of this study was to optimize the sol-gel process for synthesizing chromium doped  $\text{LiMn}_2\text{O}_4$  powders which have nanosize, narrow size distribution and high crystallinity. Chromium-doped  $\text{LiMn}_2\text{O}_4$  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 particle size was found to depend on the calcination condition 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.

#### **W9.28**

**A STUDY OF THE GROWTH CURVES OF C.XEROSIS AND E. COLI BACTERIA IN MEDIUMS CONTAINING NANOMETRIC AND MICROMETRIC SILICON PARTICLES.** Daniel Melendez, Thompson Le Blanc, Javier Avalos, Metropolitan University, Dept of

Science and Technology, San Juan, PR; Lidaris SanMiguel, 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 later inoculate in *C. xerosis* and *E. coli* bacterial strains. Recent studies indicated 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 depend on the size of the particles) for this selectivity. The growth 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 curves during the first four hours. This is possibly caused by the formation of complexes with the silicon that activated this growth. After the initial four hours, both growth curves remain under their respective standard curve. For the *C. xerosis* curve with nanometric particles, this presents 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.

#### **W9.29**

**ELECTROCHEMICAL QUARTZ CRYSTAL NANOBALANCE AND SCANNING FORCE MICROSCOPY INVESTIGATIONS OF NANOPARTICLE CATALYSTS.** Jin Luo, Mathew M. Maye, Yongbing Lou, Chuan-Jian Zhong, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY; Maria 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 nanobalance (EQCN) and atomic force microscopy (AFM) investigations. The EQCN 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.

#### **W9.30**

**XPS AND MAGNETIZATION STUDIES OF CrMn NANOPARTICLES.** W. Amdul-Razzaq, West Virginia University, Physics Department, Morgantown, WV; U. Lee, U.S. Army Research Laboratory, Adelphi, MD.

$\text{Cr}_{1-x}\text{Mn}_x$  ( $x < 6.3\%$ ) 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 particles 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  $\text{MnO}_2$  and  $\text{Cr}_2\text{O}_3$  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 all the way to 330 K, beyond the Neel temperatures of the Cr and the oxides. Even though the magnetization value is in the range of a typical antiferromagnet at all temperatures from 5 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.

#### **W9.31**

**IRON-DOPED TIN OXIDE NANOPARTICLES SYNTHESIZED BY MECHANOCHEMICAL PROCESSING.** Lara Cukrov, Paul G. McCormick, Research Centre for Advanced Mineral and Materials Processing, The University of Western Australia, AUSTRALIA;

Kosmas Galatsis, Wojtek Wlodarski, Sensor Technology Laboratory, School of Electrical and Computer Systems Engineering, RMIT University, Melbourne, AUSTRALIA.

The use of nanoparticulate or nanocrystalline materials in the preparation of gas sensors is a well established method to enhance sensor sensitivity. The benefits of such nanoscale dimensions on sensor performance have been recognised through extensive studies, with particular emphasis on tin oxide. In addition, the introduction of dopants has been recognised as a means to further increase the sensitivity. It is believed that the dopant plays a fundamental role in 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 cation. Recent studies have shown that mechanochemical processing is a suitable pathway for the production of tin oxide nanoparticles for gas sensing applications. The mechanochemical 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 soluble matrix. The nature of the process means that suitable dopant precursors may be added during the milling stage, leading to the production of doped nanoparticles. The synthesis of Fe<sub>2</sub>O<sub>3</sub>-doped SnO<sub>2</sub> nanoparticles was investigated by the mechanochemical processing of SnCl<sub>2</sub>, FeCl<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> precursor powders. Increasing Fe<sub>2</sub>O<sub>3</sub> content led to a slight decline in particle size, with XRD crystallite sizes less than 8nm measured. The nanopowders were characterised by X-ray diffraction, transmission electron microscopy, BET surface area analysis and X-ray photoelectron spectroscopy. Gas sensing measurements of the Fe<sub>2</sub>O<sub>3</sub>-doped SnO<sub>2</sub> nanoparticles revealed a 100-fold increase in the sensor resistance, in comparison to pure SnO<sub>2</sub>.

**W9.32**  
ELECTRICAL PROPERTIES OF MULTIWALL CARBON NANOTUBE/Al<sub>2</sub>O<sub>3</sub>/ALUMINUM SYSTEM. K.S. Jeong<sup>1</sup>, J.U.

Chu<sup>1</sup>, G.S. Park<sup>3</sup>, W.B. Choi<sup>2</sup>. <sup>1</sup>The National Program for Tera-Level Nanodevices. <sup>2</sup>U-Team. <sup>3</sup>Analytical Engineering Center, Samsung Advanced Institute of Technology, Suwon, KOREA.

Porous anodic aluminum oxide(AAO) template-based technique for carbon nanotube(CNT) fabrication has an advantage in growing two-dimensional CNT arrays with perfect vertical alignment on 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/Al<sub>2</sub>O<sub>3</sub>/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 annealing treatment and investigated the electrical property by measuring current-voltage(I-V) characteristics. It is shown that the I-V characteristics is linear for the as-grown sample over the whole range of voltages and the resistivity is about 1.710<sup>-1</sup>Ωcm. 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, it is found that electron tunnel junction is formed in the annealed CNT/Al<sub>2</sub>O<sub>3</sub>/Al interfaces. Transmission electron microscope image of the annealed interfaces shows that crystallized alumina layer is newly formed between CNT and aluminum substrate during annealing treatment. In this presentation electron tunneling behavior of CNT/Al<sub>2</sub>O<sub>3</sub>/Al system and its possible mechanism will be discussed.

**W9.33**  
FABRICATION OF NANO-HYDROXYAPATITE PARTICLES DOPED WITH TRANSITION METAL IONS. Kyung-Sik Oh, Jae-Young Choe, Hyun-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 anti-microbial effects in ionic states. By substituting such ions into the solid ion carrier materials, the antimicrobial effects can be integrated in the solid state, thus extending the field of applications due to its convenience. The release of the antimicrobial metallic 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 whose sizes were reduced to nano-ranges. 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 smaller than 50 nm could be obtained. The transition metal ions were doped 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, NIOBIUM OXIDE AND COMPLEX TITANATES USING CATHODIC ELECTRODEPOSITION. Igor Zhitomirsky, McMaster University, Hamilton, Ontario, CANADA.

Cathodic electrodeposition has been utilized for preparation of nanostructured thin films of titanium oxide, niobium oxide, zirconium titanate, PZT, and composites titanium oxide - ruthenium oxide, titanium oxide-aluminum oxide. Peroxoprecursor method was used in order to solve problems associated with handling of titanium and niobium salts in aqueous solutions. The important finding was that complex oxide compounds such as zirconium titanate and PZT can be deposited via corresponding peroxoprecursors. In contrast, ruthenium and titanium species precipitate from mixed solutions as 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 the precursors. Obtained deposits were studied using XRD, TG/DTA, SEM, and Auger methods. Crystallite sizes were derived at different temperatures from X-ray broadening data. Nanostructured films were obtained as monolayers or laminates 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 NANOCRYSTALLINE ITO THICK FILM. Jeung-Soo Huh, Bong-Chull Kim, Environmental Gas Monitoring Lab, Kyungpook National University, Taegu, KOREA; Jeong-Ok Lim, Medical Research Institute, Kyungpook National University, KOREA.

In nanosized materials, since the surface-to-bulk ratio is much greater than in coarse materials, surface properties become paramount. Despite nanosized semiconductor gas sensors are widely investigated, however, fundamental understanding of gas sensors remains far from being satisfactory. In particular, the effect of crystal structures on sensing characteristics of nanosized gas sensor has not been reported. Therefore, the purpose of this work is to investigate the gas sensing characteristics of two nanosized gas sensors and to attempt to correlate the performance of these sensor materials with their respective crystal structure. We selected the different two crystal structured nanosized ITO powders with same particle size. Their crystal structures are cubic and rhombohedral, respectively and particle sizes of both powders are identical, at 15nm (in diameter). Nanosized thick films for gas sensors are prepared by screen printing with 20um thickness. Gas sensing properties are examined depending on the operating temperature and gas concentration. Gaseous ethanol sensitivity is higher in rhombohedral thick film than in cubic thick film at all operating temperatures.

**W9.36**  
SYNTHESIS AND ROMP OF METAL CONTAINING NORBORNENE DERIVATIVES. James Wynne, Christopher Lloyd, Steven Bullock, Robert Cozzens, Naval Research Laboratory, Chemistry and Materials, Washington, DC.

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

**W9.37**  
PREPARATION AND MAGNETIC PROPERTIES OF FE NANOPARTICLES BY CHEMICAL VAPOR CONDENSATION PROCESS. C.J. Choi, B.K. Kim, Korea Institute of Machinery and Materials, Changwon, Kyungnam, KOREA; X.L. Dong, Laboratory of Ultrafine 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)<sub>5</sub>) as the source. We investigated the microstructures, magnetic properties of the Fe nanoparticles and their oxidation behavior during annealing systematically by means of HRTEM, DTA-TGA, Moessbauer spectroscopy and magnetization measurement. The prepared particle was nearly spherical shaped and core-shell type structure with 5-20nm in mean size. Oxidation heat treatment leads to the successive appearance of oxide phases. The magnetic states of Fe nanoparticles changed from super-

paramagnetism to ferromagnetism with the particle size and microstructure. The carrier gas containing oxygen influenced the magnetic properties and oxidation behavior of Fe nanoparticles.

#### W9.38

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

We present a study on electrical conduction in nanostructured carbon (ns-C) films produced by deposition of a supersonic beam of neutral carbon clusters. By introducing small amounts of metallorganic 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 highly porous regions mixed to 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 ( $H_2$ ,  $N_2$ ,  $CH_4$ , He) pressure and relative humidity. Conductivity vs. temperature measured in vacuum in the range 300-400K is characterized by a constant activation energy of  $\sim 0.3$  eV in nanostructured carbon films without catalysts. In samples grown with metallorganic precursors the conductivity presents a lower value at room temperature, but higher activation energy. The electrical conductivity of samples produced with molybdenum is very sensitive to changes in gas pressure and relative humidity, showing fast and reversible responses. 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 gas, suggesting a gas-film interaction dominated by physisorption. I-V characteristics at room temperature indicate an almost ohmic behavior, with a slope strongly dependent on the relative humidity.

#### W9.39

SURFACE CHARACTERIZATION OF CARBON NANO MATERIALS VIA ADSORPTION MEASUREMENTS.

Saikot Talapatra, A.D. Migone, Southern Illinois Univ at Carbondale, Dept of Physics, Carbondale, IL.

We present the adsorption isotherm results of various gases on single walled 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

PHOTOEMISSION STUDY OF THIOL-CAPPED GOLD NANOPARTICLES. T. Nagasawa, A. Tanaka, H. Sasaki, Y.

Kuriyama, S. Suzuki, S. Sato, Tohoku Univ, Dept of Physics, Sendai, JAPAN; T. Sekine, Tohoku Univ, Dept of Chemistry, Sendai, JAPAN.

A photoemission 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 2-5 nm by using the two-phase (water-toluene) reduction of  $AuCl_4^-$  by sodium borohydride in the presence of an alkanethiol [1]. The thiol-stabilized gold nanoparticles were deposited on the highly oriented pyrolytic graphite substrates and loaded into ultrahigh vacuum chamber. From the ultraviolet photoemission measurements, it is found that the spectral intensity at the Fermi energy is vanished. On the other hand, the optical absorption spectra of thus prepared gold nanoparticles exhibit a distinct plasmon resonance for all sizes. The existence of a plasmon resonance indicates that the collective motion of the valence electrons in the metal. We have analyzed the observed photoemission spectra with a simple model that takes into account the finite lifetime of the photohole remaining in the gold nanoparticle during the photoemission 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 also carried out the X-ray photoemission measurements for the dodecanethiol-capped gold nanoparticles. We discuss the chemical states of the present gold nanoparticles from detailed analyses of spectra.

[1] M. Brust *et al.*, J. Chem. Soc., Chem. Commun. 1994, 801 (1994).  
[2] H. Hovel *et al.*, Phys. Rev. Lett. 81, 4608 (1998).

#### SESSION W10: NOVEL STRUCTURES

Chair: Richard Partch

Thursday Morning, November 29, 2001

Back Bay B (Sheraton)

#### 8:30 AM \*W10.1

THE EFFECT OF INTERFACIAL VISCOSITY ON THE KINETICS OF FORMATION OF SILVER NANOPARTICLES USING WATER-IN-OIL MICROEMULSIONS AS NANOREACTORS.

D.O. Shah, R.P. Bagwe and B.S. Parmar, Center for Surface Science and Engineering, Engineering Research 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 borohydride. The silver nanoparticles formed were characterized using UV-Visible absorption spectra and TEM micrographs. Effect of addition of Arlacel-20 to the AOT/Heptane 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 in case of pure AOT whereas addition of Arlacel-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 Arlacel 20 for few hours indicating the reaction kinetics is slowed down upon addition of Arlacel-20. This observation can be explained using the concept of rigidity of surfactant film at the oil/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 Arlacel-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, Arlacel-20, microemulsion, plasmon band, interfacial fluidity, molecular packing in mixed surfactant film, reaction kinetics.

#### 9:00 AM W10.2

TIN OXIDE ( $SnO_x$ ) NANOWIRES, NANODISKETTES, NANOTUBES, AND NANOSTRUCTURES SUPPORTED ON SILICA NANOSPHERES. James L. Gole<sup>a</sup>, Zurong Dai<sup>b</sup>, J.D. Stout<sup>a</sup> and Z.L. Wang<sup>b</sup>. Georgia Institute of Technology, Atlanta, GA. <sup>a</sup>Schools of Physics, Georgia Institute of Technology, Atlanta, GA. <sup>b</sup>MS&E Dept, Georgia Institute of Technology, Atlanta, GA.

Two unique syntheses have been used to generate  $SnO_{2-x}$  nanowires, nanotubes, and nanodiskettes. Crystalline nanowires which display both a rutile and orthorhombic structure are formed from high temperature synthesis with  $SnO/SnO$  and  $Sn/SnO$  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 combined rutile and orthorhombic structures are obtained. With additional modification, it has been possible to synthesize larger ( $\sim 200$  nm) nanodiskettes and channeled nanotubes which appear to display a crystallographic structure. The latter tubes with their near cubic cross sections may contain  $SnO_{2-x}$  diskettes and thus might be used as nanoreactors. A single step mixed  $SnO/Si/SiO_2$  synthesis has been used to form silica nanospheres decorated with  $SnO_x$  nanocrystals. Partially agglomerated  $SiO_2$  nanospheres of diameter  $\sim 45$  nm have been used as nanosupports (substrates) for  $SnO_x$  crystallites of diameter 3-6 nm. The ability to disperse these extremely small  $SnO_x$  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 algacides.

#### 9:15 AM W10.3

3D HIGHLY ORIENTED ARRAY OF METAL OXIDE NANO- TO MICROPARTICULATE MATERIALS. Lionel Vayssieres, Jinghua Guo, Joseph Nordgren, Uppsala University, Dept of Physics and 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 ageing 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 thermodynamically stabilized metastable crystal phases. The experimental outcome 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 porosity 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 template-free and surfactant-free aqueous chemical growth synthesis allows to generate, at large scale and low-cost, novel designed and well-ordered metal oxide nano- to microparticulate thin film materials with a complex architecture such as for instance, 3D crystalline arrays of oriented nanorods of ferric oxide (hematite and akaganeite), 3D crystalline arrays of highly oriented nanorods, microtubes and microtubes of ZnO (zincite) 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 Mayers, 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 monodispersed nanorods from a variety of materials (such as Se, Te, Se/Te alloys, and metals). The lateral dimensions of these nanorods could be tightly controlled between 50-200 nm, with their lengths ranging from half to a few micrometers. These nonspherical 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 studies) for the formation of these monodispersed nanorods, as well as some preliminary measurements on their properties.

**9:45 AM W10.5**  
FORMATION OF FERROMAGNETIC Ni/SiO<sub>2</sub> NANOSPHERES. S.M. Prokes, W.E. Carlos, Naval Research Lab, Washington, DC; Lenward Seals, Stephen Lewis, and James L. Gole, Georgia Institute of Technology, Atlanta, GA.

Recently, it has been demonstrated that the formation of semiconductor and oxide-based nanostructures can be achieved by high temperature synthesis which, as a function of experimental conditions, can be made to produce a variety of nanospheres and nanowires. We have produced SiO<sub>2</sub> nanospheres, having an average 30 nm diameter, which have then been nickel plated using an electroless 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<sup>2+</sup> paramagnetic centers, which are most easily seen below 40K, and the formation a ferromagnetic metallic Ni coating, which can be readily seen above 40K and at room temperature. The MR results indicate only the presence of paramagnetic Ni<sup>3+</sup> in the dried Ni plating solution that does not contain any SiO<sub>2</sub> nanospheres. Using the Ni LMM transition, the presence of Ni has also been confirmed by Auger Electron Spectroscopy. Substantial amounts of oxygen (determined from the KLL transition) have also been detected, due to the SiO<sub>2</sub> and the organics present in the electroless plating solution. These results suggest that an interfacial reaction at the surface of the SiO<sub>2</sub> nanospheres leads to the formation of ferromagnetic Ni, which only deposits onto the SiO<sub>2</sub> spheres and forms a room temperature ferromagnetic Ni/SiO<sub>2</sub> 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.

Derivatization 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 covalent attachment of organic salts to the nanocrystal surfaces. Furthermore, surface passivation by organic ligands can significantly enhance the quantum yield of luminescent nanocrystals. Accurate characterization of the organic functionalities on these derivatized and/or surface-passivated nanocrystals by techniques such as infrared spectroscopy is often not possible however, since it is difficult to obtain purified samples of the derivatized nanocrystals. As-prepared, organic-functionalized nanocrystals are typically dispersed in solvent mixtures containing excess quantities the organic reactants used to functionalize and/or passivate the surface, and hence the unbound organics interfere with signals due to nanocrystal-bound organics. In order to accurately characterize organic-functionalized nanocrystals, methods must be developed to

easily isolate these derivatized nanocrystals from unbound organics. Nanoporous alumina filters prepared by anodization of very thin sheets of aluminum metal have pore sizes on the order of 20-200 nm in diameter and are commercially available. We have used these filters as "nanocontainers" to trap derivatized CdSe/ZnS nanocrystals that have been surface-functionalized with either propionate and sulfonate organic salts, and that have also been passivated with a variety of organic Lewis bases. These trapped nanocrystals were washed with solvents to remove excess unbound organics, and analyzed directly by Fourier Transform infrared spectroscopy (FTIR). We will describe this simple method to prepare clean, isolated samples of derivatized nanocrystals, and present our FTIR analysis results.

**10:30 AM W10.7**  
NANOCOATING ON POWDERS FOR COLLOIDAL CERAMIC PROCESSING: 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)<sub>2</sub> coating on Nb<sub>2</sub>O<sub>5</sub> for pyrochlore-free perovskite PMN will be given. 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, E/Ew, where -E is the attraction 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 coating 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 BIMETALLIC NANOPARTICLES. Marie-Jose Casanove, Pierre Lecante, Marie-Claire Fromen, CEMES, CNRS, Toulouse, FRANCE; Fabrice Dassenoy, Fritz Haber Institute, Berlin, GERMANY; Marc Respaud, LPMC, 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 a 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 and possibly 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 PtRu, CoRh and CoRu ultrafine bimetallic particles as a function of the composition in the whole range of stoichiometry. The particles are synthesized by simultaneous decomposition 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 effect of size reduction on the atomic organization in these ultrafine particles is evidenced. In the PtRu 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 detail the mechanism of the transition. We point out the effect of size reduction and alloying in the structure and enhanced magnetization in CoRh particles.

**11:00 AM W10.9**  
GOLD NANORODS: ELECTRIC FIELD DIRECTED GROWTH AND BENDING MODES. Paul Mulvaney, Orla Wilson, University of Melbourne, Chemistry School, AUSTRALIA; John Sader, University of Melbourne, Dept. of Maths and Statistics, AUSTRALIA; Greg Hartland, University of Notre Dame, Dept. of Chemistry, IN.

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 NUCLEATION TO REALIZE HIGH-DENSITY SI QUANTUM DOTS ON SiO<sub>2</sub> THIN FILMS.** Jianhong Zhu, W.

Thomas Leach and John G. Ekerdt, Dept of Chemical Engineering, The University of Texas at Austin, TX.

Predeposition of submonolayer Si by hot-wire CVD is found to facilitate the nucleation of Si quantum dots on SiO<sub>2</sub> thin films, which were subsequently grown by conventional UHV-CVD using disilane. Compared to growth without the predeposition step, 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 ( $9.5 \times 10^{11} \text{ cm}^{-2}$ ) 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, Sudha Madhugiri, Claudia Meek and Paul Pantano, 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 shapes and sizes including hexagons, gyroids, discoids, apheres and fibers. Novel applications that exploit the unique shapes of these particles will be described. In one case, a nanosorting device based on a microwell array etched at the distal face of an optical fiber bundle was developed. DAM-1 particles have been deposited into the microwells, 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 sieve nanofibers will be presented.

#### **11:45 AM W10.12**

**THE EFFECT OF NANOCRYSTALLINE GRAIN SIZES IN (0-2 MOL%) YTTRIA STABILIZED ZIRCONIA ON THE TETRAGONAL PHASE STABILITY.** Arun Suresh, Merrilea J. Mayo, The Pennsylvania State University, Dept. of MS&E, University Park, PA; Wallace D. Porter, Claudia J. Rawn, 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<sub>2</sub> (anatase, rutile), BaTiO<sub>3</sub> (cubic, tetragonal), Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) etc. In the present study, the effect of particle size on the tetragonal  $\rightarrow$  monoclinic phase transformation in yttria-doped zirconia was examined. The phase stability effect is important in the zirconia system, as the tetragonal phase has to be retained at 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  $\rightarrow$  M phase transformation temperature was seen to vary linearly with inverse particle size. The shift of the yttria-zirconia 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  $\rightarrow$  M transformation. Critical grain sizes below which the tetragonal phase is stable at room temperature were determined to be 70nm, 100nm, 175nm for 0.5, 1.0, 1.5 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> respectively.

#### **SESSION W11: MEDICAL APPLICATIONS**

Chairs: Dinesh O. Shah and Nobuyuki Kambe

Thursday Afternoon, November 29, 2001

Back Bay B (Sheraton)

#### **1:30 PM \*W11.1**

**ULTRATHIN COATINGS FOR PULMONARY DRUG DELIVERY.**

**Gunther Hochhaus**, Intira Coowanitong, Weon-Seok Kim, Valentin Craciun, Rajiv Singh, Departments of Pharmaceutics and Materials Science and Engineering, University of Florida, Gainesville, FL; James Talton, Nanosphere Inc. Alchua, 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 was it 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 inhalation 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 NANOPARTICLES FOR IN-VIVO BIO-MEDICAL APPLICATIONS.**

**Do-Kyung Kim**, Muhammet S. Toprak, German Salazar-Alvarez, Maria Mikhailova, Mamoun 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 conspicuity 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 materials are demanded. Based on computer-assisted chemical equilibrium calculations, several optimum operation conditions for coprecipitation process are predicted and magnetite nanoparticles have been prepared under N<sub>2</sub> flow to protect the critical oxidation. In this way, monocrySTALLINE nanoparticles of Fe<sub>3</sub>O<sub>4</sub> with size of few nanometers have been synthesized. These particles were further coated by ultra-thin films of PVA, Dextran, 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 was 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 NANOPARTICLES.** Jonghwi Lee

and Santipharp Panmai, Department of Pharmaceutical Research and Development, Merck Sharp and Dohme 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 hydrophobic 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 can be observed in all three systems. However, differential scanning calorimetry and X-ray scattering data reveal that there is significant damage 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 Moeser, Lifen Shen, T. Alan Hatton,

Paul Laibinis, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

Magnetic fluids consisting of stable colloidal suspensions of magnetite nanoparticles with tailorable surfaces provide opportunities in chemical separations. Chemical precipitation to form magnetite nanoparticles with diameters of 8 to 12 nm provides a flexible approach for designing dispersible and readily recoverable nanoparticles that are coated by a molecular or polymeric layer. The composition of this layer affords a high surface area colloidal suspension ( $\sim 1 \text{ m}^2/\text{mL}$  for a 1 vol% solution). We have prepared magnetite nanoparticles exposing charged surfaces with tunable charge densities, polymeric films of varying hydrophobicities, and molecular films expressing chiral surfaces. The particles have been characterized by a range of techniques including SANS, TEM, IR, 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 coatings) from a fluid phase. The particles are readily redispersed in a liquid phase for reuse. The talk will detail the synthesis of the particles, their properties, and their demonstrated uses in both batch and continuous separation processes, noting opportunities for their use in a variety of separations, notable for biological species and for operations performed in microscale.

### 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  $\text{BaSO}_4$  particles to optimize the properties of polymethyl methacrylate (PMMA), a cement used for orthopedic implants.  $\text{BaSO}_4$ , a relatively insoluble salt, is a radio-opaque agent that permits radiographic assessment of the stability of the implant over time. By decreasing the average size of the particles from 1-2  $\mu\text{m}$  to 0.1  $\mu\text{m}$  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 hours in the presence of various concentrations of nano- and micron sized particles of  $\text{BaSO}_4$ . 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 TNF $\alpha$ . The effects of nanoparticles on cell viability and proliferation as well as 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, Heimo Schnablegger, Wolfgang Fitz, Richard D. Scott, Thomas S. Thornhill, Anuj Bellare, Department of Orthopedic Surgery, Brigham & Women's Hospital, Harvard Medical School, Boston, MA.

Polymethyl 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 fracture 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 of identical volume fractions. Sodium citrate was used as a surfactant to improve dispersion of the barium sulfate particles in the PMMA matrix. The dispersion of the nanoparticles in each PMMA cement was characterized using low voltage scanning electron microscopy (LVSEM) and ultra-small angle x-ray scattering (USAXS) performed at the UNICAT beamline of the Advanced Photon Source, Argonne National Laboratory. Tensile tests and compact tension tests were performed to measure the work-of-fracture and fracture toughness of the cements. The mechanism of crack propagation was investigated by LVSEM examination of the region in

front of the growing crack. The effect of dispersion of barium sulfate nanoparticles on the morphology and mechanical properties of PMMA based bone cement will be presented.

### 3:45 PM W11.7

QUANTITATIVE AND REVERSIBLE LECTIN-INDUCED ASSOCIATION OF GOLD NANOPARTICLES MODIFIED WITH  $\alpha$ -LACTOSYL- $\omega$ -MERCAPTO-POLY(ETHYLENE GLYCOL). Hidenori Otsuka, Nanoarchitectonics Research Center(NARC), National Institute of Advanced Industrial Science and Technology(AIST), Tsukuba, Ibaraki, JAPAN; Yukio Nagasaki, Department of Materials Science and Technology, Science University of Tokyo, Noda, Chiba, JAPAN; Yoshitsugu Akiyama, Kazunori Kataoka, 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 heterobifunctional PEG containing both mercapto and acetal terminal groups ( $\alpha$ -acetal- $\omega$ -mercapto-PEG, acetal-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  $\text{HAuCl}_4$  in the presence of  $\alpha$ -acetal- $\omega$ -mercapto-PEG. The  $\alpha$ -acetal-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- $\beta$ -D-lactopyranoside (Lac) in the presence of  $(\text{CH}_3)_2\text{NHBH}_3$ . Lac-conjugated gold nanoparticles exhibited selective aggregation when exposed to ricinus communis agglutinin ( $\text{RCA}_{120}$ ), a bivalent lectin specifically recognizing the  $\beta$ -D-galactose residue, inducing significant changes in the absorption spectrum with concomitant visible color change from pinkish red to purple. Aggregation of the Lac-functionalized gold nanoparticles by the  $\text{RCA}_{120}$  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 quantitate lectin concentration with nearly the same sensitivity as ELISA. This simple yet highly effective derivatization of gold nanoparticles with heterobifunctional PEG provides a convenient method to construct various colloidal sensor systems currently applied in bioassays and biorecognition.

### 4:00 PM W11.8

BIOMIMETIC FABRICATION OF SILVER NANOCRYSTALS. Sarah J. Stringer, Rajesh 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 benign route for nanoscale materials. Many biological systems are capable of synthesizing nanoparticles from inorganic materials such as silica, silver and ferric oxide<sup>1</sup>. Isolation of the organic molecules involved in these processes may facilitate 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 phage peptide display system, we were able to isolate peptide sequences that specifically bind to silver particles. Both the phage particles displaying the silver-specific peptide as well as a synthetic peptide based on phage-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 nanoparticles. Currently, we are investigating ways of patterning the peptides for possible future applications in bottom-up fabrication approaches. References:

1. Klaus-Joergler et al., Trends Biotechnol 19, 15-20 (2001).