

# SYMPOSIUM Y

## Synthesis, Functional Properties, and Applications of Nanostructures

April 17 – 20, 2001

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\* Invited paper

SESSION Y1: SYNTHESIS AND SELF ASSEMBLY  
OF NANOPARTICLES

Chair: Rina Tannenbaum  
Tuesday Morning, April 17, 2001  
Metropolitan II (Argent)

**8:30 AM \*Y1.1**

**POLYMER-MEDIATED "BRICKS AND MORTAR" ASSEMBLY OF NANOPARTICLES.** Andrew K. Boal, Trent H. Galow, Vincent M. Rotello, Univ. of Massachusetts, Dept. of Chemistry, Amherst, MA; Thomas P. Russell, Univ. of Massachusetts, Dept. of Polymer Sci. and Eng., Amherst, MA.

Self-assembly based on selective control of non-covalent interactions provides a powerful tool for the creation of structured molecular-level systems. Application of this methodology to macromolecular systems supplies a potential means for the extension of this structure to the macroscopic level. In recent research, we have developed a "bricks and mortar" strategy, in which colloidal gold particles functionalized with recognition elements serve as the bricks, while polymers bearing complementary functionality serve as mortar. With this methodology, the conformational flexibility of the polymer compensates for irregularities in the size and shape of the nanoparticles, providing efficient propagation of structure. We have recently described the controlled formation of discrete micrometer-scale spherical assemblies based on 2 nm gold nanoparticle 'bricks'<sup>1</sup>. In ongoing studies, we have extended the utility of the 'bricks and mortar' method through variation in assembly protocol and recognition motifs, providing highly controlled routes to both network aggregates and mesoporous materials. Characterization of these materials, as well as their mechanism of formation, will be discussed.

<sup>1</sup>"Self-Assembly of Nanoparticles into Giant Spherical Arrays" A. Boal, F. Ihan, J. DeRouchey, T. Thurn-Albrecht, T. Russell, V. Rotello, *Nature*, 2000, 404, 746-749.

**9:00 AM \*Y1.2**

**INORGANIC NANOCRYSTALS WITH DENDRIMER TEMPLATES: MESOSCOPIC MODEL SYSTEM AND ROUTE TO NANOCOMPOSITES.** Franziska Groehn, National Institute of Standards and Technology, Gaithersburg, MD and Max Planck Institute for Polymer Research, GERMANY; Barry J. Bauer and Eric J. Amis, National Institute of Standards and Technology, Gaithersburg, MD.

"Quantum dots", semiconductor crystals of nanometer size, represent an intermediate stage between single molecules and bulk solids with special optical and electrical properties caused by quantum size effects and thereby are excellent materials for potential nanoscale optoelectronic devices and biosensors. Organic-inorganic hybrid nanostructures can combine the optical and electrical properties of the inorganic colloid with the mechanical properties, propensity for self-assembly, and functional groups of the organic compound. In order to design such hybrid structures, templating a growing inorganic crystal within a polymeric matrix - initially inspired by nature - has been evaluated as an effective synthetic route. The success of such materials requires understanding their formation mechanisms and properties. We study dendrimers, monodisperse and well-characterized molecules with a mesoscopic size of 1 to 15 nm, as "model nanoreactors". Different inorganic colloids like metal nanoparticles as well as highly fluorescent semiconductor nanocrystals are studied. Small angle neutron scattering (SANS), small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) are used to characterize the resulting hybrid structures. Dendrimers that have been incorporated into a polymeric matrix can lead to well-defined solid nanocomposites that combine special colloidal effects with the mechanical properties of polymers. Routes for further arranging the hybrid particles on surfaces are the selective deposition of the dendrimers onto hydrophilic stripes of contact printed samples or hydrophilic domains of phase separated polymer blends.

**9:30 AM Y1.3**

**ROLE OF THE INTERFACE IN NOVEL NANOSTRUCTURED VANADIA-TITANIA CATALYSTS.** Galina N. Kryukova, Galina A. Zenkovets, Borekov Institute of Catalysis, Novosibirsk, RUSSIA; Robert Schloegl, Fritz-Haber-Institute of MPG, Berlin, GERMANY.

By using nanotechnology novel nanostructured vanadia-supported catalysts have been synthesized. The main structural feature of these systems was a coherent interface between the particles of the active component, V<sub>2</sub>O<sub>5</sub>, and of the support, TiO<sub>2</sub>(anatase). These catalysts showed remarkable activity and selectivity in some reactions of mild oxidation. It seems likely that a reason for their excellent behavior is a presence of the interface being a mixed layer composed of vanadium, oxygen and titanium atoms with a possible appearance of V-O-Ti bonds. To understand a nature of the active sites we prepared the inverted system - vanadia doped with titanium atoms. In this case catalysts are in the form of thin rods the surface/subsurface layers of

those are Ti enriched. The reactivity of this material was similar to that of the vanadia-supported catalyst. Formation of V-O-Ti bonds in the titanium doped vanadia might contribute to the good catalytic behavior. Role of the interface as possible active site in the vanadia-titania catalysts is discussed.

**9:45 AM Y1.4**

**SURFACE PATTERNS OF ZEOLITE NANOCRYSTALS BY EVAPORATION-INDUCED SELF-ASSEMBLY.** Huangting Wang, Zhengbao Wang and Yushan Yan, Department of Chemical & Environmental Engineering University of California, Riverside Riverside, CA.

We have reported a novel, convenient, and versatile materials processing approach for constructing hierarchically porous structures through templated self-assembly of monodisperse zeolite nanocrystals in ethanol [1,2]. These porous crystalline structures have potential applications in separation, catalysis, and microelectronics. Here we report a new procedure that leads to spontaneous formation of hierarchically porous crystalline films with rather sophisticated patterns by self-assembly using colloidal zeolite nanocrystal suspension in EtOH-H<sub>2</sub>O. Colloidal silicalite nanocrystals suspensions are synthesized via hydrothermal procedures [2]. Self-assembly of silicalite nanocrystals was conducted on flat silicon wafer surfaces and surface patterns spontaneously formed during dispersant evaporation at ambient temperature. Typical patterns (by SEM) include knotted-rope web and wrinkled honeycomb ordered with 3-5 micron sized repeating unit. Calcined patterned materials have high BET surface area (670~750m<sup>2</sup>/g, higher than pure silicalite) and a bimodal pore size distribution (micropore (0.55 nm) volume: 0.15 m<sup>3</sup>/g, mesopore (2-3nm) volume: 0.2-0.4 m<sup>3</sup>/g). XRD patterns show typical silicalite orthorhombic lattice with broadened reflections and d spacings (d<sub>hkl</sub>=1.13 nm {011}, 1.00 nm {200}, 0.385 nm {501}, 0.373 nm {033}, 0.366 nm {133}). Low angle XRD shows peak at 2 $\theta$ ≈1.00~1.15 (d=8.83~6.68 nm) confirming presence of mesopores formed from nanoslabs in the patterned materials. FT-IR spectra show typical Si-O-Si framework bands including the characteristic double five-ring vibration at ca. 550 cm<sup>-1</sup> and a shoulder at 980 cm<sup>-1</sup> attributable to Q<sup>3</sup> Si-OH groups, and the crystallinity is estimated to be 65%~85%. TEM reveals ordered structures in the patterned materials. The patterned materials are attractive for many applications such as catalysis, adsorption, and microelectronics. The formation of surface pattern can be explained by preferential evaporation of ethanol and by supramolecular templating of TPAOH. [1] L.M. Huang, Z.B. Wang, J.Y. Sun, L. Miao, Q.Z. Li, Y.S. Yan and D.Y. Zhao, *J. Am. Chem. Soc.*, 2000, 122, 3530. [2] H.T. Wang, Z.B. Wang, Y.S. Yan, *Chem. Commun.*, 2000, in press.

**10:30 AM \*Y1.5**

**NANOSTRUCTURED INORGANIC MOLECULAR MATERIALS.** Mary Elizabeth Williams, Joseph T. Hupp, Northwestern University, Department of Chemistry, Evanston, IL.

Our group has prepared a series of molecular 'squares' and 'rectangles' based on octahedral Re coordination of bidentate bridging ligands. The size and chemical reactivity of the internal cavity is highly tunable, and the inorganic cyclophanes are actively being studied in catalytic, ultra-separation, and sensing applications. Electrochemical techniques have been primary methods for characterization of thin films of the nanostructured materials on electrodes. For example, cyclic voltammetry and rotating disk electrode voltammetry experiments have shown size-selective permeation of redox probes that is determined by the internal square dimensions. We have more recently begun to employ Scanning Electrochemical Microscopy (SECM) to spatially image micropatterned electrodes containing these thin film materials, simultaneously allowing us to obtain permeability data with topographical information. This seminar will present new data employing porphyrin-based molecular squares with chemically tailored nanocavities and using single crystals of molecular rectangles.

**11:00 AM Y1.6**

**A NOVEL LOW TEMPERATURE SYNTHESIS METHOD FOR SEMICONDUCTOR NANOWIRES.** S. Sharma, M.K. Sunkara, R. Miranda, University of Louisville, Department of Chemical Engineering, Louisville, KY; G. Lian, E.C. Dickey, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY.

We present a novel synthesis technique to grow one-dimensional semiconductor structures such as wires and whiskers at temperatures less than 550°C. In this technique, gallium, which melts at ~30°C, and remains as a low vapor pressure liquid over a broad temperature range (30-2400°C), is used as the catalytic medium in the vapor-liquid-solid (VLS) mechanism. Use of gallium allows the growth of nanowires at much lower temperatures than the traditional VLS growth technique involving silicon-transition metal eutectic. To grow silicon whiskers for example, a liquid gallium film is spread on a

cleaned p-type (100) silicon wafer, which upon exposure to a microwave generated hydrogen plasma diluted in nitrogen, agglomerates into tiny droplets. One-dimensional growth of silicon with varying sizes and shapes was observed. Resulting silicon wires ranged from several microns to less than ten nanometers in diameter. The observed growth rates were on the order of 100 microns/hr. The substrate temperature was measured to be approximately 400°C using an Infrared sensor. In this approach, unlike in traditional VLS based growth, silicon is not supplied directly through the gas phase. It is believed that atomic hydrogen in the plasma creates the necessary source for silicon in the vapor phase through silicon etch products, SiH<sub>x</sub>. Low equilibrium solubility of silicon in gallium at temperatures of 400°C and extremely low eutectic temperature and composition in atomic fraction of silicon for the Ga-Si system are unique features of this binary system. Similar results with other elemental semiconductors will be presented. The synthesized semiconductor nanowires were found to be crystalline in nature. The structural and opto-electronic characteristics of the nanowires were studied using energy dispersive x-ray spectroscopy, high-resolution transmission electron microscopy (HRTEM) and Raman Spectroscopy. This study was funded in part by NSF through CAREER grants CTS #9876251 and EPS #0083103.

#### 11:15 AM Y1.7

CHARACTERIZATION ON SELF-ALIGNED HgTe NANO-CRYSTALS INDUCED BY CONTROLLED PRECIPITATION IN PbTe-HgTe QUASI-BINARY COMPOUND SEMICONDUCTOR ALLOYS. Manjong Lee and Choong-Un Kim, The University of Texas at Arlington, MS&E Program, Arlington, TX.

This paper presents a new methodology of producing quantum-dot crystals in semiconductor alloys and evidences of its effectiveness. This method utilizes the precipitation process in alloy systems and resembles the age-hardening process used in metallic alloys. The trial of controlled precipitation on PbTe-4HgTe quasi-binary semiconductor alloys show that high-density nano crystallites of HgTe can be resulted. The HgTe precipitate forms initially as platelets along 100 direction of matrix and undergoes a gradual shape change without any noticeable coarsening, from a disk to a cube, as the aging time increases. The microstructure after full aging is found to contain almost equal size HgTe cubes, roughly 7 nm, that maintain lattice coherency with PbTe matrix. The quantum effect arising from these coherent HgTe quantum dots are investigated using FTIR spectroscopy with variation of precipitate size and shape. This investigation yields several evidences that the HgTe precipitates do behave as quantum-dots, rendering the absorption properties of the alloy in a unique manner. A strong absorption peak having several times higher intensity than that of matrix phase at around 4.2 micron of source wavelength are obtained by the presence of coherent HgTe nanocrystals. In addition, the width and intensity of absorption peak is found to vary with the shape of the precipitates. The significance of all these findings will be discussed in conjunction with the theoretical and experimental evidences.

#### 11:30 AM Y1.8

CHEMICAL INTERACTIONS BETWEEN NANOPARTICLES AND POLYMERS. Yigal D. Blum, D. Brent MacQueen, SRI International, Chemical Science and Technology Lab, Menlo Park, CA; Nobuyuki Kambe, NanoGram Corporation, Fremont, CA.

A rapid growth of applications for inorganic-organic nanocomposites is arising from the advanced technologies either currently proposed or under development. Structural, biomedical, optical coating, optoelectronic and electronic applications are envisaged. These applications require either homogeneous blending of the nanoparticles with no agglomeration or, alternatively, selective deposition of nanoparticles within a polymeric matrix. A generic approach to chemically interact nanoparticles with conventional polymers is developed to address the design and processing capability of nanocomposites. This approach induces homogeneity to the composite and can be used as a tailoring tool for microstructure architecture. Nanoparticles produced by the NanoGram<sup>TM</sup> technology are excellent for such nanocomposites.[1] Their spherical shape and narrow size distribution assists the processing capability of such homogeneous blends. High loads of particles within a polymeric matrix can be achieved without losing the homogeneity. Alternatively, the particles can be selectively attracted into desired domains.

[1]: N. Kambe, et al., in this symposium, MRS Spring 2001.

### SESSION Y2: TARGETED DESIGN AND SYNTHESIS OF NANOPARTICLES

Chair: Horst Hahn  
Tuesday Afternoon, April 17, 2001  
Metropolitan II (Argent)

#### 1:30 PM \*Y2.1

ELECTRONIC PROPERTIES OF NANOSTRUCTURES GENERATED USING ELECTROCHEMICAL/CHEMICAL SYNTHETIC METHODS. Reginald Penner, University of California-Irvine, Irvine, CA.

(ABSTRACT NOT AVAILABLE)

#### 2:00 PM \*Y2.2

ASSEMBLY AND OPTICAL PROPERTIES OF 3D COLLOIDAL CRYSTALS. Vicki Colvin, Rice University, Houston, TX.

(ABSTRACT NOT AVAILABLE)

#### 2:30 PM Y2.3

THE FACILE SYNTHESIS OF NANOCRYSTALLINE SEMICONDUCTOR QUANTUM DOTS. Michael S. Wong and Galen D. Stucky, University of California at Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

Quantum dots (QD's) are crystalline semiconductor nanoparticles that exhibit unique optical properties derived from quantum confinement effects. They luminesce with very sharp spectral resolution upon UV-vis irradiation, and have other advantages over organic fluorophores. They have potential uses in a multitude of applications, such as optical devices, fluorescence microscopy, and inventory control. The emission color of QD's can be tuned with great precision, depending on materials composition and on particle size. Current synthetic techniques for high quality QD's involve the decomposition of specialized organometallic precursors at very high temperatures (in excess of 300°C). We report a new preparation method which uses simpler, less hazardous precursors and can be carried out at much lower temperatures. Fine control of particle sizes of CdSe QD's is possible, as observed by UV-vis spectroscopy, fluorometry, and electron microscopy. Extensions to other QD compositions and their mechanism of formation under these synthesis conditions will be discussed.

#### 2:45 PM Y2.4

STRUCTURAL, OPTICAL AND CHEMICAL PROPERTIES OF ZnS AND CdS NANOPARTICLES OBTAINED BY AN IMPROVED COLLOIDAL CHEMISTRY SYNTHETIC ROUTE. M.L. Curri, A. Agostiano, M. DellaMonica, C.S. CFILM - CNR, Bari, ITALY; G. Leo, M. Lomascolo, L. Vasanelli, IME - CNR, Lecce, ITALY.

In the last decade semiconductor nanoparticles have attracted much attention because of their unique optical, electronic and photocatalytic properties due to the quantum size effects. This class of new materials has not only provided many unique opportunities for understanding the underlying physics at reduced dimensions but it also exhibits novel optical and transport properties useful for technological applications in the area of electronic and optoelectronic devices. The increasing interest towards these materials has led to develop a wide range of chemical routes to prepare nanoparticles, aiming to the careful control of nanocrystallite size and, even more important, their size distribution. Recently a great interest has been devoted to wide gap semiconductors, such as II-VI and III-Nitride compounds for application as light emitters and detectors in the UV spectral range. In this perspective nanocrystals of wide gap II-VI compounds such as CdS and ZnS are good candidate for these applications due to the possibility to further increase their band gap up to the UV region by decreasing the nanocrystal size. In this work an improved synthetic route that exploits a quaternary water-in-oil microemulsion, is used to obtain ZnS and CdS nanocrystals of high crystalline quality, small dimensions and a high degree of monodispersity. In fact the presence of pentanol, the co-surfactant in the quaternary microemulsion, results to be a key factor in regulating the size, the size distribution and the stability of the crystallites. The obtained CdS and ZnS nanoparticles have been immobilized on gold and ITO, by spin coating and self-assembly techniques, using 1,6-hexanedithiols and (4-aminobutyl)-dimethylmethoxysilane as bridging molecules. The physical and chemical properties of the CdS and ZnS nanoparticles, as obtained and after film preparation, have been investigated by UV-visible and photoluminescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS), X ray diffraction (XRD), scanning tunneling microscopy (STM) and electrochemical measurements.

#### 3:30 PM \*Y2.5

CATALYSIS USING DENDRIMER-ENCAPSULATED METAL NANOPARTICLES. Richard Crooks, Texas A&M University, College Station, TX.

(ABSTRACT NOT AVAILABLE)

#### 4:00 PM Y2.6

HYBRID ORGANIC-INORGANIC GAS SEPARATION

MEMBRANES WITH A HIERARCHICAL NANOSTRUCTURE. Asad Javaid, David M. Ford, Texas A&M Univ, Dept of Chemical Engineering, College Station, TX.

Hybrid materials based on thin organic films deposited on inorganic substrates have been proposed for many applications, including chemical sensing, catalysis, and micro-lubrication. We are employing this concept to develop improved gas separation membranes. We start with supported mesoporous inorganic membranes that are quite permeable, but not very selective (e.g. silica or alumina, with average pore sizes ranging from 2 to 200 nanometers). We then "fill" the pores to varying degrees with a selective organic material that is physically or chemically anchored to the porous surfaces. Simple organic oligomers and dendrimers with nanometer dimensions are used as filling agents. This architecture gives us a degree of simultaneous control over both the chemistry and free volume of the membrane that is difficult to attain in purely polymeric or purely inorganic membranes. In this paper, we explore the impact of organic filler size, chemistry, and surface coverage, as well as substrate pore size, on membrane separation performance. The focus is on solubility-based separations, including the removal of volatile organic compounds from air and the removal of higher molecular weight alkanes from natural gas. The performance of these hybrids compares very favorably to the best results reported for purely polymeric membranes. To help us interpret the permeation results, the membranes are characterized using X-ray photoelectron spectroscopy, FTIR diffuse reflectance spectroscopy, scanning electron microscopy, and thermogravimetric analysis.

**4:15 PM Y2.7**

SYNTHESIS OF SILICON NANO-DENDRITES. Saion Sinha, Dept. of Physics, Southern Connecticut State University, New Haven, CT; B. Gao, O. Zhou, University of North Carolina, Chapel Hill, NC.

Silicon nanostructures were synthesized by ablating Si powder mixed with metal catalysts using a 532 nm pulsed YAG Laser. The effects of various synthesis conditions on its growth were studied. It was discovered that under certain conditions branched Si- nanostructures can be produced, which we call Si nano-dendrites. The morphology of these branched Si nanostructures is strikingly similar to the dendritic structures commonly observed in metals, but in a much larger length scale. These nanostructures typically comprise of a long primary backbone with diameter of 20-100 nm with short and narrow secondary and in some cases tertiary branches that are orthogonal to each other originating from the primary backbone. The length, diameter and spacing of the secondary and tertiary arms are roughly uniform. A mechanism will be proposed that will support this kind of nano-dendritic growth, so that it can be generalized for other materials. Also probable applications of this unique structure will be discussed.

**4:30 PM Y2.8**

SELF-ASSEMBLY AND THE SOLID STATE AS DESIGN ELEMENTS FOR THE SYNTHESIS OF ORGANIC NANOSTRUCTURES. Leonard R. MacGillivray, Department of Chemistry, University of Iowa, Iowa City, IA; Jennifer L. Reid, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, CANADA.

Approaches to synthesis that employ molecules as templates for making covalent bonds are of widespread interest owing to the ability of such molecules to make available chemical transformations less available using more traditional approaches to synthesis. In this context, we have recently introduced a reliable method for making covalent bonds in solids that utilizes bifunctional molecules, in the form of linear templates based on resorcinol, to organize olefins in the solid state, by way of assembly processes directed by hydrogen bonds, such that the template, following [2+2] photoreaction, may be recycled for further synthesis (J. Am. Chem. Soc. 2000, 122, 7817). In this talk, we will demonstrate a first approach to application of this method for the solid state synthesis of organic molecular structures (e.g. cyclic molecules) and assemblies (e.g. capsules) of nanometer scale dimensions. The success of the approach relies on achieving reaction homology in the solid state, which, in turn, facilitates the stereo- and regiocontrolled alignment, and reaction, of single and multiple reactive sites in solids by design. Efforts to generalize the method, making the approach a reliable tool for making covalent bonds in solids, and permitting access to molecular products and materials not accessible in the liquid phase, will also be discussed.

**4:45 PM Y2.9**

NANOWIRE ALIGNMENT AND INTEGRATION USING MICROCHANNEL NETWORKS. Benjamin Messer, Jae Hee Song, Peidong Yang, Univ of California, Dept of Chemistry, Berkeley, CA.

Conductive  $[\text{Mo}_3\text{Se}_3^-]_\infty$  nanowires have been aligned and patterned on substrates using microchannel networks. The process relies on the

solvent evaporation induced self-assembly of  $[\text{Mo}_3\text{Se}_3^-]_\infty$  infinite chains within the microchannels. Aligned  $[\text{Mo}_3\text{Se}_3^-]_\infty$  wires as thin as several nanometers can be readily patterned using micrometer-sized channels. Multilevel junction configurations and nano-to-microscale connections were also demonstrated. Optical microscopy, field emission scanning electron microscopy, transmission electron microscopy studies and electrical measurements show that these wires are highly oriented, crystalline and conductive. The process represents a parallel approach for making nanoscale and molecular scale electronic devices using molecular wires as building blocks.

SESSION Y3: POSTER SESSION  
Chairs: Clifford P. Kubiak and Richard W. Siegel  
Tuesday Evening, April 17, 2001  
8:00 PM  
Metropolitan Ballroom (Argent)

**Y3.1**

DEVITRIFICATION OF SILICA XEROGELS INDUCED BY METALLIC NANOCCLUSERS. J.R. Martinez and G. Ortega-Zarzosa, Fac de Ciencias, O. Domínguez-Espino, Inst de Metalurgia, F. Ruiz, Inst de Física "Manual Sandoval Vallarta", Univ Autónoma de San Luis Potosi, San Luis Potosí, MEXICO.

$\text{SiO}_2$  xerogels doped with CuO, Ag, and Ag+CuO species of nanometric size were prepared. The prepared samples were annealed in air at different temperatures. By using IR absorption and X-Ray diffraction the samples structure was studied. It was found that the metal species and the heat treatments modify strongly the  $\text{SiO}_2$  structure. The appropriate metal species inclusions can yield to a relative low temperature crystallization of the glass into low-cristobalite and low-quartz.

**Y3.2**

A BUILDING BLOCK APPROACH TO MIXED-COLLOID SYSTEMS THROUGH ELECTROSTATIC SELF-ORGANIZATION. Trent H. Galow, Andrew K. Boal, Vincent M. Rotello, Dept of Chemistry, Univ of Massachusetts, Amherst, MA.

Molecular self-assembly is the association of molecules into structurally well-defined, stable aggregates via thermodynamically-controlled non-covalent interactions. Application of self-organization to multi-scale ordering of colloidal nanoparticles provides a platform for the creation of macroscopic devices. The ability to finely control the spatial arrangement of nanoscopic entities in self-assembled composites allows the creation of structured materials, with interesting electronic, optical, optoelectronic, and magnetic properties. In recent research, we have developed a building block approach to electrostatically-mediated construction of modular self-assembled colloid-colloid ensembles. Our strategy involves functionalization of one type of colloidal building block with a primary amine, and a counterpart building block with a carboxylic acid derivative (Scheme 1). By combining the two systems, acid-base chemistry followed by immediate charge-pairing resulted in the spontaneous formation of electrostatically-bound mixed-colloid constructs. The shape and size of these ensembles was controlled via variation of particle size for the two components and their stoichiometries.

**Y3.3**

NANOSTRUCTURES MADE BY ANODIC POROUS ALUMINA MASK ON SILICON SUBSTRATE. Xi-Mao Bao, Jian-Ping Zou, Jun-Hui Wu, and Lin Pu, Department of Physics, Nanjing University, Nanjing, PR CHINA.

This work presents the preparation of nanostructures for Si-based opto-electronic integration by using anodic porous alumina mask. The anodic porous alumina as a mask (or template), was directly formed on Si wafer. Amorphous Si was deposited into the holes of alumina by electron beam evaporation followed by a Xe ion beam bombardment. After annealing at different temperature, photoluminescence (PL) peaked at 583nm was measured and nanoparticles arranged in order along the holes of alumina can be observed by cross-sectional TEM. Another nanostructure is nanoscale light emitting source array made up of  $\text{SiO}_2$  islands. It was formed by anodic oxidation through the alumina mask followed by Ge ions implantation into  $\text{SiO}_2$  islands, which exhibit PL at 370, 400, and 415nm. These nanostructures can be regarded as prototype of nanoscale device and light emitting source.

**Y3.4**

FORMATION MECHANISM OF MOLYBDENUM AND MOLYBDENUM OXIDE NANOPARTICLES BY ELECTRON IRRADIATION. Bingshe Xu, College of MS&E, Taiyuan University of Technology, Taiyuan, Shanxi, CHINA.

The mechanism of molybdenum and molybdenum oxide nanoparticle formation from molybdenum oxide microparticles by electron beam irradiation using a high-resolution transmission electron microscope on a room-temperature stage have been investigated. It is found that, the microsized molybdenum oxide particles disintegrated to form nanosized molybdenum oxide particles by electron beam irradiation with an intensity of approximately  $10^{21} \text{e/cm}^2/\text{sec}$ . The molybdenum nanoparticles were formed from molybdenum oxide nanoparticles upon further electron irradiation. During the electron irradiation process, the surfaces and interfaces of molybdenum oxide nanoparticles suffered damage and defects, such as vacancy arrays showing hole like spots and a moire-like fringes in the lattice image due to oxygen loss, followed by a gradual change from molybdenum oxide to molybdenum nanoparticles. The phenomenon of molybdenum metal nanoparticle formation from nanosized molybdenum oxide is considered to be due to desorption of oxygen as a result of electron stimulation and atomic displacement via the knock-on effect. We suggest that electron irradiation is a powerful technique to create nanostructured metal, ceramic and semiconductor materials by atomic-scale control.

### Y3.5

#### A MAGNETICALLY ORDERED NON-STOICHIOMETRIC ZINC FERRITE FOR THE OXIDATIVE DEHYDROGENATION REACTIONS.

J.A. Toledo<sup>a</sup>, X.C. Sun<sup>a</sup>, N. Nava<sup>a</sup>, and X. Bokhimi<sup>a,b</sup>. <sup>a</sup>Instituto Mexicano del Petróleo, Mexico DF, MEXICO. <sup>b</sup>Institute of Physics, The National University of Mexico, Mexico DF, MEXICO.

Zinc ferrite,  $\text{ZnFe}_2\text{O}_4$ , possesses spinel structure,  $\text{AB}_2\text{O}_4$ , where tetrahedral sites (A) are occupied by diamagnetic ions, as  $\text{Zn}^{2+}$ , and the octahedral (B) positions are occupied by  $\text{Fe}^{3+}$  ions. This structure is named normal spinel and usually presents long range antiferromagnetic order above the Néel temperature ( $T_N \approx 10 \text{ K}$ ). However, recently it was found that ultrafine particles of  $\text{ZnFe}_2\text{O}_4$  prepared by coprecipitation or by ball milling methods showed unusually high magnetization even at room temperature. These types of ferrimagnetic material are technologically important since they have been used in magnetic types, microwave technology, magnetocaloric refrigeration, etc. In this study,  $\text{ZnFe}_2\text{O}_4$  nanoparticles were prepared by coprecipitation and hydrothermal reduction approach. In the hydrothermally treated samples, crystalline  $\text{ZnFe}_2\text{O}_4$  phase were observed by XRD as the main compound, but a considerable amount (30%) of  $\alpha\text{-Fe}_2\text{O}_3$  was segregated in the as-synthesized sample. Crystallite sizes, phases composition and atoms positions were refined by SRD Rietveld analysis. It was found that the  $\text{Fe}^{3+}$  of  $\alpha\text{-Fe}_2\text{O}_3$  diffuses into the tetrahedral and octahedral sites of the  $\text{ZnFe}_2\text{O}_4$  with increasing the annealing temperature. Mössbauer spectra showed that 78% of the  $\text{Fe}^{3+}$  of a  $\alpha\text{-Fe}_2\text{O}_3$  was distributed into the tetrahedral sites while the 22% was distributed to the octahedral ones. These atomic distributions around the sites correspond nearly to the theoretical density of these vacancy sites into the spinel structure. Magnetization measurements showed a typical ferrimagnetic behavior of the  $\text{ZnFe}_2\text{O}_4$  phase, even at room temperature, indicating that the  $\text{Fe}^{3+}$  ions are located in the tetrahedral sites. Therefore, iron in tetrahedral and octahedral sites orient their spins antiparallel, also since the number of octahedral sites are higher than the number of tetrahedral sites, a non compensate magnetic moment occurs. Moreover, catalytic activity was measured in the oxidative dehydrogenation of 1-butene. The activity increase as annealing temperature rose indicating those A-B interactions of  $\text{Fe}^{3+}$  also promotes the activity and selectivity to butadiene in the selected reaction. On the other hand, in the co-precipitated samples,  $\text{ZnFe}_2\text{O}_4$  was obtained by annealing the samples at  $550^\circ\text{C}$  and  $750^\circ$ , respectively. Crystallite sizes increase and a small amount of  $\alpha\text{-Fe}_2\text{O}_3$  segregates with increasing annealing temperature, contrary to the observed one for the hydrothermally treated samples.

In summary, the nonstoichiometric  $\text{ZnFe}_2\text{O}_4$  nanoparticles, synthesized hydrothermal method, exhibits high magnetic moment and catalytic activity due to the repartition of  $\text{Fe}^{3+}$  of  $\alpha\text{-Fe}_2\text{O}_3$  in the two sublattices of the spinel.

### Y3.6

Abstract Withdrawn.

### Y3.7

BIOCERAMICS AND BIOMINERALS AND THEIR NANOSTRUCTURES. Shulin Wen, Jingwei Feng, Shandong University, Dept of MS&E, Shandong, CHINA.

The characterization of microstructure of bioceramics and bioceramics may help material scientists for design of new kind of biomaterials. Bioceramics have much higher strength and hardness than that in corresponding mineral crystal and they have very high toughness due to wonderful assembly and composite at both micro- and macro-structure levels. Therefore, comparison research for these materials at

different structure level would certainly benefit to design and manufacture of new biomaterials. We characterized the nanostructure features of egg shell, strombus gigas shell, human bone and teeth. Many interesting results have been obtained. Human enamel is a kind of bioceramics which may decay; much attention has been paid to these research of dental decay and repair due to many million patients involved in the world. The main inorganic constituent of enamel is hydroxyapatite with a hexagonal structure in the form of an ordered prism. We have shown that the dental decay process appears to start at some defects. These defects are point defects aggregation, dislocations, stacking faults and some grain boundaries. The most important is that these defects always moving and their inter-reactions causing those decay. Some repair to these decay also suggested.

### Y3.8

APPLICATIONS OF  $\text{ZnS:Mn}^{2+}$  NANOCRYSTALS. J.F. Suyver, R. Bakker, A. Meijerink, J.J. Kelly, Debye Institute, Physics and Chemistry of Materials, Utrecht, THE NETHERLANDS.

The synthesis of semiconductor nanocrystals such as  $\text{ZnS}$  or  $\text{ZnO}$  (undoped or doped with a transition metal ion) in the size range of 2 to 5 nm using an inorganic chemical route is straightforward, allowing for industrial applications. An electroluminescent device consisting of conducting porous layers made from doped semiconductor nanoparticles, deposited on a conducting substrate is such an application. Majority carriers will be injected into the layer from a transparent conducting substrate, while minority carriers are provided by an electrical contact which completely penetrates the pores (such as a liquid electrolyte or a *p*-type conducting polymer). The luminescence properties of the nanocrystals, which determine the color and light output of an electroluminescent device, can be altered by varying the type of nanocrystal, the dopant ion, and the synthesis conditions. This presentation will focus on  $\text{ZnS:Mn}^{2+}$ . The synthesis is discussed in detail and a way to increase the energy transfer efficiency from the nanocrystal to the dopant is presented. The change in the energy transfer efficiency and the particle size are related to the ratio of  $\text{S}^{2-}$  to  $\text{Zn}^{2+}$  precursor. On the basis of these observations, a mechanism for the  $\text{ZnS}$  host lattice luminescence is proposed. Efficient luminescent  $\text{ZnS:Mn}^{2+}$  nanocrystals were deposited on a conducting substrate (an ITO film on glass) and their opto-electrical properties were measured in an electrochemical cell. When illuminated with 300 nm light the film gave an anodic as well as a cathodic photocurrent. This fascinating result, only observable for nanocrystals, is explained by the absence of a depletion layer in a nanocrystal. Photoluminescence measurements as a function of the applied potential are discussed. Electroluminescence from these layers was not observed and also not expected, due to the unfavorable position of the  $\text{ZnS}$  valence band.

### Y3.9

#### FABRICATION AND TEMPERATURE DEPENDENCE OF THE RESISTANCE OF SINGLE-CRYSTALLINE BI NANOWIRES.

Xiangfeng Wang, Jun Zhang, Lide Zhang, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, PR CHINA.

Single-crystalline Bi nanowires with diameter ranging from 20nm to 70nm were prepared by electrodeposition using nanoporous aluminum oxide membranes rather than the more usual track-etched polycarbonate membranes as templates. X-ray diffraction and transmission electron microscopy investigations revealed that the nanowires are essentially single-crystalline and highly oriented. The temperature dependence of zero-field resistance of different diameter nanowires indicated that these Bi nanowires undergo a semimetal-semiconductor transition due to two-dimensional quantum confinement effects. The resistance maximum was observed at 50K in zero magnetic field for 20nmBi nanowires, and the resistance minimum was observed at 258K for 50nm Bi nanowires, due to the quantum size effect.

### Y3.10

CHEMICAL PROCESSING OF NANOSTRUCTURED MATERIALS. R.N. Das, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay, Powai, Mumbai, INDIA.

Recent years have seen a surge of interest in the synthesis and processing of nanostructured materials. Often these advanced materials are tailor made to suit specific applications, and the chemical processing routes play a crucial role in their design and production. The use of chemistry in the preparation of materials can avoid three major problems-diffusion, impurities and agglomeration. In the present study, a variety of nanostructured (particle diameter less than 100 nm) materials have been prepared from metal ion complex based precursor solutions. The precursor solution was prepared at room temperature from metal hydroxides, nitrates or acetates mixed with suitable complexing agents such as amines, carboxylic acids, hydroxy carboxylic acids or poly hydroxy compounds.

Calcination of the precursor mass at low external temperatures produces the nanostructured materials. The example discussed include lead zirconate titanate  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  (PZT), Lanthanum modified lead zirconate titanate PLZT (3/60/40), lead magnesium niobate  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN), lead iron niobate  $\text{PbFe}_{1/2}\text{Ni}_{1/2}\text{O}_3$  (PFN), barium titanate  $\text{BaTiO}_3$ , calcium tungstate  $\text{CaWO}_4$ , cobalt ferrite  $\text{CoFeO}_4$  and corundum ( $\alpha\text{-Al}_2\text{O}_3$ ).

### Y3.11

COMPARISON OF THE GAS SENSING PROPERTIES OF TIN, INDIUM AND TUNGSTEN OXIDES NANOPOWDERS: CARBON MONOXIDE DETECTION AND HUMIDITY EFFECTS.

Marie-Isabelle Baraton, SPCTS CNRS, Univ Limoges, FRANCE; Lhadi Merhari, CERAMEC, Limoges, FRANCE.

It is now well established that the use of nanosized powders in the fabrication of gas sensors by screen-printing technology significantly enhances the sensor sensitivity. However, further improvements of nanosized powder-based sensors require a careful study of the surface reactions at the origin of the gas detection mechanisms. This is a necessary step toward a rigorous industrial fabrication protocol. In this work, chemical reactions occurring at the surface of semiconductor (tin, indium, and tungsten oxides) nanopowders are analyzed by Fourier transform infrared (FTIR) spectrometry simultaneously with their effects on the electrical conductivity of the materials. These surface reactions are compared for the different materials and their relation with the metal oxide sensitivity toward CO at different temperatures is discussed. In addition, because the presence of humidity is known to lead to adverse effects on the CO detection by tin oxide-based sensors, indium and tungsten oxides are specially investigated in terms of response toward humidity and their potential advantages over tin oxide are discussed. This work is funded by the European Commission under the BRITE EURAM III program (contract number BRPR-CT95-0002) and under the IST programme (contract number IST-12615).

### Y3.12

LOWER AND UPPER LIMITS OF CRYSTALLITE SIZES IN NANOSTRUCTURED MATERIALS. Rostislav Andrievski, Inst of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, RUSSIA.

Size effects in properties of nanostructured materials (NM) are of great importance from both fundamental considerations and modern practice. In this connection it seems to be important to consider the values of upper and lower limits of crystallite sizes in NM. It is assumed that the upper limit is about of 100 nm but this value is very arbitrary and is dictated by convenience considerations rather than by physical ones. Another approximations are also considered. Examples of lower limits of about 1 nm and lower in consolidated NM are described and discussed in detail.

### Y3.13

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF NANOMETRIC COMPLEXES. Kripa Modi, Bhavna Trivedi, Chemistry Department, Faculty of Science, M.S. University of Baroda, Vadodara, INDIA; Arun Pratap, Applied Physics Department, Faculty of Technology & Engr., M.S. University of Baroda, Vadodara, INDIA.

The preparation and characterization of nanostructured materials and catalysts is the subject of immense importance and interest in recent years. The microemulsion techniques is one of the chemical methods commonly used for isolation of nanosized materials of some simple compounds such as AgCl and LiF. However, very few attempts have been made to isolate nanometric coordination compounds, which are known to be good catalysts. In the present work, nanosized complexes of Cu(II), Ni(II) and Co(II) with Lucine were prepared by the reaction of metal chloride and the ligand solution in water in oil microemulsion medium. n-Heptane was used as oil and sodium salt of dioctyl sulphosuccinate (AOT) was used as surfactant. The complexes were characterized by elemental analysis and spectral studies. The crystallite size was determined by X-ray diffraction (XRD) studies using single line approximation through Scherrer equation. The XRD studies revealed that crystallite size of the complexes prepared via microemulsion technique and that of the complexes prepared by the conventional method, both were of nano-range. But, the crystallite size of the material prepared by microemulsion method was found to be still smaller (~22 nm) than that of the material prepared by the conventional method (~35 nm). The difference in particle size was also observed in differential scanning calorimetric (DSC) measurements, where the shift in peak temperature to lower value is a signature of the lower size of material obtained using microemulsion technique. The increased surface to volume ratio for lower crystallite sized specimens prepared through microemulsion are expected to show better catalytic behaviour.

### Y3.14

CHARACTERISATION AND PROPERTIES OF WET-CHEMICALLY NANOSTRUCTURED SURFACES OF IMPLANT METALS. Robin Buescher<sup>1</sup>, Thomas Sawitowski<sup>2</sup>, Herbert P. Jennissen<sup>3</sup>, Alfons Fischer<sup>1</sup>. <sup>1</sup>Materials Science and Engineering. <sup>2</sup>Institute of Inorganic Chemistry. <sup>3</sup>Institute of Physiological Chemistry, University of Essen, GERMANY.

The aim of modern implant research is to modify surfaces in order to gain a better integration into the human body. Many attempts make use of coating techniques. They improve their physiological behaviour by surface structures in the  $\mu\text{m}$  range, which enhances the mechanical and biological interlocking with the bone tissue. The effectiveness of these coatings is partly limited by their bonding strength to the substrate. This criterion is not valid for those techniques which just modify the surface material of the substrate in zones of a few m thickness. This contribution introduces a novel surface enhancement technique for steel (AISI 316 L) and Ti (cp-Ti Grade2), which is based of a wet chemical process<sup>1</sup>. The surface structures are investigated by means of Laser profilometry, metallography (SEM, TEM), as well as by other physical methods (Laser-SNMS, AFM). The physical surface properties are derived by the Wilhelmi-Plate method. Afterwards the surfaces were loaded with proteins making use of spacer molecules, which bring about a covalent bonding. The corrosive attack brings about a structuring of the surface by "chemical machining". The resulting surface profiles reaches  $R_a$ -values between 0.88 and 1.13  $\mu\text{m}$ . The surfaces are covered with oxide layers of 10 to 50 nm thickness for the steel and 50 to 150 nm thickness for Ti, which is known from Laser SNMS measurements. AFM revealed a nearly regular surface profile in the nm range. TEM light- and dark field investigations together with diffraction pattern analyses brought about, that the passivation layers generated during and after the wet chemical treatment, are nanocrystalline. In addition the real surface areas show a fractal structure within three orders of magnitude from about 5  $\mu\text{m}$  down to 5 nm. Thus, the real surface area are much larger than the apparent one. The contact angles of these surfaces are nearly zero, which gives a first hint on their excellent bioadhesive behaviour. This and the fractal structure brings about a distinct improvement of the physiological properties of implant surfaces. This is shown by the fact, that 10 times more proteins can be covalently bonded to these surfaces compared to electropolished ones.

<sup>1</sup>Jennissen, H.P., Zumbrink, T., Chatzinikolaïdou, M. and Steppuhn, J. (1999) *Materialwiss. Werkstofftech.* 30, 838-845.

### Y3.15

GRAPHITE ENCAPSULATED NICKEL AND IRON NANOCRYSTALS PRODUCED USING HIGH ENERGY BALL MILLING. Boris Bokhonov, Mikhail Korchagin, Institute of Solid State Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, RUSSIA.

The investigation of morphological and structural changes in the mechanical treatment and thermal annealing of the mixtures carbon black/iron and carbon black/nickel demonstrated that the activation is accompanied by the formation of nano-sized metal particles distributed over the amorphous carbon matrix. Prolonged mechanical activation of the carbon/iron system (for more than 3-5 min) leads to the formation of cementite phase. Mechanical activation of the compositions carbon/metal causes a substantial decrease in graphitization temperature of amorphous carbon: for carbon/iron system, temperature at which amorphous carbon starts to crystallize is 250 - 300 C while for carbon/nickel system, minimal temperature at which the crystallization of amorphous carbon was observed exceeded 600C. Morphological characteristics of the annealed, mechanically activated samples carbon/metal depend on the time of preliminary mechanical activation. The annealing of carbon/metal samples obtained after short-time mechanical activation (1 to 3 min) causes the crystallization of amorphous carbon as onion-like carbon structures. The annealing of carbon/metal samples after mechanical treatment for more than 5 min leads to the formation of metal particles encapsulated by graphite. The longer preliminary mechanical activation, the smaller the size of encapsulated nano- particles. In situ electron microscopic studies of the interaction of metal particles with amorphous carbon film showed that the interaction starts in these systems at temperatures about 600 C. The interaction in the systems iron/amorphous carbon film and nickel/amorphous carbon film proceeds via the formation of carbide phases  $\text{Fe}_3\text{C}$  and  $\text{Ni}_3\text{C}$ ; their decomposition results in the formation of crystal carbon and nano sized metal particles

### Y3.16

TEMPERATURE DEPENDENCE OF CLUSTER-CLUSTER COALESCENCE IN MONODISPERSED  $\text{Co}$  CLUSTER ASSEMBLIES. Dong-Liang Peng, Takehiko Hihara and Kenji Sumiyama, Dept of MS&E, Nagoya Inst of Tech, Nagoya, JAPAN.

Cluster-assembling method, in which nanometer-sized clusters are

directly deposited on a substrate, is a promising alternative to fabricate ideally-controlled nano-scale materials. Throughout the assembling process, it is desirable to maintain the initial size and structure of the clusters. In practice, however, interaction among the deposited clusters takes place on a substrate, preventing one from achieving this goal. This interaction is known to depend on several factors: deposited materials, cluster size, substrate temperature and contamination. Using a plasma-gas-condensation (PGC) type cluster deposition apparatus, we have succeeded in preparing monodispersed Co clusters with the mean sizes  $d = 6$  to  $15$  nm. In this work, we report the results of the study on temperature dependence of cluster-cluster coalescence in the Co cluster assemblies obtained by *in situ* electrical resistivity measurement and *ex situ* TEM observation. Although the distribution and the interface morphology of the clusters showed no marked change at substrate temperatures  $T_s < 250^\circ\text{C}$ , *in situ* electrical resistivity and percolation measurements revealed that the coalescence of the Co clusters has already started at  $T_s \approx 100^\circ\text{C}$ . For the assembly with  $d = 8.5$  nm, temperature-rising resistivity measurement shows that the temperature dependence of the resistivity reveals an irreversible behavior, and is grouped into three distinct stages in temperature-rising curve. Below  $100^\circ\text{C}$  (stage I), the resistivity linearly increases with increasing  $T$  and shows ordinary metallic temperature dependence. At  $100^\circ\text{C} < T < 250^\circ\text{C}$  (stage II), the resistivity still shows a gradual increase with temperature, but its increase rate clearly deviates from the linear behavior, until finally it starts to decrease slowly with increasing  $T$ . Above  $250^\circ\text{C}$  (stage III), the resistivity decreases dramatically with increasing  $T$ , and then exhibits a minimum at  $T_M = 275^\circ\text{C}$ . When  $T \geq 300^\circ\text{C}$ , the resistivity exhibits once again the ordinary metallic temperature dependence and coincides with that in the temperature-lowering curve, resulting in the reversible behavior. In addition, above  $T_s = 250^\circ\text{C}$ , HRTEM also detected combined clusters, whose interfacial structure indicated that the rearrangement of Co atoms took place in the contact area.

### Y3.17

**TUNABLE MAGNETIC PROPERTIES IN METAL CERAMIC COMPOSITE THIN FILMS.** D. Kumar, J. Sankar, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; J. Narayan, A. Kvit, and C. Jin, Department of MS&E, North Carolina State University, Raleigh, NC.

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 5-10 nm size range embedded in amorphous as well as crystalline alumina have been produced. Our results have shown that by controlling the size of the nanocrystalline magnetic materials, we can tune the magnetic properties from superparamagnetic to ferromagnetic. Structural characterization by transmission electron microscopy (TEM) and scanning transmission electron microscopy with  $z$ -contrast (STEM-Z) reveals the presence of a crystalline iron/nickel and an amorphous alumina phase. The particle size of Fe in  $\text{Al}_2\text{O}_3$  matrices prepared by changing the deposition time of Fe, have been found to be 9, 7 and 5 nm from TEM studies. At 10 K, the coercivities of these samples are found to be 450, 350 and 150 Oe, respectively. At 300 K, the coercivity of Fe- $\text{Al}_2\text{O}_3$  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. We will also present our recent results focused on giant and tunneling magnetoresistance effects of Fe and Ni nanoparticles embedded in insulating matrices and isolated from each other on nanometer scale.

### Y3.18

**$\text{Eu}_3$ -DOPED  $\text{Y}_2\text{O}_3$ - $\text{SiO}_2$  NANOCOMPOSITE OBTAINED BY A SOL-GEL METHOD.** Carla Cannas, Mariano Casu, Roberta Licheri, Anna Musinu, Giorgio Piccaluga, Dipartimento di Scienze Chimiche - Cittadella Universitaria di Monserrato (CA); Marco Bettinelli, Adolfo Speghini - Istituto Chimico Policattedra - Universita di Verona, ITALY.

Lanthanide ions in insulating host matrix find uses in a wide variety of applications, such as phosphors for fluorescent lighting, display monitors, X-ray imaging, laser and amplifiers for fiber-optic communication. Preparing nanoscale host materials can change the physical properties, which affect the luminescence and dynamics of the optically active dopant. The luminescence efficiency of these materials is often limited by the interactions with the insulating host (i.e. silica) and enhanced by oxides such as  $\text{Y}_2\text{O}_3$ . Investigating and understanding these interactions is important to optimize the emissive properties of the material for technological applications. The present study focuses on the preparation and characterization of  $\text{Y}_2\text{O}_3$ - $\text{SiO}_2$  nanocomposites in which  $\text{Eu}^{3+}$  ions are embedded. Preparation involve the mixing of proper amounts of tetraethoxysilan and hydroethanolic solutions of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Eu}(\text{NO}_3)_3$  (pH=1). Not aggregated

yttria nanoparticles ( $\sim 2$  nm) resulted homogeneously dispersed into the amorphous silica matrix. The characterization of nanoparticles were carried out by TEM, XRD while the influence of the silica support on the physical and structural properties of the nanoparticles was studied by medium FTIR and  $^{29}\text{Si}$  MAS and CPMAS NMR spectroscopy. The optical properties of  $\text{Eu}^{3+}$  in the  $\text{Y}_2\text{O}_3$ - $\text{SiO}_2$  nanocomposites were investigated by fluorescence and emission lifetime measurements.

### Y3.19

**ELECTROKINETIC CHARACTERISTICS OF OXIDE NANOSTRUCTURES AND VOLUME (HYDRO)OXIDES IN 1:1 ELECTROLYTES.** L. Ermakova, M. Sidorova, N. Bogdanova, A. Klebanov, V. Smirnov, St-Petersburg State Univ, Dept of Chemistry, RUSSIA.

The synthesis of nanosized oxo-layers (nanostructures) onto solid substrates by the molecular chemical modification from the gas phase allows to obtain the highly organized ultra-thin oxide layers with the beforehand structure, composition and properties. The nanosized Si-, Al-, Ti- and Fe- oxo-layers were synthesized onto silica substrates (spherical silica particles and slit vitreous quartz capillary) by the molecular chemical modification from their gas chlorides. Electrokinetic parameters (electrokinetic potential, isoelectric point - IEP) of prepared nanostructures were measured in dependence on nanostructure thickness, pH and salt level. The surface parameters of silica substrates, coated by nanostructures, were compared with characteristics of substrate and corresponded volume (hydro)oxides (anatase, boehmite, and goethite). It was obtained that the electro-surface characteristics of nanostructures not depend on the type of silica substrate. The IEP position of Al-oxo-layers gradually shifts up to the IEP of volume boehmite with an increase in nanostructure thickness; the IEP position of Ti-oxo-layers lies between the IEP values of substrate and volume anatase; the deposition of Fe-oxo-layers practically not changes the electrokinetic behaviour of coated particles.

The work funded by Russian Foundation for Fundamental Research under contract numbers 98-03-32086a and 00-15-97357.

### Y3.20

**PHOTOCATALYTIC CHARACTERISTICS OF  $\text{TiO}_2$  NANOMETER-SIZED POWDERS BY HOMOGENEOUS PRECIPITATION PROCESS.** K.R. Lee, S. Park, Myongji Univ, Dept of Inorganic Materials Engineering, Yongin, Kyunggido; S.J. Kim, Korea Atomic Energy Research Institute, Yusong, Taejeon, KOREA.

Photocatalytic characteristics of nanometer-sized  $\text{TiO}_2$  powder prepared by homogeneous precipitation process (HPP) were compared with those of commercial Degussa P-25 powder in order to remove metal ions such as Pb and Cu from aqueous equi-molar metal-EDTA solution. In aqueous Pb-EDTA solution, the  $\text{TiO}_2$  powder by HPP was 3.5 times higher and 1.5 times faster in initial adsorption and complete elimination of Pb ions, respectively, than Degussa P-25 powder. The  $\text{TiO}_2$  powder by HPP also showed a higher initial adsorption and faster elimination rate of Cu ions than Degussa P-25 powder in an aqueous Cu-EDTA solution, similar to the photocatalytic properties are enhanced with increasing specific surface area, and that the  $\text{TiO}_2$  powder by HPP, which consists of a primary particle size of 20nm coagulated with a chestnut bar shape has a larger specific surface area ( $170 \text{ m}^2/\text{g}$ ) than that ( $40 \text{ m}^2/\text{g}$ ) of Degussa P-25

### Y3.21

**HALL-PETCH RELATIONSHIP IN NANO-RUAL PREPARED BY MECHANICAL ALLOYING.** Kaiwen Liu, Frank Mücklich, Department of Materials Science, Functional Materials, Saarland University, Saarbrücken, GERMANY.

A transition from a normal Hall-Petch relationship to an abnormal one is observed at a grain size of approximately 18.5 nm for nano-RuAl. Several models each representing a controlling factor have been employed to rationalize the transition mechanism. The grain sizes corresponding to the dislocation pile-ups lower bound in grain interior are much smaller than the observed transition grain size and no apparent transition grain size has been derived from the grain size dependence of unit cell volume change. While the grain sizes corresponding to the transition of strain rate according to Coble creep and to the significant triple junction volume fraction (1%) are well consistent with the observed transition grain size. The overall results indicate that the transition of H-P relationship is dominated by the weakening effect of grain boundaries and triple junctions. The weakening and strengthening effects of the grain boundary components have been analyzed based on the detailed internal structural evolutions and the possible grain boundary structural evolutions during grain growth.

### **Y3.22**

**SYNTHESIS AND SINTERING CHARACTERISTICS OF TiC-Ni-Ti NANO-COMPOSITES.** Kai Yohwinkel and Rasit Koc, Department of Mechanical Engineering and Energy Processes, Southern Illinois University at Carbondale, IL.

This paper deals with the synthesis of submicron TiC powder from carbon coated precursor and sintering behavior with Ti and Ni binders. The TiC powders with submicron particle size, high purity and, non-agglomeration were synthesized using a new method [1]. The precursor is derived from a titania and hydrocarbon gas and provides high contact area between the reactants. This yields a better distribution of carbon within the precursor and inhibits the agglomeration among the titania particles, resulting in a more complete reaction and purer TiC powders at a comparatively low temperature. The TiC powders produced at 1550°C for 4 hours in flowing argon gas have a very fine particle size (< 100 nm) (surface area of about 60 m<sup>2</sup> / g), uniform shape and no agglomeration. The sintering behavior of the submicron TiC was investigated in a TiC-Ti-Ni system. The densification was investigated as a function of initial carbon and Ti-Ni content in flowing argon at 1500°C. DSC studies provided information on the formation of Ni<sub>x</sub>Ti<sub>x</sub> during the sintering. Both the Vickers hardness and fracture toughness will be discussed in the presentation.

1. R. Koc and G. Glatzmeier, U.S. Patent No: 5,417,952,(1995). Sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation/UT-Battelle.

### **Y3.23**

**NICKEL AND IRON NANOPARTICLES SYNTHESIZED ON SILICON AT ROOM TEMPERATURE BY PULSED LASER DEPOSITION.** Lianne Doeswijk, Vladimir I. Merkulov, Douglas H. Lowndes.

Nanoparticles of Fe or Ni are of interest as catalysts for the synthesis of carbon nanofibers and nanotubes. To grow individual nanotubes, and especially to control their diameter, very small, isolated nanoparticles should be used, preferably deposited on silicon at low temperatures in order to be compatible with other device processing steps. The size distribution of Fe and Ni nanoparticles, pulsed-laser deposited onto silicon wafers at room temperature, has been investigated as a function of the ambient argon gas pressure, target-substrate distance, number of laser pulses and laser pulse-repetition frequency (PRF). Increasing the PRF resulted in the desired smaller sizes of the metal nanoparticles. Combining this information with the dependence of nanoparticle size on the number of laser pulses, we propose a model for the formation and interaction of the particles with the ambient gas. Even smaller nanoparticles were found when the silicon substrate was placed next to and facing the same direction as the target, instead of in the customary position opposite to and facing toward the target. We will describe the size distributions achieved and their dependence on deposition conditions for these two different geometries.

This research was carried out at Oak Ridge National Laboratory (ORNL), with support from the Basic Energy Sciences program, U. S. Dept. of Energy, and from the ORNL LDRD program. Additional graduate student support was provided by the U. of Twente. ORNL is managed by UT-Battelle, LLC, for the U. S. Dept. of Energy under contract no. DE-AC05-00OR22725.

### **Y3.24**

**SYNTHESIS AND PROPERTIES OF BARIUM TITANATE/ORGANIC HYBRID FROM METAL-ORGANICS.** Toshinobu Yogo, Reimon Fukuzawa, Wataru Sakamoto, Shin-ichi Hirano, Nagoya University, Nagoya, Aichi, JAPAN.

Nanocrystalline particle/organic hybrids attract growing attentions as new inorganic/organic materials. This paper describes the processing of barium titanate/organic hybrid from metal-organic precursor. Barium titanate (BT) precursor was prepared from barium metal, titanium isopropoxide and organic modifiers. The structure of the BT precursor was analyzed by IR and NMR spectroscopy. The precursor was found to be a double metal-organics in solution. The precursor was hydrolyzed under the controlled reaction conditions. The formation conditions of nano-sized BT particles were investigated. The nanocrystalline particles in the organic matrix were analyzed by SAD, EDX and XRD. The particle size was found to depend upon the hydrolysis conditions. The hybrid was shaped into films by heating under pressure. The dielectric properties of the hybrid film were evaluated. The electro-rheological properties of the hybrid were also measured. The effects of organic modifiers on the electro-rheological properties were investigated.

### **Y3.25**

**FABRICATION OF 2D SUPERLATTICES OF SMALL GOLD NANOPARTICLES.** Toshiharu Teranishi, Mitsuyasu Haseda, Eitaro Yasuda, Mikio Miyake, Japan Adv Inst of Sci and Tech, School of Materials Science, Ishikawa, JAPAN; Masa-aki Haga, Toshitada Kato, Yoichi Shiozawa, Chuo Univ, Dept of Applied Chemistry, Tokyo, JAPAN.

Nanoscale metal particles, so-called nanoparticles, hold promise for use as advanced materials with new electronic, magnetic, optical, and thermal properties as well as new catalytic properties. These potentialities are mainly due to the quantum size effect, which is derived from the dramatic reduction of the number of free electrons in particles smaller than 5 nm. Moreover, the fabrication of ordered metal nanoparticles, superlattice, would enable us to produce the novel optical and nanoelectronic devices. Especially, the metal nanoparticles smaller than 2 nm in size are required for such devices to make use of the phenomenon of Coulomb blockade at room temperature. We successfully prepared the gold (Au) nanoparticles smaller than 2 nm by using the newly-synthesized ligand, 2,6-bis(1-(thioalkyl)benzimidazol-2-yl)pyridine (TC<sub>n</sub>BIP, n: the number of methylene groups in alkyl chain), which was designed to have disulfide group and 2,6-bis(benzimidazol-2-yl)pyridine (BIP) group, the former serving to produce small Au nanoparticles and the latter inducing the interaction between the ligands. Moreover, their two-dimensional superlattice was fabricated by the self-organization making use of an interaction between the ligands. Taking the mean interparticle spacing into consideration, the TC<sub>n</sub>BIP ligands are thought to interpenetrate each other as a result of a π-π interaction of BIP groups, resulting in contributing to the self-organization of Au nanoparticles. Using a series of the ligands with various alkyl chain lengths are expected to control the interparticle spacing of 2D self-organized Au superlattice.

### **Y3.26**

**BIFUNCTIONAL ELECTROCATALYTIC FILMS WITH GOLD NANOPARTICLES AND METALLOPORPHYRIN: PREPARATION AND CHARACTERIZATION.** Wenjun Yang, Xiaoyuan Li and Nai-Teng Yu, Department of Chemistry, Hong Kong University of Science & Technology, Hong Kong, PR CHINA.

Electrochemical transducer has been established as one of the primary sensing technologies in the selective and quantitative detection of chemical and biological species. Most of the modified electrodes provide one catalytic function for detecting only one analyte. In a living system it is often desirable to detect several analytes simultaneously at the same location. We report here the preparation and characterization of a new type of bifunctional films assembled on the electrode containing two electrocatalytic species (gold nanoparticles and metalloporphyrin) by multilayer deposition and ultraviolet light exposure. The multilayer assembly was achieved by a layer-by-layer (LbL) self assembly approach. The driving force of the assembly is the electrostatic force between the oppositely charged substrate and the assembling species. In this study, the cation, manganese (III) 5,10,15,20-tetra(4-pyridyl)-porphine chloride (MnP), and the anion, potassium tetrachloroaurate (III) were alternatively assembled on negatively charged glass and indium-doped tin oxide (ITO) supports. The assembled tetrachloroaurate ions were then converted to gold nanoparticles under the exposure of ultraviolet light (excitation peak at 240~250 nm). The film growth at each adsorption step was followed by absorption spectroscopy and cyclic voltammetry (CV). The absorbance at 468 nm (from MnP) and the reduction and oxidation waves of CV in pH 7 PBS increase linearly with the number of layers in film. The gold nanoparticles were characterized by UV-Vis absorption and X-ray photoelectron spectroscopy (XPS). Scanning electron micrographs (SEMs) were used to compare the surface morphologies of electrodes assembled with different numbers of assembling reagents. The electrocatalytic activity of the bifunctional multilayer films was studied in the detection of nitric oxide (NO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

This research has been supported in part by RGC-HK, RGC-NNSFC and HKUST.

### **Y3.27**

**AFM-BASED NANOMECHANICAL PROPERTIES AND STORAGE OF DENTIN AND ENAMEL.** Stefan Habelitz, Thomas M. Breunig, Grayson W. Marshall, Sally J. Marshall, Dept of Preventive and Restorative Dental Sciences, University of California, San Francisco, CA; Mehdi Balooch, Dept Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

AFM-based nanoindentation has become an increasingly useful technique for the determination of mechanical properties of structural features in biological hard tissues. Since nanoindentations sample only a thin surface layer, chemical changes of mineralized tissues resulting from storage solutions are important considerations for the accurate determination of mechanical properties. The present study evaluated



the affects of 6 different solutions: deionized water, saline, 3 calcium buffered saline solutions and Hanks' Balanced Salt Solution (HBSS), on nanohardness and elastic modulus of dentin and enamel from human third molars at storage times of 0, 1, 7, 14 and 28 days using a modified AFM (Triboscope). The pH values of the solutions were monitored throughout the test periods. Storing the specimens in deionized water resulted in a large decrease of mechanical properties, e.g. the reduced elastic modulus of dentin decreased from  $24 \pm 1.5$  GPa to  $21 \pm 1.6$ ,  $8.6 \pm 1.1$  and  $5.2 \pm 1.1$  GPa for storage times of 1, 7 and 14 days, respectively. In general, the mechanical properties of dentin and enamel dropped by more than 12% after one day and greater than 50% after a week when stored in deionized water, saline or calcium chloride buffered solutions. The observed changes in mechanical response were attributed to a demineralization process during storage. In contrast, storing teeth in HBSS did not significantly alter the mechanical properties of dentin or enamel over the time studied. Therefore, the use of HBSS for the storage of tooth samples prepared for nanomechanical and other mechanical tests sensitive to surface quality is recommended.

Supported by NIH/NIDCR DE09859 and DE13029.

### Y3.28

#### ULTRASOUND-ENHANCED SPRAY DRYING OF POLYMER MICRO-EMULSIONS FOR NANOPARTICLES SYNTHESIS.

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In this paper, we report how micro-emulsions of polymers, which are Newtonian at low concentrations, behave in ultrasound-modulated two-fluid (UMTF) atomization. Stable micro-emulsions of uniform nanoparticles of polymers in water can be obtained by soap-less emulsion polymerization. However, these nanoparticles often coalesce during the drying process. Since UMTF atomization is capable of producing uniform droplets, it is a potential means for drying of the micro-emulsions of polymers. UMTF atomization uses ultrasound to control the drop size and size distribution of two-fluid atomization (i.e. liquid atomization by high velocity air). At sufficiently high air velocity, the capillary wave generated by the third harmonic frequency of the ultrasound grows at a much higher rate than that generated by the fundamental. Uniform drops with a diameter determined by the third harmonic frequency are produced as a result. Contrary to the common view that viscoelastic liquids are more difficult to atomize than Newtonian liquids, we have found that the aerodynamic conditions required to produce uniform drops in UMTF atomization are less severe for viscoelastic xanthan gum solutions than for Newtonian aqueous glycerol of similar viscosity. In addition, UMTF atomization of polymer micro-emulsions at 110 kHz ultrasound frequency produced uniform spherical particles of poly(methyl methacrylate), PMMA and poly(butyl acrylate), PBA 50 nm and 1.3  $\mu$ m in diameter, respectively. These findings suggest potential applications of UMTF atomization in spray drying for synthesis of uniform polymer beads for use in catalyst templates and strength reinforcement of advanced materials.

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### Y3.29

#### RECOGNITION-MEDIATED TEMPLATING OF NANOPARTICLES USING GIANT VESICLES.

Erik J. Turnberg, Trent H. Galow, Faysal Ilhan, Mark Gray, Tomomi Sakai, Vincent M. Rotello, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA.

Adaptation of self-assembly processes to the controlled aggregation of synthetic polymers provides a useful method for the creation of novel higher order architectures. We have recently incorporated specific recognition elements into polystyrene-based polymers. Unlike biopolymers such as DNA and RNA, these synthetic polymers are highly flexible and randomly substituted. This combination of randomness and flexibility provided giant self-assembled vesicles. Proof of the vesicular nature of the aggregates formed from complementary copolymers was obtained using Confocal Laser Scanning Microscopy (CLSM). For these studies, a flavin-functionalized analog was used as a fluorescent probe. CLSM micrographs of the aggregates show that the vesicles consist of bright edges with less-fluorescent central regions indicating a hollow interior. In addition, we have successfully deposited recognition-functionalized gold nanoparticles onto surfaces using the vesicle as a template.

### Y3.30

#### GREATLY ENHANCED SECOND HARMONIC GENERATION IN DEFECTIVE PHOTONIC CRYSTAL.

Bin Shi, Zuimin Jiang, Xun Wang, Fudan Univ, Surface Physics Lab, Shanghai, CHINA.

In last decade, great attention has been paid on the investigations of photonic crystals (PC) and their applications. However, to our knowledge, there was little work on the nonlinear optical phenomena of the PC with defects. In this paper, a kind of defective PC constructed by the nonlinear optical material is studied with numerical experiments by computer simulation. Greatly enhanced second harmonic generation (SHG) is found in such structure, providing a new application area of the defective PCs. The structure of the nonlinear defective PC is an array of square rods of  $\text{LiNbO}_3$  inserted in the air surrounding. The axes of the rods are chosen along the z-direction of  $\text{LiNbO}_3$  crystal. There are 17 periods in the x direction and infinite periods in the y direction. The side length of the square is  $0.5a$ , where  $a$  is the periodicity of the array. The defects are introduced by changing the side length of some  $\text{LiNbO}_3$  rods in the PC from  $0.5a$  to  $a$ . Such rods locate at the ninth period in x direction and are separated each other by nine periods along y direction. In such a structure, the periodicity of the PC is destroyed by the defect rods, and thus some defect states will be introduced in the band gap of the PC. Using finite-difference time-domain method with some improvement for the dispersion materials, we studied the SHG process in such structure. The computer simulation results illustrate that in the defective nonlinear photonic crystal, second harmonic generation can be greatly enhanced. The SHG efficiency can be larger than 10% in a several micrometer long structure with the incident power of 2.2  $\text{MW}/\text{cm}^2$ . The above SHG efficiency is four orders of magnitude higher than that of a bulk  $\text{LiNbO}_3$  crystal with the same dimensions and under the same excitation conditions.

### Y3.31

#### SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF MOLECULAR-WIRE/SEMICONDUCTOR NANOCRYSTALS HYBRID STRUCTURES.

Edith Minkin, Marina Sirota, Efrat Lifshitz, Technion-Israel Institute of Technology, Dept of Chemistry and Solid State Institute, Haifa, ISRAEL; Volker Hensel, Meir Lahav, Weizmann Institute of Science, Dept of Materials and Interfaces, Rehovot, ISRAEL.

The extensive study of individual nanocrystals stimulated preliminary work in the development of ordered or disordered arrays of nanocrystals. The latter show new collective effects, resulting from the inter-nanocrystal or matrix-nanocrystal interactions. Thus, appropriate engineering and meticulous physical characterization of nanocrystals arrays offer the opportunity to design devices with the benefit of individual nanocrystals and the collective properties of the arrays. The present study focused on the spectroscopic properties of new molecular-wire/nanocrystalline superstructures. The molecular-wires consisted of (phenylene)<sub>n</sub>-(acetylene)<sub>(n-1)</sub>-dicarboxylate conjugated chains (acid), with a length varying between 1.9 nm to 3.3 nm. The nanocrystalline component consisted of either lead sulfide (PbS) or cadmium sulfide (CdS) or both, with an average size diameter of 2.0-3.0 nm. The photoluminescence (PL) spectra, the PL-excitation and the time-resolved PL measurements showed a typical quantum size effect of the individual nanocrystals, and additional collective effects of a superstructure. The nanocrystals are excited, both via the molecular-wires and directly into the quantized state of the nanocrystals. Simulation of the luminescence decay processes suggested an energy transfer between the organic acid and the nanocrystal, by exciton diffusion mechanism. Furthermore, the direct exciton excitation in the nanocrystals is slightly red-shifted upon variation of the length of the acid molecules. This variation is a consequence of either an acid/nanocrystals or inter-nanocrystalline electronic interactions.

### Y3.32

#### SINGLE CRYSTAL NANOWIRES ELECTRODEPOSITED FROM REVERSED LIQUID CRYSTALLINE PHASES.

Limin Huang, Yushan Yan, Department of Chemical & Environmental Engineering, University of California, Riverside, Riverside, CA.

One-dimensional nanowires have attracted much attention because of their unique electrical, magnetic, optical, and mechanical properties [1-2]. Templated synthesis with rigid templates (e.g., anodized alumina) has been used [1], but these templates are tedious to fabricate and not easy to remove after completion. Also it tends to produce polycrystalline nanowires because the template is rigid. Here we report a new, simple and versatile procedure that allows electrodeposition of single crystal nanowires (Cu, Ag, Zn, Bi, etc.) of controllable diameter and length directly from flexible reversed liquid crystalline phases. And the nanowires so-obtained can be easily collected by simple washing. Hexagonal reversed liquid crystalline phases were chosen according to classical ternary phase diagram consisting of surfactant, p-xylene and for our synthesis water was substituted by an aqueous electrolyte containing desired metallic ions. Polished stainless steel was used as working electrode, on which nanowires were deposited, and copper, silver or zinc plate was used as counter electrode. Potential of 0.5-3 V was applied across the two

narrowly spaced electrodes (500  $\mu\text{m}$  apart). SEM images show highly ordered unidimensional arrays of nanowires with uniform diameters ranging from 10 nm to 80 nm and with lengths from 2  $\mu\text{m}$  to tens of micrometer. The length and diameter of the nanowire can be controlled by varying deposition time and dimension of aqueous phase within reversed liquid crystal. TEM and XRD further show that the nanowires are single crystals. We believe that formation of single crystal nanowires is a result of the flexibility of the liquid crystalline phase that allows better supermolecular recognition among metallic ions. In addition, patterned structures of nanowires (e. g., fan, tree, ball and cone-shaped, etc.) can also be fabricated.

[1] C.R. Martin, *Science* 266, 1961 (1994).

[2] A.M. Morales, C.M. Lieber, *Science* 279, 208 (1998).

### **Y3.33**

**CHEMICALLY VAPOR DEPOSITED  $\text{TiSi}_x$  NANOISLANDS ON Si.** T.I. Kamins, R. Stanley Williams and D.A.A. Ohlberg, Hewlett-Packard Laboratories, Palo Alto, CA.

Ti can be deposited by chemical vapor deposition from the gaseous precursor  $\text{TiCl}_4$  at elevated temperatures onto Si, where it reacts with the Si substrate to form  $\text{TiSi}_x$ . Because of the large mismatch between the lattice constant of the deposited material and that of the substrate, three-dimensional nanoislands form. The deposition rate of Ti increases rapidly with increasing deposition temperature below 690°C, while it increases only slowly at higher temperatures. The number of islands after deposition varies only slowly with the amount of Ti deposited, but the number of Ti atoms in each island varies rapidly. During annealing above 800°C, the island density decreases significantly, and the islands take characteristic shapes. The island size varies only slowly with the amount of Ti deposited, and the island density varies more significantly. After annealing, three different dominant island shapes are seen on Si(001).

### **Y3.34**

**THE FORMATION, STRUCTURE AND OPTICAL PROPERTIES OF  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  AND  $\text{Zn}_{1-x}\text{Ag}_x\text{S}$  NANOPARTICLES IN LANGMUIR-BLODGETT FILMS.** Yuri N. Savin, Alexander V. Tolmachev, Oxana A. Pavlenko, Maxim B. Yemets, Institute for Single Crystals, Kharkov, UKRAINE.

The optical and electronic transport properties of semiconductor nanoparticles in dielectric matrixes draw attention now because quantum dimension effects can be observed here and such structures can be used in photonics, micro- and nanoelectronics. In this communication the formation processes of a semiconductor nanoparticles of a ternary compounds  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  and  $\text{Zn}_{1-x}\text{Ag}_x\text{S}$  in Langmuir-Blodgett (LB) films of the stearic acid are discussed. Synthesis of a nanoparticles in LB films was carried out by two methods. The first, Langmuir monolayer of a cadmium stearate was formed at the water subphase containing  $\text{CdCl}_2$  salt and was transferred on the quartz and silicon substrates. Then LB films were exposed in  $\text{Zn}(\text{NO}_3)_2$  water solution to obtain the LB films of the zinc and cadmium stearates solid solutions. Afterwards LB films were exposed in  $\text{Na}_2\text{S}$  water solution to obtain  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  solid solutions. The alternative was the forming of the cadmium stearate LB films with the following treatment in  $\text{Na}_2\text{S}$  solution, than in  $\text{Zn}(\text{NO}_3)_2$  or  $\text{AgNO}_3$  solutions and again in  $\text{Na}_2\text{S}$ . As a result  $\text{CdS}$ ,  $\text{ZnS}$  or  $\text{Ag}_2\text{S}$  particles or nanoparticles  $\text{CdS}$  covered by  $\text{ZnS}$  or  $\text{Ag}_2\text{S}$  layers were obtained. The elemental compositions were studied by XPS. The nanoparticle size, their distributions and structures were investigated by electron microscopy and X-ray diffraction. Optical absorption spectra of nanoparticles depending on their sizes and compositions are discussed.

### **Y3.35**

**SUSTAINED POSITIVE DRUG RELEASE ON NANO-STRUCTURED THERMOSENSITIVE CERAMIC/HYDROGEL HYBRIDS (NANOGELES).** Yongsoon Shin, Jun Liu\*, Jeong Ho Chang, Rick Williford, Pacific Northwest National Laboratory, Richland, WA.

Hybrid nanostructured thermosensitive ceramic/hydrogels (nanogels) shows great potentials for a wide range of biomedical applications. This paper will discuss the preparation of the hybrid nanogels and the new thermal sensitive on-and-off mechanism associated with the nanogel. When the temperature rises, the polymer gel shrinks, squeezing the drug into the porous channels, and at the same time, opening the pore to the outside media. The drug delivery into the media is controlled by the diffusion of the drug out of the porous channels. The proposed squeezing-diffusion mechanism allows uniform release rates when the temperature is maintained at the high temperature. In addition, by changing the composition during the nanogel preparation, the pore volume and channel sizes can be reduced, significantly extending the effective release over a long period of time.

### **Y3.36**

**STRUCTURAL TRANSITIONS IN THIN METALLIC MULTILAYERS.** Gregory B. Thompson, Rajarshi Banerjee, Hamish L. Fraser, Dept of MS&E, Ohio State University, OH.

Thin metallic multilayers have found application in a wide variety of fields. These include metallization layers in semiconductor devices, giant magnetoresistive devices, optical and x-ray mirrors, and as coatings for structural applications. Each application requires that the properties of the films be well understood. In recent years, it has been reported that a variety of multilayered structures, such as Co/Cr, Ti/Al, and Nb/Zr exhibit structural transitions, when the layer thicknesses are reduced to the nanoscale regime. Such structural transitions are expected to significantly alter the physico-chemical properties of the system thereby enhancing or diminishing its potential application. By understanding the mechanisms that cause these transitions it is possible to model and consequently predict the critical transition thicknesses in these systems. Furthermore, modeling affords the possibility to manipulate the multilayer to get the desired structure with optimal properties. This paper focuses on the experimental characterization, using transmission electron microscopy and x-ray diffraction, and modeling of structural transitions in thin multilayers.

### **Y3.37**

**MAGNETIC NANOCOMPOSITES BY ALKALIDE REDUCTION.** Jennifer A. Nelson, Micheal J. Wagner, George Washington Univ, Dept of Chemistry, Washington, DC.

The goal of this research is to develop a magnetic nanocomposite that will be important to the construction of a magnetic refrigeration system that can operate in the range of ambient atmospheric temperatures and be applied to practical consumer refrigeration systems. A relatively new and unexplored method, the reduction of metal salts by alkalides and electrides, is being employed to synthesize Gd and Dy nanocomposites. Magnetic nanocomposites offer important advantages over either paramagnetic or ferromagnetic materials for magnetic cooling, producing large entropy changes for smaller magnetic fields, having a more uniform distribution of  $\delta S(t)$  as a function of temperature, and allowing high cycling frequency to be utilized while minimizing any eddy current losses. The magnetic properties of these materials are being tested as is their ambient temperature cooling capability in a magnetic refrigerator.

### **Y3.38**

**EFFECTS OF SIZE AND SHAPE OF MAGNETIC NANO PARTICLES ON ELECTRICAL AND MAGNETIC PROPERTIES OF MAGNETIC PARTICLES/POLYMER NANO-COMPOSITE.** Jin-Ho Kang, Chan-Eon Park, Pohang University of Science and Technology, Polymer Research Institute, Department of Chemical Engineering, Division of Electrical and Computer Engineering, Pohang, KOREA.

Magnetic particles/polymer nano-composites have been actively studied because of their electrical, optical and magnetic properties for various applications such as microelectronic device, storage material and optics. However these studies have been based on spherical nano particles synthesized by sol-gel method or simple coprecipitation. In this study, we have synthesized spherical and non-spherical (disk-like) nano particles and studied the effects of size, shape and alignment of nano particles on electrical and magnetic properties. Ferrite and Ni-Zn ferrite nano particles have been synthesized by chemical method and then dispersed homogeneously into polymer matrix such as hydrogen silsesquioxane and polyimide for nano-composite. The size and shape of magnetic particles have been controlled by the concentration of mixed surfactants and mole ratio of anionic surfactant (sodium dodecylsulfate) to cationic surfactant (cetyltrimethylammonium bromide). For stable dispersion of nano particles, surface charges have been introduced by applying various acids, alkalies and coupling agents ( $\gamma$ -APS) to nano particles. The shape, size, dispersity and structure of nano particles have been analyzed by transmission electron microscopy and x-ray diffraction. Magnetic properties have been measured by vibrating sample magnetometer. Superparamagnetic property with 5.6 nm and ferri or ferromagnetic property with more than 10 nm of nano particle have been obtained. Electrical properties such as permittivity of nano-composites have been measured using network analyzer from 10 MHz to 5 GHz. Especially, the effects of particle shape and size have been investigated on permittivity of nano-composite.

### **Y3.39**

**GLASS TO ICOSAHEDRAL-PHASE TRANSFORMATION IN Zr-BASED GLASSY METALS.** Osami Haruyama, Dept of Physics, Science University of Tokyo, JAPAN; Junji Saida, Japan Science and Technology Co, Inoue Superliquid Project, JAPAN; Akihisa Inoue, Inst for Material Research, Tohoku, JAPAN.

I-phase crystallization in Zr-based metallic glasses has been examined first by Koster et al.[1]. Hereafter, new alloy systems such as  $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{10}(Pd, Ag)_{10}$ ,  $Zr_{70}Pd_{20}Ni_{10}$  and  $Zr_{70}Pd_{30}$  were found out. The calorimetric experiment was clarified that two exothermic transformations have been occurred in these glasses. One corresponded to I-phase crystallization from glassy phase and another to the precipitation of crystallite from I-phase. It is very interesting that I-phase crystallization in several glasses was performed in a polymorphic manner. In this case, a single I-phase was precipitated in a glassy phase without the variation of composition. We present the change in the electrical resistivity due to the polymorphous I-phase transformation. In  $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{10}(Pd, Ag)_{10}$  glasses, the electrical resistivity decreased as I-phase crystallization proceeded. On the other hand,  $Zr_{70}Pd_{20}Ni_{10}$  and  $Zr_{70}Pd_{30}$  glasses showed the increment of resistivity which has been reported for polymorphous I-phase transformation in Al-Cu-V and Al-Mn-Si glasses. Low temperature resistivity experiment was also performed to examine the difference of electron transport property between glass and icosahedral phases. The resistivity data suggested that the electron transport was controlled by the weak localization of conduction electron in both glass and icosahedral phases.

[1] U. Koster, J. Meinhardt, S. Roos and H. Liebertz: Appl. Phys. Lett. 69(1996)179.

### Y3.40

**SYNTHESIS OF INDIUM OXIDE NANOPARTICLES BY REACTIVE LASER ABLATION.** Amith Murali, Anirudha Barve, Valerie J. Leppert, Subhash H. Risbud, University of California, Davis, Dept of Chemical Engineering and Materials Science, Davis, CA.

Indium oxide nanoparticles were synthesized by pulsed laser ablation of 99.9999% pure indium metal in flowing air. The ablation was performed in a stainless steel chamber. The air pressure was maintained at 25 Torr with a flow rate at about 0.6l/min. The laser source was the fourth harmonic of a pulsed Nd:YAG laser ( $\lambda = 266\text{nm}$ ) with a pulse width of 10 ns, repetition rate of 10 Hz, and a pulse energy of typically 50 mJ. The laser beam was focused down to a  $\sim 1\text{mm}$  diameter spot on the indium target causing the ablation. The reaction product was collected downstream on a microporous cellulose nitrate membrane filter. The phase and size of the particles were characterized using x-ray diffraction (XRD), and transmission electron microscopy (TEM). Diffraction data from both the XRD and the TEM confirmed the cubic phase of indium oxide and the dark field data from TEM showed particle size of about 5 nm. Photoluminescence spectroscopy was used to determine the optical property of the particles.

### Y3.41

**NANOPARTICLE AGGREGATED FILMS OF IRON OXIDE PREPARED BY LASER ABLATION.** Leszek Zbronic, Takeshi Sasaki, Naoto Koshizaki, Natl Inst of Mats and Chemical Research Agency of Industrial Sci and Tech, MITI Tsukuba, JAPAN.

Iron oxide nanoparticle aggregated films were prepared using excimer laser ablation technique by adopting off-axis configuration and gas condensation process. Sintered  $Fe_2O_3$  targets were ablated in Ar,  $O_2$ , He,  $N_2$ , Ne and Xe by ArF excimer (193 nm) under various pressures. It was found that both the ambient gas and its pressure strongly affect the composition of the deposition product. Depending on the ablation parameters the product of ablation was comprised of  $Fe_2O_3$  or  $Fe_2O_3$  and FeO. In the 13.3 Pa - 6.67 kPa pressure range of argon and in the 13.3 - 997 Pa range for oxygen the oxide phases exhibited well-defined peaks whereas in the 0.667 - 13.3 Pa range the phases had rather poor crystallinity often being amorphous in argon and oxygen. In Ar, He, Ne and Xe the XRD peak intensity ratios, defined as  $R = I(Fe_2O_3(311)) / I(FeO(200))$ , showed high sensitivity to changes in gas pressure. In Ar, at the lowest fluence, the most pronounced change in product chemistry was observed in the 13.3 - 267 Pa pressure range. Changing Ar pressure from lower to upper limit of this range varied the product chemistry from being close to a single phase ( $Fe_2O_3$ ) to being a two phase ( $Fe_2O_3$  FeO). On the other hand, varying oxygen pressure had little effect on the product chemistry. In Ar the dominating phase of the ablation product tended to be the same as that of the target whenever the fluence was sufficiently high and with increasing argon pressure this required fluence for stoichiometric (Fe/O ratio the same as that of the target) deposition also became higher. When the irradiation fluence was sufficiently high the deposition became stoichiometric within pressure range specific for each gas. With further increase in fluence these pressure ranges within which the deposition was stoichiometric became broadened. Ambient gas also affected the film thickness distribution and film length. The latter decreased exponentially with the atomic mass of the inert gas with data points for  $N_2$  and  $O_2$  lying far off this dependence. Additionally, it was found that in  $O_2$  at very specific conditions, the target surface state strongly affected the composition of the product of ablation.

### Y3.42

**PRODUCTION AND CHARACTERISATION OF RADIO FREQUENCY SUSPENSION PLASMA SPRAYED NANO-SIZED HYDROXYAPATITE POWDERS FOR BIO-MEDICAL APPLICATION.** Rajendra Kumar, P. Cheang, Nanyang Technological University, School of Materials Engineering; K.A. Khor, School of Mechanical and Production Engineering, SINGAPORE.

RF suspension plasma spraying was utilised to produce nano-sized HA powders. This technique utilises the inherent properties of the RF plasma to inject an atomised spray of HA suspension axially into the plasma producing ultra-fine powders. The effect of process parameters and concentration of suspension on the resulting properties of the powders were studied to understand the spraying process and define operating windows for the production of powders with different properties. Particle sizing, XRD, SEM and TEM, DSC and FTIR were employed to characterise the as-sprayed powders and the HA suspension feed stock. Rietveld analysis was carried out on selected powders to determine the quantity of phases present. The powders were spherical and in the size range of 10nm to 4 microns. Particles below 150nm were completely amorphous and larger than 400nm were nano-crystalline. XRD results revealed that as-sprayed powders contained HA, alpha and beta tri-calcium phosphate (TCP), tetra-calcium phosphate (TTCP), CaO and an amorphous phase. Average particle size was inversely proportional to plate power. Decomposition rose up to a plate power of 15kW and then decreased at higher powers. The amorphous content increased with plate power except at 15kW at which it dipped. Spraying at lower chamber pressure and gas flow rates increased the average particle size and lowered decomposition. DSC analysis revealed that the powders recrystallised between 550-630 degrees Celsius and that the other phases reverted back to HA. FTIR revealed that the as-sprayed powders contained varying amount of carbonate and hydroxyl groups. Rietveld quantitative analysis revealed detailed phase composition and unit cell parameter changes as a function of plate power. Results thus far have defined operating windows for the production of nano-sized HA powders and shed light on the mechanism of phase transformation taking place during suspension plasma spraying.

### Y3.43

**HYDROGEN EVOLUTION FROM WATER DISPERSING TITANIA OR ALUMINA NANOPARTICLES ENHANCED BY GAMMA-RAY.** Satoshi Seino, Takao A. Yamamoto, Ryosuke Fujimoto, Kensuke Hashimoto, Masahiro Katsura, Osaka Univ, Dept of Nuclear Engineering, Osaka, JAPAN; Shuichi Okuda, Osaka Univ, ISIR, Osaka, Japan; Ryuichiro Oshima, Osaka Prefectural Univ, RIAST, Osaka, JAPAN.

Hydrogen gas evolution from water dispersing nanoparticles induced by  $^{60}Co$  gamma-ray irradiation was studied. Nanoparticles of  $TiO_2$  and  $Al_2O_3$  with average sizes of 7 - 200 nm supplied from several suppliers were employed. These nanoparticles were characterized by the following methods. Primary particle size distributions and their shapes were investigated by a TEM, and their crystal structures were determined with XRD. Agglomerated particle size in the aqueous phase was investigated with laser doppler method. Before gamma-ray irradiation, distilled water and nanoparticles were closed in a glass vial, and argon gas purged air in the vial and dissolved in the dispersion. During the irradiation, the vials were continuously stirred to maintain the dispersion. After the irradiation, hydrogen gas was measured by a gaschromatograph. In some experiments, pH of the dispersion was controlled by phosphoric acid and sodium hydroxide. The low pH of the dispersion resulted in low hydrogen evolution yield, which might be explained by the relatively large size of agglomerated nanoparticles under acidic condition. On the basis of these experimental results and characteristics of nanoparticles, reactions occurring in this heterogeneous system are discussed taking account of radiolysis and photocatalytic effects. Radiolysis process seems dominant in the system.

### Y3.44

**SURFACE INITIATED POLYMERIZATION (SIP) ON NANOPARTICLE SURFACES: DEMONSTRATION OF FIRST PRINCIPLES AND PREPARATION OF NANOCOMPOSITE LAYERS AND MATERIALS.** Qingye Zhou, Xiaowu Fan, Chuanjun Xia, Jimmy Mays and Rigoberto Advincula, Chemistry Department, University of Alabama at Birmingham, Birmingham, AL.

Surface initiated grafting of polystyrenes from Si-gel and clay nanoparticles have been made by both free radical and living anionic polymerization method. For anionic SIP, 1,1-diphenylethylene (DPE) initiation sites were attached to Si-gel and clay particle surfaces by using chlorosilane and amino functional groups which are separated from the DPE by an alkyl spacer. After polymerization of styrene, polymers were cleaved from Si-gel and clay particle surfaces and analyzed. We have characterized these polymers by FTIR, NMR,

AFM, TGA and SEC. Polymers grafted from particle surfaces show a higher polydispersity than in solution. Molecular weight of polymers obtained from clay surfaces is much lower than in solution. It seems that diffusion of styrene monomer and stability of the initiator attachment to the surface controls the propagation of styrene in the interlayer of clay. We have also prepared Clay-polymer nanocomposites mainly using the layer-by-layer alternate assembly approach. These films are being used as test surfaces for investigating SIP. Analysis of these films is done with techniques such as X-ray, AFM, SPS, and QCM.

### Y3.45

**MAGNETIC PROPERTIES OF COBALT NANOPARTICLES IN AN AIMCM41 MESOPOROUS HOST.** Jin-Seung Jung, Kangnung National Univ, Dept of Chemistry, Kangnung, KOREA; Yong-Rok Kim, Yonsei Uni, Dept of Chemistry, Seoul, KOREA; Leszek Malkinski, Weillie Zhou, Marilena Viciu, John Wiley, Charles O'Connor, AMRI/Dept of Chemistry, Univ. of New Orleans, New Orleans, LA.

Ultrafine cobalt particles in AIMCM41 silica tubes have been synthesized by ion exchange and the reduction with sodium borohydride. The role of this stable host matrix of AIMCM41 silica is to prevent agglomeration of the magnetic particles attached to the walls of AIMCM41 silica pores. The size of the host pores naturally limits the particle dimensions and thus improves their size distribution. The Co particles in silica tubes exhibit superparamagnetic properties with blocking temperature around 4K. The coercive field below the blocking temperature was 600 Oe at 2K. Existence of Co-oxide was detected in the first series of samples, however improvement of synthesis method made possible to get rid of this undesirable effect. Both magnetic susceptibility measurements and transmission electron microscopy show a narrow distribution size of the nanoparticles. Well controlled insertion of the magnetic material to the host channel excludes formation of bulk particles outside the host material grains, which was confirmed by the TEM studies. X-ray diffraction data did not show peaks corresponding to a crystalline cobalt, but this maybe due to small size of particles and their relatively small volume fraction. The content of Co in the AIMCM41 host was measured using both magnetic measurements and elemental analysis.

### SESSION Y4: NANOLITHOGRAPHY AND FUNCTIONAL NANOMATERIALS

Chairs: L. Andrew Lyon and Pulickel M. Ajayan  
Wednesday Morning, April 18, 2001  
Metropolitan II (Argent)

### 8:30 AM \*Y4.1

**CHEMICAL LITHOGRAPHY.** M. Grunze, W. Eck, A. Goelzhaeuser, W. Geyer, and V. Stadler, Angewandte Physikalische Chemie, Universitaet Heidelberg, INF, Heidelberg, GERMANY.

Densely packed Self Assembled Monolayers (SAMs) provide well defined model systems to study electron beam effects in organic interfaces, and can be used as high resolution electron beam resist. I will present examples of negative and positive resist systems based on SAMs, and then discuss our recent work using derivatized biphenyl SAMs to prepare, by direct electron beam writing or projection lithography, multifunctional chemical structures on noble metal, semiconductor and ITO glass surfaces. These chemical nanostructures can be used to place, with a lateral precision of better than 20 nm, identical or different molecules (or macromolecular objects) in a predefined pattern on a surface.

### 9:00 AM \*Y4.2

**CONSTRUCTIVE NANOLITHOGRAPHY: NANOFABRICATION VIA SELF-ASSEMBLY ON STABLE MONOLAYER SURFACES PATTERNED WITH AN ELECTRICALLY BIASED AFM TIP.** R. Maoz<sup>1</sup>, S.R. Cohen<sup>2</sup> and J. Sagiv<sup>1</sup>. <sup>1</sup>Department of Materials & Interfaces. <sup>2</sup>Chemical Services Unit, The Weizmann Institute of Science, Rehovot, ISRAEL; S. Höppener, L.F. Chi and H. Fuchs Physikalisches Institut, Interface Physics, Münster, GERMANY.

We present a new approach to nanofabrication, based on self-assembly processes of both organic (e.g. mono-, multilayer) and inorganic (e.g. metal, semiconductor nanoparticles) materials taking place on template patterns generated by the non-destructive local electrochemical modification (with a conducting AFM tip operated in normal ambient conditions) of selected sites on the top surface of a highly stable, defect-free base monolayer self-assembled on silicon. This pure "synthetic" approach differs in principle from the usual etch-development techniques employing organic monolayers as passive ultrathin resists that are removed after the desired pattern is generated. In constructive nanolithography, the patterned organic film plays an active role as template throughout the entire fabrication

process, which consists of self-assembly and surface chemical modification steps only. It will be shown that such in-situ self-assembly provides new build-up options, allowing fabrication of nanostructures that combine diverse materials and architectural motifs in a manner not easily realizable by other techniques. This aspect is particularly promising with regard to the possible future fabrication of novel electronic devices with precisely defined nanometric dimensions.

Related recent publications:

R. Maoz, S.R. Cohen, J. Sagiv, Adv. Mater., 1999, 11, 55. R. Maoz, E. Frydman, S.R. Cohen, J. Sagiv, Adv. Mater. 2000, 12, 424. R. Maoz, E. Frydman, S.R. Cohen, J. Sagiv, Adv. Mater. 2000, 12, 725.

### 9:30 AM Y4.3

**LASER WRITING OF NANO-STRUCTURE ON SILICON (100) SURFACES WITH PARTICLE ENHANCED OPTICAL IRRADIATION.** L. Zhang, Y.F. Lu, W.D. Song, Y.W. Zheng and B.S. Luk'yanchuk, Laser Microprocessing Lab Department of Electrical and Computer Engineering and Data Storage Institute, National University of Singapore, Singapore, SINGAPORE.

0.5  $\mu\text{m}$  spherical silica particles were placed on Silicon (100) substrate. After laser irradiation with a 248 nm KrF excimer laser, hillocks with size of about 100 nm were obtained at the original position of the particles. Mechanism of the formation of the sub-wavelength structures were investigated and found to be the near-field optical resonance effect induced by particles on surface. Theoretical prediction of the near-field light intensity distribution was presented, which was in agreement with the experimental result. The method of particle enhanced laser irradiation has potential applications in nanolithography.

### 9:45 AM Y4.4

**GOLD NANOARRAYS FOR LITHOGRAPHY AND TETHERING OF SINGLE MOLECULES.** Vanessa Z-H. Chan, Joachim P. Spatz and Martin Möller, Univ. of Ulm, Dept. Organic and Macromolecular Chemistry, Ulm, GERMANY.

The study of structures with nanometer dimensions and their use in the fabrication of nanoscale devices is of intense scientific and technological interest. Through the combination of top-down (e-beam lithography) and bottom-up (macromolecular chemistry) approaches, we are able to produce nanometer sized gold patterns with controlled spacings that now allow the study of fundamental phenomena in the biological and physical sciences. To this effect, gold islands with diameters ranging from 2 nm to 200 nm can be precisely patterned in periodic and artificial arrays on a wide variety of substrates, including GaAs, glass and silicon. The gold can then be used as an anchor point for the tethering of functional molecules to yield a wide range of chemical nanopatterns. The versatility of this method allows the use of these nanopatterns for a variety of applications. The gold nanoarrays have been used to make quantum wells in InGaAs substrates by using the gold as etch masks for the underlying substrate. Columns with aspect ratios of up to 8:1 have been produced. We have also shown the formation of fluorescent patterns through the binding of a lissamine molecule to the gold dots which will allow a non-ensemble study of fluorescent species resulting in statistically significant dynamic information on these molecules. With the appropriate choice of dyes one can also imagine the use of such substrates as optical storage devices. Currently, these gold nanoarrays are also being used to study the interaction of single protein molecules with living cells. To this effect, nanosized patterns of RGD proteins are formed through the tethering of RGD to the gold islands using thiol end groups. By culturing cells modified with green fluorescent proteins on these substrates, the influence of the pattern of specific contact adhesion points on the cell cytoskeleton can be studied. It is hoped that through these single protein molecule patterns, direct communication to the cell can be realized which will ultimately allow the understanding of the mechanisms that govern cell adhesion and movement on the molecular level.

### 10:30 AM \*Y4.5

**NANOCRYSTALLINE Mg-BASED HYDRIDES FOR HYDROGEN STORAGE.** R. Bormann, T. Klassen and W. Oelerich, Institute for Materials Research, GKSS-Research Center, Geesthacht, GERMANY.

Hydrogen is the ideal means of energy storage for transportation and conversion of energy in a comprehensive clean-energy concept. However, appropriate storage facilities, both for stationary and for mobile applications, are complicated, because of the very low boiling point of hydrogen (20.4 K at 1 atm) and its low density in the gaseous state (90 g/m<sup>3</sup>). Furthermore, the storage of hydrogen in liquid or gaseous form imposes safety problems, in particular for mobile applications, e.g. the future zero-emission vehicle. Metal hydrides are a safe alternative for H-storage and, in addition, have a high volumetric energy density that is about 60% higher than that of liquid hydrogen. Mg hydride has a high storage capacity by weight and is

therefore favoured for automotive applications. However, so far light metal hydrides have not been considered competitive because of their rather sluggish sorption kinetics. Filling a tank could take several hours. Moreover, the hydrogen desorption temperature of about 300°C is rather high for most applications. A breakthrough in hydrogen storage technology was achieved by preparing nanocrystalline hydrides using high-energy ball milling. These new materials show very fast ab- and desorption kinetics within few minutes, thus qualifying lightweight Mg-based hydrides for storage application. In this talk, we present recent detailed results on the sorption behaviour of nanocrystalline Mg and Mg-based alloys. In a following research effort the sorption kinetics of nanocrystalline Mg has been further enhanced by catalyst additions. Furthermore, different transition metals have been added to Mg to achieve a thermo-dynamic destabilisation of the hydride, thus lowering the desorption temperatures to about 230°C. The newly developed materials are currently being tested in a prototype storage tank.

#### 11:00 AM \*Y4.6

SUPPORTED ON NANOCRYSTALLINE OXIDE CATALYSTS FOR METHANE OXIDATION. Gar B. Hoflund<sup>a</sup>, Johannes Seydel<sup>b</sup>.

<sup>a</sup>University of Florida, Dept of Chem. Eng., Gainesville, FL.

<sup>b</sup>Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERMANY.

Nanocrystalline oxides including CeO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> have been shown to be excellent catalysts for methane oxidation under lean conditions. The bare oxides exhibit considerable activity and the addition of Pd greatly enhances their activities. On a mass basis the Pd/nano catalysts are significantly more active than the corresponding Pd/poly catalysts, and, in fact, they are the most active methane oxidation catalysts that have ever been made. In comparing nano and poly catalysts, there are two considerations: surface area and activity per specific area. Although the nano catalysts have higher surface areas, their activity per surface area has been shown to be lower. This result is consistent with surface characterization studies which demonstrate that the surface chemistry is different for nano and poly catalysts. This negative result implies that there is a significant margin for improving nano catalysts if the surface chemistry can be made more similar to the poly catalysts. In this study the same nano-oxides have been made using several different preparation techniques, and the resulting Pd/nano catalysts are being tested for catalytic activity and characterized using multiple techniques. This study will result in improved methane oxidation catalysts and a better understanding of the factors which are important with respect to the surface chemistry.

#### 11:30 AM Y4.7

FABRICATION OF NANOSTRUCTURE ON GOLD SURFACE BY SPM TIPS UNDER LASER IRRADIATION. B. Hu, Y.F. Lu, Z.H. Mai, NUS, Department of Electrical and Computer Engineering, Singapore, SINGAPORE.

In this paper, we present a novel method of nanofabrication by scanning probe microscope (SPM) tips under laser irradiation. The SPM has an open architecture that allows an external laser beam incident on the tip at an incident angle between 0 to 45°. In our investigation, the SPM tips are fixed and the sample moves via a tube scanner. Nanolithography software controls the scanner movement in x and y directions. A vertical polarized Nd: YAG pulsed laser with duration of 7 ns was focused on the tip. An electrical shutter was introduced to switch the laser irradiation. Alignment between the laser beam and the tip was performed under a high power charge coupled device (CCD) microscope. The fabrication work was carried out on gold films deposited on n-type Si substrates using the physical deposition method. Pits of nanometer scale were created in air ambient under different laser pulse numbers, pulse energies and tip force. The feature size of the pits increases with the pulse number, pulse energy and the tip force. Nano-patterns were obtained by this method. This technique may have potential applications in the high-density data storage.

#### 11:45 AM Y4.8

CONTROLLED GROWTH OF SILICON NANOWIRES. Yiyi Wu, Peidong Yang, University of California at Berkeley, Dept of Chemistry, Berkeley, CA.

Based on our mechanism study of vapor-liquid-solid (VLS) process, it's now possible to rationally control the diameter, position and orientation of Si nanowires using Au as catalyst. The diameter is controlled by the size of Au clusters. To prevent the cluster aggregation at high temperature, the Au clusters were embedded in mesoporous SiO<sub>2</sub>. Experiments showed that uniform nanowires with average diameter of 19 and 29 nm could be synthesized using uniform 17 and 25 nm Au clusters respectively. Electron beam lithography was used to accurately define the position of Au catalyst, which further control the growth position of Si nanowires. In addition, orientation control is accomplished by epitaxial growth of Si nanowires on single

crystalline Si wafer. Si nanowires prefer to grow along <111> direction. Hence, epitaxially grown Si nanowires are perpendicular to the (111) Si wafer and form arrays. The as-made regular array of Si nanowires can be used as electron field emitter and 2-dimensional photonic crystal.

### SESSION Y5: NANOTEMPLATES AND NANOSTRUCTURES

Chair: Michael H.H. Grunze

Wednesday Afternoon, April 18, 2001

Metropolitan II (Argent)

#### 1:30 PM \*Y5.1

ELECTRICAL TRANSPORT IN BIOPOLYMER TEMPLATE-PATTERNED METAL NANOPARTICLE ARRAYS.

Laura Clarke, Christopher A. Berven, Martin N. Wybourne, Department of Physics and Astronomy, Dartmouth College, Hanover, NH; Jana Mooster, Marvin G. Warner, James E. Hutchison, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR.

Nanostructures in which inherent single electron tunneling and charging effects can be exploited for device applications are receiving much attention as alternatives to the conventional semiconductor device paradigm. Although nanostructures fabricated at the limits of electron-beam lithography (ca. 15 nm) are too large to achieve clear single electron effects at room temperature, assemblies of metal or semiconductor nanoparticles that have well-defined dimensions are small enough that single electron effects can be exploited at room temperature. In order to utilize nanoparticle building blocks, or even to explore their electrical properties, it was necessary to develop methods to assemble arrays and make electrical contact to them. To date, few measurements of the lateral transport through spatially defined nanoparticles arrays have been reported. Our method for nanofabrication involves the assembly of functionalized metal nanoparticles onto rigid biomolecular scaffolds cast upon an insulating substrate and bridged between narrowly spaced electrodes. This simple, wet chemical approach yields one- and two-dimensional arrays of gold nanoparticles that exhibit more stable electrical behavior (Coulomb blockade) compared with non-patterned samples. Current-voltage measurements and AFM imaging suggest that electron transport is dominated by one-dimensional nanoparticle chains. Further, the electrical response shows clear, robust single electron charging effects that are insensitive to defects within the chemical assembly. Given the simple assembly method used, the transport properties and defect tolerance are unexpected. The structural parameters that lead to the unique properties of these arrays, including defect tolerance, will be presented.

#### 2:00 PM \*Y5.2

MOLECULE CORRALS AS TEMPLATES FOR NANOSTRUCTURES. Thomas Beebe, University of Utah, Salt Lake City, UT.

(ABSTRACT NOT AVAILABLE)

#### 2:30 PM Y5.3

COMPLEX FLUIDS AS ORGANIZING MATRICES FOR THE FORMATION OF HETEROSTRUCTURED NANOPARTICLE ARRAYS. Millicent A. Firestone, Dixy E. Williams, Roseann Csencsits, Materials Science Division, Argonne National Laboratory, Argonne, IL; Soenke Seifert, Chemistry Division, Argonne National Laboratory, Argonne, IL; P. Thyagarajan, Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, IL.

Recently, we described the preparation and characterization of polymer-grafted phospholipid-based complex fluids that possess the unique ability to interconvert between a low viscosity, 2-D hexagonal array of prolate micelles to a lamellar gel phase as the temperature is raised above 16°C. These complex fluids are non-covalent aggregates characterized by both a high degree of anisotropy and segregated aqueous and organic domains organized on a micrometer length scale. These properties permit facile introduction and spatial compartmentalization of both semiconductor (CdS) and metal (Au and Ag) nanoparticles. Heterostructured arrays of these nanocrystals can be readily prepared by chemically tailoring the nanoparticle surface, which allows for site-directed localization into one of three physico-chemically distinct regions of the complex fluid: the bulk water channel, the palisade region, or the alkane region of the bilayer. Small angle X-ray and neutron diffraction studies, together with phosphorus NMR, demonstrate minimal perturbations of the encapsulating matrix structure upon nanoparticle doping. Examination of the structural organization of the encapsulated nanoparticles by anomalous small angle X-ray scattering and absorption spectroscopy provide insights into the structural arrangement of the nanoparticles within the host matrix. Most

significantly, it has been found that by adjustment of the complex fluid composition, the interactions of the encapsulated nanoparticles and therefore, their electronic properties, can be 'fine-tuned'. Complex fluids are thus shown to provide a viable scaffolding for the organization of inorganic nanoparticles.

Work supported by Office of Basic Energy Sciences, Division of Materials Sciences, United States Department of Energy, under contract W-31-109-ENG-38.

#### 2:45 PM Y5.4

##### RAMAN STUDIES OF ORIENTATION DEVELOPMENT IN ELECTROSPUN MICRO- AND NANOFIBERS. Jean Stephens,

Simon Frisk, John F Rabolt, University of Delaware, Dept of MS&E, Newark, DE; Bruce Chase, Central Research and Development Department, DuPont Experimental Station, Wilmington, DE.

The development of orientation and microstructure in electrospun polymeric fibers has been investigated by polarized Raman spectroscopy. Studies have shown that solution viscosity, nature of the solvent, and spinning voltage have an effect on the structure and properties of electrospun fibers<sup>1,2</sup>. However, no "real time" analysis of the orientation of these fibers has been carried out as has been demonstrated in melt-spun fibers<sup>3</sup>. It is well known that polymer chain alignment in the fiber direction directly impacts the mechanical properties of fibers with chain orientation along the axis of the fiber yielding fibers with high strength and low elongation<sup>4</sup>. The optimization of fiber orientation in individual static electrospun fibers and in fibers while they are spinning will help us to better understand the electrospinning process and help establish structure/property relationships. Our results indicate that molecular weight and molecular weight distribution also have an impact on fibers that are electrospun from solution. Molecular weight directly influences solution viscosity which in turn affects the ease of spinning uniform fibers. Molecular weight distribution is also important in conventional fiber spinning with a larger molecular weight distribution adding flexibility and strength to polymeric fibers. The effect of using samples with narrow or broad molecular weight distributions in the electrospinning process has also provided insight on the limitation of using certain polymer architectures.

1. Reneker D.H., Fong H., Chun I., Polymer 1999;40:4585-4592.
2. Deitzel J.M., Klienmeyer J, Harris D., Beck Tan NC, Polymer 2001;42:261-272.
3. Lesko C.C.C., Rabolt J.F., Ikeda R., Chase B.D., Kennedy A., J. Molecular Structure 2000;521:127-136.
4. Rodriguez F., PRINCIPLES OF POLYMER SYSTEMS, 2nd ed. McGraw-Hill Book Company, 1982.

#### 3:30 PM \*Y5.5

HIGH VOLUME-FRACTION COLLOIDAL CRYSTALS FROM HYDROGEL NANOPARTICLES. Justin D. Debord, Mark T. Lofye, L. Andrew Lyon, Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA.

The assembly and characterization of high volume fraction colloidal crystals composed of hydrogel particles (microgels) is described. Specifically, thermoresponsive microgels composed of lightly crosslinked poly-N-isopropylacrylamide are used to create colloidal crystals over a range of 4.5 to 10 wt% polymer in aqueous solutions. When the large swelling factors of these microgels (>16-fold volume increase) are taken into account, we find that the theoretical volume fractions are physically unrealistic, ranging from 80 to 160% occupancy. This apparent contradiction is alleviated if we assume that the soft hydrogel spheres are deformed and desolvated upon being forced to occupy this small volume. Because of this deformation and the elastic restoring force of the particles, these materials display unusual stability with respect to shock and shear disordering. Furthermore, the temperature responsivity of the component particles renders the array similarly thermoresponsive and thermoprocessable. Finally, the optical properties of these materials are of high quality, displaying transmission Bragg peaks with FWHM values of 5-10 nm at visible wavelengths, tunability over ~80 nm, and extinctions of ~0.6 AU per mm of crystal thickness. These results and their interpretations will be discussed in the context of soft sphere crystallization.

#### 4:00 PM \*Y5.6

EARLY STAGES OF CARBON NANOTUBE GROWTH AND NANOTUBE CRYSTALS. P.M. Ajayan, Z. Zhang, B. Wei, G. Ramanath, Dept of MS&E, Rensselaer Polytechnic Inst, Troy, NY.

The growth of vertically aligned carbon nanotubes on flat substrates is important for applications such as field emission displays. Although this has been done, the initial stage of nanotube growth and the understanding of the growth process still remains a mystery. In this talk we will report certain fascinating growth features that dominate the initial stages of carbon nanotube growth on planar substrates during chemical vapor deposition (CVD). The hydrocarbon precursor

(xylene) and the catalyst (ferrocene) are both introduced through the vapor phase in this process, which grows nanotubes on planar silica. For the first time, we show that nanotubes can nucleate and grow as islands of tiny well-faceted, two-dimensional crystals.

#### 4:30 PM Y5.7

GROWTH AND CHARACTERIZATION OF MAGNETIC NANO-WIRES ON CARBON NANOTUBE TEMPLATES. Yihong Wu, Peiwen Qiao, and Towchong Chong.

Experiments performed so far showed that carbon nanotubes have extraordinary electrical and mechanical properties. The potential application of nano-tubes has been discussed or explored in literature in several areas: atomic force microscopy, electronic devices at molecular level, non-volatile memory, flat panel display, and energy storage. There have also been reports on the utilization of carbon nanotubes as templates for fabricating other type of nano-structures. In this work, we have tried to fabricate magnetic nanowires with nanotubes as the supporting materials. Vertically aligned multiple wall carbon nanotubes were first grown on NiFe-coated Si substrate by using a microwave CVD technique. The reaction gas is a mixture of hydrogen (80 SCCM) and methane (20 SCCM). The typical process pressure and growth temperature are 1.7 Torr and 800°C, respectively. The typical length of the nanotubes is about 1µm for a 5 minutes growth. The FE-SEM observation shows that the nanotubes are separated from each other though they tend to form clusters. After the SEM analysis the sample was re-loaded to the NiFe deposition system equipped with an e-beam gun at a base pressure of  $3 \times 10^{-9}$  Torr. After a deposition of about 60nm of NiFe, the nanotubes were found to be self-arranged into assembly of "micro-umbrellas"; each of them is supported by 10 to 20 nanotubes. The diameter of the tubes has increases significantly as compared to the original carbon nanotubes though they are still separated from each other except for the top tips. This suggests that magnetic nano-wires with carbon at the cores have been formed during the second NiFe deposition process. This is also supported by the magnetic measurement which revealed that the magnetic nano-wires have a hard axis in the normal direction of the substrate and an easy axis in the film plane. Detailed studies on the electrical property of the magnetic nano-wires are in progress and their applications in magnetic sensors will be explored.

#### 4:45 PM Y5.8

SYNTHESIS OF ORDERED ARRAYS OF SIZE-CONTROLLED Ga-NITRIDE NANOCCLUSERS IN A BLOCK COPOLYMER MATRIX. V.J. Leppert, A.K. Murali and S.H. Risbud, UC Davis, Dept. of Chem. Eng. and Mat. Sci., Davis, CA; M. Stender and P.P. Power, UC Davis, Dept. of Chemistry, Davis, CA; H.W.H. Lee, LLNL, Livermore, CA; X. Lu, J. Colton and P. Yu, UC Berkeley, Dept. of Physics, Berkeley, CA; P. Banerjee, Y.Y. Won and A.M. Mayes, MIT, Dept. of MS&E, Cambridge, MA.

The group-III nitrides have seen tremendous recent development in the form of thin films for light emitting devices (LEDs) and laser diodes. Quantum dot structures of these materials are predicted to luminesce with much greater efficiency due to localization of charge carriers. Indeed, the superior performance of InGaN devices has been attributed by some investigators to variations in indium concentration forming quantum dot structures. We report here the novel synthesis of Ga-nitride nanoclusters, less than 10 nm in diameter and in an organized array, through the decomposition of cyclotrigallazane in a block copolymer matrix. The block copolymer matrix serves as a self-organizing ordered array for the formation of uniformly sized Ga-nitride nanoclusters. We have characterized the nanoclusters using an array of advanced microstructural techniques, including HRTEM, AEM, XPS, Raman and photoluminescence. The possibilities for tailoring the block copolymer matrix to control particle size, interparticle distance, and packing arrangement are explored.

#### SESSION Y6: OPTICAL AND ELECTROCHEMICAL PROPERTIES OF NANOPARTICLES

Chair: Thomas Beebe

Thursday Morning, April 19, 2001  
Metropolitan II (Argent)

#### 8:30 AM \*Y6.1

TUNING THE OPTICAL PROPERTIES OF LARGE GOLD NANOPARTICLE ARRAYS. Beomseok Kim, Steven L. Tripp, Alexander Wei, Purdue Univ, Dept of Chemistry, West Lafayette, IN.

Large (15-100 nm) resorcinarene-coated gold nanoparticles self-organize at the air-water interface into monoparticulate films with long-range order. Films can be transferred onto glass or quartz substrates by Langmuir-Blodgett deposition techniques to produce planar arrays with continuities on the millimeter length scale. Large gold nanoparticle arrays exhibit a number of intriguing optical properties: plasmon resonances shifted to near-infrared wavelengths,

variable reflection and light-scattering properties, and extremely high surface-enhanced Raman scattering (SERS) with efficiency factors as large as  $10^8$ . The dependency of these properties as a function of particle size and interparticle spacing will be discussed.

#### 9:00 AM Y6.2

**NANOPARTICLES FOR OPTICS AND NANOSCALE ELECTRONICS: CONTROL OF THEIR SYNTHESIS WITH ION BEAMS.** Karl-Heinz Heinig, Bernd Schmidt, Torsten Mueller, Research Center Rossendorf, Inst. of Ion Beam Physics and Materials Research, Dresden, GERMANY.

New physical processing routes based on ion irradiation will be presented which result in an improved control of nanoparticle size distributions and spatial arrangements. The talk will focus on two examples: (i) Recently the authors predicted theoretically and proved experimentally (see MRS 2000 Fall Meeting, inv. talk O14.6/R9.6) that nanocluster ensembles evolve under ion irradiation by inverse Ostwald ripening (IOR). Unlike conventional ripening, IOR leads (according to XTEM analysis) to a narrow size distribution which is preferred for different applications. The same fundamental processes causing IOR are responsible for pattern formation at flat interfaces. This controllable interface instability can be employed for nanoscale engineering. For instance, a controlled decay of a nanowire into a chain of equidistant nanoclusters can be predicted. Metallic nanocluster chains in  $\text{SiO}_2$  could be used for new microoptical devices based on "plasmonics". (ii) In  $\text{SiO}_2$  films on Si we found recently the formation of a monolayer of nanoclusters which is well-aligned to and equidistant from the  $\text{SiO}_2/\text{Si}$  interface. This nanocluster arrangement is ideal for a new nonvolatile memory device. The so-called nanocluster  $\delta$ -layer appears after ion implantation of Ge, Sn or As into the  $\text{SiO}_2$  film and subsequent annealing in case that quite specific implantation and annealing conditions are chosen. Thus, the number of collisional displacements per atoms (dpa's) has to be a few dpa's in the interface region. The mechanisms of the formation of the nanocluster  $\delta$ -layer will be illustrated by means of kinetic lattice Monte-Carlo simulations.

#### 9:15 AM Y6.3

**SYNTHESIS AND OPTICAL PROPERTIES OF CORE/SHELL AND ALLOY NANOCLUSTERS.** Jess Wilcoxon, Jim Martin and Paula Provencio, Nanostructures and Advanced Materials Chemistry Dept, Sandia National Laboratories, Albuquerque, NM.

We describe the synthesis and chromatographic characterization of core/shell and alloy metal nanoparticles. Alloy nanoparticles were synthesized by co-reduction of the respective simple metal salts encapsulated in inverse micelles using a strong metal hydride reducing agent in an inert, water-free, oil environment. Sequential reduction is used to form core-shell nanoparticles. Following formation, strong passivating agents are added to the solutions allowing the composite clusters to be purified using size exclusion liquid chromatography (SEC). Their size and size-dispersions were obtained by SEC and HRTEM. The optical properties were studied using a photodiode array spectrometer during the SEC process. The absorbance of the Au/Ag nanoparticles differs substantially from Ag/Au particles of the same size. The size dependence of the optical properties such as plasmon linewidth, energy, and resonance peak symmetry of the core/shell and alloy particles are compared to their pure counterparts and extant theoretical descriptions. The chemical, nanostructural, and optical features of base metal/noble metal nanoparticles (e.g. Ni/Au) will also be described.

Acknowledgement:

This work was supported by the U.S. Department of Energy under contract DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. Department of Energy.

#### 9:30 AM Y6.4

**NONLINEAR OPTICAL PROPERTIES OF (Cd,Zn)S NANOPARTICLES.** Dmitri V. Petrov, Beate S. Santos, Giovanna A.L. Pereira, Celso de Mello Donegá, Dept of Fundamental Chemistry, Federal University of Pernambuco, Recife, BRAZIL.

A semiconductor nanoparticle is an example of low-dimensional structure. In these structures one can use bulk materials with already desirable properties and improve or tailor these properties using quantum confinement effects. The availability of large nonlinear optical coefficients in semiconductor nanoparticles may lead to applications in ultra fast optoelectronic devices. Another possible application is in biological labeling. We measured the first hyperpolarizability  $\beta$  by the Hyper Rayleigh Scattering (HRS) technique for aqueous suspensions of CdS nanoparticles of different mean diameters, of 9 nm  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  nanoparticles ( $x = 0, 0.25, 0.75, 1$ ), and of 9 nm CdS nanoparticles after surface modification with  $\text{OH}^-$ . The values of  $\beta$  are among the largest observed for solution samples. Luminescence spectra obtained upon 1064 nm excitation

show that the fluorescence contribution due to multiphoton excitation is negligible. We report the first experimental observation that  $\beta$  decreases as the band gap energy increases. We have also established the size dependence of  $\beta$  for CdS. Although  $\beta$  increases with the particle size, the  $\beta$  values normalized per CdS pair increase with decreasing of size, leading to an enhancement by one order of magnitude for 2 nm particles in comparison with bulk. This is ascribed to quantum confinement effects on the oscillator strengths. A two-level model can explain both the band-gap and the size dependences. Finally, the surface modification of CdS nanoparticles with  $\text{OH}^-$  is observed to increase  $\beta$  by a factor 1.7. This can be explained by the new Cd-OH $^-$  chemical bonds formed at the nanoparticle surface, which enable a considerable amount of second harmonic generation. Further, the hydroxyl groups also induce an increase in the absorption. These results suggest that the HRS technique may be used as a probe of nanocrystal surfaces.

#### 9:45 AM Y6.5

**PECULIARITY OF PROPERTIES AND SOME APPLICATIONS OF ULTRA DISPERSED (NANO-) MATERIALS.** Vadim F. Petrunin, Moscow State Physical Engineering Institute, Moscow, RUSSIA.

Tree next arguments are considered as main for peculiarity of nanosized materials properties [1]. Firstly, commensurability of morphological elements (particle, grain, domain) with a characteristic correlation scale of one or another physical phenomenon or with characteristic distance of some transport process (length of electron or phonon free path, electric or magnetic domain, dislocation or disclination etc.) leads to limited efficiency of classic physics laws. Secondly, increasing surface energy can not be neglected in general energy balance. At third, extreme conditions of synthesis contribute to non-equilibrium (metastable) state. These are why an unusual and unique combination of properties can be feasible in ultra dispersed (nano-) materials, for examples, high hardness and superplasticity [2]. Lowering of melting and phase transition temperatures and increasing of thermal capacity versus the crystallite size decreasing are characteristic of them also. Single-domain ferro- and antiferro-magnetic materials become superparamagnetic. Ultra dispersed isolated metallic particles have semiconductor type of electric conductivity. Optical and other physical and chemical properties are changed very often. Some examples of ultra dispersed materials applications working out by Atomic Energy Industry program are following. Addition of ultra dispersed metallic powder to motor oil allows decreasing the friction, to restore the working surfaces, to increase the recourse of friction pair at 1,5 - 2 time. Covering of tools, calibers, filliers, neutron counters by strong nanoceramic materials or nanodiamond prolongs their working time. Highlight manufactured goods from nano-beryllium for X-ray windows of medicine and science equipments and for thermal nuclear reactor target are developed. Soft magnetic ferrites, piezoelectric ceramic materials for electronic industry, high porous filter materials for cleaning of water, technical liquids, oil products and other applications are studied.

1. I.D. Morokhov, V.I. Petinov, L.I. Trusov, V.F. Petrunin, Sov. Phys. Usp. 24 (4) (1981) 295. 2. G.M. Gryznov, V.F. Petrunin, Conversion in Machine Building of Russia 1 (4) (1996) 24.

#### 10:30 AM \*Y6.6

**DIFFUSION AND IONIC CONDUCTION IN NANOCRYSTALLINE CERAMICS.** Paul Heitjans, Sylvio Indris, Universitaet Hannover, Institut fuer Physikalische Chemie und Elektrochemie, Hannover, GERMANY.

Nanocrystalline materials can show enhanced diffusivity as compared to their microcrystalline counterparts due to the large fraction of atoms or ions located in interfacial regions. In the case of ceramics, resulting properties with potential applications are, e.g., fast ionic conductivity, high mechanical creep rate and increased catalytic activity. Mixing with a different phase, being an ion conductor or not, offers additional freedom to tune atomic transport by varying the composition and grain sizes. Mainly Li ion conductors, both monophase and composite systems, were studied. The nanocrystalline materials were mostly prepared by high-energy ball milling. NMR lineshape and relaxation spectroscopy was used to measure number fractions and activation energies of the mobile ions in the interfacial regions. Impedance spectroscopy was applied to measure dc and ac ionic conductivities and the corresponding activation energies. Some of the materials show surprising results. Whereas in general the activation energies are reduced as compared to those in the corresponding microcrystalline system, e.g., they are constant in the ceramic composite  $(1-x)\text{Li}_2\text{O}:x\text{B}_2\text{O}_3$ . Nevertheless, with increasing insulator fraction  $x$ , the conductivity increases in the nanocrystalline and decreases in the microcrystalline material. The results for the various systems are discussed with respect to their microstructure.

**11:00 AM Y6.7****NANOCOMPOSITE POLYMERIC ELECTROLYTES.**

Władysław Wieczorek, D. Świerczyński, Aldona Zalewska, Zbigniew Florjańczyk, Norbert Langwald, Warsaw University of Technology, Faculty of Chemistry, Warsaw, POLAND.

Polymer electrolytes have been intensively studied over the last two decades mostly due to the possibility of their application in a variety of electrochemical devices working at ambient conditions. In order to improve physical-chemical characteristics of polymeric electrolytes towards their application in electrochemical systems various methods of modification have been applied. Among these methods the use of inorganic fillers is one of the most successful. The addition of fillers results in an increase in ionic conductivity, extends thermal and mechanical stability ranges and limits the formation of interfacial passive layers usually formed at the alkali metal electrode-polymer electrolyte interface.

Although the relation between physical-chemical characteristics of polyether electrolytes and structural changes are accepted the micro-mechanism of polymer-filler-salt interactions is still under discussion. The increase in conductivity is often related to the decrease in the fraction of crystalline phase in semi-crystalline PEO based electrolytes and changes in the polymer flexibility and ionic associations in the case of high or low molecular weight amorphous polyether based systems.

In the present work the effect of addition of nanosize fumed silica to low molecular weight polyether electrolytes is explored. It is shown that the addition of fumed silica results in the formation of gel-like polymer electrolytes. In spite of quasi solid structure of composite systems compared to the liquid base PEG-LiClO<sub>4</sub> electrolyte the increase in conductivity is observed for several salt concentration in composite systems compared to the base PEG-LiClO<sub>4</sub> electrolytes. The increase in conductivity is related to the reduction in the fraction of ion-pair as revealed from FT-IR experiments and Fuoss-Kraus type analyses of the salt concentration dependence of ionic conductivity. Acknowledgements: This work was financially supported by the MSC fund (MEN/DOE-97-317) and Warsaw University of Technology (504/G/1020/0126).

**11:15 AM Y6.8****PAIR-STATE FORMATION IN NANOCRYSTALS: A****THEORETICAL PERSPECTIVE. J.F. Suyver, J.J. Kelly, A.**

Meijerink, Debye Institute, Physics and Chemistry of Materials, Utrecht, THE NETHERLANDS; R. Meester, Division of Mathematics and Computer Science, Free Univ. Amsterdam, THE NETHERLANDS.

The intriguing optical properties of nanocrystalline semiconductors have prompted much research on the luminescence of the dopants in these nanocrystals. More and more experimental evidence has been published in the last few years indicating the formation of *dopant pair-states*. These states explain adequately the observed luminescence characteristics, which are different from those of nanocrystals with low dopant concentrations. These altered properties with respect to the bulk systems include a change in photoluminescence emission energy and a decrease in luminescence lifetime. No theoretical analysis of the statistical properties of random sets of dopants in a nanocrystal have been published until now. Since the probability for pair-formation is strongly influenced by the presence of surface states (less neighbors), models that have been developed for bulk semiconductors do not work for nanocrystals. To solve the problem numerically, a generic nanocrystal of an extended radius  $\rho = (r/a)$  was parameterized through the complete set of lattice positions  $\{\mathbf{p}\}$  inside the nanocrystal. From this complete set, a random subset  $\{\mathbf{q}\}$  was chosen, indicating the dopants present in the nanocrystal. An algorithm, based on a statistical average of  $10^5$  nanocrystals with the same size and dopant concentration, is presented that uses  $\{\mathbf{q}\} \subset \{\mathbf{p}\}$  to extract the probability for the formation of at least one pair-state as well as the percentage of pair-states that is to be expected. Furthermore, several statistical properties of the nanocrystals are presented and the large  $\rho$  limits are discussed. The presentation will end with several results from the recent literature and their comparison with the theory will be described.

**11:30 AM Y6.9****TEM INVESTIGATION OF NANO ELECTRODES MADE BY****ELECTROMIGRATION OF GOLD ATOMS. M.S. Kabir, S.H.**

Magnus Persson, Chalmers University of Technology, Dept. of Micro Electronics and Nanoscience, Gothenburg, SWEDEN.

Electromigration is a failure mechanism of conductors, advantageously used for fabricating gold electrodes with nanometer separation. We have designed and fabricated a Transmission Electron Microscopy (TEM) sample holder with an array of electrodes that fits with the contact pads of the chips with nanowires made on SiN membrane windows. We are fabricating nanowires and electrodes with nanometer

separation and concurrently observing the structural changes of the gold nanowire. Small gaps are made by driving a large current through the nanowires until a small gap opens, which results in a large increase of resistance and a termination of the electromigration process. The present work is aimed at investigating the electrical properties of single conducting molecules placed in-between the electrodes and simultaneously observed in TEM.

**11:45 AM Y6.10****SURFACE CHARGE INFLUENCED STRUCTURAL PROPERTIES****OF ELECTRICALLY CONNECTED PLATINUM NANO-****PARTICLES. R.N. Viswanath<sup>a</sup>, J. Weissmüller<sup>a</sup>, R. Würschum<sup>a,b</sup>**

and H. Gleiter<sup>a</sup>. <sup>a</sup>Forschungszentrum, Karlsruhe GmbH, Institut für Nanotechnologie, Karlsruhe, GERMANY. <sup>b</sup>Technische Universität Graz, Institut für Technische Physik, Graz, AUSTRIA.

When the grain size of a material is reduced to the nanometer-scale then the number of atoms at the surface or in the core of grain boundaries will become comparable to the number of atoms in the interior of the crystals. Since the earliest studies of nanomaterials there has been the prospect of achieving novel properties in materials where the modified properties of the matter at the surface or at internal interfaces contributes measurably to the overall materials properties. Recently, there has been a growing body of evidence suggesting that space-charge layers at interfaces can have a significant influence on a wide variety of physical properties. The notion that suitable experimental setups can allow space-charge layers to be induced and manipulated by an externally applied voltage suggests the prospect of preparing nanocrystalline materials with tunable structure and electronic properties [1]. We present experimental results which circumstantiate this concept. We have studied the reversible variation of the lattice constant of Pt nanoparticles immersed in an electrolyte as a function of the applied voltage. It is found, that reversible volumetric strains of up to 1.5% can be induced, corresponding to pressures of up to 3.5GPa. We present the experimental setup for in-situ x-ray diffraction with an electrochemical cell, and the characterization of the interfacial reactions by cyclic voltametry. The relevant consequence of the variation of the space-charge at the metal-electrolyte interface is the variation of the surface stress,  $f$ , (i.e., the derivative of the interface excess free energy,  $\gamma$ , with respect to the bulk strain tangential to the interface) as a function of the applied potential. We shall present values for  $f$  computed from the measured bulk strain by use of the capillary equation for solids, Ref. [2]. [1]. H. Gleiter, J. Weissmüller, O. Wollersheim and R. Würschum, 'Nanocrystalline Materials - A Way to Solids With Tunable Electronic Structures and Properties?', Acta mater. (2000), in press. [2]. J. Weissmüller and J.W. Cahn; 'Mean Stresses in Microstructures due to Interface Stresses: A Generalization of a Capillary Equation for Solids'. Acta mater. 45 (1997), 1899.

SESSION Y7/U6: JOINT SESSION  
MAGNETIC PROPERTIES OF NANOMATERIALS

Chairs: James E. Hutchison and Franziska Groehn

Thursday Afternoon, April 19, 2001

Metropolitan II (Argent)

**1:30 PM \*Y7.1/U6.1****MAGNETISM IN THE NANOTECHNOLOGY WORLD.**

Robert D. Shull, Magnetic Materials Group, National Institute of Standards and Technology, Gaithersburg, MD.

The National Nanotechnology Initiative (NNI) in the United States this year has caused renewed attention to the area of nanometer length-scale materials and devices, even internationally. Why all the interest? And where does magnetism fit into this flurry of activity? Here, a description will be presented of the properties and applications of materials possessing nanometer-thick films, particles, or crystals of a ferromagnet intimately mixed with magnetically-dissimilar materials. Such nanoscale morphology has been found to result in novel magnetic behavior. Why does this occur and how will it impact your present and future lives? Particular attention will be devoted to the fabrication and use of magnetic "nanocomposites" for magnetic recording. In this application, use is made of a novel phenomenon called the "Giant Magnetoresistance (GMR) Effect" which derives from nanometer-thick layering of dissimilar materials. The reasons for our group's world leading magnetic "spin valve" structures and behind the unusual magnetic switching behavior of certain key elements in these "spin valve" structures (using the GMR effect) will also be included. Mention will be made of the first successful preparation of magnetic dendrimers, very attractive nanocomposites for targeted drug delivery and magnetic imaging contrast, along with how nanocomposites can play a role in the development of advanced high energy density permanent magnets, or even of the "softest" soft ferromagnets. If time permits, a description will also be provided on how nanolayering can be used to develop very large magnetic anisotropies and on how magnetism can be used to develop high



efficiency refrigerators, using the "Giant Magnetocaloric Effect" in magnetic nanocomposites, applications also pioneered at NIST. As a result of this presentation, it should become obvious what makes magnetism a particularly special case for nanotechnology excitement.

#### 2:00 PM Y7.2/U6.2

**SUPERPARAMAGNETISM AND MICROSTRUCTURAL PROPERTIES OF CARBON ENCAPSULATED Ni NANO-PARTICLE ASSEMBLIES.** Xiang-Cheng Sun, J.A. Toledo, Prog. Simulación Molecular, Instituto Mexicano del Petróleo, México, MÉXICO; M.J. Yacamán, ININ, México, MÉXICO.

Superparamagnetism is a unique and important features of magnetic nanoparticles. Novel carbon encapsulated Ni nanoparticles offer us great opportunities for studying the mechanism of superparamagnetic properties.

Carbon encapsulated Ni nanoparticles were synthesized by modified arc-discharge reactor under methane atmosphere. The presence of carbon encapsulation was identified by HR-TEM lattice imaging, nano-diffraction and X-ray microanalysis. The grain size is typically 10-3 nm with spherical shape, neither gaps nor intermediate phases were observed between the outer carbon layers and the core metallic Ni nanocrystals. The intimate and contiguous carbon fringes around these Ni nanocrystal particles is good evidence for complete encapsulation by carbon shell layers. Superparamagnetic properties studies for an assembly of carbon encapsulated Ni nanoparticles using DC-SQUID magnetometer. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements display a divergence below the blocking temperature at a certain applied magnetic field. The blocking temperature ( $T_B$ ) is determined to around 115K at 1000Gs applied field. Below  $T_B$ , the temperature dependence of the coercivity is given by  $H_c = H_{ci}[1-(T/T_B)^{1/2}]$ , with  $H_{ci} \approx 500$ Oe. Above  $T_B$ , the magnetization  $M(H,T)$  can be described by the standard Langevin function  $L$  using the relation,  $M/M_s(T=0) = \text{cloth}(\mu H/kT) - kT/\mu H$ . The particle size can be inferred from Langevin Fit (particle moment  $\mu$ ) and blocking temperature theory ( $T_B$ ), which values are bigger than HR-TEM observations. It is suggested, this assemblies of carbon encapsulated Ni nanoparticles have been showed typical single-domain, field-dependent superparamagnetic relaxation properties; and these typical superparamagnetic behaviors are consistent with the Stoner-Wohlfarth theory on single-domain particles. These interesting superparamagnetic properties studies indicates, this novel carbon encapsulated Ni nanoparticles have many potentials for application such as ferrofluids, magnetocaloric refrigeration, and magnetic resonance imaging (MRI) enhancement.

#### 2:15 PM Y7.3/U6.3

**NANOSTRUCTURES WITH VARIABLE MAGNETIC PROPERTIES.** Igor P. Suzdalev, Yuri V. Maksimov, Vladimir N. Buravtsev, Vladimir K. Imshennik, Sergey V. Novichikhin, Institute of Chemical Physics, Russian Academy of Sciences, Moscow, RUSSIA.

An assembling of nanocluster systems causes new properties of the matter that can be varied by means of cluster organization and interfacial interactions. This work deals with novel type of magnetic and structural phase transitions in iron oxide nanocluster systems induced by interface and strain effects. New nanostructure systems composed of alpha, gamma-iron oxide nanoclusters with sizes of 20-50 nm were synthesized by solid-state chemical reaction. The systems were loaded by shear stress (250 grade) under high pressure (up to 20 Kbar) as well as by the stresses combined with polymerization in acrylamide. The nanostructures were found to compose of nanoclusters that strong interact with each other and matrix. The magnetic properties of systems were determined by intercluster interaction, by density of defects in clusters and by intercluster strain. We observed new type of magnetic phase transition: jump-like first order magnetic phase transition at which the magnetization and magnetic order disappeared by jump with temperature at  $T_{cc} \sim 120-300$ K ( $T_c$  for the bulk is  $\sim 900$ K). The studied nanostructures showed collective transition into the unusual twin structure just above the Morin temperature,  $T_m$ , typical of  $\alpha$ -ferric oxide. The values of  $T_m$  were found to vary from 120 to 260K depending on intercluster interaction. An action of shear stress under high pressure leads to change  $T_{cc}$  and the character of magnetic phase transition (first or second order phase transition) depending on the presence or absence of polymeric matrix. For nanoclusters of 20-30 nm in size the character of magnetic phase transitions and variation of the Curie or Neel points were treated and explained by the thermodynamic model of magnetic phase transition with regard for intercluster strain effects, intercluster interaction and density of defects.

#### 2:30 PM Y7.4/U6.4

**PRODUCTION OF MAGNETIC-ORDERED SPIN SYSTEMS BY THE FORMATION OF TWO - DIMENSIONAL OXIDE NANOSTRUCTURES OF VARIOUS TOPOLOGY ON THE SILICA**

**SURFACE.** Vladimir M. Smirnov, Igor V. Murin, St. Petersburg State University, Dep. of Chemistry, St. Petersburg, RUSSIA.

Theoretical bases and experimental data confirmed a possibility of a synthesis of ordered spin systems are discussed in the communication. Chemical designing of specified steric arrangement of surface atoms in the matrix of two-dimensional nanostructure (nanolayer) is considered as the base of the procedure. In the instance of oxide nanostructures we evaluate a possibility to use the resources of modern precision synthesis for the dissolving of the production problem of solid chemical compounds with various steric distribution of atoms (structural topology) within the high order artificial substance like oxide superlattice. The phenomenon of two-dimensional ferromagnetism which was discovered by us is discussed.

Two-dimensional magnetization area is supposed to arise from aggregation of certain amount of  $Fe^{3+} - O$  group on the surface of diamagnetic support. Problems of production of high ordered spin systems are considered in the relation to magnetic properties of two samples series: i) two-dimensional oxide nanostructures containing in the plane of two-component monolayer various element-oxygen groups with their designed ratio ( $Fe^{2+} - O$  and  $Fe^{3+} - O$ ,  $Fe^{3+} - O$  and  $Ni^{2+} - O$ ,  $Fe^{3+} - O$  and  $Ti^{4+} - O$  etc.); ii) two-dimensional oxide nanostructures containing alternating element-oxygen monolayers of various chemical composition ( $Fe^{2+} - O$  and  $Fe^{3+} - O$ ,  $Fe^{3+} - O$  and  $Ni^{2+} - O$ ,  $Fe^{3+} - O$  and  $Zn^{2+} - O$  etc.), the monolayers are deposited in the designed order.

The data obtained confirm a possibility to control vigorously the ordered spin states (states of magnetic moments) within given oxide nanostructures. Work is supported by RFBR (RUSSIA) under the Grant No 99-03-32010.

#### 2:45 PM Y7.5/U6.5

**NANOCRYSTALLINE Co NEEDLES MADE BY NON-AQUEOUS ELECTRODEPOSITION.** C.-S. Yang, A. Sokolov, J.R. Jennings, J. Redepenning, B. Doudin Dept. of Physics and Astronomy, Dept. of Chemistry, University of Nebraska Lincoln, Lincoln, NE.

This research investigates the synthesis and properties of magnetic materials made by electrodeposition in non-aqueous solvents. Very little is known on this synthesis method, mostly because aqueous deposition is easy. However, the use of non-aqueous solvent has been found to be of primordial importance when plating over a thin oxide for the purpose of making tunnel junction by electrochemical methods. Our initial research concentrates on the magnetic properties of nanometer-sized wires, of diameters down 30 nm, obtained by template synthesis in filtering membranes. Wires have the ideal needle-type geometry for which the shape contribution of the magnetic anisotropy energy is dominant. Our results show surprisingly small crystallite size when using different solvents. Wires of Co plated in an ethylene glycol solvent show properties similar to those observed with aqueous solvents. However, a decrease in magnetization and coercive force for the other solvents is evident. Electron microscopy studies show that the crystallites size is not exceeding 3 nm for the DMF produced Co, and even lower for the acetonitrile bath. Non-aqueous plating offers a unique possibility to make ferromagnetic materials with very low crystallites dimensions. The decrease of the saturation magnetization is more likely due to an increasing number of Co surface atoms. A model of chain-of-grains become more accurate to explain the magnetic properties of low-crystallinity samples.

#### 3:30 PM \*Y7.6/U6.6

**FROM NEAR-SURFACE AND INTERFACE MAGNETISM TO THE MAGNETISM IN SMALL PARTICLES.** B. Stahl, M. Ghafari, H. Hahn, Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERAMANY.

To understand magnetic phenomena in small particles not seen in bulk materials, especially in the vicinity of critical points, surface, interface, shape, volume and structural effects have to be taken into account. Experiments on different particle sizes in order to distinguish between these effects have to start with infinite large particles, i.e. the near-surface region of single crystals and interfaces of layered structures. These near-surface and interfaces properties give a significant contribution to the magnetic properties of particles in the nanometer range. From this it is clear that the experimental methods have to cope with this scaling with respect to depth resolution, magnetic and structural characterisation. This gives the field a largely interdisciplinary character, especially if one aims at applications as is the case for instance in magneto-resistance devices. Experiments on the near-surface magnetism of single crystals as well as on nano-structured materials will be presented, laying special attention on a surface sensitive and depth resolved Moessbauer technique.

#### 4:00 PM Y7.7/U6.7

**SIZE-DEPENDENCE OF MAGNETIC PROPERTIES OF BISMUTH**

FERRITE NANOPOWDERS. H. He, J. Li, Lanzhou Univ, Dept of Materials Science, Lanzhou, CHINA.

$\text{BiFeO}_3$  is a magnetoelectric material in which antiferromagnetic and ferroelectric orderings coexist.  $\text{BiFeO}_3$  has a cycloidal spiral modulated magnetic structure with an abnormal long period of 62 nm. So it would be interesting if the crystal dimension decreases to nanometer scale, especially below 62 nm.  $\text{BiFeO}_3$  nanopowders with average grain sizes from 20 to 60 nm are supposed to be single-crystal particles and have narrow size distributions. The cell edge increases markedly and the axis angle deviates increasingly from  $60^\circ$  as the particle size decreases. The change of magnetic susceptibility with temperature is characteristic of antiferromagnetic ordering. However, its high magnitude is indicative of weak ferromagnetism. The magnetization and magnetic susceptibility increase with decreasing particle size. Mössbauer studies reveal that the spin canting angles in the smaller particles are bigger and have a wider distribution. The magnetic structure in these particles is an uncompensated antiferromagnetic spin ordering. Therefore, as the particle size decreases, the lattice distortion, the spin canting and the weak ferromagnetism of the  $\text{BiFeO}_3$  nanopowders increase.

#### 4:15 PM Y7.8/U6.8

MAGNETIC BEHAVIOUR OF INTERACTING SUPERPARAMAGNETIC IRON OXIDE NANOPARTICLES IN FERROFLUIDS. Wolfgang Voit, Royal Institute of Technology, Engineering Materials Physics Division, Stockholm, SWEDEN and XaarJet AB, Jarfalla, SWEDEN; Do Kyung Kim, Mamoun Muhammed, Royal Institute of Technology, Materials Chemistry Division, Stockholm, SWEDEN; Werner Zapka, XaarJet AB, Jarfalla, SWEDEN; K.V. Rao, Royal Institute of Technology, Engineering Materials Physics Division, Stockholm, SWEDEN.

We present a magnetic study of ferrofluids containing superparamagnetic magnetite ( $\text{Fe}_3\text{O}_4$ ) particles in a size range from 6 to 10 nm. The iron oxide particles were produced using a controlled co-precipitation technique, preventing undesirable oxidation of  $\text{Fe}^{2+}$ . After coating with sodium oleate or PVA, the nanoparticles were dispersed in a water-based solution forming a stable ferrofluid. The magnetic properties of ferrofluids with different particle concentration were studied using SQUID magnetometry and AC-susceptibility, and compared to the magnetic properties of the solid iron oxide nanoparticles. The measurements reveal a dependency of the blocking temperature on the particle concentration. In addition, the dc-susceptibility for the zero-field-cooled and field-cooled magnetisation show irregularities near the transition point from the frozen to the liquid state for ferrofluids, due to different relaxation mechanisms (Néel relaxation and Brownian relaxation). The AC-susceptibility measurements in the frequency range from 10 Hz to 4 kHz complement this study. A correlation of the magnetic properties to the chemical environment around the particles is investigated. Recent results of these studies will be presented.

#### 4:30 PM \*Y7.9/U6.9

MAGNETIC PROPERTIES OF SINGLE MOLECULE MAGNETS. Andrew D. Kent, Louisa Bokacheva, Dept of Physics and Marc Walters, Dept of Chemistry, New York University.

Single molecule magnets (SMM) are a new type of magnetic nanostructure that consist of a core of strongly exchange-coupled transition metal ions with a large collective magnetic moment per molecule, thus far up to about  $20 \mu_B$ . Their molecular nature enables experimental studies of monodisperse ensembles of nanomagnets with well-defined size, shape, chemical composition, and magnetic anisotropy. Such materials are of interest for investigations of the interplay between classical and quantum effects in nanomagnets, as well as potential applications in quantum computing. This talk will present results of our recent magnetic studies of the crossover between thermal activation (superparamagnetism) and quantum tunneling of the magnetization in the prototype SMM  $\text{Mn}_{12}$ -acetate [1]. Some open questions in magnetic quantum tunneling in SMMs and perspectives for new SMM materials will also be discussed. [1] L. Bokacheva, A.D. Kent and M. Walters, Phys. Rev. Lett. **85**, 4803 (2000).

#### SESSION Y8: POSTER SESSION

Chairs: Rina Tannenbaum and Horst Hahn

Thursday Evening, April 19, 2001

8:00 PM

Metropolitan Ballroom (Argent)

#### Y8.1

CURRENT INDUCED ORGANIZATION IN THIN NANOPARTICLE GOLD FILMS DURING DEPOSITION. P. Chaoung, J. Ederth, L.B. Kish, J. Kopniczky, S. Zhao, C.G. Granqvist, Uppsala

Univ, Dept of Materials Science, Uppsala, SWEDEN; S.J. Savage, Swedish Defence Research Establishment, Dept of Electromagnetic and Optic Materials, Linköping, SWEDEN.

In-situ electrical transport measurements were carried out in nanocrystalline gold films during inert gas deposition. The time dependence of the conductivity showed various self-organization phenomena, including aspects of: - biased percolation: conductor-insulator transition; - biased percolation: bad conductor - good conductor transition; - annealing; - sintering; - electromigration. The different effects were identified by recording the time-dependence of the conductance, by varying the deposition conditions, and by structural analysis using atomic force microscopy.

#### Y8.2

STRUCTURE AND GIANT MAGNETORESISTIVE PROPERTIES OF CO-BASE NANO-PARTICLES IN A Au MATRIX. B.J. Kooij, T. Vystavel, J. Th. M. De Hosson, Dept. Applied Physics, Groningen, The NETHERLANDS.

Alloys with Co, CoFe and CoPt nano-particles dispersed in a Au matrix were prepared under various conditions, characterized by HRTEM and their giant magneto-resistive properties determined (fields up to 5 Tesla and temperatures down to 10 K). Co particles have the fcc structure, truncated octahedral shape and their size can be smaller than 4 nm or after annealing were grown to an average size of up to about 20 nm. CoFe particles have the bcc structure, show a Bain orientation relation with the Au matrix and have a plate shape. After annealing at 573 K these plates have a thickness of typically 2 CoFe{100} layers and a length of 20 nm and after annealing at 673 K have a thickness of about 4 nm and a length of 40 nm. Due to these marked difference in predominantly the precipitate shape, the GMR properties of the  $\text{Au}_{80}\text{Co}_{20}$  and  $\text{Au}_{80}\text{Co}_{10}\text{Fe}_{10}$  alloys are very different. The Co particles are under most conditions superparamagnetic and as a consequence the GMR effect is largely proportional to the square of the magnetization measured. On the other hand the larger CoFe plates developed at 673 K result in GMR effect that gives a relative larger decrease in resistance at small magnetic fields and start to resemble the spin-valve effect of nano-structured multi-layers.

#### Y8.3

Abstract Withdrawn.

#### Y8.4

Abstract Withdrawn.

#### Y8.5

SUBSTRATE BASED "BRICKS-AND-MORTAR" SELF-ASSEMBLY OF SPHERICAL NANOPARTICLE AGGREGATES.

Andrew K. Boal, Faysal Ilhan and Vincent M. Rotello, University of Massachusetts, Amherst Department of Chemistry, Amherst, MA.

Polymer-mediated "Bricks-and-Morta" self-assembly of nanoparticles is a useful and versatile procedure for the fabrication of multi-scale materials. (Boal, A.K.; Ilhan, F.; Boal, A.K.; Ilhan, F.; Thurn-Albrecht, T.; Russell, T.P.; Rotello, V.M. *Nature* **2000**, *404*, 746-748). In this process, engineered molecular recognition complementarily between functionalized nanoparticles and polymers is used to provide the basis of self-assembly. Use of this methodology furnishes spherical assemblies whose size can be thermally controlled: structures ranging from 60 nm to  $1.5 \mu\text{m}$ , comprised of 7000 to 2.5 million nanoparticle components, are formed. In recent studies, we have extended this assembly process to thin polymeric films. In these studies, films of recognition element-functionalized polymers of varying thickness were cast on TEM grids. These grids were then suspended in solutions of the complimentary nanoparticle (in a solvent in which the polymer was insoluble) and the resulting structures were characterized by TEM. The quality of the resulting aggregates was found to be strongly dependant on assembly conditions: the process was optimized for the production of regular, spherical constructs, with decreasing film thickness and increasing nanoparticle concentration. Control experiments demonstrated that this process was based on the specific molecular recognition events which occur between the polymer and nanoparticle. Insight into the assembly mechanism was also gained by studying structural evolution as a function of assembly time and nanoparticle solution concentration. Applications of this process to the discovery of novel nanoparticle aggregates *via* a combinatorial screening process will also be discussed.

#### Y8.6

SPRAY AND INK JET PRINTING OF COMPOSITE NANOPARTICLE-ORGANOMETALLIC INKS FOR Ag AND Cu METALLIZATIONS. Calvin Curtis, Alex Miedaner, Jeff Alleman, Tanya Rivkin, John Perkins and David Ginley, National Renewable Energy Laboratory, Golden, CO.

There are a large number of thin film conductor applications requiring medium to low resolution lines ( $>200 \mu\text{m}$ ). These include solar cells, printed circuit boards, toys, and microelectronic packaging, for example. Current ink jet technology is capable of 20 to 50  $\mu\text{m}$  definition and is a low cost alternative to conventional photolithographic or screen printing approaches. We are using organometallic and nanoparticle-organometallic composite inks to deposit Ag and Cu metallizations using both spray and ink jet printing. An organometallic ink comprised of Ag(hfa)(COD) (where hfa = hexafluoroacetylacetonate and COD = 1,5-cyclooctadiene) dissolved in ethanol has been used to print lines and patterns on heated glass and Si substrates using a commercial Epson piezoelectric ink jet printer. After annealing outside the printer at 300°C for 20 minutes in air, pure Ag features with good adhesion and resistivities  $\sim 5 \mu\Omega\text{-cm}$  were obtained. The deposition rate with this ink is  $\sim 700 \text{Å}$  per pass. To achieve higher deposition rates, we are using inks containing metal nanoparticles mixed with organometallic metal precursors. Metallizations using nano-Ag/Ag(hfa)(COD) and nano-Cu/Cu(hfa)VTMS inks (where VTMS = vinyltrimethylsilane) will be discussed. The challenges of this approach are to achieve good electrical contact between particles and good adhesion of the particles to the substrate. The organometallic component serves as a metal glue that helps to meet these requirements. These low temperature direct write approaches offer a real alternative to current process methodologies for semiconductor and related metallizations. This work was funded by the National Center for Photovoltaics at NREL.

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**Y8.7**  
FILM FORMATION FROM COMPLEX NANOPARTICLES.  
N. Kambe, NanoGram Corporation, Fremont, CA.

NanoGram<sup>TM</sup> Process has produced an unparalleled range of materials in nanoscale. Multi-component materials as well as materials with rare-earth element dopants have been synthesized. Volume-production capability can be achieved. Compositions of materials cover metal-oxides/carbides/nitrides/sulfides, metals and transition metals and carbons. These nanomaterials are extremely uniform and suitable as building blocks for submicron-scale device structures. We have developed several methods to form thin and thick films comprising synthesized nanomaterial building blocks. One method is indirect formation of films based on blending with binders, while the other is direct deposition of nanoparticles over a substrate. Both are found to provide a broad range of film compositions and design capability for electronic and photonic device structures. More significant in terms of device performance is improvement of surface and interfacial flatness and smoothness. Microscopic images of the surfaces taken by electron microscopy and atomic force microscopy are rendered to demonstrate the structural superiority in these film formation processes.

**Y8.8**  
Abstract Withdrawn.

**Y8.9**  
NANOMETER-SIZED BISMUTH CRYSTALLITES SYNTHESIZED FROM A HIGH-TEMPERATURE REDUCING SYSTEM. Jiye Fang, Kevin L. Stokes, Weilie L. Zhou, Christopher B. Murray\* and Charles J. O'Connor, Advanced Materials Research Institute, University of New Orleans, New Orleans, LA. \*IBM T. J. Watson Research Center, Yortown Heights, NY.

Nanometer-sized bismuth has successfully been prepared using a high-temperature organic reducing system by presence of proper capping/stabilizing agents. Various synthetic conditions, which may significantly affect the formation of nanocrystalline bismuth, have been optimized and discussed in this paper. The as-prepared nanocrystallites exist in a single rhombohedral phase with high crystallinity, and oxidation problem has been efficiently overcome within limited period by employing this method. We also reported that the size-selected bismuth particles (15nm in size) tend to be self-assembled.

**Y8.10**  
SMALL SILVER CLUSTERS IN ZEOLITES: A NOVEL ORDERED NANOMATERIAL. Nina Bogdanchikova, Vitalii Petranovskii, Miguel Avalos, National Autonomous Univ of Mexico, Center of Condensed Matter Science, Ensenada, B.C., MEXICO; Annette Quiroz, Sonia Martinez, Mario Del Valle, Jose Guillermo Rodriguez, Autonomous Univ of Baja California, Tijuana, MEXICO; Nancy Martin, Univ Autonoma Metropolitana - Iztapalapa Mexico-city, MEXICO; Valerij Gurin, Belarusian State Univ, Physico-Chemical Research Institute, Minsk, BELARUS; Beatriz Concepcion, Gerardo Rodriguez-Fuentes, Habana Univ, Habana, CUBA.

Zeolites possessing nanometer-sized voids in the crystal lattice are an example of natural nanomaterial. Ordered cavities and channels provide possibility to produce materials with ordered metal inclusions those essentially change physical properties of obtained composite. In this report we collect recent experimental and theoretical results on silver containing zeolites (mordenite, erionite, clinoptilolite, L-, beta-, Y-zeolites, ZSM-11, etc.) on incorporation of silver inside the voids. Some of these zeolites provide the formation of well-defined monosized Ag<sub>8</sub> clusters. The size and geometry of the clusters are determined, mainly, by the cavity geometry. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (MR) varied in the broad range from 2.5 to 1000 and silver concentration have the effect upon the contribution of silver particles formed on the external zeolite surface as the result of reduction of Ag-exchanged forms of the zeolites. Electronic and geometric structures of Ag<sub>8</sub> were described on the basis of MOLCAO HF calculations, and optimum geometrical configurations of clusters consisting with observed optical and EXAFS spectra were determined. The optical manifestation of these monosized clusters inside of zeolite cavities is similar to Ag<sub>8</sub> species in solutions and gaseous phase. Ag-mordenite samples reveal the MR dependence of the catalytic properties in the reaction of dehydration of isopropyl alcohol. Ag-clinoptilolites show a significant sterilizing action with respect to bacteria Coli.

**Y8.11**  
THE CHARACTERISATION AND REACTIVITY OF NANOSTRUCTURED Ce-Cu-O COMPOSITES FOR ENVIRONMENTAL CATALYSIS. Othon Adamopoulos, Yu Zhang, Mamoun Muhammed, Royal Institute of Technology, Dept of Materials Science and Engineering, Stockholm, SWEDEN; Mark Croft, Rutgers Univ, Dept of Physics, Piscataway, NJ; Thomas Tsakalakos, Igor Zacharenko, Rutgers Univ, Dept of Ceramics and Materials Engineering, Piscataway, NJ.

The nanostructuring of CeO<sub>2</sub> has shown to greatly enhance its performance properties, such as oxygen storage capacity and redox reactivity, which render it suitable for environmental catalysis. Ceria can be heavily doped with several iso-valent and noniso-valent cations, and the resulting solid solutions have different chemical reactivity. In this work, we report some new results on the doping of ceria by copper oxide. Nanophase powder has been synthesised via co-precipitation approach, where computer-assisted thermodynamic modelling was used to predict the optimum experimental criteria. The properties of Ce-Cu-O composite (10 mol% CuO) have been extensively investigated by a variety of techniques, including TGA, TPR, SEM, TEM, EDX, XRD and EXAFS. The obtained materials have shown to have different morphology from other doped ceria salts, with highly uniform distribution of Ce and Cu throughout the powder. The TRP study indicated that Ce-Cu-O mixture has an enhanced oxygen storage capacity compared to pure ceria or pure copper oxide. On the other hand, the detailed characterisation of the nanophase powder does not show the formation of solid solution and the composites consists of two metal oxides. EXAFS study shows a variation of the existence of Cu and Ce in several oxidation states. Copper oxide seems to exist evenly distributed along the surfaces and boundaries of the crystal grains of CeO<sub>2</sub> on the nanoscale. Such nanostructuring may be responsible for the significant enhancement of the reactivity of the materials. Detailed results of the characterizations and the correlations of structure-surface-catalytic reactivity will be presented.

**Y8.12**  
Transferred to Y4.7.

**Y8.13**  
LASER FABRICATION OF NANO-STRUCTURES ON SILICON (100) SURFACES WITH PARTICLE-ENHANCED OPTICAL NEAR-FIELD IRRADIATION. Liang Zhang, Y.F. Lu, W.D. Song, Y.W. Zheng and B.S. Luk'yanchuk Laser Microprocessing Lab Department of Electrical and Computer Engineering, National University of Singapore, Singapore, SINGAPORE.

0.5  $\mu\text{m}$  spherical silica particles were placed on Silicon (100) substrate. After laser irradiation with a 248 nm KrF excimer laser, hillocks with size of about 100 nm were obtained at the original position of the particles. Mechanism of the formation of the sub-wavelength structures were investigated and found to be the near-field optical resonance effect induced by particles on surface. Theoretical prediction of the near-field light intensity distribution was presented, which was in agreement with the experimental result. The method of particle enhanced laser irradiation has potential applications in nanolithography.

**Y8.14**  
THIN YSZ NANOLAYERS PREPARED BY CHEMICAL VAPOR DEPOSITION. Johannes Seydel, Markus Winterer, Horst Hahn, Darmstadt University of Technology, Institute of Materials Science, Darmstadt, GERMANY.

Yttria-stabilized zirconia (YSZ) is a technologically important material for solid electrolyte in fuel cell systems. We have prepared thin YSZ electrolyte layers by chemical vapor deposition (CVS) on a pre-sintered NiO/YSZ fuel cell anode substrate. Structural analysis by scanning electron microscopy (SEM) and X-ray-diffraction shows a homogeneous, nanostructured layer. Conventional electrolyte films reach desired electrical properties only at elevated temperatures, typically 1000°C to 1100°C. The YSZ films grown by CVS on rough anode substrates show better growth behaviour and less defects at the anode/electrolyte interface than films deposited by conventional methods (laser deposition, sputtering). First results on electrical properties of such nanostructured YSZ films at lower working temperatures (< 900°C) are presented.

#### **Y8.15**

**LOW-TEMPERATURE SOLVOTHERMAL ROUTE TO GALLIUM NITRIDE NANOPARTICLES.** Jianjun Wang, Luke Grocholl, Edward G. Gillan, University of Iowa, Department of Chemistry, Iowa City, IA.

Gallium nitride ( $E_g = 3.4$  eV) has many potential applications such as high intensity blue or ultraviolet lasers or nanoscale optoelectronic semiconductor devices. Gallium nitride films can be prepared by vapor phase processes from a variety of dual or single-source precursors. Bulk GaN crystal growth remains elusive however, often requiring high temperatures and pressures. We will present recent results on the preparation of gallium nitride via a simple, one-step solvothermal reaction of gallium trichloride with sodium azide at low temperatures (225-300°C) in non-coordinating and polar solvents such as toluene or THF. Upon annealing at 750-1000°C, crystalline nanorods, nanoparticulates (~50 nm), and larger hexagonal crystals are observed.

#### **Y8.16**

**SYNTHESIS OF FUNCTIONAL ENGINEERING PARTICLES WITH ELECTROLESS DEPOSITION.** Hui Ma, Rajiv K. Singh, University of Florida, MS&E, Gainesville, FL.

Tungsten Carbide/Co is widely used in cutting tools for metal removal operations as well as new applications such as cutting of polymer and composite materials. Current fabrication status involves mechanically mixing of metal and carbide powders in large ball mills by means of liquid media to disperse powders or using plasma thermal spray of dispersed metal and carbide powders in the chamber. Both of them produce non-uniform cobalt coating on the tungsten carbide particles which result in the subsequent segregation of cobalt and tungsten carbide during consolidation. The mechanical properties, like fracture strength and fracture toughness are very related to homogeneity of composition. The segregation will lead to the poor mechanical properties. To improve the homogeneity of composition in the composites, electroless deposition was implemented to form uniform coating on the fine particles of irregular geometry shapes. Typically, the nonconductive particles need to be activated by Pd before deposition. Sub-micron tungsten carbide powder was employed to plate cobalt coating. The morphology and distribution of cobalt coating was observed by Scanning Electron Microscope (SEM) and X-Ray mapping. Energy Dispersive X-Ray (EDX) provides another evidence of cobalt coating. The composition of cobalt was characterized with Inductively Coupled Plasma (ICP).

#### **Y8.17**

**SYNTHESIS AND OBSERVATION OF 5 NANOMETER GOLD CLUSTERS IN SOLUTION.** Olivier Balmes, Jan-Olov Bovin, Jan-Olle Malm, Chemical Center Lund Univ, Dept Inorganic Chemistry 2, Lund, SWEDEN; Gunnel Karlsson, Chemical Center Lund Univ, Biomicroscopy Unit, Lund, SWEDEN.

Nanotechnology is promised to be one of the leading techniques for fabrication of new materials with improved properties. These new materials find applications in many fields of interest from microelectronics to hydrogen storage or electro-optical devices. In a number of cases, precise positioning of the nano-elements with respect to the substrate or with respect to each other is required. We have investigated the 3-dimensionnal ordering of 5-nm ligand protected gold clusters in solution or deposited on a carbon film. Using Cryo Transmission Electron Microscopy (Cryo-TEM), we show evidence that the ordering already exists in solution. Gold clusters organize in 3-dimensionally ordered superstructures. Deposition of the same sample on a carbon film for conventionnal electron microscopy shows that not all the ordering is retained, thus showing that the interaction between gold clusters is weak enough to be disturbed by the deposition process. Interaction between the substrate and the protecting ligand shell are also playing a role in retaining the structure upon deposition.

#### **Y8.18**

**HYDROTHERMAL FABRICATION OF ROD-LIKE RUTILE**

**NANO-PARTICLES.** Juan Yang, Sen Mei, and José M.F. Ferreira  
Department of Ceramics and Glass Engineering, UIMC, University of Aveiro, Aveiro, PORTUGAL.

Rutile phase exhibits higher refractive index and hiding power, good chemical stability, and is becoming a candidate material for the high-temperature separation and catalysis applications. The thermodynamically stable feature of rutile among the three polymorphs of TiO<sub>2</sub> usually hinders obtaining nano-sized rutile phase by a conventional calcining way. However, acid peptization of amorphous TiO<sub>2</sub> is favorable to the formation of rutile phase. In this work, well-crystallized and well-dispersed rod-like rutile particles with specific surface areas of 49.1 and 35.0 m<sup>2</sup>/g were prepared by hydrothermally treating the acid peptized TiO<sub>2</sub> amorphous sols at relatively low temperatures of 200°C or 240°C, respectively. The formation of non-touching rutile particles is attributed to high long-range electrostatic forces between particles in the presence of the high concentration of the peptizer. The acid peptization would easily break the ≡Ti-O-Ti≡ bonds to form ≡Ti-OH or HO-Ti-OH species depending on the amount of acid, and create conditions for the formation of rutile nuclei after structural rearrangements.

#### **Y8.19**

**FABRICATION OF NANO-FERRITE THROUGH HEAVY DEFORMATION.** Zhiguang Liu, Keichi Masuyama, Koichi Tsuchiya, Minoru Umemoto, Dept of Production Systems Engineering, Toyohashi Univ of Technology, Toyohashi, JAPAN; Xinjiang Hao, Dept of MS&E, Northeastern Univ, Shenyang, CHINA.

Nanocrystalline materials have been attracting more and more attention since its foundation in 1980's. A number of novel nanocrystalline materials have been produced through various processes and found their application or prospective application. However, little attention has been paid to the most popular materials in the world, steel. Although endeavor has been made to produce sub-microcrystalline steels, no practical progress was made in the field of nanocrystalline steel. It is no doubt that nanocrystalline materials own improved or novel mechanical and physical property than coarse-grained microcrystalline materials. The improved properties of nanocrystalline steels are expected as well. The present work will be devoted to the fabrication and characterization of nanocrystalline ferrite through heavy cold work. Starting materials including pure iron and steels with carbon content up to eutectoid steels were subjected to heavy cold work, which includes heavy cold rolling, three dimensional compression and mechanical milling. Based on the previous work that cementite can dissolve after heavy deformation, the complete dissolution of cementite and formation of nanocrystalline ferrite was expected. It was found that under heavy cold rolling, nano-ferrite could be produced as strips in steels, although the complete dissolution of cementite could not be realized in the high-carbon steels. However, mechanical milling leads to the complete dissolution of cementite after various milling time for steels with different carbon contents in the present study. Aging the as-milled powders leads to the precipitation of fine cementite particle, as small as several tens of nanometers, in ferrite matrix. On the contrary, if the cementite was not dissolved completely, aging the as-milled powders leads to the formation of big cementite particles of several micrometers. The formation of nano-ferrite through mechanical milling and its subsequent recovery to ferrite-cementite nano-composite was analyzed in view of structure and thermodynamics.

#### **Y8.20**

**HIGH BRIGHTNESS WHITE LIGHT PHOSPHORS FROM CADMIUM SELENIDE NANOPARTICLE-POLYMER COMPOSITES.** David J. Cole-Hamilton, Andrea V. Firth, Stuart J. Williams, University of St. Andrews, Dept. of Chemistry, St. Andrews, UNITED KINGDOM; John W. Allen, University of St. Andrews, Dept. of Physics and Astronomy, St. Andrews, UNITED KINGDOM.

Polymer encapsulated cadmium selenide nanocrystals have been prepared at room temperature by direct reaction of dimethyl cadmium with hydrogen selenide gas, using a polyphosphine matrix as encapsulation medium. The particle size of the encapsulated nanocrystals can be controlled by either reaction duration or reagent (Cd:P) ratio. The resulting composite materials have been cast directly from solution to form films with high optical transparency. The semi-conductor nanocrystals encapsulated within these films exhibit bright luminescence. The specific emission properties of these particles are highly dependent upon crystal size. Larger particles (>3 nm) exhibit near band edge luminescence, whilst smaller particles display a broader emission, covering most of the visible spectrum. These particles display a moisture sensitivity, with quenching of luminescence occurring upon exposure of the composite to wet argon or air. Subsequent exposure of water quenched material to UV/Visible light has been observed to induce a reversal of the initial quenching.

The result of this process is a composite material which now displays stable luminescence upon exposure to moisture. In some systems the total regenerated luminescence quantum yield has exceeded that of the sample prior to quenching and regeneration. The combination of broad emission, high brightness and the ability to regenerate these materials to a moisture stable form suggests applications in the area of 'white' phosphors.

#### **Y8.21**

**X-RAY INVESTIGATION OF EPITAXIAL OVERGROWTH ON GERMANIUM QUANTUM DOTS.** David W. Greve and Qian Zhao, Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA.

Self-assembled germanium quantum dots on silicon (QD) have been the subject of considerable research, in part because of their potential application in quantum cellular automata. This application will require smaller and more uniform quantum dots than typically reported. Consistent with some other groups, we have found that predeposition of carbon results in smaller and more uniform dots under some circumstances. Here, we report on the quality of a silicon epitaxial layer which is overgrown on quantum dots formed with and without carbon predeposition. Samples were prepared by UHV/CVD on (100) silicon substrates using silane, germane, and methylsilane as the reactants for silicon, germanium, and carbon respectively. Before initiating growth the oxide layer was thermally desorbed, followed by growth of a silicon cap layer for 10 minutes, followed by a 2 min pause before initiating the germane flow. When predeposition of carbon was performed, exposure to methylsilane took place after the pause and was followed by a second 2 min pause before starting the germane flow. After the deposition of Ge layer, we deposited an additional silicon cap and then a layer of  $\text{Si}_x\text{Ge}_{1-x}$  on top. We used HRXRD and reciprocal space mapping to study the quality of the  $\text{Si}_x\text{Ge}_{1-x}$  layer. HRXRD results showed that (113) peaks of the overgrown layers are broadened compared with the same content  $\text{Si}_x\text{Ge}_{1-x}$  layer directly grown on a Si wafer. Even though predeposition of C will make the QDs smaller and more uniform, the peak of the overgrown epitaxial layer is wider. This indicates that the carbon has an adverse effect on the quality of the epitaxial layer. We will also present the results of detailed characterization of the overgrown epitaxial layers using reciprocal space mapping.

#### **Y8.22**

**INDEX ENGINEERING OF NANO-POLYMER COMPOSITES.** Nobuyuki Kambe, Sujeet Kumar and Shiv Chiruvolu, NanoGram Corporation, Fremont, CA; Yigal D. Blum, D. Brent MacQueen and Gregory W. Faris, SRI International, Chemical Science and Technology Lab, Menlo Park, CA.

Highly homogeneous nanoparticles-polymer composite materials have been developed<sup>1</sup> to meet high demands of photonic materials covering a broad range of the refractive index. Index engineering can be achieved by controlling loading level of metal-oxide nanoparticles within an organic host material. Uniformity and smallness of nanoparticles are critical to maintain low level of light scattering, particularly in visible to infrared regions. We have developed LASER-driven nanomaterials synthesis tools to generate a versatile range of nanomaterials that have an extremely narrow size distribution. These nanomaterials can be blended at various loading levels, to at least 50 wt% in a conventional polymer matrix. In addition to homogeneous blending and transparent or translucent behavior, some selective attraction of nanoparticles to polymer sites is also found.<sup>1</sup> Optical characterization results are discussed for these photonic nanocomposites.

<sup>1</sup>Y. Blum, et al., in this symposium, 2001 MRS Spring Meeting.

#### **Y8.23**

**ELECTRONIC STRUCTURE OF MoS<sub>2</sub> CLUSTERS USING X-RAY ABSORPTION AND EMISSION SPECTROSCOPES.** T. van Buuren, Lawrence Livermore National Laboratory, Livermore, CA; J.P. Wilcoxon, Sandia National Laboratory, Albuquerque, NM; C. Bostedt, N. Franco, J.E. Klepief, Lawrence Livermore National Laboratory, Livermore, CA; T.D. Callcott, Physics Department University of Tennessee, TN; D.L. Ederer, Physics Department Tulane University.

Molybdenum disulfide (MoS<sub>2</sub>) nanoclusters have demonstrated to be effective photocatalysts for the detoxification of chemical waste. In such an application the cluster would absorb light creating electron-hole pairs and thus catalyze specific chemical reactions. For these applications the cluster must have a band gap that is matched to the visible spectrum and the valence and conduction band edges must be compatible with the redox potentials for the reactions involved. To tailor these properties for a specific application we measure the valence and conduction band edges of well-defined MoS<sub>2</sub> clusters using x-ray absorption and emission spectroscopies. MoS<sub>2</sub> clusters from 1-10nm in diameter were formed using the inverse micelle synthetic process at room temperature in inert oil. The cluster size and

distribution could be precisely controlled using a high-pressure liquid chromatography system. By measuring the S 2p absorption we are able to measure the change in the conduction band edge of the MoS<sub>2</sub> clusters as a function of particle size. We found that the conduction band edge was blue shifted with decreasing clusters size with shifts up to 1.2 eV measured for clusters 2nm in diameter. These results agree with earlier predictions of the conduction band shifts as a function of particle size. The valence band density of states was determined by measuring the soft x-ray emission from the S 2p core hole. Effective mass calculations, which predict little or no shift in the valence band edge are compared to our valence band shift measurements. We compare all these results to recent optical measurements. This work is supported by US Department of Energy under contract number DE-AC04-AL8500 and W-7405-ENG-48.

#### **Y8.24**

**OPTICAL AND STRUCTURAL PROPERTIES OF VERTICAL ALIGNED SELF-ASSEMBLED InAs QUANTUM DOTS MULTILAYERS.** J.C. González, M. I.N. da Silva, North Carolina State University, Analytical Instrumentation Facility, Raleigh, NC; W.N. Rodrigues, F.M. Matinaga, M.V.B. Moreira, A.G. de Oliveira, R. Magalhaes-Paniago, Universidade Federal de Minas Gerais, Dept de Física, Belo Horizonte, BRAZIL; D. Ugarte, Laboratório Nacional de Luz Síncrotron, Campinas, Sao Paulo, BRAZIL.

In this work, we report optical and structural properties of vertical aligned self-assembled InAs quantum dots multilayers. The InAs quantum dots samples have been grown by Molecular Beam Epitaxy. Employing Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Grazing Incident X-ray Diffraction (GID) we have studied the structural properties of samples with different number of periods of the multilayer structure, as well as different InAs coverage. The optical properties have been studied using Photoluminescence (PL) and Magneto-Photoluminescence (Magneto-PL) Spectroscopy.

#### **Y8.25**

**SYNTHESIS AND SELF-ORGANIZATION OF NANORODS.** Franklin Kim, Jae Hee Song, Serena Kwan, Jennifer Akana, Peidong Yang, University of California Berkeley, Dept of Chemistry, Berkeley, CA.

One-dimensional (1D) nanostructures are of both fundamental and technological interest. Major challenge remains in order to fully exploit the 1D nanostructures, namely, the development of suitable chemical strategies for the synthesis and organization of the nanoscale building blocks with uniform sizes and aspect ratios. We've chosen uniform nanorods as model systems to study the effect of dimensionality on the self-assembly behavior as compared with nanoclusters. Au, Cu, BaCrO<sub>4</sub>, BaWO<sub>4</sub> nanorods have been prepared using either electrochemistry or reversed micelle template chemistry. These nanorods are very uniform in both their sizes (~ 10 nm) and aspect ratios (3 ~ 10). Various methods have been employed to examine their assembly behaviors, including Langmuir-Blodgett monolayer formation, solvent-evaporation induced superstructure formation, and soft lithography surface patterning. The effect of aspect ratio on the superstructure formation will be discussed. In addition, superstructure formed from mixture of nanoclusters and nanorods will also be presented.

#### **Y8.26**

**MECHANICAL STRENGTHENING BY ELECTROCHEMICAL CODEPOSITION OF NICKEL/ALUMINA NANOCOMPOSITES.** Ingrid Shao, P.M. Vereecken, P.C. Searson, R.C. Cammarata, Johns Hopkins Univ, Dept of MS&E, Baltimore, MD; C.L. Chien, Johns Hopkins Univ, Dept of Physics and Astronomy, Baltimore, MD.

Oxide dispersion strengthened (ODS) materials are widely used for high temperature and high stress applications due to their high yield strength and high creep resistance. Powder metallurgy is the conventional processing method to synthesize ODS materials. We have produced ODS materials embedded with nanoscale oxide particles using a novel electrochemical deposition process. Advantages of electrochemical codeposition of metal/nanoparticle composites are the low cost, low energy requirement, and high yield. Nickel/alumina nanocomposites were deposited from an aqueous nickel sulfamate solution containing a suspension of 300 nm alumina particles using a rotating disk electrode. Different alumina volume fractions were obtained using different deposition current densities and rotation rates of the working electrode. The volume fraction of particles incorporated into the nickel film was found to depend on the rate of metal deposition and the flux of particles to the cathode surface. A kinetic model for the rate of particle incorporation will be presented. A homogeneous and well-dispersed distribution of ceramic particles was observed. The hardness of nickel/alumina films increased significantly with the alumina concentration in the film, while the saturation magnetization, normalized for the volume of nickel in the

film, was not degraded significantly. The magnetic coercivity was observed to linearly increase as a function of particle concentration in the films. A scaled-up cell setup was used to produce large nickel/alumina samples 2-inch in diameter and 250- $\mu\text{m}$  in thickness.

#### **Y8.27**

**PHOTO-ASSISTED PROCESSING OF MULTI-COMPONENT OXIDE NANO-PARTICLES.** H.F. Lu, W. Lo, Texas Center for Superconductivity and Department of Mechanical Engineering, University of Houston, Houston, TX; K. Ravi-Chandar, Center for Mechanics of Solids, Structures and Materials, Department of Aerospace Engineering and Engineering Mechanics, University of Texas, Austin, TX.

Multi-component oxides have various functionalities such as ferroelectric, electronic, magnetic and optical properties that are being exploited for different engineering devices. Some of these functionalities (e.g. optical properties) are expected to be enhanced when nano-scale structures are introduced to these materials. A "bottom-up" approach of the development of such nano-structured devices requires the availability of nano-particles with engineered phase compositions, morphologies and size distributions so that materials in different forms can be fabricated. The present paper presents the development of a photo-assisted processing technique for the synthesis of complex oxides from solution precursors. This technique involves the generation of fine aerosols from solutions, drying of the aerosols to form solid powders and in situ decomposition and reaction of the solid powders by photo-irradiation to form final oxide nano-particles. By incorporating electric fields in this process, the spatial distribution of the particles could also be manipulated. In view of the multi-component oxide nano-particle processing as well as the spatial distribution controlling capabilities, this technique will have important implications on the fabrication of nano-structured, patterned devices for various applications.

#### **Y8.28**

**BULK NANOSTRUCTURED Al-Pb COMPOSITE WITH NOVEL MECHANICAL PROPERTIES.** Fei Zhou, Enrique Lavernia, Univ of California at Irvine, Dept of Chemical and Biochemical Engineering and Materials Science; Ke Lu, State Key Laboratory of RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, PR CHINA.

Aluminum alloys with proper distribution of lead have potential as materials for plain bearings because of the lubrication ability of lead in the aluminum matrix. The present study is devoted to develop bulk nanostructured Al-Pb composite with novel mechanical properties. Powders of  $\text{Al}_{90}\text{Pb}_{10}$  (wt.%) with a mixture of nanostructured fcc-Al and fcc-Pb phases were produced by ball milling of elemental Al and Pb blends. The as-milled powders were successfully consolidated into bulk, fully dense samples (>99.5% theoretical density) while the average grain sizes of Al and Pb in the compacted samples remain unchanged with respect to those in the as-milled powders (7 nm for Pb and 24 nm for Al). Compared with conventional Al-Pb alloys, an increase in microhardness by a factor of 2 was achieved in the as-consolidated sample. The compressive tests indicated a yield stress value as high as about 400 MPa in the as-consolidated state. With an increase of the grain size of Al in annealed samples, a reduction of the compressive yield stress was observed. The novel mechanical performance was attributed to the strengthening effect of the nanometer scale Al grains following the Hall-Petch relationship.

#### **Y8.29**

**SYNTHESIS AND CHARACTERIZATION OF AEROSOL SILICON NANOPARTICLE NONVOLATILE FLOATING GATE MEMORY DEVICES.** Michele L. Ostraat, Richard C. Flagan, Mark L. Brongersma, Julie D. Casperson, Harry A. Atwater, California Institute of Technology, Pasadena, CA; L. Douglas Bell, Jet Propulsion Laboratory, Pasadena, CA; Jan De Blauwe, Martin L. Green, Lucent Technologies/Bell Labs, Murray Hill, NJ.

Silicon nanoparticle-based floating gate MOS field effect devices have potential for terabit  $\text{cm}^{-2}$  density nonvolatile memory applications. We have fabricated nanoparticle memory devices in a conventional MOS ULSI process with channel lengths from 0.18-10 $\mu\text{m}$  with a silicon nanoparticle floating gate fabricated by aerosol deposition.  $\text{SiO}_2$  passivated silicon nanoparticles have been synthesized in an ultra-clean two-stage aerosol reactor that is interfaced to a 200 mm wafer deposition chamber in a class 100 cleanroom. We synthesize silicon nanoparticles by thermal decomposition of silane gas at 950 $^\circ\text{C}$  to produce single crystal, nonagglomerated nanoparticles. The second reactor stage passivates the silicon particles with a thin thermal oxide grown at 1050 $^\circ\text{C}$ . Particles are thermophoretically deposited onto 200 mm wafers with densities from  $10^{13}$  particles  $\text{cm}^{-2}$  at the wafer center to  $10^{11}$  particles  $\text{cm}^{-2}$  at the wafer edge in tens of minutes. We have fabricated floating gate memory devices in which the dielectric layer contains a discontinuous nanoparticle layer containing (i) 2 - 4

nm crystalline core diameter with 1 nm thermal oxide; (ii) 6 - 10 nm crystalline core diameter with 2 nm thermal oxide; (iii) bimodal distribution of 4 nm crystalline core diameter with 1 nm thermal oxide and 8 nm crystalline core diameter with 2 nm thermal oxide. Cross-sectional transmission electron microscopy verifies the presence of a crystalline silicon nanoparticle floating gate layer. Aerosol nanoparticle floating gate devices exhibit normal transistor behavior. Aerosol nanoparticle devices with 0.2 $\mu\text{m}$  channel length exhibit intrinsic threshold voltages  $\sim 2.5\text{V}$  with large threshold voltage shifts  $> 5\text{V}$  after submicrosecond program times and millisecond erase times. No degradation in program/erase threshold voltage swing was seen during 100,000 program and erase cycles, although some threshold shift due to charge trapping was observed. Retention times on the order of 100,000 seconds have been documented. The effect of nanoparticle size and density on memory characteristics will be discussed. Results on devices with bimodal particle size distributions and with high k-dielectric materials incorporated into the control gate oxide will also be presented. The results of physical and electrical characterization indicate that nanoparticle memories fabricated by aerosol deposition of the silicon nanoparticle floating gate have device performance characteristics comparable to the best current floating gate nonvolatile memory devices and are fully scaleable to nanometer scale dimensions.

#### **Y8.30**

**TOMOGRAPHIC PROFILING OF INTERNAL STRESSES IN NANOSTRUCTURED COATINGS.** Thomas Tsakalacos, Igor Zakharchenko, Zvi Kalman, Yuriy Gulak, Dept of Ceramics and Materials Engineering, Rutgers University, NJ; Mark Croft, Physics Dept, Rutgers University, NJ; R. Rigney, R. Brunhouse, Jr., R. Shroshire, A&A Company Inc., So. Plainfield, NJ; R. Holtz, K. Sadananda, NRL, Washington, DC; Z. Zhong, J. Hastings and J.Z. Hu, National Synchrotron Light Source.

We have been successful in the development of a synchrotron based technique to profile residual stress versus depth, directly and accurately utilizing energy dispersive x-ray diffraction (EDXRD). In addition a second new technique, this work is greatly facilitated by a second new technique, scattered Intensity profiling (SIP), which allows tomographic profiling (by scattering strength) of composite materials/interfaces under study. These methods allow the evaluation of internal stresses in nanocrystalline solids (and composites). This represents a promising advance in the field of nondestructive evaluation of localized and global strains in nanomaterials for large depths. We have performed control experiments using cantilever beam specimens, which have proved the feasibility and sensitivity of the strain profiling method. Examples of residual stresses profiles of Nanostructured Coatings on grit blasted steel substrates will be presented. The results 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. Grit blasting of one of the steel surface resulted in significant compressive stresses near the blasted surface but still tensile in the other. The deposition of Nanostructured Coating altered the magnitude of the compressive stress distribution. 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. We have correlated the residual stress profiling to fatigue deformation processes. Large compressive stresses in WC/Co coatings correlate well with extended fatigue lives observed in four point bending fatigue experiments in same specimens. Also, our measured internal stress relaxations for fatigued steels coated with WC/Co nanocoatings, up to one million cycles deformation, point to new approach for understanding the mechanism(s) of internal fatigue damage in these materials. We have also related fatigue deformation to structural parameters of nanocoatings. These include microstructural evolution of nanocoatings, phase changes during processing, initial nanopowder characteristics and plasma spray processing parameters. Systematic studies showed the various influences of these parameters to fatigue damage of these structural materials. Finally, a new approach to the methodology that could lead to fatigue life prediction Nanostructured Coated components will be introduced. The EDXRD mapping of a three-dimensional space distribution of local residual stresses at the crack tip produced by overload and other transient effects, is a promising step toward the success of the Unified Approach (K,  $K_{\text{max}}$ , Kint) for fatigue life predictions of load bearing components.

#### **Y8.31**

**ELECTRON TRANSPORT PROPERTIES OF METAL-SEMICONDUCTOR NANO-COMPOSITES.** Scott L. Cumberland, Geoffrey F. Strouse, Univ of California, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

Nano-materials such as CdSe nanocrystals and gold and silver nanoparticles are of great interest in sensing and electronic technologies due to their unique size dependent optical and electronic properties. The proximity of the band gap energy of CdSe

nanocrystals and the excitation energy of the metal nanoparticle surface plasmon offers the opportunity to produce nano-composite materials with potentially novel optical and electronic properties. We have been able to produce crystalline nanocomposite materials composed of CdSe and Au nanoparticles via a ligand-directed self-assembly methodology. The lattice structures of these assemblies and their electron transport properties are affected by such factors as the ratio of their core sizes and the ligand chain length and functionality. Here we report the transport properties of Au-CdSe nanomaterials with various core size ratios and connecting ligands.

#### **Y8.32**

**APPLICATION OF FERROFLUIDS CONTAINING MAGNETITE NANOPARTICLES FOR MAGNETIC INKS AND BIOMEDICAL APPLICATIONS.** Wolfgang Voit, Royal Institute of Technology, Engineering Materials Physics Division, Stockholm, SWEDEN and XaarJet AB, Jarfalla, SWEDEN; Do Kyung Kim, Mamoun Muhammed, Royal Institute of Technology, Materials Chemistry Division, Stockholm, SWEDEN; Werner Zapka, XaarJet AB, Jarfalla, SWEDEN; Börje Bjelke, MRI Research Center, Dept. of Clinical Neuroscience, Karolinska Institutet, Stockholm, SWEDEN; K.V. Rao, Royal Institute of Technology, Engineering Materials Physics Division, Stockholm, SWEDEN.

A controlled co-precipitation method is introduced to prepare uniformly monodispersed colloidal ferrofluids. The ferrofluids contain magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles with a controlled particle size. Computer-assisted chemical equilibrium calculations were carried out to predict undesired critical oxidation of  $\text{Fe}^{2+}$ . The magnetic nanoparticles were coated with functional groups to modify the surface charge and stabilize the colloidal suspension. The colloidal ferrofluids as well as the nanosized magnetic iron oxide particles were characterized by SQUID magnetometry and AC-susceptibility. The studies indicate superparamagnetic behaviour for small particles with a mean particle size of 5-10 nm, which makes them suitable for biomedical applications. Larger nanoparticles exhibit remanent magnetisation at room temperature, and are possible for applications as magnetic inks. For the biomedical purpose, ferrofluids with superparamagnetic magnetite nanoparticles were investigated for the use as MR contrast agents. The nanoparticles were injected via a glass capillary pipette into the dorsal hippocampus of rat brains. One hour after the injection the rats were examined in vivo using a 4.7 Tesla / 40 cm Bruker Biospec Advance spectrometer, equipped with a standard 12 cm self-shielded gradient system. Animals were imaged using a 35 mm birdcage coil. The distributions of the particles were characterized using multi-slice MRI protocol with a Rapid Acquisition with Relaxation Enhancement (RARE) sequence. The results indicate that the nanoparticles used have a superparamagnetic property that is easily detectable in a MRI scanner. A second application is the use of ferromagnetic magnetite particles in magnetic inks. The ferrofluid containing the nanoparticles was adjusted to a suitable range in viscosity and surface tension, to enable possible usage for drop-on-demand inkjet printheads.

#### **Y8.33**

**SHAPE CONTROL OF CdSe NANOCRYSTALS.** Erik C. Scher, Liberato Manna, A. Paul Alivisatos, Dept of Chemistry, University of California, Berkeley, CA and Materials Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA.

Shape control of CdSe nanocrystals is demonstrated using binary surfactant mixtures. Single crystal nanoparticles shaped like rods, arrows, tetrapods, and branched tetrapods can be synthesized in large quantities and narrow shape distributions. The ratio and type of surfactants, initial injection conditions, and the time dependent monomer concentration can be manipulated to exact precise control over the nanocrystal shape. Shape control is characterized via TEM and high resolution TEM. This shape control of semiconductor nanocrystals will allow for the development of novel new materials, since CdSe nanocrystals exhibit size and shape dependent properties. Shape control also provides insight into the growth mechanism of the nanocrystals.

#### **Y8.34**

**STRONG ROOM TEMPERATURE LUMINESCENCE OF InAs QUANTUM DOTS SELF-ASSEMBLED ON AlAs.** V. Tokranov, M. Yakimov, L. Senapati, K. Dovidenko, S. Oktyabrsky, University at Albany Institute for Materials, University at Albany - SUNY, Albany, NY.

Using photoluminescence (PL) and transmission electron microscopy (TEM) techniques we studied the influence of growth temperature and 2ML thick AlAs cladding layers on the formation of self-assembled InAs quantum dots (QDs). Single sheets of InAs QDs with 2.4 monolayers (ML) average coverage were grown by molecular beam epitaxy at 0.05 ML/sec growth rate on a 2ML-AlAs/8ML-GaAs short-period superlattice. QD samples grown at 475°C with

AlAs-cladding layers were shown to have the highest room temperature PL intensity with a peak at 960 nm and the narrowest linewidth. Integral PL intensity of this QD ensemble was almost equal to that of  $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  quantum well (QW) excited with  $10\text{W}/\text{cm}^2$   $\text{Ar}^+$ -laser. The PL intensity of the QD's showed very weak (similar to that of QW's) dependence on temperature between 77K and room temperature. Growth of the QD structures at even higher temperatures exceeding 475°C greatly reduced ground state PL intensity at 1050nm. In-situ RHEED measurements of the critical InAs coverage for QD formation showed to be 15% higher on AlAs than on GaAs. TEM analysis showed more gradual temperature dependence of the QD density ( $4 - 20$ )  $\bullet 10^{10}\text{cm}^{-2}$  when formed on AlAs as compared to GaAs surface.

#### **Y8.35**

**ASSESSMENT AND CONTROL OF NANOSTRUCTURE AND COMPOSITION IN  $\text{Bi}_2\text{Te}_3$  NANOWIRE ARRAYS.** M.S. Sander, A.L. Prieto, M.S. Martin-Gonzalez, A.M. Stacy, UC Berkeley, Dept of Chemistry, Berkeley, CA; R. Gronsky, T. Sands, UC Berkeley, Dept of MS&E, Berkeley, CA.

Due to the effects of reduced dimensionality, bismuth telluride nanowires are expected to have increased thermoelectric efficiency relative to bulk  $\text{Bi}_2\text{Te}_3$ , one of the best thermoelectrical materials known. However, nanowire properties will depend strongly on structure and composition because transport is confined to one dimension. We have studied in detail the characteristics of nanowire arrays fabricated by electrodeposition of wire material into porous anodic alumina templates. Arrays of wires with diameters from 20 to 200nm have been assessed employing transmission electron microscopy (TEM) and analytical electron microscopy (AEM). Electrodeposition allows for careful control of the wire characteristics through various deposition parameters. Grain size in the wires is controlled by the deposition temperature, potential, and post-deposition annealing, resulting in average grain sizes of a few nanometers to several times the wire diameter. Composition along the wire is particularly sensitive to the concentrations of species in solution and the deposition potential, as determined from energy dispersive x-ray spectroscopy of localized regions ( $\sim 1\text{nm}$ ). Variations in grain size and stoichiometry strongly affect the properties of bulk  $\text{Bi}_2\text{Te}_3$  and are expected to have an even greater effect on the properties of these nanostructured materials.

#### **Y8.36**

**FABRICATION OF HIGH DENSITY THERMOELECTRIC NANOWIRES ARRAYS BY ELECTRODEPOSITION.** M.S. Martin-Gonzalez<sup>1</sup>, A.L. Prieto<sup>1</sup>, M.S. Sander<sup>1</sup>, M. Chan<sup>1</sup>, R. Gronsky<sup>2</sup>, T. Sands<sup>2</sup>, A.M. Stacy<sup>1</sup>, <sup>1</sup>Department of Chemistry, <sup>2</sup>Department of Materials Science and Mineral Engineering, University of California, Berkeley, Berkeley, CA.

Interest in thermoelectric materials has increased recently because it has been postulated that quantum confinement improves the efficiency of these materials, which have applications as solid state refrigerators and power generators. One way to achieve quantum confinement is by fabricating one-dimensional (1-D) nanowires.  $\text{Bi}_2\text{Te}_3$  is a good candidate for nanowires because it has one of the highest Seebeck coefficients in bulk at room temperature. One of the possible methods to fabricate nanowires is by electrodeposing the material into anodic  $\text{Al}_2\text{O}_3$  templates. For the porous  $\text{Al}_2\text{O}_3$  to be used as a cathode in an electrochemical cell, a metal film is attached to the back. This material plays an important role in the quality of the nanowires arrays to be used as a future device. The influence of different metals (i.e. platinum and silver) and diverse electrode treatments (for example, faceting and electrode activation) in order to improve the wire density in the arrays has been assessed.

#### **Y8.37**

**FABRICATION OF Al-Zr-O NANOCOMPOSITE BY PECHINI PROCESS FOR THE REINFORCEMENT OF BIOCERAMIC IMPLANT.** Young-Min Kong, In-Seop Lee, Hyoun-Ee Kim, School of MS&E, Seoul Nat'l Univ, Seoul, KOREA; Doh-Hyung Riu, Korea Institute of Ceramic Engineering and Technology, Seoul, KOREA.

Hydroxyapatite (HAP) has attracted much attention as a substitute material for damaged bone, because of its similarity to various calcified tissue of vertebrates. But its poor mechanical properties have been obstacles for load bearing applications.

Tetragonal-Zirconia-Polycrystal (TZP) has been widely used as a reinforcement of brittle ceramics because of its excellent mechanical properties. However, when TZP was added to HAP as a reinforcing agent, interfacial reactions between HAP and TZP made the tetragonal phase stabilize into the cubic phase, decreasing the transformation toughening effect. Pechini process is well known method of homogeneous and very fine powders or mixtures, however, there has been no attempt to make composite powder. We produced the TZP- $\text{Al}_2\text{O}_3$  nanocomposite powder with varying the amount of

esterification agents, in order to investigate the effects of the addition of the TZP-Al<sub>2</sub>O<sub>3</sub> composite powders into HAP.

#### **Y8.38**

**OPTOELECTRONIC, PHOTONIC, NANO-ELECTRONIC, AND BIOLOGICAL APPLICATIONS OF SILICON AND GERMANIUM QUANTUM DOTS.** Howard W.H. Lee, Boyd R. Taylor, Lawrence Livermore National Laboratory, Advanced Photonics Materials Group, Physics and Advanced Technologies Dept, Livermore, CA; Paul T. Steele, Peter A. Thiel, University of California at Davis, Dept of Applied Science, Livermore, CA.

Quantum dots (QDs) composed of direct bandgap semiconductors have received considerable attention for many years. Examples include mainly II-VI semiconductors such as CdSe, CdS, and CdTe. As a result, the fundamental understanding of direct bandgap QDs have matured tremendously, giving rise to innovative applications in fields that include optoelectronics, photonics and biotechnology. However, the situation with QDs composed of indirect bandgap materials, e.g., Group IV semiconductors such as Si and Ge, is not nearly as advanced. An understanding of their fundamental properties is only now beginning to emerge, and applications based on their unique properties are slowly being realized. However, fundamental differences in the phonon-assisted nature of their lowest optical transition lead to a rich variety of physics, making this nanostructured material system scientifically and technologically interesting. We will describe our recent results on the unique optical, nonlinear optical, electronic, and electrical properties of stable and quantum confined silicon and germanium QDs in a variety of configurations. We will also present results on how these fundamentally different properties can be capitalized on for applications in optoelectronics, photonics, nanoelectronics, and biology. Examples include thin film LEDs and lasers, ultrafast all-optical switches and logic gates, single electron nanoelectronics, and fluorescent biological labels and biosensors.

#### **Y8.39**

**ELECTROCHEMICAL SYNTHESIS OF CoSb<sub>3</sub> NANOWIRE ARRAYS WITH THREE-DIMENSIONAL PERIODICITY.**

A.L. Prieto, M.S. Sander, M.S. Martín González, A.M. Stacy, Dept. of Chemistry; J.F. Behnke, R. Gronsky, T. Sands, Dept. of Materials Science and Mineral Engineering, University of California, Berkeley, CA.

Dimensionally restricted materials present a wide range of potential applications, ranging from thermoelectric power generation to information storage and processing. Nanowires are promising materials for thermoelectric applications because quantum confinement has been shown to increase thermoelectric efficiency. We have used porous anodic alumina as a template to make nanowires of thermoelectric materials. We have used electrochemical methods to synthesize and fill the template with CoSb<sub>3</sub>, a thermoelectric material. Electrodeposition of material into the pores of anodic alumina templates ensures that the as-deposited wires are electrically continuous, and provides a wide range of control via anodization potentials, electrolytes, and temperature. We have electrodeposited nanowires of varying diameters of CoSb<sub>3</sub>. Characterization of the nanowire/porous Al<sub>2</sub>O<sub>3</sub> composite materials using X-Ray diffraction (XRD) to determine the phase, degree of crystallinity, and orientation of the nanowires will be presented. We have also used scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS) to determine the extent of pore-filling, the morphology, and the composition of the resulting composite material. We have discovered an interesting three-dimensional periodicity of the CoSb<sub>3</sub> wires as a result of our electrodeposition methods, which will be presented.

#### **Y8.40**

**PROCESSING AND MAGNETIC PROPERTIES OF Ni-Fe ALLOY DISPERSED ALUMINA NANOCOMPOSITES.** Jai-Sung Lee, Sung-Tag Oh, Seok Namkung, Hanyang Univ, Dept of Metallurgy and Materials Science, Ansan, KOREA.

Ceramic matrix composites with nanocrystalline dispersion provide new opportunities, both scientific and technological. For example, fracture strength of alumina could be increased three times by the dispersion of 5 vol% SiC nanophase. Based on this processing, ceramic based composites dispersed with nano-sized phases were studied to introduce ferromagnetism into structural ceramics. The entire study has focused on the synthesis kinetics of nanocrystalline alloy and understanding of the role of alloy nanoparticles in microstructure evolution during densification process, because they are prerequisite to realize fabrication of nanocomposites with required microstructural characteristics and properties. In this approach, alumina, which has been well examined as a structural ceramic, and Ni-50 wt% Fe alloy as a material having ferromagnetic property were selected for the ceramic matrix and dispersion, respectively. The composites were fabricated by the hot-pressing of powder mixtures of alumina and nanocrystalline Ni-Fe alloy, in which the alloy was prepared by the

mechanochemical process comprising high-energy ball-milling of NiO-Fe<sub>2</sub>O<sub>3</sub> powders and a subsequent hydrogen reduction process. Microstructural observation revealed that the nanocrystalline Ni-Fe alloy was homogeneously dispersed in the alumina matrix. The composite showed improved mechanical properties and magnetic response such as coercive force dependent on the dispersion size. The formation mechanism of Ni-Fe nano-sized alloys during oxide reduction and phase evolution was explained based on two kinetic processes; the nucleation-growth and diffusion control at low- and high temperatures, respectively. The mechanical and magnetic properties of composites are discussed in terms of microstructural characteristics such as the distribution and size of Ni-Fe dispersion.

#### **Y8.41**

**STRUCTURE AND OPTICAL PROPERTIES OF (InGa)(AsN) NANOSTRUCTURES SYNTHESIZED BY ION IMPLANTATION.** X. Weng, S. Clarke, S. Kumar and R.S. Goldman, Dept. of Dept of MS&E; V.H. Rotberg, Dept. of Nuclear Engineering and Radiological Science; S. Krishna and P.K. Bhattacharya, Dept. of Electrical Engineering and Computer Science; J. Holt, J. Sipowska, and A. Francis, Dept. of Chemistry; A. Daniel and R. Clarke, Dept. of Physics, University of Michigan, Ann Arbor, MI.

Mixed anion nitride-arsenide compound semiconductor heterostructures are promising for light-emitting devices operating throughout the near infrared range. However, due to the large N-As size difference, a limited miscibility of (InGa)(AsN) on the anion sublattice is predicted. Furthermore, alloy phase separation resulting in the formation of quantum dot-like nanostructures has been reported in GaAsN/GaAs [1] and InGaAsN/GaAs [2] superlattices. We have investigated the structure and optical properties of (InGa)(AsN) quantum dot-like nanostructures synthesized by N ion implantation into GaAs and InAs, using a variety of implantation and rapid thermal annealing (RTA) conditions. High-resolution cross-sectional transmission electron microscopy reveals both crystalline and amorphous nanostructures surrounded by either amorphous or crystalline matrices, depending on the energy and dose of the implanted ions and the post-implantation RTA conditions. Electron diffraction indicates that the crystalline GaAsN nanostructures are randomly-oriented cubic or hexagonal phases, with lattice parameters close to that of pure GaN. These nanostructures exhibit significant photoluminescence in the near-infrared range. The apparent lowering of the fundamental band gap is consistent with strain-induced band gap narrowing of a GaN-rich spherical cluster [1]. We will discuss the mechanisms of formation and coarsening of these nanostructures, as well as correlations between their optical and structural properties. [1] R.S. Goldman, R.M. Feenstra, B.G. Briner, M.L. O'Steen and R.J. Hauenstein, Appl. Phys. Lett. 69, 3689 (1996), J. Electr. Mater. 26, 1342 (1997). [2] H.P. Xin, K.L. Kavanagh, Z.Q. Zhu, and C.W. Tu, Appl. Phys. Lett. 74, 2337 (1999).

#### **Y8.42**

**RESONANT TUNNELING BEHAVIOUR IN MULTILAYERED COLD CATHODES MADE OF NANOSEEDED DIAMOND AND NANOCLUSTER CARBON.** B.S. Satyanarayana and A. Hiraki. KUT Academic & Industrial Collaboration Centre, Kochi University of Technology, Kochi, JAPAN.

There is an increasing interest in carbon based nanostructured materials like the nano-diamond, nanotubes and nanocluster or nanostructured carbon. The interest stems from the diverse fields of application envisaged for these materials which include, vacuum microelectronics, energy storage systems, MEMS, electronics and sensors. Presented in this paper is a study on novel heterostructured cold cathodes made of nanoseeded diamond and cathodic arc process grown nanocluster carbon. The nanocrystalline diamond with varying diamond concentration was first coated on to the substrate. The nanocluster carbon films were then deposited on the nanoseeded diamond coated substrates using the cathodic arc process at room temperature. Some of the resultant heterostructured microcathodes were observed to exhibit low field electron emission (emission currents of 1mA/cm<sup>2</sup> at low fields of 1.2 - 5 V/μm). Further some of the samples seem to exhibit I-V characteristics with a negative differential resistance region at room temperature conditions. This negative differential resistance or the resonant tunneling behaviour was observed to be dependent on the nanoseeded diamond concentration and size. The behaviour is further analysed on the basis of the electrical and structural characteristics of the material.

#### **Y8.43**

**DIRECT ELECTRONIC CONTROL OF BIOMOLECULAR SYSTEMS.** Kimberly S. Hamad, Aaron Santos, Joseph M. Jacobson, The Media Lab, Cambridge, MA; John J. Schwartz, Shuguang Zhang, Center for Biomedical Engineering; Massachusetts Institute of Technology, Cambridge, MA.



The authors present experimental results on the direct electronic control of a biomolecular system. Specifically, direct control of the dehybridization of DNA oligonucleotides is demonstrated. This is achieved by means of radiofrequency coupling to inorganic nanostructures covalently bound to the biomolecule. We present data showing the ability to selectively increase the molecular temperature of biomolecules covalently linked to nanostructures while leaving unlinked biomolecules in the same solution unchanged. Applications of this technique in molecular biology, computing, and nanotechnology will be discussed.

#### SESSION Y9: NANOPARTICLES IN BIOLOGICAL SYSTEMS

Chair: Dan L. Feldheim  
Friday Morning, April 20, 2001  
Metropolitan II (Argent)

##### 8:30 AM \*Y9.1

CORE-SHELL NANOPARTICLES FORMED FROM RING-OPENING METATHESIS POLYMERIZATION AND FUNCTIONAL BIOMOLECULES. Chad A. Mirkin, So-Jung Park, Keith Watson, Jin Zhu, and Son-Binh Nguyen, Northwestern University, Chemistry Department, Evanston, IL.

The use of ring-opening metathesis polymerization (ROMP) to form inorganic nanoparticles with discrete blocks of oligomers and polymers surrounding the inorganic core will be described. Methods for interfacing such structures with DNA and proteins will be presented. Structure, characterization, and properties of these novel materials will be discussed.

##### 9:00 AM \*Y9.2

NANOFUNCTIONALIZED PARTICLES FOR SUSTAINED RELEASE PULMONARY DRUG DELIVERY SYSTEMS. Rajiv K. Singh, K. Rau, M. Ollinger, W. Kim, Univ of Florida, Dept of MS&E, Gainesville, FL; G. Hochhaus, I. Coowanitwong, Univ of Florida, Dept of Pharmaceutics, Gainesville, FL; J. Talton, NanoCoat Inc., Gainesville, FL.

The clinical success of drugs with short biological half lives depend on sustained release of active species to induce desired pharmacological effects. The high polymer loading used in conventional microsphere technology severely limits its application to pulmonary drug delivery systems. We demonstrate that the use of nanofunctionalized particulates or particles formed by the attachment of nanoparticles of degradable polymer to the drug particle represents a viable method for pulmonary drug delivery systems. Studies on the sustained release of antiasthmatic drugs by this method will be discussed. The formation of the nanofunctional particulates by the Pulsed Laser Deposition on Particles (PLDP) will be discussed in detail. The laser solid interaction and control of the chemical functionality of the polymer will also be addressed.

##### 9:30 AM Y9.3

IMAGING OF GOLD DENDRIMER NANOCOMPOSITES IN CELLS. Lajos Balogh, Jonathan D. Eichman, and James R. Baker, Jr., Center for Biologic Nanotechnology; Theodore S. Lawrence, Mohamed K. Khan, Department of Radiation Oncology; Dorothy R. Sorenson, Chris A. Edwards, Department of Cell & Development Biology; University of Michigan, Ann Arbor, MI.

Poly(amidoamine) (PAMAM) dendrimers have a great potential in biomedical and materials science applications due to their biofriendly composition, predetermined size, shape and surface functionalities. These spherical artificial proteins may be further functionalized and used as nanoscopic building blocks. However, PAMAM dendrimers are aliphatic, therefore are extremely difficult to observe directly in cells or in tissue. Generally, fluorescent markers or surface complexes of metal ions, such as  $Gd^{3+}$ , are used to overcome this obstacle. Nonetheless, conjugation of markers to the surface of the macromolecule may dramatically change the solubility and other surface-related properties. This problem can readily be solved by using dendrimer nanocomposites (DNC) that may be synthesized with various surface properties and are easy to observe by transmission electron microscopy. In this work gold(0) PAMAM dendrimer nanocomposites, Au(0)n-PAMAM have been used to demonstrate this nanoparticle based concept of imaging. Gold nanocomposites offer the high electron density of the guest atoms, while their interactions with the environment are determined by the surface of the host dendrimer molecule. As a consequence, an inorganic particle can be manipulated as if it was an organic one, and monodisperse nanoparticles with various surfaces may readily be created. Au(0)n-PAMAM gold dendrimer nanocomposites with a well-defined size have been synthesized with various surfaces and have been imaged by TEM both in vitro and in vivo. The results demonstrate the advantages of this technique: Au(0) nanocomposites readily penetrate into cells, are well

observable in TEM, and their interaction with the biological objects may be influenced by the properties of the template dendrimers. This project has been funded with Federal funds in part from the National Cancer Institute, National Institutes of Health, under Contract No. NOI-CO-97111 and in part from the U.S. Department of Energy, under Award No. FG01-00NE22943.

##### 9:45 AM Y9.4

BLOCK COPOLYPEPTIDE MEDIATED GROWTH OF SEMI-CONDUCTOR NANOPARTICLES. Jennifer N. Cha, Larken E. Euliss, Daniel E. Morse, Timothy J. Deming, Galen D. Stucky, University of CA, Santa Barbara, Depts. of Chemistry, Materials and Molecular, Cellular & Developmental Biology, Santa Barbara, CA.

It was earlier demonstrated at UCSB that block copolypeptides could synthesize amorphous, inorganic materials such as silica at ambient pressure and temperature. Recently, we have discovered that block copolypeptides can also be used to organize crystalline materials, including semiconductor nanoparticles. Using a novel, low temperature aqueous route, we have successfully demonstrated that by tuning the lengths and specific compositions of AB diblock copolypeptides, we can easily produce different sizes of CdS and ZnS quantum dots with characteristic optical properties. The synthesis of these nanoparticles involves both block copolypeptide self-assembly as well as direct nucleation of the semiconductor materials from the organic template. This is in contrast to the typical use of organic molecules as capping agents to control nanoparticle growth. Also, because of the versatility of these diblock copolypeptides, different nanoparticles can be organized into arrays. We are also currently working on controlling the final shape of the semiconductor materials by going beyond the AB diblock copolymers and using both ABA and ABC triblock copolypeptides.

##### 10:30 AM \*Y9.5

ELECTROPHORETIC ISOLATION OF Au NANOPARTICLE/DNA CONJUGATES. Daniela Zanchet, Christine M. Micheel, Wolfgang J. Parak, Daniele Gerion, Shara Williams, A. Paul Alivisatos; University of California, Berkeley, Dept of Chemistry, Berkeley, CA; Lawrence Berkeley National Laboratory, Materials Science Division, Berkeley, CA.

Nanocrystal bio-polymer conjugates hold great promise both for biological diagnostics, where the nanocrystals can provide unique detection signatures, and for nanotechnology, where the information content of the bio-molecule can be harnessed for spatial patterning of nanocrystals. Among the many biological polymers that can be coupled to nanocrystals, DNA is of particular interest, because of its inherent programmability. To fully extract the most use from nanocrystal/DNA conjugates, it is first necessary to prepare nanocrystals with a discrete and known number of single-stranded oligonucleotides attached. The attachment of DNA to the Au via a terminal thiol on the oligonucleotide is straightforward but statistical, and a distribution of the number of the oligonucleotides per particle is always present. Using Au nanocrystals with mean particle size between 2-10 nm, we demonstrated that gel electrophoresis is a very powerful probe to study and isolate several Au nanocrystal/ DNA conjugates (DNA length between 30-100 bases). When DNA is attached to the particle, the particle mobility changes leading to the appearance of discrete bands in the same lane. Each band corresponds to a specific number of DNA strands per particle; these bands can be recovered from the gel, producing purified samples of nanocrystal/DNA conjugates. Each conjugate can be seen as a new building block, and different conjugates have been combined to produce several nanocrystal structures, formed by a defined number of particles. This method can also be extended to different systems, such as water-soluble semiconductor nanoparticles.

##### 11:00 AM \*Y9.6

NANOBAR CODE<sup>TM</sup> IDENTIFICATION TAGS: A VERSATILE NANOPARTICLE-BASED PLATFORM FOR MULTIPLEXED BIOANALYSIS. Michael J. Natan, Chief Technical Officer, SurroMed, Inc.

The information revolution in biology, largely catalyzed by innovations in multiplexing and miniaturization of biological assays, has to date been mostly confined to the realm of genes and genomic information. There is a huge need to quantitate cells, proteins, and low-molecular weight species in biological samples; in blood alone, there is thought to be at least 5000 different secreted proteins and another 5000 or more low MW organic species. This presentation concerns synthesis, optical properties, and applications of Nanobar Codes tags (NBCs), very novel nanoparticulate materials. NBCs are segmented, cylindrically-shaped metal nanoparticles with a variable composition along their length. Because the number and width of stripes can be varied, as can the overall particle dimensions, there are an enormous number of unique NBCs that can be fabricated. I will describe progress in both manual and computer-controlled approaches

to electrochemical particle synthesis. We have developed automated software for optical identification of NBCS based on differential reflectivity of adjacent segments; the performance of this software in real-world samples will be described. Finally, I will highlight applications of NBCs in the realm of immunoassays, mass spectrometry, and genomics.

**11:30 AM Y9.7**

**BIOLOGICALLY-INSPIRED NANOCERAMICS AS THE FUTURE BONE PROSTHETIC MATERIAL.** Thomas J. Webster, Purdue University, Dept of Biomedical Engineering, W. Lafayette, IN; Richard W. Siegel, Rensselaer Polytechnic Institute, Dept of MS&E, Troy, NY; Rena Bizios, Rensselaer Polytechnic Institute, Dept of Biomedical Engineering, Troy, NY.

Clinical complications with conventional orthopaedic/dental implant devices composed of metal and metal alloys are often due to insufficient bonding to juxtaposed bone. Ceramics have long been appreciated for their biocompatibility with bone cells and tissue; poor mechanical properties (such as low fracture toughness) have, however, limited their wide use as orthopaedic/dental implants. One approach to increase bone implant efficacy is to design and synthesize "biologically-inspired" ceramics that possess grain size distributions similar to those of physiological bone (i.e., less than 100 nm in diameter). The present series of studies demonstrated that, compared to conventional (that is, grain sizes greater than 100 nm) formulations, nanophase ceramics (specifically, alumina, titania, and hydroxyapatite) exhibited bending properties on the same order of magnitude as physiological bone. Most important, compared to conventional ceramics, the functions (such as adhesion, proliferation, and deposition of calcium-containing mineral) of osteoblasts (the bone-forming cells) were significantly enhanced while functions of fibroblasts (cells that contribute to fibrous encapsulation and callus formation events that lead to implant loosening and failure) were minimized on all nanophase ceramics tested. These studies also provided the first evidence of enhanced functions (specifically, synthesis of tartrate-resistant acid-phosphatase and formation of bone-resorption pits) of osteoclasts (the bone-resorbing cells) on nanophase compared to conventional ceramics. Investigation of the mechanism(s) of the observed, select, enhanced osteoblast adhesion (a crucial prerequisite for subsequent, anchorage-dependent-cell function) on all ceramic formulations tested in the present study revealed that the concentration, conformation, and bioactivity of vitronectin (a protein that mediates and promotes osteoblast adhesion) were important parameters mediating osteoblast adhesion exclusively on nanoceramics. By demonstrating that bioceramics can be designed (through, for example, control of grain size) to possess improved mechanical properties and also promote select osteoblast and osteoclast function, the results of the present study demonstrated, that nanophase ceramics have great potential to become the next generation, choice orthopaedic/dental biomaterial to enhance bonding to juxtaposed bone and, thus, increase implant efficacy.

**11:45 AM Y9.8**

**SURFACE MODIFICATION OF SUPERPARAMAGNETIC NANOPARTICLES WITH PEG FILMS AND MEMBRANE TRANSLOCATING PEPTIDES FOR PARTICLE IMPREGNATION IN CELLS.** Yong Zhang, Nathan Kohler, Miqin Zhang, University of Washington, Seattle, WA.

Surface modification of superparamagnetic nanoparticles with PEG films and membrane translocating peptides for particle impregnation in cells Yong Zhang, Nathan Kohler, and Miqin Zhang Abstract Biocompatible superparamagnetic nanoparticles such as iron oxide are widely used for medical applications such as magnetic cell separation, hyperthermic therapeutics, drug delivery, and in vivo diagnostics via the enhancement of magnetic resonance imaging contrast. For these applications, a technique able to efficiently incorporate the superparamagnetic nanoparticles into the cells is highly desirable. In this work, we have developed a simple and effective technique to modify superparamagnetic iron nanoparticles with PEG films and membrane translocating peptides, which allow the impregnation of the nanoparticles in non-specific or specific cells, respectively. PEG and PEG-fluorescein were chemically immobilized on the surfaces of superparamagnetic iron nanoparticles using a self-assembly technique, and characterized using FTIR. The immobilization of membrane translocating peptide-fluorescein on the nanoparticle surfaces was also studied. Several cell lines were cultured in the media with the PEG-fluorescein and peptide-fluorescein coated nanoparticles and the uptake of the nanoparticles into the cells were visualized using fluorescence optical and confocal microscopes.