

# SYMPOSIUM Z

## Chemistry of Nanomaterial Synthesis and Processing

March 29 - April 1, 2005

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\* Invited paper

**8:30 AM Z1.1**

**Room-Temperature Growth of Carbon Nanofibers.**

Jeffery E. Raymond, Kristin L. Gabby, Jason K. Vohs, Robert L. Paddock and Bradley D. Fahlman; Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan.

Nanostructural carbon allotropes, with tunable dimensions below 100 nm, are of increasing interest for applications such as molecular electronic devices, field-emission display panels, hydrogen storage, and micro-electromechanical systems (MEMS). Ordered carbonaceous growth typically requires high-energy methods such as arc discharge or decomposition of hydrocarbon-based precursors using laser, plasma, or thermolytic techniques. For the latter technique, temperature regimes on the order of 600-1000 °C are most common, with a few recent reports citing slightly lower temperatures using halogenated precursors, or through alkali-metal catalyzed transformation of bulk carbon allotropes. We have recently reported the lowest reported temperature to date for growth of multi-walled nanotubes (MWNTs), from the catalytic decomposition of carbon tetrachloride under high-pressure conditions. Herein, we report the growth of amorphous carbon nanofibers grown directly from metal-encapsulated dendrimer catalysts at ambient temperature/pressure conditions. Lengths of the nanofibers range from 15 - 20 nm, with lengths in excess of 20 microns. We will discuss the proposed mechanism for our mild process, as well as ongoing research to control the morphology of the nanostructures.

**8:45 AM Z1.2**

**Continuous Spinning of a Single-Walled Carbon Nanotube-Nylon Composite Fiber and Large Scale Fabrication of Aligned Single-Walled Carbon Nanotube Assembly.** Robert C. Haddon<sup>1</sup>, Junbo Gao<sup>1,2</sup>, Mikhail Itkis<sup>1</sup>, Elena Bekyarova<sup>1</sup>, Aiping Yu<sup>1</sup>, Bin Zhao<sup>1</sup> and Sandip Niyogi<sup>1</sup>; <sup>1</sup>Center for Nanoscale Science and Engineering, Departments of Chemistry and Chemical & Environmental Engineering, University of California, Riverside, California; <sup>2</sup>Carbon Solutions, Inc, Riverside, California.

The high tensile strength, unique electrical and thermal properties and nanometer-scale dimensions of single-walled carbon nanotubes (SWNTs) make them ideal candidates for polymer composite reinforcing agents and 1-D nanowires for electronic devices. The limited solubility and graphene-like atomically smooth, non-reactive surface of the SWNTs usually leads to an inhomogeneous SWNT distribution and a weak SWNT-matrix interfacial interaction in composites. Furthermore it is extremely difficult to align SWNTs along predetermined directions in a form suitable for nanoelectronic devices. In the first part of this talk, we will present a chemical process for SWNT-nylon composite synthesis that allows the continuous spinning of single-walled carbon nanotube (SWNT)-nylon 6 (PA6) fibers by the in-situ polymerization of caprolactam in the presence of SWNTs which simultaneously optimizes the morphology of the composite. We show that caprolactam is an excellent solvent for carboxylic acid-functionalized SWNTs (SWNT-COOH), and that this allows the efficient dispersal of the SWNTs and subsequent grafting of PA6 chains to the SWNTs through condensation reactions between the carboxylic acid group on SWNT-COOH and the terminal amine group of PA6. The existence of a graft copolymer between the PA6 chains and the SWNTs is demonstrated by IR, TGA, AFM studies, and we show that the solubility of the polymerized material in formic acid is controlled by the degree of graft copolymerization. The amount of grafted PA6 chains which are attached to the SWNTs can be adjusted by controlling the concentration of the initiator (6-aminocaproic acid). The process leads to a uniform dispersal of the SWNTs, and the presence of the graft copolymer increases the polymer/SWNT compatibility while strengthening the interfacial interaction between filler and matrix. The Young's modulus, tensile strength and thermal stability of pure nylon 6 are significantly improved in the continuous fibers that can be produced by this process, which can be readily scaled to produce fibers of any length and diameter. In the second part of the talk, we will demonstrate a method to fabricate SWNT assemblies in which we simultaneously realize the directional control of SWNT alignment and the de-bundling of SWNTs into individual tubes. We make use of the electrospinning technique to fabricate aligned SWNTs/polymer composite fibers, and the high fiber elongation and high DC electric field applied during the electrospinning process results in the orientation of the SWNTs along the axial direction of the fiber. The alignment of the electrospun composite fiber transfers this local SWNT orientation to macroscopically aligned SWNTs. After removing the polymer component from the aligned composite fiber by heating or chemical vapor etching, large area aligned SWNTs are produced.

**9:15 AM Z1.3**

**Optical Properties of Aligned Arrays of Multiwalled Carbon Nanotubes.** Brian Ralph Kimball<sup>1</sup>, Joel B. Carlson<sup>1</sup>, Diane

Steeves<sup>1</sup>, Krzysztof Kempa<sup>2</sup>, Zhifeng Ren<sup>2</sup>, Pengfei Wu<sup>3</sup>, D. V. G. L. N. Rao<sup>3</sup>, Glenda Benham<sup>4</sup>, A. Herczynski<sup>2</sup>, Thomas Kempa<sup>2</sup>, Wenzhi Li<sup>2</sup>, J. Rybczynski<sup>2</sup> and Yang Wang<sup>2</sup>; <sup>1</sup>Nanomaterials Science Team, US Army Natick Soldier Center, Natick, Massachusetts; <sup>2</sup>Physics Department, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>Physics Department, University of Massachusetts, Boston, Massachusetts; <sup>4</sup>MegaWave Corporation, Boylston, Massachusetts; <sup>5</sup>Physics Department, Florida International University, Miami, Florida.

Aligned carbon nanotube arrays were grown on silicon and quartz substrates using plasma enhanced chemical vapor deposition method. Both periodic and non-periodic arrays were fabricated with varying spacing and carbon nanotube height. Periodic arrays were created using self-assembly nanosphere lithography. Optical properties of the arrays were studied and related to array geometry. Diffraction and polarization studies were performed with both monochromatic and white light sources. The results indicated strong polarization dependence for both periodic and non-periodic arrays. Three dimensional diffraction maps were created that reveal the manner in which the nano-arrays interact with visible light. Polarized diffracted light is described in terms of efficiency. A peak in diffracted light intensity in the direction of the source has been experimentally observed and is reported here. We also report a polarization-dependent resonant effect due to the intra-action of visible light with nonperiodic arrays that appears as bright colors to the observer. Results indicate that visible light interacts with the aligned arrays similar to the way in which radio waves interact with a radio antenna. Periodic CNT arrays such as these have the potential for applications in optical computing and energy conversion

**9:45 AM Z1.4**

**Carbon Nanotubes: Synthesis, Properties and New Directions.** Hongjie Dai, Department of Chemistry, Stanford University, Stanford, California.

This talk will present our latest research on single walled carbon nanotubes. We have been using carbon nanotube as a model system to study interesting nanoscale problems concerning materials synthesis, solid-state physics and devices, and surface science. This presentation will cover our latest results in, (1) Controlled synthesis of nanotubes. (2) Ballistic electron transport in both metallic and semiconducting nanotubes. (3) Pushing the performance limit of nanotube transistors, and (4) quantum transport phenomena, (5)interfacing carbon nanotubes with biological systems

**10:30 AM Z1.5**

**Electronics and Optoelectronics with Single Carbon Nanotubes.** Phaedon Avouris, Physical Sciences, IBM T.J. Watson Research Center, Yorktown Heights, New York.

Carbon nanotubes (CNTs) are one-dimensional nanostructures with unique properties that make them ideal for applications in nanoelectronics and optoelectronics. Particularly strong emphasis has been placed on the fabrication and optimization of carbon nanotube field-effect transistors (CNTFETs). In general, charge-transfer at the CNT-metal interfaces leads to band-bending and the formation of Schottky (SB) barriers, which adversely affect the performance of the FET, in particular the gate swing. Another bothersome effect appears upon scaling of the gate insulator thickness ( $t_{ox}$ ). At small  $t_{ox}$ , unipolar CNTFETs turn ambipolar with large OFF currents. We have been able to eliminate these remaining problems by: (a) electrostatic doping of the contact regions in double-gate CNTFET devices, and (b) chemical doping through charge-transfer interactions with adsorbed molecules. The resulting unipolar CNTFETs have outstanding operational characteristics exceeding those of the state-of-the-art silicon devices. While ambipolar (a-) CNTFETs may be undesirable in logic applications, they are particularly valuable for photonic applications. We have used a-CNTFETs to simultaneously inject electrons and holes from the opposite terminals of the FET. A fraction of these confined carriers recombine by a radiative process. This allowed us to produce an electrically-excited and controlled single nanotube molecule light source. The spectra, polarization, and dependence on applied bias of the radiative recombination process were determined. Unlike conventional p-n diodes, a-CNTFETs are not doped and there is no fixed p-n interface. By spatially resolving the emission we found that the emitting region can be translated at will (by at least 100 micrometers) along a CNTFET channel by varying the gate voltage. Study of the properties of the emission as a function of applied bias provides new insights on the electrical transport in CNTs. Stationary light spots are also observed and their generation mechanism involving defects is analyzed. Finally, I will demonstrate the reverse process of recombination, i.e. the photogeneration of e-h pairs in the single CNTFET channel. The corresponding

photoconductivity spectra provide information on the nature of the excited states of the CNTs and the difference between optical transition energies and the electrical band-gap.

**11:00 AM \*Z1.6**

**Carbon Nanotubes for Highly Efficient Transfection in Mammalian Cells.** Dong Cai<sup>1</sup>, J. Mataraza<sup>2</sup>, J.-Y. Huang<sup>3</sup>, Zh-P. Huang<sup>1</sup>, T. Chiles<sup>2</sup>, David Carnahan<sup>1</sup>, K. Kempa<sup>3</sup> and Zh-F. Ren<sup>3</sup>; <sup>1</sup>NanoLab Inc, Newton, Massachusetts; <sup>2</sup>Biology Department, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>Physics Department, Boston College, Chestnut Hill, Massachusetts.

Vertically aligned nanotubes grown by plasma enhanced chemical vapor deposition have ferromagnetic catalyst particles of Co, Fe, or Ni, located in their tips. Therefore, nanotubes can be accelerated when placed in a magnetic field. We show, that nanotubes in a solution can be driven by a magnetic field to penetrate cell membranes, which remain intact after the spearing. We found, that varied in time polarization of the magnetic field enhances the effect, and that there are no significant differences in viabilities of speared cells, and those from a control group. Gene transfection was conducted with green fluorescent protein (GFP) plasmids immobilized on the spearing nanotubes, and a very high transfection efficiency, up to 100% in lymphoma cells, was achieved. This study is the first step in the development of a magnetically drivable nano-vehicle, which could deliver various molecules, such as DNA and proteins, directly to selected cells. This would revolutionize the biomolecule and drug delivery.

**11:30 AM \*Z1.7**

**Synthesis and Characterization of Double-Walled Carbon Nanotubes and their Field Emission Properties.** Cheol Jin Lee, Su Hwan Lee, Seong Il Jung, Tae Jae Lee, Sang Kyu Choi, Chang Bae Kong, Jung Hee Cho, Hyun Jung Kang, Gwangmin Kwon and Sung Ho Seo; Department of Nanotechnology, Hanyang University, Seoul, South Korea.

We demonstrate the synthesis and characterization of high-quality double-walled carbon nanotubes (DWNTs) using a catalytic chemical vapor deposition (CVD) method and a hydrogen arc discharge method. For the synthesis of DWNTs using a catalytic CVD, we used various carbon containing molecules such as benzene, alcohol, hexane, propanol, THF over Fe-Mo embedded MgO or Al<sub>2</sub>O<sub>3</sub> support material. The produced carbon materials indicated high-purity DWNTs bundles free of amorphous carbon covering on the surface. The diameters of DWNTs were mainly dependent on carbon sources, support materials, catalyst concentration and growth temperature. Typically, DWNTs had larger diameters over 2.5 nm and the large interlayer spacing of 0.35 - 0.5 nm. By adopting a hydrogen arc discharge method, we could obtain high-purity DWNTs in large scale. In this work, we used FeS and Fe bicatalyst to promote the synthesis of DWNTs. The purity and yield of the produced DWNTs were largely dependent on catalyst concentration and reaction pressure. TEM, Raman analysis and TGA showed that the produced carbon materials had high purity and low defect level. To evaluate field emission properties from DWNTs, we distributed DWNTs on Ti coated Si substrate using a spray method. Field emission from DWNTs indicated the low turn-on voltage about 2-3 V/ $\mu$ m and the high emission current density of several mA/cm<sup>2</sup> similar to SWNTs. Moreover they showed high emission stability like MWNTs. The emission current density mainly dependent on the density of DWNTs on Si substrate. We will discuss field emission properties from DWNTs in detail.

**SESSION Z2: One-Dimensional nanostructures II:  
Nanowires and Nanotubes**

Chairs: William Buhro and Peidong Yang  
Tuesday Afternoon, March 29, 2005  
Room 3016 (Moscone West)

**1:30 PM \*Z2.1**

**High-Yield Catalytic Synthesis of Thin Multi-Walled Carbon Nanotubes.** Young Hee Lee, Physics Department and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon, South Korea.

We have synthesized thin multi-walled carbon nanotubes (t-MWNTs) using a catalytic chemical vapor deposition (CCVD) method with FeMoMgO catalyst. The number of tube walls were 2 ~ 6 with the corresponding diameters of 3 ~ 6 nm. We obtained high production yield of over 3000 wt% compared to the weight of the supplied catalyst. These t-MWNTs revealed the intermediate structural characteristics between single- and multi-walled carbon nanotubes (SWNTs and MWNTs). Critical issues for high yield synthesis of t-MWNTs were further discussed in terms of reduction procedure, growth time, and gas species. Application of this material to field

emitters will be further discussed in comparison with those of singlewalled and multiwalled carbon nanotubes.

**2:00 PM Z2.2**

**Characterizations of Carbon Aerogels and Their Structurally-Modified Derivatives.** Dafei Kang<sup>1</sup>, Ying Zhang<sup>2</sup>, Carl D. Saquing<sup>2</sup>, Can Erkey<sup>2</sup> and Mark Aindow<sup>2</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Carbon aerogels (CAs) are a type of novel nanoporous material, with open porosity the length scale of which is adjustable at nanometer scale. CAs are characterized by high specific surface area, low mass density, and high electrical conductivity, which makes them particularly well suitable for various applications ranging from electrode materials in supercapacitors and fuel cells, to host material such as heterogeneous catalyst support. The morphology of carbon aerogels can be modified as a function of the different synthesis variables. In this work, we will present some recent progress on the comprehensive characterization of carbon aerogels prepared with controlled conditions. Some instrumentations used are: high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), Raman infra-red spectrometry, liquid nitrogen adsorption/desorption, etc. Further information is given in the structural modification of as-synthesized carbon aerogels for a selected array of potential applications.

**2:15 PM Z2.3**

**Formation of Piezoelectric Single-Crystal Nanorings and Nanobows.** William L. Hughes and Zhong Lin Wang; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Bending of polar-surface-dominated (PSD) nanobelts of ZnO can be explained by one of two processes: electrostatic neutralization of the dipole moment via deformation (called an electrostatic polar-charge model), or imbalances between surface tensions via surface-terminated induced stresses. This work presents experimental data on the structural features of nanorings and nanobows formed by bending single-crystal, PSD ZnO nanobelts. Our data exclusively supports the electrostatic polar-charge model as the dominant mechanism for bending. We first present nanorings and nanobows that are formed by bending PSD nanobelts with a radial direction (originated from the ring center) of  $\pm[0001]$ . The inner surface of the rings can be oxygen-terminated (000-1) or Zn-terminated (0001). A model calculation is then given for predicting the thickness-to-radius ratio of nanorings formed by the spontaneous polar-charge model. The results of the calculation are in excellent agreement with experimental data. The surface charge density of ZnO  $\pm(0001)$  is derived to be  $\sigma = \pm 0.033 \text{ C/m}^2$ , demonstrating an experimental approach for measuring the surface charge density on the polar surfaces of nanobelts. Finally, we illustrate a PSD, single-crystal, zig-zag structure of ZnO, which is a result of growth kinetics. The nanorings and nanobows of single-crystal ZnO presented here are potential candidates for applications in nano-scale sensors, transducers and electro-mechanical coupling devices. [1] W.L. Hughes and Z.L. Wang "Formation of Piezoelectric Single-Crystal Nanorings and Nanobows", J. Am. Chem. Soc., 126 (2004) 6703-6709. [2] For information see [www.nanoscience.gatech.edu/zlwang](http://www.nanoscience.gatech.edu/zlwang)

**2:30 PM Z2.4**

**Hierarchically Templated Synthesis of Highly Ordered Mesostructured Nanowires and Nanowire Arrays.** Yiyang Wu, Tsachi Livneh, Martin Moskovits and Galen D. Stucky; Chemistry, UC Santa Barbara, Santa Barbara, California.

Nanowires have attracted extensive interest in view of their interesting electronic and optical properties, and potential applications as building blocks for nanoelectronic and nanophotonic devices. Here we present a broadly applicable methodology that utilizes confined mesoporous silica as a template for preparing highly ordered mesostructured nanowires with meso-ordering periodicity of  $\sim 13$  nm. The prepared Ag, Ni, and Cu<sub>2</sub>O nanowires, with unprecedented mesostructures of coaxially multi-layered helical, and stacked-donuts structures, have the unique features of hierarchical organization, modulated surface morphology, high surface area, and chirality. This method based on electrochemical deposition can be readily applied to the preparation of nanowires of a broad of materials: metals, semiconductors, oxides and polymers. Specifically, we demonstrate the effectiveness of the Ag mesostructured nanowires synthesized using this technique as nano-engineered substrates for surface-enhanced Raman spectroscopy (SERS). Compared to those for solid nanowires, the SERS spectra from rhodamine 6G (R6G) molecules adsorbed on an aligned mesostructured nanowire bundle show significantly less sensitivity to the excitation light polarization, due to their unique modulated surface morphologies.

2:45 PM Z2.5

### **Germanium-Catalyzed Growth of Zinc Oxide Nanowires: A Semiconductor Catalyst for Nanowire Synthesis.**

Zhengwei Pan<sup>1</sup>, Sheng Dai<sup>2</sup>, Christopher M. Rouleau<sup>1</sup> and Douglas H. Lowndes<sup>1</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The vapor-liquid-solid (VLS) crystal growth mechanism [1] has been widely used to guide the growth of a wide range of semiconductor [2,3] and oxide [4,5] nanowires. In this mechanism, a catalyst nanoparticle serves as a preferential site for absorbing and dissolving reactants from the vapor phase, directs the growth direction of the nanowire, and defines the diameter of the nanowire. The catalysts used so far are metals, with the most popular ones being gold and iron. Here we report that germanium, a group-IV semiconductor, can be used as an efficient catalyst for high-yield growth of very long, extremely straight, and quasi-aligned arrays of ZnO nanowires. The germanium-catalyzed ZnO nanowires are structurally uniform and single-crystalline, with lengths of up to several hundred micrometers and diameters ranging from 50 to 400 nanometers. The nanowires are terminated at their growing ends with large germanium particles (0.5 to 4 micrometers) having diameters about 5 to 15 times that of the nanowires. Furthermore, patterned growth of ZnO nanorods was achieved on photolithographically-prepared germanium-dot patterns, further confirming the catalytic effect of germanium on ZnO nanowire growth. [1] R.S. Wagner and W.C. Ellis, *Appl. Phys. Lett.* 4, 89 (1964). [2] A.M. Morales and C.M. Lieber, *Science* 279, 208 (1998). [3] J. Westwater, D.P. Gosain, S. Tomiya, S. Usui, and H. Ruda, *J. Vac. Sci. Technol. B* 15, 554 (1997). [4] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science* 292, 1897 (2001). [5] H. T. Ng, J. Li, M. K. Smith, P. Nguyen, A. Cassell, J. Han, M. Meyyappan, *Science* 300, 1249 (2003). [6]

3:00 PM Z2.6

### **Integrated Metal-catalyzed Bridging Silicon Nanowires.**

Shashank Sharma, M. Saif Islam, Theodore I. Kamins and R. Stanley Williams; Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

Nanometer-scale Ti-silicide islands and Au-Si eutectic droplets have been previously shown to catalyze the growth of silicon in one dimension to form free-standing nanowires by chemical vapor deposition (CVD). The nanowires typically grow epitaxially along the  $\langle 111 \rangle$  crystallographic directions, therefore, perpendicular to  $\{111\}$ -oriented silicon surfaces. We have demonstrated lateral growth of Au- and Ti-catalyzed silicon nanowires from a vertical sidewall of a trench on a silicon-on-insulator (SOI) substrate ( $\{011\}$ -oriented silicon layer). Upon impinging on the other sidewall, the nanowires attach to this "opposing" sidewall, thus bridging across the trench and making strong mechanical connection. The nature of the connection at the impinging end will partially determine the electrical and mechanical behavior of the electronic device. We will report current-voltage (I-V) measurements of Au-catalyzed silicon nanowires that were doped during the growth using diborane mixed with the SiH<sub>4</sub>/HCl/H<sub>2</sub> ambient in the CVD reactor. The I-V dependence was observed to be linear, indicating good electrical contact formed in-situ between the nanowires and the electrodes. I-V measurements also indicated boron concentrations in thicker nanowires (diameter >100 nm) in the mid-1018 cm<sup>-3</sup> range, corresponding to those observed for epitaxial silicon deposition on a plane silicon surface, with boron concentration increasing with increasing diborane partial pressure in the gas phase. To understand the electrical characteristics of the bridging connection at the opposing sidewall, we observed this connection using high-resolution transmission electron microscopy (TEM) to be epitaxial and coherent silicon-to-silicon. We will also demonstrate selective growth of Au- and Ti-catalyzed silicon nanowires on vertical silicon surfaces compared to horizontal silicon dioxide surfaces. In the case of Au-catalyzed nanowires, for a particular set of annealing conditions and nanowire growth conditions, there is a critical Au film thickness, below which we did not observe nanowire growth. We used angled evaporation of Au to utilize this observation to enable nanowire growth selectively on vertical surfaces. In the case of Ti-catalyzed nanowires, the desired selectivity was achieved by CVD of Ti using liquid TiCl<sub>4</sub> source. Controlled, selective growth of nanowires in particular geometries within a device is critical to enable functional devices, such as sensors, based on bridging semiconductor nanowires.

3:30 PM \*Z2.7

### **Structure Analysis of Nanowires and Nanobelts.**

Zhong L. Wang and Yong Ding; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

One-dimensional (1D) nanostructures, such as nanowires, nanobelts and nanorods, are attracting a great deal of research interest due to their unique properties and novel applications. Structure analysis of

1D nanostructures is an essential part of research because achieving structural control is the key step in controlling properties and device performances. Using ZnO, CdSe and ZnS as examples, this paper addresses the technical details of how to use transmission electron microscopy for correctly analyzing the structure of nanowires and nanobelts, including growth direction, side/top surfaces, surface polar direction, surface reconstruction, point defects, dislocations, planar defects, and twin/bicrystal structures. The methodologies introduced can be applied to a wide range of 1D nanostructures. [1] Y. Ding and Z.L. Wang "Structure Analysis of Nanowires and Nanobelts by Transmission Electron Microscopy", *J. Phys. Chem. B*, 108 (2004) 12280-12291. [2] *Electron Microscopy of Nanotubes*, edited by Z.L. Wang, C. Hui, Kluwer Academic Publisher (2003). [3] *Nanowires and Nanobelts - materials, properties and devices*; Vol. I: Metal and Semiconductor Nanowires, edited by Z.L. Wang, Kluwer Academic Publisher (2003). [4] *Nanowires and Nanobelts - materials, properties and devices*; Vol. II: Nanowires and Nanobelts of Functional Materials, edited by Z.L. Wang, Kluwer Academic Publisher (2003). [5] *Handbooks of Microscopy for Nanotechnology*, edited by Nan Yao and Z.L. Wang, Springer (2004). [6] For details please visit: [www.nanoscience.gatech.edu/zlwang](http://www.nanoscience.gatech.edu/zlwang)

4:00 PM \*Z2.8

### **Role of Facet-Sensitive Reactivity in Promoting Nanorod, Nanodisk and Nanowire Growth.**

Brian A. Korgel, Aaron Saunders, Felice Shieh, Michael Sigman and Ali Ghezelbash; Chemical Engineering, University of Texas at Austin, Austin, Texas.

It is now well-established that arrested precipitation can yield anisotropic nanocrystals, such as rods, disks, wires, and even tetrapods for semiconductor and metal materials with anisotropic crystal structure. A general understanding of the crystallization and colloidal growth processes, however, remains somewhat elusive. One of the most prevalent ideas relates to the concept of facet-sensitive capping ligand adsorption, which is believed to aid the growth of the nanostructure along a preferred crystallographic orientation while inhibiting growth along others. Another idea relates to the role of precursor supersaturation and crystallization kinetics on nanocrystal shape. Although ligand-crystal adsorption and supersaturation are certainly important (and perhaps related), we have found that facet-sensitive reactivity appears to be the dominant factor that controls shape anisotropy in a variety of nanocrystals, including the cadmium chalcogenides (CdS, CdSe, CdTe), and other metal sulfides, such as Cu<sub>2</sub>S, NiS, and Bi<sub>2</sub>S<sub>3</sub> produced by arrested precipitation in solution and solventless environments. In the case of the cadmium chalcogenides, anisotropic nanorod and nanowire growth can be promoted in solution by using a sequential precursor injection route, in which seed particles are first nucleated and then "added to" epitaxially by the addition of more precursor. The  $\{002\}$  planes of the hexagonal crystal structure are reactive and promote crystal growth preferentially along the c-axis. The sequential injection approach is sufficiently general to create nanorod heterostructures consisting of a core of CdSe with ends of CdTe for example. Dark field STEM images of these nanorod heterostructures that confirm their formation will be presented. In the solventless environment, the nanocrystal morphology (i.e., nanorod, nanodisk or nanowire) depends on the nature of the material and the existence of preferred crystallization directions. For example, hexagonal Cu<sub>2</sub>S forms nanodisks, with growth quenched in the  $[002]$  direction, whereas orthorhombic Bi<sub>2</sub>S<sub>3</sub> forms high aspect ratio nanowires (>100) extended in the  $[110]$  direction. The influence of the crystal structure, reaction conditions, and the interplay of facet-sensitive reactivity on the nanocrystal morphology—as well as how to control them synthetically—will be presented.

4:30 PM Z2.9

### **Ternary Semiconductor Nanowire Arrays For Optoelectronic Applications.**

Qiguang Li and Reginald Penner; Chemistry, UC Irvine, Irvine, California.

The efficiency of a light emission device is determined both by the internal factors, such as the chemical nature of the material, and external factors, such as the shape and dimension affecting the re-absorption of the emitted light. Here we designed a new type of nanowire arrays to improve both the internal efficiency and the external efficiency. The ternary semiconductor compound, Cd<sub>x</sub>Se<sub>1-x</sub>, has adjustable band gap, high quantum efficiency and fast response time, compared to the corresponding binary compounds. In this work, Cd<sub>x</sub>Se<sub>1-x</sub> nanowires were synthesized by a two-step method: First, electrochemical step edge decoration (ESED) was employed to deposit CdSe nanowires onto highly ordered pyrolytic graphite (HOPG) surface. Second, the electrodeposited CdSe nanowires were exposed to H<sub>2</sub>S at elevated temperatures to fabricate Cd<sub>x</sub>Se<sub>1-x</sub> nanowires by diffusing sulfur into the nanowire body. The nanowires fabricated by this method are hemispherical in shape, continuous over 50 μm and organized into arrays, with their diameters controlled from 20 nm to 300 nm by the electrodeposition duration. The rough convex surface of the nanowires can minimize the internal

reflection of the emitted light. The re-absorption of the emitted light can be reduced both by its nanoscale dimension and by creating a bandgap gradient, with the bandgap of the material increasing from center to the surface, realized by the sulfur concentration gradient. The photoluminescence spectra of these nanowires with various compositions have confirmed their band gap adjustability and high quantum efficiency. Light emission can be adjusted from 1.85eV to 2.45eV when increasing the sulfur concentration in the nanowires. The emission intensity is more than 50 times stronger than their binary counterparts with similar shape and crystal structures. This high quantum efficiency is due to the localized excitons bounded to compositional defects, which suppress the energy migration to nonradiative recombination and thus increase the radiative recombination probability. The  $\text{CdS}_x\text{Se}_{1-x}$  nanowires can be easily transferred from conductive HOPG surface to an insulator surface for device fabrication purpose. The electrical measurement shows these nanowires are electrically continuous and have photoconductivity. These strong emissions ranging from red to green and the photoconductive nature make these nanowires promising for optoelectronic applications.

4:45 PM **Z2.10**

**Issues in the Synthesis of III-Nitride Heterostructure Nanowires via MOCVD.** George T. Wang, J. Randall Creighton and Paula P. Provencio; Sandia National Laboratories, Albuquerque, New Mexico.

Nanowires based on the direct bandgap semiconductor Group III nitride (AlGaInN) materials system are attractive due to their potential in novel optoelectronic applications, including LEDs, lasers, high power transistors, and sensors. We have employed a MOCVD process to synthesize single-crystalline GaN nanowires in a standard cold-wall rotating disk reactor on 2-inch diameter wafer substrates coated with Ni catalysts. Notably, we have also been able to synthesize using MOCVD novel core-shell heterostructure nanowires consisting of a GaN cores and various III-nitride shell materials, including AlN, InN, and AlGaIn, and InGaIn. In this presentation, several challenges and issues regarding control of the growth process will be discussed, including selectivity of VLS growth versus film nucleation, control of nanowire alignment and spacing, and effects of various process variables. Additionally, the ability to control shell-layer uniformity in heterostructure nanowires will be discussed. The growth processes and reactor environment employed in this study are typical of those used to synthesize device-quality III-nitride films and should be scalable to larger commercial reactors and substrates. Data on the optoelectronic and electrical properties of the nanowires and heterostructure nanowires will also be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

SESSION Z3: Poster Session: Synthesis,  
Characterization, and Applications of Nanostructures  
Chair: James Voigt  
Tuesday Evening, March 29, 2005  
8:00 PM  
Salons 8-15 (Marriott)

### **Z3.1**

**Improved Crystallinity of Zinc Sulfide Nanoparticles in Aqueous Environment.** Navendu Goswami and P. Sen; School of Physical Sciences, Jawaharlal Nehru University, New Delhi, Delhi, India.

The thermodynamic behavior of nanoparticles differs from their bulk counterpart due to the surface free energy term  $\gamma A$  - the product of the surface (or interfacial) free energy and the surface (or interfacial) area. Due to larger surface to volume ratio, surface contribution to the total energy becomes more important for smaller particles. Therefore, the surface energy plays a vital role in deciding the final structure of these nanoscale-materials [1-2]. Here we present direct evidence of water-induced structure buildup and stabilization of nanocrystalline ZnS. Free-standing ZnS nanoparticles are synthesized by employing the exploding wire method, also known as, electro-explosion of wire (EEW). In this method of preparation, pure ZnS particles in the size range 1.67 - 3.86 nm are stabilized through electro-explosion of Zn wires in a sodium sulfide solution. Broadening of the characteristic x-ray powder diffraction (XRD) lines reveal the reduced-size nature of ZnS particles. Moreover, changes in the XRD data were observed on keeping in water after the explosion. This illustrates the remarkable structural development of ZnS derived in this fashion, in an aqueous environment. Real space topographic images recorded by atomic force microscope (AFM) partly reflect the particle sizes but show aggregation. Fourier transform infrared (FTIR) spectroscopy allows us to establish the principal cause of this

stabilization through evolution of hydrogen-bonded sulfur peaks and oxygen-bonded metal peaks whose intensity and peak positions scale with the amount of ZnS prepared. Our non-equilibrium route of preparation enhances the surface energy term of ZnS nanoparticles and hence, provides an ideal platform to investigate its influence in microscopic details. The results presented here demonstrate the role of S-H interactions in the time-evolution of crystalline behavior of these particles [3]. These particles may possibly be used as an ideal water sensor due to the observed gigantic changes seen in XRD and FTIR. [1] H. Zhang, B. Gilbert, F. Huang, J. F. Banfield, *Nature* 424 (2003) 1025. [2] F. Huang, B. Gilbert, H. Zhang, J. F. Banfield, *Phys. Rev. Lett.* 92 (2004) 155501. [3] Navendu Goswami & P. Sen, *Volume 132, Issue 11, pp. 791-794 Solid State Communications* (DOI information 10.1016/j.ssc.2004.09.022)

### **Z3.2**

**Synthetic Chemistry on Controlling the Structure of Cerium-Titanium Composite Oxide Nanoparticles.** Jin Lu<sup>2</sup>, Curt A. Hoffman<sup>1</sup>, Yie-Shein Her<sup>1</sup> and Xiangdong Feng<sup>1,2</sup>;

<sup>1</sup>Electronic Materials System, Ferro Corporation, Independence, Ohio; <sup>2</sup>CAMP, Clarkson University, Potsdam, New York.

Nano-ceria and its composite particles have generated lots of interest due to their unique physical and chemical properties and multiple applications such as solid electrolytes in oxide fuel cells, catalysts, optical additives, cosmetic materials, and abrasives for chemical mechanical planarization. However, the synthetic chemistry and particle formation mechanism are still not well understood. The physical and chemical properties prepared from various chemical processes differed significantly due to the presence of different chemical speciation, which promote different chemical reactions and impact different nuclei formation and growth of the particles. In this paper, we present a systematic study of the chemical species and their reaction mechanism during hydrothermal synthesis of cerium-titanium composite oxide nanocrystalline particles starting from cerium (IV) ammonia nitrate, titanium isopropoxide, acetyl acetone, and ammonia hydroxide solution. Each reaction step and chemical intermediate are studied using GC-MS, FT IR, 1H NMR, 13C NMR, XPS, XRD, SEM, and TEM. This study confirms that the hydrothermal synthesis of the cerium-titanium composite oxide nanoparticles consists of the following four steps: 1. Titanium di-acetylacetone isopropoxide is formed through ligand exchange reaction between acetyl acetone and Ti(iso-Pro)4 to enhance the stability of the starting materials in an aqueous system 2. Formation of homogenous Ce(IV)/III)/Ti(IV) solution or coupled =Ce-O-Ti= molecular solution to promote uniform distribution of Ce and Ti before hydrolysis 3. Formation of mixed hydroxide HO-Ce-O-Ti-O-Ce-OH by reaction with ammonium hydroxide before hydrothermal treatment 4. Conversion of mixed hydroxide into composite oxides O-Ce-O-Ti-O-Ce-O through in situ dissolution and recrystallization A good understanding of these chemical speciation and reaction mechanism enables us to have precise control of the nanoparticle structure (primary and secondary particle sizes, particle shape, and crystallinity) and also improve the production efficiency and economics in commercializing the nanoparticles.

### **Z3.3**

**Sol Gel Preparation of Ta2O5 Nanorods using DNA as Structure-Directing Agent.** Carlos Alberto Martinez<sup>1</sup>, Perla Elvia Garcia<sup>1</sup>, Humberto Alejandro Monreal<sup>2</sup> and Alberto Martinez-Villafane<sup>2</sup>; <sup>1</sup>Ciencias Basicas del IIT, Universidad Autonoma de Cd. Juarez, Juarez, Chihuahua, Mexico; <sup>2</sup>Deterioro de Materiales, Centro de Investigacion en Materiales Avanzados, Chihuahua, Chihuahua, Mexico.

Nanostructured materials have attracted considerable attention because of their novel properties and applications unlike those of conventional macroscopic materials. Recent progress in the synthesis and characterization of nanowires and nanorods has been driven by the need to understand the novel physical properties of onedimensional(1-D) nanomaterials, and their potential applications in constructing nanoscale electronic and optoelectronic devices. In particular, nanostructured materials transition-metal oxides such as tantalum, titanium, and vanadium oxides are generally accepted as the next generation materials in fields such as electronics, and advanced catalysts. There are several reports on the preparation of TiO2 particles of nanometer size, otherwise, there are a few reports in the preparations of tantalum and vanadium oxides materials in the nanoscale size. In this work we present an easy route for the synthesis of Ta2O5 nanorods by sol gel method using circular DNA as directing agent, the DNA used as template was extract from the plasmid pBR322 4,361 pb. The size of the nanorods were in the order of 40 to 150 nm in diameter and several microns in length. This easy preparation method can be useful in the synthesis of nanomaterials for electronics and optoelectronics as well as catalysts.

### Z3.4

**Space Charge Conduction in Gallium Arsenide Nanowires and the Meyer Neldel Rule for DC Conductivity in Gallium Arsenide, Germanium Nanowires and Bi<sub>2</sub>S<sub>3</sub> Nanowire Bundles.** April Dawn Schricker, Forrest M. Davidson, Michael B. Sigman, Tobias Hanrath and Brian A. Korgel; Chemical Engineering, Center for Nano- and Molecular Science and Technology, and Texas Materials Institute, University of Texas, Austin, Texas.

Large quantities of nanowires can easily be synthesized and used as active components in device structures for various applications, including sensing, information storage, computing, thermoelectric refrigeration, photovoltaics, and illumination. For these applications, having a thorough understanding of nanowire electrical properties is critical. Although electrical transport through bulk semiconductors and heterostructures is very well-studied, there is currently little data on the transport properties of single-crystal semiconductor nanowires. In this work, the temperature dependent electrical properties of GaAs, Ge nanowires and Bi<sub>2</sub>S<sub>3</sub> nanowire bundles were investigated and compared. The GaAs and Ge nanowires were synthesized by the supercritical fluid-liquid-solid (SFLS) approach seeded by gold nanoparticles where as the Bi<sub>2</sub>S<sub>3</sub> was synthesized by a solventless synthesis technique. In each case, the nanowires were deposited on device substrates pre-patterned by electron beam lithography (EBL) with Au/Cr contact electrode arrays. Electrical contact between the nanowires and the electrode arrays was made by depositing local Pt interconnects using focused ion beam (FIB) assisted metal deposition. Specifically, in the case of the GaAs, at temperatures higher than ~428 K, the current-voltage (IV) curves exhibited linear (Ohmic) behavior with activation energies for transport ranging from 0.12 to 0.18 eV, consistent with expectations for doped nanowires. At lower temperatures, the IV curves exhibited nonlinear behavior consistent with the onset of space-charge limited conduction. The observed voltage dependence of the current density,  $J \propto V^{1/2}$ , indicated that the space charge limited conduction in GaAs was controlled by trapped charge. The characteristic trap energies ranged from 0.05 eV to 0.10 eV. In addition, the Ge, GaAs nanowires and Bi<sub>2</sub>S<sub>3</sub> nanowire bundles all showed a Meyer-Neldel relationship due to variation in defect concentration from wire to wire. The Ge nanowires exhibited an inverse Meyer-Neldel behavior with a characteristic Meyer-Neldel energy ( $E_{MN}$ ) of -0.018 eV. The GaAs nanowires and Bi<sub>2</sub>S<sub>3</sub> nanowire bundles that were not annealed exhibited Meyer-Neldel behavior with an  $E_{MN}$  of 0.044 eV and 0.038 eV, respectively. In comparing the characteristic Meyer-Neldel energies of all three wire types, our results indicated that the orientation of nanowire lattice defects to current flow and thick amorphous surface coatings increase the electrically active defect concentration which increases the nanowire variability in resistivity.

### Z3.5

**Self Assembled Silver Nanoparticles on Nanostructured Surfaces for Surface Enhanced Raman Scattering.** Surojit Chattopadhyay<sup>1</sup>, Shih-Chen Shi<sup>3</sup>, Hung Chun Lo<sup>1,3</sup>, Kuei-Hsien Chen<sup>1,2</sup>, Chih-Hsun Hsu<sup>2</sup> and Li-Chyong Chen<sup>2</sup>; <sup>1</sup>Institute of Atomic and Molecular Sciences, Academia, Sinica, Taipei, Taiwan; <sup>2</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; <sup>3</sup>Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Surface enhanced Raman spectroscopy (SERS) has evolved as a powerful and sensitive tool for detection and identification of a wide range of adsorbate molecules down to the limit of single molecule detection. In this paper we report the self assembly of silver nanoparticles, with less than 10 nm diameter, on a variety of nanostructured surfaces. The surface energies offered by these templates namely, silicon nanotips (SiNNT), aluminum nitride nanotips (AlNNT), nanorods (AlNNR) and carbon nanotubes (CNT) to an incident flux of silver atoms culminates in organizing silver nanoparticles at an extremely high density on their surfaces that readily exhibit SERS. These one dimensional nanostructured templates are prepared by conventional plasma or thermal chemical vapor deposition (CVD) techniques. Silver has been deposited on these surfaces via ion beam sputtering technique. These specially prepared substrates containing the nanoparticulates on the one dimensional nanostructured surfaces are SERS active. Molecules such as Rhodamine 6G, or BPE adsorbed on these substrates show SERS reproducibly. Such small size (10 nm) silver clusters are generally prepared by wet chemical techniques which are not suitable in device processes. However our technique in generating SERS active substrates are entirely plasma based and compatible to device processes. The large surface area of the nanostructured substrates and the extreme high density of the nanoparticulates distributed on them enable the substrate to behave as reliable and reproducible SERS active substrates even at very low concentrations of the molecules under study. A range of Raman enhancement factors could be obtained using these substrates in the range of 10<sup>5</sup> to 10<sup>8</sup>.

### Z3.6

**Self-Catalyzed Growth of Gallium Nitride Nanowires.** Blake S. Simpkins<sup>1</sup>, Lars M. Ericson<sup>1</sup>, Rhonda M. Stroud<sup>2</sup> and Pehr E. Pehrsson<sup>1</sup>; <sup>1</sup>Tribology Section 6176, Naval Research Lab, Washington, District of Columbia; <sup>2</sup>Magneto-electronic Materials and Devices Section 6361, Naval Research Lab, Washington, District of Columbia.

Research activity on semiconductor nanowire (NW) structures has surged recently due to advances in growth techniques [1] and an increased demand for their applications, which include biological [2] and chemical [3] sensors. The present work describes a new method for producing self-catalyzed nanowires that has the potential to overcome several disadvantages of conventional metal catalyzed growth. In past reports on NW growth, precursor materials have been delivered in the form of metal-organics, [4] heated pure metals, [5] and even laser ablated species, [6] however, metal catalysts were also needed to initiate nucleation and growth in these studies [7] introducing the danger of chamber or wire contamination. To address these shortcomings, we have pursued the growth of GaN:NWs using a Ga-based catalyst. This novel approach will potentially simplify growth procedures and eliminate the risks of wire and chamber contamination. In this work, we will present and compare structural and electrical characterization of both gallium nitrate (Ga(NO<sub>3</sub>)<sub>3</sub>)- and Ni film-catalyzed GaN:NWs. We have employed CVD growth using NH<sub>3</sub> and metallic Ga as precursors to grow GaN:NWs on Si and a-Al<sub>2</sub>O<sub>3</sub> substrates and have grown wires using either a Ga(NO<sub>3</sub>)<sub>3</sub> solution or a Ni film as catalyst. Wire size and areal density were characterized using SEM while TEM with EDS and SAED were used for compositional and crystallographic interrogation verifying the presence of wurtzite GaN. Carrier type, density, and mobility in the wires were evaluated through gated I-V measurements. These results indicate that Ga-catalyzed growth of GaN:NWs is possible and further studies of substrate effects and growth parameters are in progress. The significance of this work can be appreciated by considering the possibility of completely catalyst-free growth of GaN:NWs. Within an MOCVD growth chamber, Ga droplets could first be accumulated on the growth surface by introducing a high flux of Ga precursor. This step would be followed by standard NW growth procedures. The Ga droplets would act as the NW catalysts completely removing the need for any ex-situ deposited catalyst. 1. X. Duan and C. M. Lieber, Adv. Mat., 12, 298 (2000). 2. G. Steinhoff, et.al., Adv. Funct. Mat. 13, 841 (2003). 3. P. Qi, et.al., Nano Lett. 3, 347 (2003). 4. T. Kuykendall, et.al., Nano Lett. 3, 1063 (2003). 5. C. H. Liang, et.al., Appl. Phys. Lett. 81, 22 (2002). 6. A. M. Morales and C. M. Lieber, Science, 279, 208 (1998). 7. R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. 4, 89 (1964).

### Z3.7

**Novel Spray Technique for the Formation of Semiconductor Nanocrystals.** Lilac Amirav and Efrat Lifshitz; Chemistry and Solid State Institute, Technion - Israel Institute of Technology, Haifa, Israel.

We present a novel spray technique for the formation and production of semiconductor nanocrystals that offers an attractive alternative to conventional production methods, epitaxial growth and colloidal synthesis. According to this spray method, mainly thermospray, aqueous or organic solutions of semiconductor salts are first sprayed into monodispersed droplets, which subsequently become solid particles by solvent evaporation. The concept of the spray process assumes that one droplet forms one product nanocrystal upon the full vaporization of the liquid. The average diameter and size distribution of the final nanocrystals can be controlled and determined by the solute concentration of the sprayed solution and the droplet size, hence by spray production parameters. The spray produced nanocrystals are collected on any selected solid support. In this presentation we shall show preliminary results that demonstrate the formation of CdS nanocrystals in the zinc blend phase. These nanocrystals were obtained in the size range of 3 to 6 nanometer with a size distribution of as low as five percents, which demonstrates the usefulness of this novel technique. In addition, we also obtained CdS crystal oval rings with a width of a few nanometers and a length varying from a few nanometers to a few hundred nanometers. The appearance of rings can serve as evidence for the potential of the novel technique to show new and previously unobserved structures. The spray technique is further characterized by several new and unique features and benefits such as: (a) production of free uncoated semiconductor nanocrystals, which have the potential of creating the densest possible assemblies; (b) the opportunity to dope the nanocrystals, enabling the combination of quantum confinement with the introduction of extra carriers or spins.

### Z3.8

**Synthesis in Supercritical Fluids of Functionalized Palladium Nanoparticles for Catalysis.** Cyril Aymonier<sup>1</sup>, Sandy Moisan<sup>1</sup>, Victor Martinez<sup>2</sup>, Stefan Mecking<sup>2</sup> and Francois Cansell<sup>1</sup>; <sup>1</sup>Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), CNRS,

Pessac Cedex, France; <sup>2</sup>Fachbereich Chemie, Universitat Konstanz, Konstanz, Germany.

Over the past decade, chemistry of nanoscale metal colloids and clusters has retained significant interest, especially in the field of catalysis. As an intermediate form between homogeneous and heterogeneous catalysis, colloidal catalysis, based on soluble transition metal nanoparticles is more and more studied [1]. One of the challenges in the development of this new kind of catalysts concerns their synthesis in a control way, mainly, in term of size, morphology, structure, chemical composition and surface properties. As a new alternative, the synthesis of functionalized palladium nanoparticles in supercritical fluids is investigated in our laboratory. Beyond an important environmental aspect, supercritical fluids exhibit a range of unusual properties that can be exploited for the development of new reactions which are, in the field of nanomaterials synthesis, different from those performed with classical way of solution chemistry. The main interest of supercritical fluids as reaction media to synthesize nanomaterial is the possibility to tune continuously the fluid properties from gas to liquid with small pressure and temperature variations [2]. Moreover, supercritical fluid technology of nanomaterials synthesis offers the possibility of massive production which is, today, one of the major limiting factors to their industrial development. After a brief overview of supercritical fluid properties and their implication in the field of nanomaterials synthesis and functionalization, we propose to describe the process, developed in our laboratory, to synthesize functionalized nanomaterials. The synthesis of functionalized palladium nanoparticles is based on a chemical transformation of a palladium precursor in supercritical CO<sub>2</sub> in presence of a functionalizing agent, being, in this study, a modified hyperbranched polyethyleneimine. Different kinds of modified hyperbranched polyethyleneimine are investigated. The influence of the process operating conditions (pressure, temperature, residence time, metal precursor concentration, metal precursor to modified hyperbranched polymer ratio) on the functionalized Pd nanoparticles properties will be presented by means of transmission electron microscopy, electron diffraction, X-ray photoelectron spectroscopy. [1] R. Sablong, U. Schlotterbeck, D. Vogt, S. Mecking, *Adv. Synth. Catal.*, 2003, 345, 333-336. [2] F. Cansell, C. Aymonier, A. Serani-Loppinet, *Curr. Opin. Solid State Mater. Sci.*, 2003, 7, 331-340.

### Z3.9

**Preparation of Nano-Materials Using Pulsed Laser Ablation and Arc Discharge in Water.** Hiroharu Kawasaki, Yoshiaki Suda and Tamiko Ohshima; Sasebo National College of Technology, Sasebo, Japan.

Interest in nanomaterials has been rapidly growing for the past several years. In particular, carbon nanomaterials including fullerene molecules, carbon nanotubes, nanohorns and nanoonions are promising new materials for a variety of potential applications. This paper describes a simple production method of carbon nanoparticles by intermittent arc discharge in water between pure graphite electrodes. The carbon nanoparticles were obtained in the form of floating powders on water surface. High resolution TEM observations of them revealed that the floating powders were of the shape of spherical carbon nanotubes and multi-walled carbon nanotubes. Spectroscopy of the intermittent arc discharge emission in water was performed to assess the arc plasma components (i.e. H, C+ etc). The result indicates that the carbon vapor produced by arc discharge is transformed to CO gas by the reaction with water. The rates between carbon soot products and graphite electrodes consumption by the arc discharge mode (dc or intermittent) in water are discussed.

### Z3.10

**Nano-Alumina Particle Dispersions in Polymers.** Dongsik Kim<sup>1</sup>, Carol F. Barry<sup>1</sup>, Julie Chen<sup>2</sup> and Joey L. Mead<sup>1</sup>;

<sup>1</sup>Plastics Engineering, U Mass Lowell, Lowell, Massachusetts;

<sup>2</sup>Mechanical Engineering, U Mass Lowell, Lowell, Massachusetts.

Nanocomposites become more important as they could have improved mechanical properties. Alumina is frequently used for strengthening purpose as filler. Although the size of filler particles is critical, breakdown of agglomerates and dispersion are the essential part of the improvements. For commercial applications, continuous process is better than batch process. Alumina/polyethyleneterephthalate (PET) nanocomposites were prepared using 38 nm nanoparticles by a twin screw extruder. The nanoparticles were dispersed up to 5 wt%. The effects of nano particles on the morphology of crystalline polymers and the effects of the crystallinity of polymers on the degree of nanoparticles dispersion in the composites were studied. The composites were sampled in front of the exit of the twin screw extruder and they were frozen for preventing change of morphology. The samples were analyzed by a transmission electron microscopy (TEM) and atomic force microscopy (AFM). The degrees of dispersion were measured with the TEM images by the image analyzing program Scion<sup>®</sup>, which measured the average particle size in the composites.

The crystallinity of PET measured by a differential scanning calorimeter (DSC) was changed by the amount of nanoparticles from 51% to 45%. These changes seem to indicate that the nanoparticles interfere with the motions of molecular chains so that the degree of crystallization in polymers was lowered. The degrees of dispersion in the different crystallinity of matrix polymers were hardly correlated.

### Z3.11

**Doping and Planar Defects in the Formation of Single-crystal ZnO Nanorings.** Yong Ding, Xiangyang Kong and Zhonglin Wang; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The important characteristics of the wurtzite structured ZnO are the non-central symmetry and the polar surfaces. However, for a general case, one-dimensional ZnO nanostructures usually grow along the c-axis and the side surfaces are {01-10} and/or {2-1-10} due to their lower energies than that of (0001), resulting in the vanishment of dipole moment and much reduced piezoelectricity. To maximize the effect of polar surfaces and the piezoelectricity, nanobelts grow along [01-10] or [2-1-10] are preferred. We have previously reported freestanding ZnO nanobelts that grow along [01-10], and we pointed out that the [01-10] nanobelts are always accompanied with basal plane stacking faults. This study indicates that energy barrier set by the polar surfaces may be overcome by basal-plane planar defects introduced by ions doping, such as In ions. Recently, we have demonstrated a large-yield and high purity growth of polar surface dominated ZnO nanobelts and nanorings by introducing In and/or Li ions in the raw material in the vapor-solid growth process. An important fact is that each and every nanoring is made of a nanobelt that has basal-plane planar defects, which are suggested to be important for leading the fastest growth of the nanobelt as well as lowering its elastic deformation energy. Using high-resolution transmission electron microscopy (HRTEM), we have investigated the nature of the planar defects in the nanobelts and in nanorings. The data show that the planar defects were initiated and formed by single-layer segregation of the doping element, such as indium, which was introduced in the growth process. The accumulation of impurity ions forms two vicinal In-O octahedral layers. They serve as head-to-head and tail-to-tail polar-inversion domain boundaries (IDBs). The defects are considered to take a key role in controlling the growth direction of the polar-nanobelt. The head-to-head and tail-to-tail paired IDBs do not change the polarity of the nanobelt. Therefore, the nanoring is initiated by circularly folding a nanobelt due to long-range electrostatic interaction between the surface polar-charges on the two sides, and a loop-by-loop winding of the nanobelt forms a complete ring. This analysis supports the mechanism proposed for the formation of nanorings. References: 1. O. Dulub, L.A. Boatner and U. Diebold, *Surf. Sci.*, 519, 201 (2002). 2. Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science*, 291, 1947 (2001). 3. P. Gao, Y. Ding, and Z.L. Wang, *Nano Lett.*, 3, 1315 (2003). 4. Z.L. Wang, Z.W. Pan and Z.R. Dai, *Microscopy and Microanalysis*, 8, 467 (2002). 5. X. Y. Kong, Z. L. Wang, *Nano Lett.*, 3, 1625 (2003). 6. X. Y. Kong, Y. Ding, R. S. Yang and Z. L. Wang, *Science*, 303, 1348 (2004). 7. For details please visit [www.nanoscience.gatech.edu/zlwang](http://www.nanoscience.gatech.edu/zlwang)

### Z3.12

**Self-Assembly of Nanowires for Making Nanoscale Organic Transistors.** Shuhong Liu and Zhenan Bao; Chemical Engineering, Stanford University, Stanford, California.

Considerable efforts have been placed on searching for alternatives to conventional silicon electronics in recent years. Present photolithographic techniques grow exponentially more expensive with decreasing feature size, and may never reach the dimensions required for new technologies. In our work, we design a new nanopatterning method that relies on self-assembly of nanowires to make nanoscale electrode gaps. Metal nanowires are prepared through electrochemical deposition of metal ions into porous alumina template and are derivatized by using positively and negatively charged self-assembled monolayers. Self-assembly of nanowires on metal electrodes are studied by controlling surface chemistry of the bottom electrode contacting the nanowires, surface topography of the bottom electrodes, microfluidic conditions, or the combination of them. Several approaches such as microcontact printing, topographically directed etching and cold welding are employed here. Devices are fabricated by using nanowires as source and drain electrodes, and growing organic semiconductors selectively between them. Electronic properties from transistors with different channel lengths are reported.

### Z3.13

**Surface Chemistry at Size-Selected, Aerosolized Silicon Nanoparticles.** Jeffrey Roberts<sup>1,2</sup>, Amanda Nienow<sup>1</sup> and Uwe Kortshagen<sup>2</sup>; <sup>1</sup>Chemistry, University of Minnesota, Minneapolis, Minnesota; <sup>2</sup>Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota.

A new method is described to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. Results will be presented on the oxidation of silicon nanoparticles of initial mobility diameter between 5 and 20 nm. The particles were investigated for changes in surface area and morphology using on- and off-line nanoparticle characterization instrumentation. Experiments will be reported on the oxidation of crystalline silicon nanoparticles by molecular oxygen and by water vapor. The particles were formed from silane in a microwave plasma reactor, and were extracted directly from the synthesis chamber into an aerosol flow tube reactor. We believe these to be among the first measurements of reaction kinetics that have been conducted on size-selected, aerosolized nanoparticles. The results are important because gas-to-particle conversion is a potentially important method for synthesizing nanoparticles for materials science applications. The principal elements of the atmospheric pressure aerosol flow reactor were as follows. Free flowing-streams of silicon particles were extracted from the synthesis chamber. The particle streams were sent through a bipolar diffusion charger to establish a known charge distribution, and then a specific particle size was selected with a differential mobility analyzer (DMA). The monodisperse particle streams were swept by a carrier gas into a reaction zone. The reaction zone was designed for maximal flexibility, with variable temperature (25-1200 °C), particle residence time (1-10 s), and gas-phase composition (0-100% oxygen and 0-50% relative humidity). Particles that exited the reaction zone were analyzed in two ways: (1) for size changes, with a second DMA capable of measuring diameter changes as small as 1% (i.e., less than one monolayer), and (2) for nano-structural and nano-morphological changes that are induced by surface processing, using transmission electron microscopy (TEM). Silicon oxidation results in an increase of particle size. The size increase measurements were analyzed using the Deal-Grove model, and assuming a shrinking silicon core surrounded by an oxide shell. Results indicate that under the conditions studied, the extent of oxidation was largely controlled by diffusion through the oxide shell.

### **Z3.14**

Transferred to Z11.8

### **Z3.15**

**Magnetic Particle Formation by Rapid Expansion of Supercritical Solutions.** Silvia De Dea<sup>1,2</sup>, Dominic Graziani<sup>2</sup>, David R. Miller<sup>1</sup> and Robert E. Continetti<sup>2</sup>; <sup>1</sup>Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California; <sup>2</sup>Chemistry and Biochemistry, University of California, San Diego, La Jolla, California.

Rapid Expansion of Supercritical Solutions (RESS) was used to produce small magnetic particles by expanding a supercritical solution of carbon dioxide and an organometallic compound. RESS is a well-known method to obtain small particles of uniform size. In fact when a solution of a dissolved solute in a supercritical fluid is expanded across a micro-orifice, the density of the solution decreases dramatically and the solute precipitates uniformly due to high supersaturation ratios. Fine magnetic particles have many applications as, for example, recording media, ferrofluids and targeted drug delivery. Still unresolved in RESS type depositions is the difficult question of quantifying where the final observed particles are formed and grown, in the expansion and/or on the substrate. In this study the formation of Fe<sub>2</sub>O<sub>3</sub> by expanding a supercritical solution of carbon dioxide and iron acetylacetonate on a hot silicon substrate has been investigated. The temperature of the substrate was set above the decomposition temperature of the compound so that the decomposition would occur at the surface with subsequent formation of Fe<sub>2</sub>O<sub>3</sub> in an oxidizing atmosphere. Many parameters (temperature, pressure and expansion conditions) influence particle size and distribution. A very important aspect of RESS is that accurate solubility data are necessary to completely characterize the supercritical solution. For this purpose a viewing cell was introduced in the process to allow both solubility and concentration measurements using UV-visible absorption spectroscopy just before the expansion. The solubility data obtained will be presented and compared with a fit using the Peng-Robinson equation of state for the supercritical mixture. The current RESS apparatus includes two supercritical pumps, an extraction chamber, a UV-vis cell followed by an orifice nozzle and an expansion chamber into which the supersonic expansion occurs. The experimental apparatus allows control on all the process variables: pre-expansion temperature, pressure and composition of initial solution, temperature of the substrate, position of the substrate with respect to the nozzle, and the expansion chamber pressure. The latter two variables significantly affect the shock wave structure of the expansion. At higher expansion chamber pressures there are well-defined shockwaves in the expansion, which have been recently studied in the current system, and the effect of the expansion jet structure on particle morphology will be discussed. Recording the experimental parameters and correlating them with the morphology of the particles deposited on the substrate will allow optimization of the

RESS process for specific nanoparticles deposits. The deposited particles were analyzed using scanning electron microscopy and it was found that the size distribution ranged from microns to nanometers depending on the expansion conditions. In general smaller particles are formed when the expansion is into vacuum.

### **Z3.16**

**Temperature, Pressure, and Catalytic Effects on the Morphology of CdSe Nanostructures.** Christopher Ma, Georgia Institute of Technology, Atlanta, Georgia.

Cadmium Selenide (CdSe) is an important optoelectronic, luminescent, and lasing material. The successful synthesis of CdSe nanobelts, nanosaws, and nanowires have previously been reported [1]. The nanosaws are suggested to be a result of atomic-termination induced asymmetric growth due to the cation-terminated, catalytically active (0001), while the anion-terminated (000-1) is chemically inactive. By controlling the growth direction, selection of the ionic side surfaces can be achieved, yielding the saw-like nanostructure. Empirical evidence indicates that temperature and pressure have a strong affect on the growth kinetics of these nanostructures. We present research demonstrating a systematic investigation of the effects of pressure, temperature, and catalyst on the morphology of one-dimensional CdSe nanostructures. [1] Chris Ma, Yong Ding, Daniel Moore, Xudong Wang and Z.L. Wang\* "Single-Crystal CdSe Nanosaws", J. Am. Chem. Soc., 126 (2004) 708-709 (featured by Nature 427 (2004) 497). [2] For more details, please visit: [www.nanoscience.gatech.edu/zlwang](http://www.nanoscience.gatech.edu/zlwang)

### **Z3.17**

**Synthesis of Si/metal One-dimensional Heterostructures.** Yang Jiao and Quan Li; Physics Department, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Si-based one-dimensional (1D) heterostructures have attracted much attention in recent years as they may be easily integrated into the current Si technology and thus serve as building blocks for various nanodevices. In this study, we demonstrate that several different types of Si/metal 1D nanostructures, including Si/metal nanowires, metal-core/Si-sheath nanocables, and aligned metallic nano dots in silicon oxide nanowires, can be fabricated using thermal evaporation by controlling the supersaturation of the Si-containing vapor phase. A detailed microstructure study of the nanostructure is presented. Several critical growth parameters such as the amount and the morphology of the catalyst material have been systematically investigated in order to understand the growth mechanism. Such synthetic method can be widely applied to a variety of other materials so that different Si-based 1D heterostructures can be readily obtained. Novel electrical and optical properties are expected in these nanomaterials due to their special 1D morphology.

### **Z3.18**

**Surface Modified Boehmite Aluminas: A Versatile Approach to Nano-scale Particle Dispersion and Nanocomposites.** Steven L. Baxter<sup>1</sup> and Olaf Torno<sup>2</sup>; <sup>1</sup>R&D, Sasol North America Inc., Westlake, Louisiana; <sup>2</sup>Sasol Germany, Hamburg, Germany.

Certain forms of monohydrate aluminum oxide, commonly known as boehmite or pseudoboehmite alumina, are known to disperse in water at low pH to nano-scale dimensions. The upsurge of interest in nano-scale structures has prompted our study of the surface modification of nano-scale boehmite aluminas with organic acids in order to achieve dispersion of these materials in non-aqueous systems and alkaline aqueous systems. This paper discusses the variety of modifiers used to achieve compatibilization and dispersion of nano-sized particles of these boehmite aluminas in aqueous and organic matrices, including: - Polymeric systems - Low pH aqueous systems - High pH aqueous systems - Polar organic systems - Non-polar organic systems Organic modification of a variety of crystallite sizes (3-50 nm) and shapes (plates, needles, blocks) has been achieved, including materials of high aspect ratio. We describe the properties of these dispersions, including primary particle size, dispersed particle size, and surface charge. Finally, we present physical property data of polymer nanocomposites prepared from these materials. These materials are based on a commercial process which has been in operation for over 40 years and which has global production capacities of 70,000 tons per annum.

### **Z3.19**

**Mass-productive Synthesis of Large-grained Multicrystalline Inorganic Electrider C12A7:e<sup>-</sup> by Melt Crystallization Method and its Application to Field-emission Light-emitting Device.** Yoshitake Toda<sup>1</sup>, Sung Wng Kim<sup>2</sup>, Takashi Sakai<sup>1</sup>, Masashi Miyakawa<sup>2</sup>, Toshio Kamiya<sup>1,2</sup>, Masahiro Hirano<sup>2</sup> and Hideo Hosono<sup>1,2,3</sup>; <sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; <sup>2</sup>Hosono Transparent Electro-Active Materials, Japan Science and Technology Agency,



Inorganic electride C12A7:e<sup>-</sup> is a crystalline salt in which electron anions are served as anions. Its base material is a nano-porous crystal 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C12A7), having twelve positively-charged cages (0.4 nm in inner-diameter) in a unit cell. It may clathrate active anion species such as O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, H<sup>-</sup> and electron (e<sup>-</sup>) in the cages, causing various novel functions. C12A7 incorporating e<sup>-</sup> forms the inorganic electride C12A7:e<sup>-</sup> (1). This material is air-stable even at 500°C and exhibit excellent electron emission properties that originate from electrons loosely confined in the cages at a high density  $\sim 10^{21}$  cm<sup>-3</sup> (2). However, it takes 2 weeks or longer to prepare a 0.5-mm-thick single crystalline C12A7:e<sup>-</sup> sample because substitution of electron for clathrated free oxygen ions is limited by bulk diffusion and extraction reaction at the sample surface. This process is not applicable to powder or ceramics C12A7 and requires single-crystalline materials. Therefore, we need to seek another method to prepare C12A7:e<sup>-</sup> at lower cost and higher throughput if aimed at mass-production use of the inorganic electride. Recently, we developed a simple method to prepare large-grained (maximum grain size is  $\sim 3$ mm) multicrystalline C12A7:e<sup>-</sup> with electrons at  $\sim 10^{19}$  cm<sup>-3</sup>. It just solidifies melt of C12A7 sintered body in a reducing atmosphere (melt crystallization method). In this study, we examined electron emission properties of multicrystalline C12A7:e<sup>-</sup> synthesized by the melt crystallization method and compare the results with those obtained on single-crystalline C12A7:e<sup>-</sup>. Multicrystalline C12A7:e<sup>-</sup> was sliced into 10x10x0.5mm<sup>3</sup> plates. Electron emission was measured at  $\sim 6 \times 10^{-5}$  Pa using a mirror-polished surface to examine the fundamental material properties. The distance between the emitter surface and an extraction electrode was adjusted precisely to be 0.05 mm using a 0.05-mm-thick mica plate with a hole 6 mm in diameter. It was observed that electron emission was controlled by thermionic emission at low extraction voltages, while Fowler-Nordheim (FN) field-emission dominated at voltages higher than 2000 V and emission current reached 12 mA cm<sup>-2</sup>. Field-emission light-emitting devices were fabricated using the multicrystalline C12A7:e<sup>-</sup> as electron emitter, which displayed bright light emission clearly visible in typical ambient light. These properties are almost the same as single crystalline C12A7:e<sup>-</sup>. (1) S. Matsui et al., Science 301, 626-629 (2003) (2) Y. Toda et al., Adv. Mater. 16, 685-689 (2004)

### Z3.20

**Preparation of Mesoporous Pd/Si<sub>3</sub>N<sub>4</sub> Nano-composites via a Non-aqueous Sol-gel Route.** Fei Cheng, Stephen M. Kelly, Nigel A. Young, Stephen Clark, M. Grazia Francesconi and John S. Bradley; Chemistry, University of Hull, Hull, United Kingdom.

There has been considerable interest in the preparation of transition metal-loaded porous materials due to their potential applications in heterogeneous catalysis, catalytic gas filters and other fields. In our group, we have developed a non-oxide sol-gel method for the preparation of high-surface-area mesoporous silicon nitride, silicon boron nitride and silicon aluminum nitride composites.<sup>1,2,3</sup> In this work, we report the preparation of mesoporous Pd-Si<sub>3</sub>N<sub>4</sub> nano-composite materials via a new sol-gel process as part of the NANOSOFLEX program. All the experimental procedures were performed under an anhydrous nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glove box. First, a high-surface-area silicon diimide gel was prepared by the acid-catalyzed ammonolysis of tris(dimethylamino)silylamine H<sub>2</sub>NSi(NMe<sub>2</sub>)<sub>3</sub>.<sup>1</sup> The silicon diimide gel was then reacted with 5% of palladium (II) chloride to give a light yellow powder. Finally, pyrolysis of the yellow powder under NH<sub>3</sub> flow at 1000 °C gave the final product. The FTIR, <sup>29</sup>Si CP-MAS NMR, powder X-ray diffraction and Pd K-edge EXAFS studies indicated that the final product was a composite of crystalline Pd metal and α-Si<sub>3</sub>N<sub>4</sub>. N<sub>2</sub> adsorption analysis showed that the composite ceramic material exhibited a mesoporous structure with a surface area higher than 400 m<sup>2</sup>/g. The heating rate of the pyrolysis under NH<sub>3</sub> has a great effect on the pore size distribution. Only one pore size distribution at 6 - 12 nm was observed for the product pyrolyzed at a heating rate of 2 °C/min, but pyrolysis at a heating rate of 5 °C/min led to the formation of a second pore size distribution at 15 - 25 nm. <sup>1</sup> F. Cheng., S. Clark, S. M. Kelly, J. S. Bradley and F. Lefebvre, J. Am. Ceram. Soc., 2004, 87, 1413. <sup>2</sup> F. Cheng, B. Toury, F. Lefebvre and J. S. Bradley, Chem. Comm., 2003, 242. <sup>3</sup> F. Cheng., S. M. Kelly, F. Lefebvre, S. Clark, R. Supplitt and J. S. Bradley, J. Mater. Chem., in press

### Z3.21

**Synthesis of Well Aligned ZnO Nanowires using Simple Physical Vapor Deposition without Catalysts or Additives.** Xiaozhong Zhang<sup>1</sup>, Lisheng Wang<sup>1</sup>, Y. L. Zhou<sup>2</sup>, Junjie Qi<sup>1</sup> and Guoyuan Zhou<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Tsinghua University, Beijing, China; <sup>2</sup>Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing,

Well aligned ZnO nanowires have been synthesized by simple physical vapor deposition (PVD) approach using c-axis directed ZnO thin films as substrate without the assistance of any catalysts or additives. The synthesized nanowires have two typical average diameters: 60nm in majority and 120nm in minority. The ZnO nanowires are about 4μm in length and well aligned along the normal direction of the substrate. XRD and HRTEM results confirmed that most of the ZnO nanowires are single crystalline with a hexagonal structure and grow along the [001] direction. It is believed that the ZnO nanowires grow following VS mechanism and the c-axis ZnO thin films control the growth direction. We also proved that foreign atoms are not necessary during the growth procedure. In addition, PL spectrum has been measured showing a single strong UV emission (380nm). Such result indicates the ZnO nanowire arrays we report can be applied to optoelectronic devices.

### Z3.22

**Growth of ZnO Nanowires Selectively on a Si Substrate without a Metal Catalyst.** John F. Conley, Lisa Stecker, Yoshi Ono and Greg Stecker; IC Process Technology Lab, Sharp Labs of America, Camas, Washington.

Although nanostructured inorganic materials such as nanowires have shown promise for many applications, much of this work has been accomplished using crystal matched substrates such as sapphire or SiC. Despite the promise of nanowires and other "bottom-up" nanotechnologies it is very likely that, at least initially, they will have to be integrated onto a traditional "top-down" silicon CMOS platform. Therefore, nanostructure formation and placement should be compatible with standard Si based processing and devices. Fabrication of nanowire devices on Si substrates has typically involved either dispersal of nanowires from solution or a metal catalyst. Dispersal from solution typically results in random placement of nanowires on the substrate and requires either that a wire fortuitously span previously formed electrodes or subsequent electron beam lithography on an individual nanowire in order to form a device. By using either dispersed nanoparticles or a patterned thin film ( $\sim 3$  nm) of a metal catalyst (such as Au), one may grow nanowires selectively onto a Si substrate. The metal catalyst is required for vapor-liquid solid (VLS) transport, one of the primary methods of nanostructure growth. Unfortunately, particles are never welcome in an ultra clean fabrication environment and thin films of typical nanostructure catalyst materials are difficult to pattern via standard processes such as etching and chemical mechanical planarization (CMP). In addition, catalyst metals are a potential source of contamination that is detrimental to device performance (e.g. many metals act as efficient recombination centers in Si) and are thus best avoided in a CMOS process. None of the above approaches is ideal for integration into Si CMOS manufacturing environment. In this work, we demonstrate a simple method to achieve highly selective patterned growth of ZnO nanowires directly on a (100)Si substrate without the use of a metal catalyst. Instead of a metal catalyst, a patterned thin film ZnO layer is used to initiate and define regions of nanostructure growth. Zn vapor is supplied via carbothermal reduction of a ZnO/graphite mixture. ZnO films are deposited via atomic-layer or metal-organic spin-on-deposition. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), reveal selective growth of vertically aligned high quality single crystalline NW with preferred c-axis orientation. The absence of catalyst balls at the end of the nanowires indicates that growth likely occurs via a vapor-solid rather than a VLS mechanism, with the thin ZnO film acting as a seed. Photoluminescence (PL) measurements reveal a strong intrinsic near-band edge PL peak at 380 nm with no detectable visible spectrum PL, indicating a lack of defects. ZnO nanostructure morphology was sensitive to ZnO seed layer deposition technique and subsequent annealing conditions, as well as Si substrate preparations such as implantation.

### Z3.23

**Interactions of Ge Atoms with Hi-k Oxide Dielectric Surfaces.** Scott K. Stanley and John G. Ekerdt; Department of Chemical Engineering, The University of Texas Austin, Austin, Texas.

Germanium is becoming an increasingly important material in electronic applications due to superior carrier mobility, lower band edge, and enhanced quantum confinement ability when compared with silicon. Next generation flash memory devices with Ge nanocrystals encapsulated in SiO<sub>2</sub> or other dielectrics have been demonstrated in the literature. However, unlike Si upon which a high-quality oxide may be formed, Ge forms unstable and volatile oxides complicating the use of Ge. Despite the increasing interest in Ge applications, surprisingly little is known about the reactions of Ge with various oxide dielectric materials. In this work, GeH<sub>4</sub> is thermally cracked over a hot filament depositing 0.7-15 ML Ge onto SiO<sub>2</sub>, HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> substrates. Ge bonding changes are analyzed during

annealing sets from 300-1000 K with X-ray photoelectron spectroscopy. Ge, GeH<sub>4</sub>, GeO, and GeO<sub>2</sub> desorption is monitored through temperature programmed desorption in the temperature range 300-1000 K. Low temperature desorption features are seen on all substrates and attributed to GeH<sub>4</sub> desorption. Various temperature and substrate dependant surface reactions lead to Ge, GeO, and GeO<sub>2</sub> desorption. Interestingly, GeO<sub>2</sub> (thought to be the more stable oxide of Ge) actually desorbs before GeO on some substrates. The stability of Ge, GeO, and GeO<sub>2</sub> on oxide surfaces and the chemical vapor deposition of Ge on oxide surfaces are discussed.

### **Z3.24**

#### **Morphology-Controlled Synthesis of Platinum**

**Nanostructures.** Jingyi Chen, Thurston Herricks, Matthias Geissler and Younan Xia; Department of Chemistry, University of Washington, Seattle, Washington.

We have synthesized Pt nanostructures with different morphologies by controlling the reduction kinetics of a polyol process. Morphological control was achieved by limiting the reduction rate from Pt(II) to Pt(0) through coupling with the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox pair and/or blocking of self-catalytic sites with oxygen. X-ray photoelectron spectroscopy (XPS) and UV-Vis spectral analysis helped to elucidate the reaction mechanism. As a general trend, a slow reduction rate for the Pt (II) species ultimately led to the formation of Pt nanostructures with morphologies deviated from the thermodynamic shape of a face-centered cubic metal. To date, platinum nanorods, nanowires, nanocubes, tetrapods, and octapods have been obtained. It is expected that this approach can also be extended to the shape-controlled synthesis of other noble metals.

### **Z3.25**

**Abstract Withdrawn**

### **Z3.26**

**Carbothermal Reduction of Titanium Dioxide Powder by Solid Carbon.** Gil-Geun Lee<sup>1</sup>, Gook-Hyun Ha<sup>2</sup> and Byoung-Kee Kim<sup>2</sup>; <sup>1</sup>Div. of Materials Science and Engineering, Pukyong National University, Busan, South Korea; <sup>2</sup>Korea Institute of Machinery and Materials, Changwon, South Korea.

The titanium carbide powder is commercially produced primarily by the carbothermal reduction of titanium dioxide powder by carbon, especially carbon black, over a temperature range of 1700-2100K. The reaction behavior of the titanium dioxide/carbon mixture, especially titanium carbide formation, in the carbothermal reduction method is very important to obtain nanosized titanium carbide powder. The manufacturing of the ultrafine titanium carbide powder with a nonagglomerated state by this method should know to be the reaction mechanism. The chemical mechanism of this reaction is often unknown, however, this is highly dependent on the conditions of the process parameters such as atmosphere, pressure and temperature. However, the parameters related to the particle characteristics of starting material of the titanium dioxide, such as particle size and phase structure, have been rarely studied exhaustively. In the present study, the focus is on their role in the carbothermal reaction of the titanium dioxide/carbon system. Four types of titanium dioxide powders with various phase structures and mean particle sizes were mixed with carbon black. These mixtures were heat treated under a flowing argon atmosphere. The changes in the phase structure and thermal gravity of the mixtures during heat treatment were analyzed using XRD and TG-DTA. Titanium dioxide powders with 100% anatase phase structure exhibit a higher titanium carbide formation ability than titanium dioxide powders with the mixed phase structure of the anatase and rutile structures. It was concluded that the phase structure of the titanium dioxide plays a more important role than the particle size on the carbothermal reduction of the titanium dioxide/carbon system.

### **Z3.27**

**Synthesis of Au Coated Fe Nanopowders by Microemulsion Process.** Yong-Jin Kim<sup>1</sup>, Ji-Hun Yu<sup>1</sup>, Gwi-Yang Chung<sup>2</sup> and

Jung-Ho Ahn<sup>3</sup>; <sup>1</sup>Department of Materials Technology, Korea Institute of Machinery and Materials, Kyungnam, South Korea; <sup>2</sup>School of Information System Engineering, Dongseo University, Busan, South Korea; <sup>3</sup>Department of Materials Engineering, Andong National University, Kyungbuk, South Korea.

Nanopowders are one of the most attractive materials because their properties are very different from those of relatively large particles or bulk materials. The nanometer-sized iron powders have attracted much attention due to their potentials application in magnetic-electronics and biotechnologies. However, the powders are easily changed to iron oxide phase when contacting with air due to their high reactivity. Many researchers try to prevent oxidation of the nano sized particles by coating inert materials such as SiO<sub>2</sub> or polymers on the powder. But these coated materials also reduce the

magnetic properties. Gold is one of the interesting coating materials to prevent oxidation of nanoparticles without reducing the magnetic properties and also prevent the corrosion from any kind of environment. In this work, we have synthesized Au coated Fe nanopowders by mixing two microemulsion solutions containing the metallic salt and reduction agent solution. The particle size, structure and magnetic properties of the synthesized nanopowders have been characterized by transmission electronic microscopy, X-ray diffraction and VSM. The microemulsion solutions were prepared by stirring a mixture of CTAB, 1-butanol and octane with an aqueous solutions of HAuCl<sub>4</sub> and FeCl<sub>3</sub>, respectively. For reducing the metallic ions, another microemulsion solution containing reduction agents was prepared in the same way but substituting NaBH<sub>4</sub> aqueous solution to metallic ion containing solutions. Both solutions were then vigorously mixed. After the completion of the reduction reaction, the resulting solution was centrifuged to separate the solid phase products. These were then washed several times with a mixture of chloroform and methanol. The washed particles were dried in vacuum at 70°C for 2 hours. The Au coated Fe nanopowders were successfully synthesized by water in oil microemulsion system consisting of water/CTAB and 1-butanol/octane. The synthesized nanopowders were less than 10 nm in average powder size. The powder size was mainly controlled by the molar ratio of the water to surfactant. The coating thickness of Au was also controlled by changing the amount of aqueous solution containing Au and Fe. The XRD results show the particles were composed of the alpha iron and pure gold without any oxide phase. The Au coated Fe particles also show superparamagnetic state at above the blocking temperature.

### **Z3.28**

**Formation of Self-assembled Monolayers (SAMs) in Vacuum by using TiO<sub>2</sub> Interfacial Layer.** Kwang M. Lee, Won S. Hwang and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. They have been shown to be useful as passivating layers and also for the modification of surface properties. Potential applications include wetting, adhesion, friction, chemical sensing, ultrafine scale lithography, and protection of metals against corrosion. Alkylsiloxane monolayers are formed on SiO<sub>2</sub> and TiO<sub>2</sub> surface in vacuum. The TiO<sub>2</sub> thin films were grown on Si(100) substrate by atomic layer deposition from titanium isopropoxide and water. Monolayers formed on SiO<sub>2</sub> and TiO<sub>2</sub> have been studied using X-ray photoelectron spectroscopy(XPS), atomic force microscopy(AFM), and contact angle analysis. Densely packed alkylsiloxane monolayers similar in quality to those on SiO<sub>2</sub> in liquid phase are formed on TiO<sub>2</sub> in vacuum. SAMs are more efficiently and well formed on the TiO<sub>2</sub> surface as compared to those on the SiO<sub>2</sub>.

### **Z3.29**

**Ostwald Ripening Kinetics and Photoluminescence Shifts in CdS-ZnS and CdSe-ZnSe Alloy Nanocrystals.** Yun-Mo Sung, Yong-Ji Lee, Kyung-Soo Park and Jung-Joon Na; Materials Sci. & Eng., Daejin University, Pochun-si, Kyunggi-do, South Korea.

Semiconductor (II-VI) nanocrystals (CdSe, CdS, CdTe, ZnS, ZnSe, ZnTe, etc.) have been intensively studied for their unique photo absorption and emission characteristics. They show specific quantum confinement effects and thus visible range emissions with a particle size. To improve quantum efficiency those semiconductor nanocrystal cores are covered with another semiconductor with a high-energy band gap and core/shell nanocrystals have been achieved. Some research results show that alloying of two semiconductors can improve stability of nanocrystals compared to core/shell structures. Alloying could be performed for II and VI elements, respectively. Although the optical and electrical properties of nanocrystals are size dependent, the Ostwald ripening kinetics of the alloyed nanocrystals have not been defined in detail. In this study the CdS-ZnS and CdSe-ZnSe alloyed nanocrystals were prepared by mixing the starting precursors. The Lifshitz-Slyozov-Wagner (LSW) theory was applied for Ostwald ripening kinetics analyses of the alloyed nanocrystals, and transmission electron microscopy (TEM) and photoluminescence (PL) data were used for this purpose. The diffusion constant (*D*) values were determined from the rate constant (*K*) values in the LSW kinetics equation. Using Arrhenius-type plots the activation energy values for the diffusion were determined and the diffusion mechanism was discussed in the alloy systems. Also, the PL characteristics of the alloyed nanocrystals were analyzed and compared to those of each alloy component (CdS, ZnS, CdSe, and ZnSe). The systematic energy band gap shifts, measured from PL data in the alloyed nanocrystals, were considered and compared to those obtained from the Brus' theoretical estimation of a band-gap energy.

### **Z3.30**

**Highly Luminescent and Photostable ZnS/CdSe/ZnS Quantum Wells for Biological Labeling via a Single Source**

**Approach.** Yang LI<sup>1</sup>, Steven M. Daniels<sup>1</sup>, Jianguhua Feng<sup>2</sup>, Nigel L. Pickett<sup>1</sup> and Paul O'Brien<sup>1</sup>; <sup>1</sup>School of Chemistry, University of Manchester, Manchester, United Kingdom; <sup>2</sup>Division of Neuroscience, Faculty of Life Sciences, University of Manchester, Manchester, United Kingdom.

Quantum wells (QWs) of ZnS/CdSe/ZnS were prepared via single source precursor method. QWs with emission from blue to red can be obtained with quantum yields ranging from 20 to 40%. Successive injections of aliquots of Zn and sulfur precursors achieve several monolayers thick ZnS shell for good photostability and high quantum yields. This synthetic method can be readily performed on a multigram scale. The nanoparticles were transferred into aqueous solutions by encapsulation with an amphiphilic polymer coating. The coating was prepared by the hydrophobic modification of polyacrylic acid with hexadecylamine using N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDAC) as a crossing reagent. This polymer and bis(3-aminopropyl) terminated poly(ethylene glycol) were used to overcoat the surface of ZnS/CdSe/ZnS to obtain the aqueous solution, which possessed similar optical properties to original QWs toluene solution. These QWs sodium borate solutions were conjugated with tuftsin peptide, which only has cell surface receptors on neutrophils and monocyte-macrophages. Labeling these circulating pro-inflammatory cells can be monitored.

### **Z3.31**

**Alloying Kinetics of CdSe/ZnSe and CdS/ZnS Core-Shell Nanocrystals.** Yun-Mo Sung, Kyung-Soo Park, Yong-Ji Lee and Jung-Joon Na; Materials Sci. & Eng., Daejin University, Pochun-si, Kyunggi-do, South Korea.

II-VI semiconductor nanocrystals (CdSe, CdS, CdTe, ZnS, ZnSe, ZnTe, etc.) have been intensively studied for their unique photo absorption and emission characteristics. They show specific quantum confinement effects and thus show visible range emissions depending on each particle size. To improve quantum efficiency a semiconductor nanocrystal core is often covered with another semiconductor shell with a high-energy band gap. Some research results show that alloying of two semiconductors can improve photoemission stability of nanocrystals compared to core/shell structures. However, sometimes alloying of two semiconductors with different atomic size is incomplete and alloying effect is not fully achieved. In this study, CdSe/ZnSe and CdS/ZnS core/shell nanocrystals were synthesized and further heated at different temperatures for different time periods. The kinetics of alloying was investigated using X-ray diffraction (XRD). The XRD peaks from CdSe and ZnSe, and those of CdS and ZnS were shifted with alloying temperature and time. The XRD quantitative analyses were performed to obtain the volume fractions of alloying and these values were used for Johnson-Mehl-Avrami (JMA) isothermal kinetic analyses. The JMA plots were produced and Arrhenius plots were also produced using the y-intercepts of JMA plots. The activation energy for alloying was obtained and discussed based upon diffusion of Cd<sup>2+</sup> ions in CdSe-ZnSe and CdS-ZnS systems. Also, a kinetics equation for Cd<sup>2+</sup> ions was derived based upon an interfacial diffusion couple model. The diffusion rates of Cd<sup>2+</sup> ions in ZnSe and ZnS, respectively were estimated and activation energy values for diffusion were determined. The activation energy values were compared with those from JMA analyses. The alloying mechanisms were suggested in detail for the core/shell systems.

### **Z3.32**

**CdS and ZnS Nanoparticles Growth in Different Reaction Media: Synthesis and Characterization.** Francesco Antolini<sup>1</sup>, Enrico Trave<sup>2</sup>, Luciana Mirengi<sup>1</sup>, Marielena Re<sup>1</sup>, Giovanni Mattei<sup>2</sup>, Leander Tapfer<sup>1</sup> and Paolo Mazzoldi<sup>2</sup>; <sup>1</sup>Material Science Unit, ENEA, Brindisi, Italy; <sup>2</sup>Dip. di Fisica, Università di Padova, Padova, Italy.

In this work we report on the growth of cadmium sulfide and zinc sulfide nanocrystals following three different synthesis routes. In particular the nanocrystals were synthesized starting from a metal thiolate (i) in a solventless way by thermolysis, (ii) by a novel route in tryoctylphosphine oxide (TOPO), and (iii) by direct synthesis in a polystyrene matrix. The structural, morphological and microanalytical properties were investigated in detail by x-ray diffraction (XRD), transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS). The experimental results show that the nanocrystals fabricated by the different methods are under optimized growth conditions single crystals of zincblende structure and of regular spherical shape. The average size can be tuned between 1.5nm to 3.0nm and the size dispersion is less than 10%. The XPS results indicate that for the nanoparticles obtained via solventless strategy the sulfur is present both as bonded to the metal atom and to the organic residue while in the TOPO synthesized nanoparticles the sulfur signal has only one component associated to the metal-sulfide bond. These evidences suggest that the role of capping agent in the absence of TOPO is played by the alkyl group bound to

the sulfur atom on the surface. The optoelectronic properties were investigated by absorption spectroscopy, photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE) at RT and at low temperature (T=77K). The photoluminescence spectroscopy results clearly evidence the typical emissions of nanosized zincblende CdS and ZnS monocrystalline particles. Furthermore, the optical spectroscopy data indicate that the size distribution of the (Cd, Zn)-sulfide - TOPO nanoparticles seems to be generally larger than that ones grown directly in polymer matrix. The metal-sulfide nanocrystals dispersed in polystyrene exhibit an excitonic transition at about 2eV that can be attributed to the hole-electron recombination at the nanocrystal/matrix interface.

### **Z3.33**

**Synthesis of Nanocarbon Materials by Carburization of Nanocrystalline Iron.** Urszula Narkiewicz<sup>1</sup>, Walerian Arabczyk<sup>1</sup>, Iwona Kucharewicz<sup>1</sup>, Krzysztof J. Kurzydowski<sup>2</sup>, Michal J. Wozniak<sup>2</sup>, Hubert Matysiak<sup>2</sup> and Nikolaous Gouskos<sup>3</sup>; <sup>1</sup>Institute of Chemical and Environment Engineering, Technical University of Szczecin, Szczecin, Poland; <sup>2</sup>Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland; <sup>3</sup>Department of Physics, University of Athens, Athens, Greece.

Carbon nanomaterials are fascinating due to their unique physical properties offering possibility for a wide range of applications. A number of preparation methods of nanomaterials were developed during last decade. Among them simple and non-expensive is a chemical vapor deposition (CVD) with use of transition metal-based catalysts. The preparation conditions are mild and the process is easy to control. The method can also be up-scaled to industrial relevance. The paper presents an example of such a preparation method based on the carburization of nanocrystalline iron with ethylene. Nanocrystalline iron was obtained by fusion of magnetite with small amount of promoter oxides, followed by reduction under hydrogen. The mean size of iron crystallites, determined using XRD, was 17 nm. The carburization process was carried out under pure ethylene at 550 °C and controlled using a thermobalance. The samples after carburization were characterized using XRD, SEM, AFM, HRTEM and FMR methods. It has been found that the carburization reaction at 550 °C is very fast and results in formation of iron carbide (cementite) and residual carbon deposit which, as reveal AFM images, encapsulates the crystallites of iron carbide. HRTEM studies show the presence of multi-wall carbon nanotubes with a crystallite of iron carbide at the end. The fine structure of graphene sheets encapsulating iron carbide crystallite is visible in HRTEM images. The FMR (ferromagnetic resonance) for the synthesized materials have been found intense and asymmetric. It has been also found that the FMR signals depend strongly on the carbon concentration. It can be explained in terms of the carbon influence on the separation of the Fe-rich magnetic particles. Applications of the obtained materials are discussed for drug delivery targeting and/or ferro-fluids.

### **Z3.34**

**Synthesis of Crack Free Highly Ordered Cubic Mesostructured TiO<sub>2</sub> Thin Films.** Daniel Brian Carew<sup>1</sup>, Sung Yeun Choi<sup>1</sup>, Marc Mamak<sup>1</sup>, Srebri Petrov<sup>1</sup>, Naveen Chopra<sup>2</sup> and Geoffrey A. Ozin<sup>1</sup>; <sup>1</sup>Chemistry, University of Toronto, Toronto, Ontario, Canada; <sup>2</sup>Xerox Research Centre of Canada, Toronto, Ontario, Canada.

Described herein is a novel room temperature synthetic route capable of producing crack-free highly ordered cubic mesostructured titania thin films. This synthetic strategy involves the use of an alternate solvent that enhances the ordering of the liquid crystal phase, thereby allowing the use of lower amounts of surfactant template and correspondingly higher concentrations of the inorganic precursor at ambient conditions. Evaporation induced self-assembly (EISA) under specific temperature and humidity conditions for a relatively short period of time determines the liquid crystalline phase of the resulting mesostructure, which has a large pore diameter, narrow pore size distribution and high surface area. This room temperature synthesis is the quickest of comparable synthetic routes while still having relative simplicity. The cubic mesostructure compared to the hexagonal one is optimal for many diverse applications. Key characteristics of this cubic mesostructure are the robust walls between pores exhibiting nanocrystalline anatase composition, large structural domains and thermal stability above 400°C. The resulting films are crack free over all length scales.

### **Z3.35**

**Electrodeposition of Bi<sub>1-x</sub>Sb<sub>x</sub> Nanowire Arrays for Thermoelectric Devices.** Jennifer Keyani<sup>1</sup>, J. W. Sharp<sup>2</sup> and Angelica M. Stacy<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of California, Berkeley, Berkeley, California; <sup>2</sup>Research and Development Division, Marlow Industries, Inc., Dallas, Texas.

Thermoelectric materials (TE) have the unique property that

application of an electric voltage results in the formation of a temperature gradient across the material, and vice versa.  $\text{Bi}_{1-x}\text{Sb}_x$  is the best n-type, low-temperature bulk TE material and is well suited for refrigeration applications, but it is not efficient enough to make large-scale use feasible. Dresselhaus *et al.* predict that quantum confinement of  $\text{Bi}_{1-x}\text{Sb}_x$  as nanowires will lead to an increase in the TE efficiency. We have fabricated nanowire arrays of  $\text{Bi}_{1-x}\text{Sb}_x$  ( $0.07 \leq x \leq 0.6$ ) by electrochemical deposition within porous  $\text{Al}_2\text{O}_3$  templates (100 and 40 nm diameter pores). The as-deposited nanowires are polycrystalline and have a smooth morphology. Larger diameter nanowires have aspect ratios on the order of 500, and smaller diameter nanowires have aspect ratios well over 1000. We have constructed TE couples incorporating  $\text{Bi}_{1-x}\text{Sb}_x$  nanowires, and have measured AC resistance, DC voltage and  $\Delta T$  of the couples to estimate the properties of the  $\text{Bi}_{1-x}\text{Sb}_x$  nanowire / porous  $\text{Al}_2\text{O}_3$  composite.

### Z3.36

**Synthesis and Aggregation of Bi<sub>2</sub>S<sub>3</sub> Nanocapsules.** Marina Gonzalez Vega<sup>1</sup>, X. Bokhimi<sup>1</sup>, A. Garcia-Ruiz<sup>2</sup>, M. Aguilar-Franco<sup>1</sup> and A. Morales<sup>1</sup>; <sup>1</sup>Institute of Physics, The National University of Mexico A.P. 20-364, 01000, Mexico DF, Mexico; <sup>2</sup>UPIICSA-COFAA, National Polytechnic Institute. Te No. 950 Esq. Resina, 08400, Mexico DF, Mexico.

Nanocapsules of Bi<sub>2</sub>S<sub>3</sub> with diameters between 5 and 10 nm were synthesized at room temperature; they had shells with an amorphous atom distribution. Bismuth precursor was bismuth nitrate, while sulfur precursor was thiourea; both were dissolved in dimethylformamide before its mixing. Capsule interaction depended on bismuth concentration; in the samples prepared with 0.4 M bismuth nitrate a black powder precipitated after aging the solution for several days, because of capsules aggregation. This powder produced a X-ray diffraction pattern containing a mixture of an amorphous and the crystalline phase Bi<sub>2</sub>S<sub>3</sub>, which was confirmed with the high resolution images of the samples obtained with a field emission transmission electron microscope. Micrographs also provided information about the morphology of capsule aggregates: When this occur at room temperature, the dominant aggregate were capsules about 20 nm in diameter made from the capsules with diameters between 5 and 10 nm; the shell of these capsules continue having an amorphous atom distribution, when they interacted between each other, however, the contact regions of the capsules crystallized into the crystalline structure of bismuth sulfide, which explains the origin of the crystalline phase observed in the X-ray diffraction pattern. At this temperature coalescence of the small nanocapsules also gave rise to necklaces of capsules, and bundles of them, which eventually gave rise to nanotubes. When the solution was annealed at temperatures lower than 100°C, coalescence gave rise to capsules as large as 1 μm in diameter, and tubes with similar diameters; in this case aggregation occurred between small and large nanocapsules. Because of the monomers aggregating had an external spherical symmetry and the low annealing temperatures, which were not high enough to produce sintering, all capsules and tubes formed during aggregation had porous walls, making these materials interesting for many applications.

### Z3.37

**Self Catalyzed Growth of Nanocones during DC Magnetron Sputtering of an ITO Target.** John F. Conley<sup>1</sup>, Devon McClain<sup>2</sup>, Lisa Stecker<sup>1</sup>, Chun Fei<sup>2</sup>, Jun Jiao<sup>2</sup>, Wei Gao<sup>1</sup>, Dave Evans<sup>1</sup> and Yoshi Ono<sup>1</sup>; <sup>1</sup>IC Process Technology Lab, Sharp Labs of America, Camas, Washington; <sup>2</sup>Dept. of Physics, Portland State University, Portland, Oregon.

$\text{In}_2\text{O}_3$ , a transparent wide bandgap semiconductor material with high gas sensitivity, is an excellent candidate for nanostructure device applications such as gas sensors or electrodes. We present a novel low temperature method for uniform growth of  $\text{In}_2\text{O}_3$  nanostructures on 6" Si substrates that does not require separate catalyst materials, high temperature, or template-assistance.  $\text{In}_2\text{O}_3$  nanotips are uniformly deposited on either bare or  $\text{SiO}_2$  thin film coated Si substrates via DC magnetron sputtering at 200-400°C using a 90%  $\text{In}_2\text{O}_3$  / 10%  $\text{SnO}_2$  (ITO) target. The nanocones are investigated with scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), field emission (FE), and photoluminescence (PL). Nanotips are conically shaped and sit atop a 100 nm conductive film. The tips are about 500 nm in length and ~80 nm in diameter at the base, tapering to a point that is capped with a spherical "ball", suggestive of a vapor-liquid-solid (VLS) growth mechanism. XRD patterns indicate a cubic  $\text{In}_2\text{O}_3$  phase. TEM images and electron diffraction patterns show a single crystalline structure for the cone, while the ball appears to be amorphous. Micro-spot EDX results indicate that the cone is composed only of In and O while the ball contains In, Sn, and O. The segregation of Sn in the ball strongly suggests a VLS mechanism in which growth of  $\text{In}_2\text{O}_3$  nanocones is self-catalyzed by the Sn / In / O ball. (A similar mechanism was proposed by Yumoto, et al. for ITO

whiskers observed during e-beam evaporation of an ITO target.) Field emission was observed at a base pressure of  $10^{-8}$  Torr with average turn-on fields from 45-75 V/cm and average threshold fields from 64-105 V/cm. Excitation with a 266 nm wavelength Nd:YAG laser excited no PL in as deposited samples in the wavelength range of 300 nm to 700 nm. Deposition morphology was investigated with respect to  $\text{O}_2$  and Ar flow rates, temperature, power, pressure, wafer rotation, and time. Oxygen flow rate (partial pressure), growth temperature, and Ar flow rate were found to have the biggest impact. Nanocone growth was observed at low  $\text{O}_2$  partial pressure ( $\leq 1\%$ , suppressed for  $\text{O}_2 \geq 2\%$ ), at growth temperatures  $\geq 200^\circ\text{C}$ , and at high Ar flow rate (100sccm, suppressed at 50 sccm). Longer time depositions resulted in longer rods. Chamber pressure, sputtering power, rotation, and throw distance did not have a large impact on morphology.

SESSION Z4: One-Dimensional nanostructures III:  
Nanowires  
Chair: Zhong Lin Wang  
Wednesday Morning, March 30, 2005  
Room 3016 (Moscone West)

### 8:30 AM Z4.1

**Growth of [001] Oriented ZnO Nanorod Arrays with Electric Field Assisted Nucleation.** Huamei Shang<sup>1</sup>, Young J. Kim<sup>1,2</sup>, Ying Wang<sup>1</sup> and Guozhong Cao<sup>1</sup>; <sup>1</sup>MSE, University of Washington, Seattle, Washington; <sup>2</sup>Materials System, Sun Moon University, Seoul, South Korea.

Highly oriented ZnO nanorod arrays were grown on ITO glass substrate from zinc nitrate solution. An external electric field was applied during the initial nucleation stage, and was found to be critical in the orientation of initial crystal seeds. The presence of other cations, such as Ni<sup>2+</sup>, Al<sup>3+</sup>, and Nb<sup>5+</sup> in the solution, was also found to have appreciable influence on the nucleation process and the crystal orientation. Polymer additive, hexamethylenetetramine (HTM), was added to promote anisotropic growth along [001] direction. X-ray diffraction demonstrated that the nanorods have wurtzite crystal structure and the texture coefficient was found to be 0.99 in [001] direction. The diameter and length of single crystal ZnO nanorod arrays can be well controlled and can vary from 50 nm to 700 nm and 0.5 μm to 3 μm respectively depending on the growth conditions applied. However, in given growth conditions, ZnO nanorods have near uniform sizes in both diameter and length. Photoluminescence measurements revealed a broad yellow PL band in the wavelength range of 450-780 nm range, while no observable PL peak at 380 nm. These results strongly suggest that the grown ZnO nanorods consist of interstitial oxygen but little or no oxygen vacancies. Possible mechanisms of oriented nucleation under an externally applied electric field and the relationships between the size and density of ZnO nanorods, crystallinity, and growth condition are discussed.

### 8:45 AM Z4.2

**Polyaniline Nanofibers: Synthesis and Unusual Photothermal Properties.** Jiaying Huang<sup>1,2,3</sup> and Richard B. Kaner<sup>1,2</sup>; <sup>1</sup>Chemistry and Biochemistry, UCLA, Los Angeles, California; <sup>2</sup>California NanoSystems Institute, UCLA, Los Angeles, California; <sup>3</sup>Chemistry, UC-Berkeley, Berkeley, California.

Mechanistic studies reveal that nanofibers of polyaniline form naturally in the early stage of chemical polymerization. The key to making pure polyaniline nanofibers is to prevent secondary growth on the nanofibers which leads to irregularly shaped particles as obtained in conventional polymerization. This has been achieved by either interfacial polymerization or rapidly mixed reactions. Both syntheses are template-free, yet capable of producing pure polyaniline nanofibers with relatively uniform size distributions. The average diameters of the nanofibers can be tuned from 30 to 120 nm by using different doping acids in the polymerization. An unusual photothermal phenomenon has been observed with these nanofibers, in which strong pulsed light, e.g. a camera flash, causes instantaneous welding and turns a random network of polyaniline nanofibers into a smooth and continuous film. This photothermal effect can potentially be useful for making asymmetric nanofiber films, melt-blending polymer-polymer nanocomposites and photo-patterning polymer nanofiber films.

### 9:00 AM Z4.3

**Controlled Growth of Silicon Nanowires for Device Integration.** Allon I. Hochbaum<sup>1</sup>, Rongrui He<sup>1</sup>, Rong Fan<sup>1</sup> and Peidong Yang<sup>1,2</sup>; <sup>1</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>2</sup>Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Silicon nanowires (SiNWs) have been identified as promising

components for nano-scale devices. To realize their full potential in applications, however, SiNW must be integrated efficiently and economically into various device architectures. Devices have been constructed around single, or several, dispersed SiNWs, and methods have been developed to manipulate as-grown SiNWs into geometries amenable to large-scale device fabrication. Alternatively, controlled growth of SiNWs in predetermined configurations would eliminate much of the processing associated with device fabrication. Furthermore, vertical growth (perpendicular to the substrate) would allow three-dimensional integration of these wires in more complex structures, such as vertical field-effect transistor (VFET) arrays. Such arrays could afford higher transistor densities and novel multidimensional logic or memory architectures. The vapor - liquid - solid (VLS) growth mechanism is an ideal synthetic technique to control SiNW growth. VLS growth by chemical vapor deposition (CVD), using SiCl<sub>4</sub> as the precursor gas, produces epitaxially-aligned, single-crystalline wires. Here we demonstrate how gold colloids were used as the VLS metal catalyst to precisely control SiNW diameter and placement. Using a thin adsorbed polyelectrolyte layer, bare gold colloids were deposited from an aqueous solution onto a Si(111) wafer to act as seeds for SiNW growth. The diameter of the colloids precisely dictated the nanowire diameter, and the colloid solution concentration set the density of wire growth. SiNWs of thickness 39, 43, and 93 nm exhibited the same diameter distributions, proportionately, as their respective seed colloids, and their growth density was predictably varied over an order of magnitude. Patterned growth was achieved by micro-contact printing the polyelectrolyte layer. Colloid deposition was limited to 2 $\mu$ m lines stamped with polymer, as were the SiNWs grown from these samples. Moreover, vertically aligned SiNWs were directly grown into microfluidic devices to demonstrate the potential and flexibility of these techniques.

#### 9:15 AM \*Z4.4

**Photoluminescence of Colloidal Semiconductor Quantum Wires.** Fudong Wang<sup>1,2</sup>, Rui Tang<sup>1,2</sup>, John J. Glennon<sup>1,2</sup>, Hooi Ling Kim<sup>1</sup>, Christine Kirmaier<sup>1</sup>, Dewey Holten<sup>1</sup>, Richard A. Loomis<sup>1,2</sup> and William E. Buhro<sup>1,2</sup>; <sup>1</sup>Department of Chemistry, Washington University, St. Louis, Missouri; <sup>2</sup>Center for Materials Innovation, Washington University, St. Louis, Missouri.

Fundamental studies of two-dimensional quantum confinement in semiconductor quantum wires will benefit from wire specimens having well-passivated surfaces, to minimize surface trapping of electrons and holes. As for 3D-confined quantum dots, the quality of quantum-wire surface passivation will likely be best assessed by the photoluminescence (PL) quantum yields and lifetimes, the higher and longer the better, respectively. Typical room-temperature PL quantum yields for CdSe quantum dots are now 30-50%, and may reach as high as 80-90%. PL lifetimes are typically 20-30 ns. One should expect PL quantum yields to be lower in quantum rods and wires, because photoexcited carriers are delocalized over larger volumes and thus sample larger defect-containing surface areas. Indeed, the best PL quantum yields measured in quantum rods are on the order of 15-30%. We are now determining how the PL quantum yields and lifetimes of quantum wires compare to those of the corresponding quantum dots and rods. Colloidal quantum wires having diameters in the strong-confinement regime have been prepared by catalyzed solution-liquid-solid growth, using precursors, conditions, and surfactants closely analogous to those employed in the best quantum-dot syntheses. Analyses of absorption spectra establish that the size dependences of the quantum-wire bandgaps are consistent with 2D confinement. We have observed weak room-temperature PL from both CdSe and InP quantum wires. Our studies show that the quantum-wire PL quantum yields are influenced by several factors previously known to influence the quantum yields of quantum dots. These factors include preparative conditions, use of long-chain primary amine surfactants, post-synthesis photoetching and photoannealing, and introduction of wider-band-gap inorganic shells. The best PL quantum yields we have achieved to date are in the range of 0.5-2.0%. We have determined a PL lifetime of 1.4 ns for a CdSe quantum-wire specimen having a PL quantum yield at the higher end of our observed range. We are also determining how single-nanowire spectroscopic behavior compares to the ensemble spectroscopic measurements. These and related studies will be described.

#### 9:45 AM \*Z4.5

**Semiconductor Nanowires: Rational Synthesis and Optical Properties.** Peidong Yang, Univ. Calif. Berkeley, Berkeley, California.

Semiconductor nanowires exhibit novel electronic and optical properties due to their unique structural one-dimensionality and possible quantum confinement effects in two other dimensions. With a broad selection of compositions and band structures, these 1-dimensional semiconductor nanostructures are considered to be the critical components in a wide range of potential nanoscale device applications. To fully exploit these 1-dimensional nanostructures, our

current research has been focused on rational synthetic control of 1-dimensional nanoscale building blocks, novel properties characterization and device fabrications based on nanowire building blocks, and integration of nanowire building blocks into complex functional architectures. The understanding of the general nanocrystal growth mechanism serves as the foundation for the rational synthesis of semiconductor heterostructures in 1-dimension. The availability of these high quality semiconductor nanostructures allows systematic structural-property correlation investigation, particularly those size- and dimensionality-controlled ones.

#### SESSION Z5: Surface and Interfacial Chemistry of Nanostructures

Chair: James Voigt

Wednesday Morning, March 30, 2005

Room 3016 (Moscone West)

#### 10:30 AM \*Z5.1

**Interfacial Chemistry in the Fabrication of Complex Nanostructures.** Jun Liu<sup>1</sup>, Qisheng Huo<sup>1</sup>, Zhengrong Tian<sup>2</sup> and James A. Voigt<sup>1</sup>; <sup>1</sup>Chemical Synthesis and Nanomaterials, Sandia National Labs, Albuquerque, New Mexico; <sup>2</sup>Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

Understanding and control of the interfacial chemistry is critical for developing functional nanomaterials. In this talk we will discuss three important aspects involved in the fabrication of complex nanostructures: (1) nucleation, (2) morphology control, and (3) renucleation and self-assembly. Controlling the nucleation size and density is important in controlling the dimension and the orientation of the nanostructures. Large arrays of oriented nanowires (oxides and polymers) are prepared by controlling the nucleation density. The morphologies of the nanocrystals are determined by the surface chemistry. Appropriate growth modifiers can be used to systematically control the nanocrystal shapes. Finally, complex nanostructures with long range ordering are prepared by controlled renucleation and self-assembly. We hope that our low-temperature, environmentally friendly approaches can be implemented for a wide range of applications. Sandia National Laboratories is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the Department of Energy under Contract DE-AC04-94AL85000.

#### 11:00 AM \*Z5.2

**Organometallic Approach to Metal Nanoparticles: Synthesis and Surface Chemistry.** Bruno Chaudret, Laboratoire de Chimie de Coordination, CNRS, Toulouse, France.

The use of organometallic precursors allows the synthesis in mild conditions of metal nanoparticles displaying a controlled size, shape and surface environment. The nature of the surface ligands will have a strong influence on the shape of the particles and on their ability to change size and shape in solution. The surface ligands will also influence the chemical reactivity of the particles as well as their organization. The lecture will focus on the synthesis of ruthenium and platinum nanoparticles and to their evolution in solution as well as on the characterization of surface ligands (hydrides, ancillary ligands such as amines and phosphines) and of their dynamics. The use of various characterization methods will be described including tools of molecular chemistry such as gas phase, solution and solid state NMR. Finally, the influence of ligands on the shape and organization of selected particles will be evidenced. References : 1) K. Philippot, B. Chaudret *Dendrimers et Nanosciences* (D. Astruc Ed), *Compte-Rendus Acad Sciences* 2003, 6, 1019. 2) K. Soulantica, A. Maisonnat, M.-C. Fromen M.-J. Casanove, B. Chaudret, *Angew. Chem. (Int Ed)* 2003, 42, 1945 3) F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Fejes, P. Renaud, P. Zurcher, *Angew. Chem. (Int Ed)* 2003, 42, 5213. 4) F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, P. Fejes *Science*, 2004, 303, 821. 5) S. Jansat, M. Gomez, K. Philippot, G. Muller, E. Guieu, C. Claver, S. Castillon, B. Chaudret *J. Am. Chem. Soc.* 2004, 126, 1592.

#### 11:30 AM Z5.3

**Controlling the Capping Agent on Gold NPs.** Adil Kassam, Glen Bremner, Carl Bartels and R. Bruce Lennox; Chemistry, McGill, Montreal, Quebec, Canada.

After the initial report of a relatively facile method to synthesize gold nanoparticles (Au-NPs) by Brust et al.[1], the research into these systems has exploded. In order for these Au-NPs to be used in biological and materials applications, their surface ligand composition must be known and readily manipulated. The place-exchange reaction of the surface-bound thiol is one reaction that enables the functionalization of particles for these applications.[2] By developing a methodology to study place exchange reactions of alkyl thiols of

different chain length using gas chromatography, we have been able to study the entire course of the place exchange reaction with great accuracy and precision. The kinetics of the place exchange reactions have been fitted via diffusion controlled Langmuir kinetics. In addition, the observed reactions proceed to a thermodynamic equilibrium governed by the ratio of the incoming thiol concentration to the amount of thiol on the starting Au-NPs. These results should enable researchers in the field to be able to make Au-NPs with known composition. Other aspects of the reaction including temperature and chain length dependence of the reaction will be discussed. (1) Brust et al. *J. Chem. Soc. Chem. Commun.* 1994 801-802. (2) Hostetler, M., Templeton, A., Murray, R.W.. *Langmuir* 1999, 15, 3782-3789

#### 11:45 AM Z5.4

**Effect of Thiols on the Photophysical Properties of CdSe/ZnS Quantum Dots in Solution.** Soheg Jeong, Marc Achermann, Jagjit Nanda, Sergei Ivanov, Victor I. Klimov and Jennifer A. Hollingsworth; Los Alamos National Lab, Los Alamos, New Mexico.

The impact of thiols on the photophysical properties of CdSe nanocrystal quantum dots (NQDs) is complicated and often deleterious. It is commonly observed that thiol-derivatized CdSe NQDs are not temporally stable, losing both photoluminescence efficiency (initial decrease and additional loss over time following thiol exchange reactions) and solubility. This has been attributed to photocatalytic oxidation of the thiol ligands to disulfides (Peng, *JACS*, 2001). Recently, Hohng and Ha (*JACS*, 2004) reported an unexpected effect of thiol ( $\beta$ -mercaptoethanol) when they added small amounts to streptavidin-conjugated CdSe NQDs. They observed complete suppression of blinking in the thiol-treated NQDs. The issue of NQD blinking is critical for any application that relies on single-dot emission. The process was completely reversible, and the authors attributed the effect to passivation of surface electron traps by the thiol moiety. In order to understand the contradictory reports regarding thiol's contribution to NQD photophysics, we have conducted an extensive study of the impacts of thiol concentration, time, and pH. We studied carrier (electron and hole) dynamics using transient absorption spectroscopy and photoluminescence up-conversion measurements. Focusing primarily on water-soluble CdSe/ZnS, we nevertheless avoided the use of thiols as the solubilizing agent, as thiol ligand-exchange reactions require exposure of the NQDs to high thiol concentrations. Instead, we prepared standard nonpolar-soluble CdSe/ZnS core/shell NQDs and subsequently transferred them to the aqueous phase using a polymer encapsulation method. Our results indicate that the //active// moiety is not the thiol but the deprotonated thiolate. Further, we observe that the effect of //thiols// on NQD PL can be favorable or adverse depending on the concentration of thiolate anion, where the thiol-thiolate equilibrium is influenced by absolute initial thiol concentration, pH conditions, and/or exposure times. Lastly, our studies help point the way to stable, bright thiol-derivatized CdSe/ZnS NQDs.

SESSION Z6: Nanocrystals and Nanoparticles I  
Chairs: Park Hongkum and Dimitri Talapin  
Wednesday Afternoon, March 30, 2005  
Room 3016 (Moscone West)

#### 1:30 PM \*Z6.1

**Shadow Nanosphere Lithography: Simulation and Experiment.** Michael Giersig, Center of Advanced European Studies and Research (CAESAR), Bonn, Germany.

In this letter we describe the preparation of large-area, two-dimensional metallic structures, using shadow nanosphere lithography. By varying the position of the substrate with respect to the evaporation source during the sample preparation, we make morphologies such as cups, rods, and wires, that are not accessible by the standard nanosphere lithography. This technique also allows for an encapsulation of the metallic structures, in order to prevent them from oxidation. Morphologies predicted by our computer simulations have been subsequently confirmed experimentally.

#### 2:00 PM \*Z6.2

**Shape-Controlled Synthesis of Metal Nanostructures.** Younan Xia, Chemistry, University of Washington, Seattle, Washington.

The concept of shape-controlled synthesis will be discussed by elaborating on the nucleation and growth mechanisms for silver nanostructures produced through a polymer-mediated polyol process. It has been found that the experimental parameters such as the concentration of AgNO<sub>3</sub> (the precursor to silver), the molar ratio between poly(vinyl pyrrolidone) (PVP, the capping agent) and AgNO<sub>3</sub>, the strength of chemical interaction between PVP and various crystallographic planes of silver, and the presence of trace

amounts of contaminants all play important roles in determining the crystallinity of seeds (e.g., single crystal vs. decahedral multiply twinned particles). In turn, the crystallinity of a seed and the extent of PVP coverage on the seed were both instrumental in controlling the morphology of final product. In addition to silver, I will also discuss shape-controlled synthesis of gold and platinum nanostructures.

#### 2:30 PM Z6.3

**A Novel Approach for Metallic Nanoparticles Synthesis.** Chunwei Wu and Taofang Zeng; North Carolina State University, Raleigh, North Carolina.

A large variety of synthetic methods for nanoparticles have been developed. The emphasis of synthesis has been on the preparation of monodisperse particles with well-defined size, shape and surface properties. Unfortunately, little success has been achieved to realize all these goals by one synthesis method. We have developed a facile and flexible method for synthesizing stable suspension of polymer protected metal nanoparticles. It is a wet reductive synthesis with the aid of fluid dynamics control. Nearly monodisperse nanoparticles of Ag, Cu, and Ni with sizes ranging from 5 nm to 50nm were produced. The particle size and particle size distribution (PSD) can be fine tuned by controlling the concentration of metallic cations, the relative molar ratio of capping reagent poly(vinylpyrrolidone) (PVP) to the cations, and the average reaction time of the continuously agglomerating particles in liquid phase. Particle morphology and structure were characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD) and electron diffraction (ED).

#### 2:45 PM Z6.4

**Synthesis of Co/Au and Co/Ag Bimetallic Nanoparticles.** Guangjun Cheng, Danilo Romero and Angela Hight Walker; Physics, NIST, Gaithersburg, Maryland.

Bioconjugated magnetic nanoparticles have shown the great potential applications in medical sensors and drug delivery. Here we present the synthesis of Co/Au and Co/Ag bimetallic nanoparticles. These bimetallic nanoparticles are expected to maintain their magnetic properties of Co component, while Au or Ag part can improve their biocompatibility. Co/Au and Co/Ag Nanoparticles are prepared by growing Au or Ag on the pre-synthesized Co nanoparticles. Transmission electron microscopy (TEM), UV-Vis spectroscopy, and a superconducting quantum interference device (SQUID) magnetometer are used to characterize as-prepared bimetallic nanoparticles.

#### 3:00 PM Z6.5

**Electrochemical Synthesis of Size-Controlled Metal Nanoparticles as Catalysts for 1-D Materials.** Sreekar Bhaviripudi<sup>1</sup>, Jifa Qi<sup>1</sup> and Angela M. Belcher<sup>1,2</sup>; <sup>1</sup>Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Biological Engineering Division, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We report a simple, efficient, room temperature nanoparticle synthesis technique using electrochemical method to achieve size and shape monodispersity for controlled material properties. The physical properties of one-dimensional materials such as carbon nanotubes and semiconducting nanowires are largely dependent on diameter. Moreover the diameter of these 1-D systems depends on the size of the catalyst from which they are grown using CVD. Thus achieving uniform electronic properties for 1-D systems entails narrow size distribution for the catalyst particles. However, this has been the problem at hand for many researchers. Secondly, monodisperse nanoparticles on substrates can result in uniform electronic, magnetic and optical properties, which could be exploited for various materials science and biological applications such as detection and separation of biomolecules. We have used novel electrochemical methods to deposit nanoparticles of Fe, Al, Zn and Au on n-Si (100) substrates. The nanoparticle size and monodispersity are dependent on the applied current density and the deposition time. These parameters are being modulated to achieve narrow size distribution. The nanoparticles have been characterized using AFM, TEM, EDX and XPS. AFM results indicate monodispersity and uniform deposition of nanoparticles. Samples with different nanoparticle sizes were synthesized which included 5nm, 15nm, 25 nm and larger. As anticipated, the longer the time scale for deposition and the higher the deposition voltage, the larger the nanoparticle size. Moreover the different particle sizes that could be obtained during synthesis were found to be material specific. One of the exciting results that we obtained during synthesis occurred during aluminum deposition where we observed self-aligned parallel arrays of Al nanoparticles with average interarray spacing of 100nm. TEM results not only corroborate AFM results, but also reveal the crystalline nature of these particles. We are currently investigating magnetic properties of Fe nanoparticles on the silicon surface and the SQUID results suggest ferromagnetic behavior above a certain size and paramagnetic below it. Furthermore, we intend to evaluate the interactions between such functionalized nanoparticles and

biomolecules for separation and detection.

### 3:30 PM \*Z6.6

**Transition Metal Oxide Nanocrystals and Bimodal Nanocrystal Superlattices.** Stephen O'Brien, Applied Physics and Applied Mathematics, Columbia University, New York, New York.

Nanocrystals of the transition metal oxides are of interest because of numerous potential applications related to their size, surface, and size dependent properties. Our materials chemistry techniques have allowed us to prepare oxide nanocrystals of some of the first row transition metals very successfully, with high yields, crystallinity and monodispersity. Control over the quality of the nanocrystals can then allow a rigorous understanding of the material properties at the nanoscale. Control over monodispersity also allows the treatment of nanocrystals as "hard spheres" in the assembly of an amazing variety of close packed structures, so called superlattices, that can consist of more than one type of nanocrystal. Such methods could lead to the rational design of functional materials based on nanocrystal assembly.

### 4:00 PM \*Z6.7

**Doped Semiconductor Nanocrystals.** S. C. Erwin<sup>1</sup>, M. Haftel<sup>1</sup>, T. A. Kennedy<sup>1</sup>, Al. L. Efros<sup>1</sup>, Lijun Zu<sup>2</sup> and David J. Norris<sup>2</sup>; <sup>1</sup>Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Chem. Eng. & Mater. Sci., Univ. of Minnesota, Minneapolis, Minnesota.

This talk will address the intentional incorporation of impurities (or dopants) into semiconductor nanocrystals (or colloidal quantum dots). While a variety of doped nanocrystals have recently been synthesized, no detailed understanding exists about how this process works or how it can be controlled. Moreover, it is not clear why it is possible to introduce impurities into some semiconductor nanocrystals but not into others. These difficulties have hindered the development of a whole class of new materials, including n-type and p-type nanocrystals. Here we report a new model that addresses the doping problem. This model is intriguing because not only can it explain prior results, but it also provides several key predictions that can be tested by experiment. We use Mn-doped II-VI semiconductor nanocrystals to explore these predictions. The results, including the influence of several key parameters on the efficiency of doping, will be discussed.

### 4:30 PM Z6.8

**Electroless Deposition of Silver Particles by Galvanic Displacement on Aluminum Alloyed with Copper.**

Dmitri A. Brevnov, Tim S. Olson and Plamen B. Atanassov; Chem & Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico.

In this presentation, we report a procedure for the electroless deposition of silver particles on films containing 99.5 % aluminum and 0.5 % copper. The deposition proceeds in the absence of external reducing agents via the galvanic displacement mechanism by which silver cations are reduced and copper is oxidized. Although aluminum is a stronger reducing agent than copper, the galvanic displacement of aluminum by silver is not observed with pure (99.997 %) aluminum substrates. By alloying aluminum with copper, aluminum films are made amenable to electroless deposition of silver by galvanic displacement. Electroless deposition of silver becomes possible because copper is pre-concentrated on the surface of the substrate. Enrichment of copper just beneath the film of anodic aluminum oxide is typically observed during anodization of aluminum / copper alloys. In order to generate a clean surface for electroless deposition with a controlled and minimal thickness of surface oxide, the aluminum films alloyed with copper are anodized in oxalic acid and etched in a mixture of chromic and phosphoric acids. Thinning of the barrier aluminum oxide during etching and deposition of silver particles are monitored with electrochemical impedance spectroscopy (EIS). Analysis of EIS data indicates that deposition of silver particles for 3 hours dramatically increases the interfacial capacitance from 5-6  $\mu\text{F}/\text{cm}^2$ , characteristic for a thin layer of barrier aluminum oxide, to 30 - 40  $\mu\text{F}/\text{cm}^2$ , typical for metal electrode surfaces. Scanning electron micrographs show that electroless deposition results in the formation of films composed of silver particles. The method for electroless deposition of silver and electrodeposition of other metals on aluminum / copper alloys can be utilized to synthesize quantum dots supported on electrically conductive substrates. In addition, the silver particles deposited on aluminum / copper films can be employed for the fabrication of miniature silver-zinc batteries, optical devices for surface enhanced Raman scattering and FT-IR spectroscopy, composite materials with photo-catalytic properties and surfaces with anti-microbial properties.

### 4:45 PM Z6.9

**Synthesis and Characterization of Novel Core-Shell CdSe/Zn1-xMnxS and CdSe/Cd1-xMnxS Quantum Dots.**

Shizhong Wang<sup>1</sup>, Angelique Louie<sup>1</sup> and Susan M. Kauzlarich<sup>2</sup>;

<sup>1</sup>Department of Biomedical Engineering, University of California, Davis, California; <sup>2</sup>Department of Chemistry, University of California,

Davis, California.

Doping Mn into CdSe quantum dots could produce a novel material of dual properties of paramagnetism and luminescence. However, previous research showed that the direct doping of a high level Mn was restricted by the large difference of crystal lattice parameters between Mn and CdSe. In this work, we present the design and synthesis of novel core-shell CdSe/Zn1-xMnxS and CdSe/Cd1-xMnxS quantum dots. In comparison with Cd1-xMnxSe quantum dots from the direct doping, these materials take the advantage of controllable Mn-doping amount due to the optional shell thickness and the more comparable crystal lattice parameters of Mn and ZnS (or CdS). In addition, the presence of wider band-gap shell of Zn1-xMnxS or Cd1-xMnxS on CdSe core greatly improved its luminescent efficiency. Synthesis was performed via high-temperature pyrolysis in trioctylphosphine and hexadecylamine system. Structure, optical properties, and paramagnetic properties were characterized by a combination of techniques including transmission electron microscope, UV-vis absorption, photoluminescence, and electron paramagnetic resonance spectroscopy.

SESSION Z7: Poster Session: Synthesis,  
Characterization, and Applications of Nanostructures  
Chair: Zhifeng Ren  
Wednesday Evening, March 30, 2005  
8:00 PM  
Salons 8-15 (Marriott)

### Z7.1

**A Facile Synthetic Route using Autogenerated Air Bubbles for the Spontaneous Formation of Nanostructures.**

Seok Min Yoon and Hee Cheul Choi; Department of Chemistry, Pohang University of Science and Technology, Pohang, South Korea.

Inorganic nanostructures are of great interests due to their possible role as a building block for next generation electronic components and sensor applications. Several synthetic methods have been developed for the formation of quantum dots (QD), quantum wires and tubes (1D) via gas phase reactions at high temperature as well as solution phase reactions. With some obvious advantages such as low energy consumption, varieties of precursor selection, opportunity of various in situ analyses during the reaction, etc., more efforts are currently being focused on the development of synthetic routes which can run at a milder condition. Here we present a new simple method which utilizes auto-generated bubbles for the generation of nanorod and nanoring type structures at room temperature. Nanorod and nanoring of iron are formed by simply mixing Fe(III) ion containing water solution with ethanol followed by hydroxylamine solutions under vigorous mechanical shaking. The formation of nanorod structures was confirmed by atomic force microscope (AFM) as well as transmission electron microscope (TEM). It seems that the role of bubble is critical for the nanostructure formation at room temperature. Micro- or nano-sized bubbles are spontaneously generated by mixing and shaking two solutions, water and ethanol. Because of difference in densities, micro or nano-sized bubbles are generated through the penetration of water molecules into the void space of ethanol layer. Possible arrangement of bubbles into the microchannel array can confine Fe(III) ions and further treatment with hydroxylamine increases intermolecular interactions to make them rigid rod or filament shape.

### Z7.2

**Cupreous ZnO Nanoclusters: Synthesis and Gas Sensing**

**Properties.** Kaluram G. Kanade<sup>1</sup>, Bharat B. Kale<sup>2</sup>, Yogesh Sonawane<sup>3</sup> and Rohini C. Aiyer<sup>3</sup>; <sup>1</sup>Department of Chemistry, Mahatma Phule College, Pune, India; <sup>2</sup>Nanocrystalline Materials, Center for Materials for Electronics Technology, Pune, India; <sup>3</sup>Department of Physics, Pune University, Pune, India.

Methanol mediated Cu doped ZnO clusters were synthesized by co-precipitation method. Dopant percentage of Cu was optimized from copper chloride to achieve the desired percentage of copper in ZnO and same was confirmed with ICP-OES analysis. The ZnO cluster size of 16 to 19 nm having hexagonal structure was obtained. UV-visible, SEM, XRD and Photoluminescence were used for material characterization. From UV-Visible, a single sharp peak corresponding to 362nm, equivalent to a band gap of 3.42 eV shows high monodispersivity. Spherically shaped particles of synthesized powders were observed in SEM and TEM. The synthesized powder was used in the form of pellet for its gas sensing properties of CO and home cooking gas (LPG). These sensors showed lowest optimum operating temperature, which is in the range 125°C -150°C. To the best of our knowledge, this is the lowest operating temperature for ZnO based sensors in the pellet form. The pellets having 1.0 % Cu have shown high sensitivity response for CO gas, while that with 0.5% Cu showed

more sensitivity for LPG gas. The response time of the sensors was observed around 12-15 seconds. Keywords: Nano-clusters, zinc oxide, gas sensors, crystal structure, copper For correspondence : Dr. B. B. Kale\*: Email: kbbb1@yahoo.com Prof. (Mrs.) R.C. Ayer \*\*E-mail: rca@physics.unipune.ernet.in Presenting Author: Prof. K.G. Kanade : Email: kgkanade@yahoo.co.in

### 7.3

**A Systematic Study on Cadmium N-Alkyldithiocarbamate Complex for the Synthesis of CdS Nanomaterials.** Ashfaq Ahmed Memon<sup>1</sup>, Mohammad Afzaal<sup>2</sup>, Mohammad Azad Malik<sup>2</sup> and Paul O'Brien<sup>2</sup>; <sup>1</sup>Shah Abdul Latif University, Khairpur, Pakistan; <sup>2</sup>Chemistry, University of Manchester, Manchester, United Kingdom.

Group II-VI semiconductor nanomaterials have continued to be an active area of research because of their potential applications in optoelectronic devices. In this study, cadmium sulfide nanoparticles, nanorods, and nanotriangles capped with hexadecylamine (HDA) were synthesized by using an air-stable single-source precursor based on cadmium dithiocarbamates; [Cd(S<sub>2</sub>CNHC<sub>12</sub>H<sub>25</sub>)].<sup>1</sup> This is the first such study on cadmium dithiocarbamates where resulting morphologies are analysed as a result of monomer concentration and temperature. Such route also offers safer, low cost, high yields and more controllable synthesis. It was established that shapes and sizes of the CdS nanoparticles vary considerably on the concentration of precursor and growth temperature. Nanomaterials were characterized by various techniques including UV/Vis, PL, XRD and HR-TEM/EDAX. Reference 1) L. H. V. Poppel, T. L. Groy, M. T. Caudle, Inorg. Chem. 2004, 43, 3180.

### 7.4

**Synthesis of Ni(II), Pt(II) and Pd(II) Sulfide Nanoparticles from Metal Ethyl Xanthate Precursors.** Neerish Revaprasadu<sup>1</sup>, Phumudzo Musetha<sup>1</sup>, Mohammad Azad Malik<sup>2</sup> and Paul O'Brien<sup>2</sup>; <sup>1</sup>Chemistry, University of Zululand, Empangeni, South Africa; <sup>2</sup>Chemistry, University of Manchester, Manchester, United Kingdom.

The use of single molecule precursors (SSP) is a well established route to monodispersed, high-quality nanoparticles.<sup>1</sup> The xanthates as a class of precursors have recently attracted interest in the preparation of metal sulfides with varying morphologies.<sup>2,3</sup> In this paper we extend our initial work on cadmium xanthates [Cd(S<sub>2</sub>COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] to other metals such as Ni(II), Pt(II) and Pd(II).<sup>2</sup> These compounds were used as SSP for the synthesis of Ni, Pt and Pd sulfide nanoparticles. The size and shape of the nanoparticles was achieved by controlling parameters such as the reaction temperature, reaction time and concentration of the monomer. The nanoparticles have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). References 1. T. Trindade, P.O'Brien and N. Pickett, Chem. Mater., 2001, 13, 3843. 2. P. Sreekumari Nair, N. Revaprasadu, T. Radhakrishnan, G.A. Kolawole and P.O'Brien, J. Mater. Chem., 2002, 12, 2722. 3. N. Pradhan, B. Katz and S. Efrima, J. Phys. Chem.B, 2003, 107, 13843.

### 7.5

**Fabrication of Gold Nanowire by Self-Assembled Supramolecule Template.** Seung-a Kim and Hee-tae Jung; Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Gold nanowire was fabricated by thermotropic supramolecule template at room temperature under air condition. Supramolecule was used form an inverted hexagonal phase with several micrometer length. Supramolecule dissolved in ethyl acetate and acetone and added NaOH aqueous solution to exchange H<sup>+</sup> with Na<sup>+</sup>. The solution was mixed with hydrogen tetrachloroaurate(III) trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) aqueous solution to exchange Na<sup>+</sup> ion with Au<sup>3+</sup> ion by stirring. Then, deposits were arised in the solution. The solution was separated in two phases. Gold nanowire was prepared by reduction of HAuCl<sub>4</sub> using UV irradiation. Ingredients of each phase in the solution were investigated by Thermal Conductivity Detector (TCD) and X-ray Photoelectron Spectroscopy (XPS). TEM images show the fabrication of nanowire.

### 7.6

**A Study of the Influence of Precursor Concentration, Reaction Temperature and Capping Groups on the Morphology of CdS and PbS Nanoparticles.** Sibusiso Mlondo<sup>1</sup>, Neerish Revaprasadu<sup>1</sup>, Paul Christian<sup>2</sup> and Paul O'Brien<sup>2</sup>; <sup>1</sup>Chemistry, University of Zululand, Empangeni, South Africa; <sup>2</sup>Chemistry, University of Manchester, Manchester, United Kingdom.

Research in materials with critical dimensions of the order of nanometers has made a huge impact in the scientific community in the past decade. The intense interest in these materials is attributed to their unique chemical and electronic properties which make them potentially useful in a wide range of applications, including nonlinear

optics, solar cells, electronics, biotechnology and optoelectronics. The control of particle size and morphology is an important for the use of nanoparticles in various applications. Recently, CdS and PbS nanoparticles have attracted attention due to their variation in one dimensional morphology with changes in reaction conditions<sup>1</sup>, and their interesting applications in the near-IR communications (PbS) and in solar cells (CdS). We report the synthesis of metal sulfide nanomaterials with varying morphologies using single source precursors based on the thiosemicarbazide ligand. The single crystal x-ray structures of [Cd(NH<sub>2</sub>CSNHNH<sub>2</sub>)Cl<sub>2</sub>]<sub>n</sub> precursor complex is reported, along with results from related lead complexes. The precursors were thermolysed in a hot co-ordinating solvents such as hexadecylamine (HDA) using the one-pot single-molecule precursor route.<sup>2</sup> By varying the important parameters such as precursor concentration, growth time and reaction temperature we have been able to prepare various nanomaterials with a range of morphologies and sizes. UV/Vis and photoluminescence spectra were used to study the materials optical properties. The structural properties of the materials were studied by X-ray diffraction and TEM. References 1. S. M. Lee, S. N. Cho, and J. Cheon, Adv. Mater., 15(5), 2003 2. M.A. Malik, N. Revaprasadu, and P.O'Brien, Chem.Mater.,13(3),2001

### 7.7

**Morphology and Properties of Tetraleg ZnO Nanostructures Fabricated by Zn-Powder Evaporation without Catalyst at Lower Temperature.** Yue Zhang<sup>1,2</sup>, Yunhua Huang<sup>1</sup>, Jian He<sup>1</sup>, Ying Dai<sup>1</sup>, Sen Wang<sup>1</sup> and Cheng Zhou<sup>1</sup>; <sup>1</sup>Department of Materials Physics, University of Science and Technology Beijing, Beijing, China; <sup>2</sup>State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing, China.

Through precisely controlling temperature, gases flow rates, partial pressures of argon, oxygen and zinc vapor, different morphology and sizes of tetraleg ZnO nanostructures have been fabricated respectively through pure zinc powder evaporation without catalyst at temperature of 600~800 degrees centigrade. Such ZnO nanostructures were fabricated by the following procedure. The silicon substrate was placed face down on an alumina ceramics boat loaded with metal zinc powder (99.9%) with thickness of 1~3 mm. The vertical distance between the zinc source and the substrate was about 5~8 mm. And then the alumina ceramics boat was inserted into the quartz tube (30 mm inside diameter) of a tubular furnace under a constant flow of argon and oxygen. The total flow rate was 250~350 standard cubic centimeters per minute (scm), and the fraction of oxygen was 3 ~ 10% according to changes of the conditions. The quartz tube was heated up to 600 ~ 800 degrees centigrade, i. e. the reaction temperature, for 20~40 minutes. No catalyzer was utilized in all the deposition process. The fabricated tetraleg ZnO nanostructures exhibited several types in morphology with different shapes and sizes of the legs. The shapes of the legs include hexagonal and columnar rod, trumpet-like, needle, pin-like, etc. Some of the structures had not been described in previous works. Some multi-leg structures were also synthesized. The length of the legs was about 2~10 micron and the diameter was in the range of several tens to several hundreds nanometers. The key of the fabricating method is to control the flow rates of gases, partial pressures of argon, oxygen and zinc vapor. The flow rates and partial pressures of argon and oxygen influence the size and the shape. Experiments revealed that the synthesis temperature influences the shapes by changing the partial pressures of Zn, and affects the size too. As the temperature or partial pressure Zn vapor increases, the nanostructures prefer being large size. The growth mechanisms of the nanostructures were proposed and discussed. The nucleation accords with the octahedral multiple twin (octa-twin) nucleus models put forward by Iwanaga. The growth of ZnO nanostructures is controlled by vapor-solid mechanism. Photoluminescence spectra and field emission property have been measured. UV and green emission peaks were observed at room temperature. Such ZnO nanostructures are likely to be candidates as building blocks for constructing photonic and field emission crystals.

### 7.8

**Synthesis and Electrochemical Properties of V<sub>2</sub>O<sub>5</sub>/nH<sub>2</sub>O Nanotube Arrays and Ni-V<sub>2</sub>O<sub>5</sub>/nH<sub>2</sub>O Core-shell Nanocable Arrays.** Ying Wang<sup>1</sup>, Katsunori Takahashi<sup>1,2</sup>, Huamei Shang<sup>1</sup>, Kyoungho Lee<sup>1</sup> and Guozhong Cao<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Washington, Seattle, Washington; <sup>2</sup>Steel Research Laboratory, JFE Steel Corporation, Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan.

Orthorhombic vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is well-known for applications in electrochemical supercapacitors because of its Li-ion intercalation ability, whereas low-crystalline or amorphous hydrated vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>/nH<sub>2</sub>O) is generally considered to have higher Li<sup>+</sup> intercalation capacity than crystalline V<sub>2</sub>O<sub>5</sub>. We have prepared nanostructured electrodes of V<sub>2</sub>O<sub>5</sub>/nH<sub>2</sub>O using the template-based electrodeposition method. Nanotubes of V<sub>2</sub>O<sub>5</sub>/nH<sub>2</sub>O were deposited from VOSO<sub>4</sub> solution into the pores of a



polycarbonate filtration membrane. This procedure produced an array of ~200 nm dia and 10  $\mu$ m long nanotubes of V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O. In similar processes, Ni-V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O nanocable arrays were achieved in two steps: first, Ni nanorod arrays were prepared through the template-based electrochemical deposition; then a coating of V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O was applied over the Ni nanorods through electrophoretic deposition from a V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O sol. TEM micrographs clearly showed each Ni core was covered completely and uniformly by a V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O shell. Electrochemical analysis demonstrated that the intercalation capacities and charge/discharge rates of both nanotube-array and nanocable-array electrodes were much higher than those of V<sub>2</sub>O<sub>5</sub> film electrode. With the Ni core diameter as ~200 nm and the average V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O shell thickness as 40 nm, the Ni-V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O nanocable arrays delivered 40 times the capacity of the film electrode. Both energy density and power density of such nanocable array electrodes were higher than the film electrode by at least one order of magnitude. Such significant improvement in electrochemical performance is due to the large surface area and short diffusion path offered by the nanostructured V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O.

#### **Z7.9**

**Synthesis of CdS@TiO<sub>2</sub> Coaxial Nanotubular Materials Using Liquid Phase Deposition with Precise Control of the Sheath Thickness.** Ming-Chi Hsu, Ing-Chi Leu, Yu-Ming Sun and Ming Hsiung Hon; Materials Sci. & Eng., National Cheng Kung University, Tainan, Taiwan.

TiO<sub>2</sub>/CdS composites have been extensively investigated for their applications in solar energy cells, catalysis, and electrochromic devices. It has been well established that in the composites, CdS and TiO<sub>2</sub> serve for light collection and photo-induced charge transfer, respectively. Due to the expanded contact area and excellent capacity of charge transport in 1D nanostructures, the CdS@TiO<sub>2</sub> composite nanowires can be expected to present eminent prospects for both fundamental study and applications. In this study, a novel fabrication route of CdS@TiO<sub>2</sub> with the wall thickness controlled precisely hybrid coaxial nanowires could be prepared using liquid phase deposition (LPD) method with porous anodic aluminum oxide (AAO) as templates. Using LPD method, the thickness of the TiO<sub>2</sub> sheaths could be controlled precisely by adjusting the reaction conditions. Sequentially, the continuous and polycrystalline CdS nanorods were deposited onto titanium oxide nanotubes by chemical bath deposition in order to form the coaxial CdS@TiO<sub>2</sub> nanowires. The core/sheath nanowires were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-visible spectroscopic techniques. And a possible growth mechanism of the formation of the composite nanowires was also proposed.

#### **Z7.10**

**A New Family of High-Temperature Thermal Insulators: IR Opacified, Fiber-Reinforced Silica Aerogel Composite Blankets.** Dmitry Fomitchev, Roxana Trifu, Irene Melnikova, Wendell Rhine and George Gould; Aspen Aerogels Inc., Northborough, Massachusetts.

The thermal stability and high-temperature thermal conductivity of the fiber-reinforced, IR opacified silica aerogel composite blanket, commercially available from Aspen Aerogels Incorporated as AR5223, are described. The aerogel composite blanket is fabricated via sol-gel processing and supercritical drying with carbon dioxide. The material has a mesoporous structure with the average pore diameter 8 nm, surface area 550 m<sup>2</sup>/g, and density 0.11-0.12 g/cm<sup>3</sup>. It is designed for applications with the maximum continuous use temperature not higher than 650 °C. The composite contains zirconium silicate powder, which is the IR opacifier that effectively reduces the radiative component of heat transfer. Nanometer sized dopants help to mitigate shrinkage and pore collapse upon exposure to high temperature. Although the commercially available product is hydrophobic, it irreversibly loses hydrophobicity after exposure to temperatures above 450 °C. Thermal conductivity data up to 700 °C demonstrate that AR5223 outperforms many types of non-load bearing thermal insulation of comparable density such as Saffil and Q-fiber felt. Thermal conductivity data were also obtained for similar composites opacified with titanium dioxide and carbon black. The data show that carbon black is the most effective IR opacifier among the tested pigments. Its utility, however, is limited to non-oxidizing environments or short term applications. Thermal conductivity data at 1 torr and 0.001 torr imply that gaseous component of heat transfer in Aspen's composites is very small at these pressures. The possibility of extending limits of performance for short-term exposure to temperatures up to 1000 °C was investigated. Shrinkage, after exposure to 1000 °C for short periods of time, was studied as a function of density and dopant concentration.

#### **Z7.11**

**Nanomaterials Synthesis by Nanoparticle Beam Pulsed Laser**

**Deposition.** Mevlut Bulut and Renato P. Camata; Dept of Physics, Univ. of Alabama - Birmingham, Birmingham, Alabama.

Naturally occurring materials often derive their outstanding properties from optimal anisotropic arrangements of nanoscale constituents. This requires a hierarchical organization of matter over several length scales, which is exceedingly difficult to achieve in artificial materials made by conventional physical and chemical methods. The combination of laser and aerosol processes offers a promising platform for creating thin film materials with a level of microscopic organization similar to that found in nature. In this work we describe how we have used laser deposition principles and aerosol technology to develop a novel nanomaterials synthesis technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD). Contrary to conventional PLD, this approach allows decoupling of deposition of nanoparticles and gas-phase species that often coexist in ablation plumes so that these two processes are manipulated independently. This is achieved by operating two independent PLD-based sources, such that one source exclusively generates nanoparticles while the other employs a gas-phase dominated plume. In the NBPLD source gas-suspended nanoparticles are generated by the ablation of a solid target in inert or reactive ambient using the focused beam of an excimer laser. A complex interplay of gas-phase nucleation, vapor condensation, and Brownian coagulation gives rise to a nanoparticle aerosol with average size in the 1-30 nm range. Through proper choice of target material, background gas reactivity and temperature, and turbulent mixing conditions, gas-suspended particles with well-controlled chemical composition and stable number concentration are produced. This nanoparticle aerosol goes through an ionization zone where it acquires an equilibrium charge distribution. The charged nanoparticles are then sorted according to size based on their different migration velocities in an electric field across a particle-free laminar gas stream. Size-selected nanoparticles are extracted from this classification region and delivered to a substrate either as an unfocused nanoparticle spray (through free expansion) or as a tightly focused nanoparticle beam (through aerodynamic focusing). Gas-phase species of different materials are simultaneously or sequentially deposited by conventional PLD using an independent laser source. We have used this technique in the fabrication of metal nanoparticles that can be incorporated in matrices for property modulation as well as nanostructured zinc oxide thin films and biocompatible calcium phosphate nanostructures for biomedical applications. Atomic force microscopy on samples produced by this method using silver nanoparticles size selected at (8.0±0.6) nm and deposited on a silicon [110] surface show remarkable uniformity of the nanoparticle ensembles, which extends to regions several millimeters across. Nanoparticle size is tunable in the 3-20 nm range while nanoparticle concentration may be adjusted between 10<sup>8</sup> and 10<sup>12</sup> cm<sup>-2</sup>.

#### **Z7.12**

**Synthesis of TiO<sub>2</sub> Nanoparticles Using Chemical Vapor Condensation.** Jie Wu, Guoren Bai and Jeffrey A. Eastman; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Nano-sized TiO<sub>2</sub> particles are of interest for many applications, including use as photocatalysts and in heat transfer fluids (nanofluids). In the present study, TiO<sub>2</sub> nanoparticles with controllable phase and particle size have been obtained through homogeneous gas-phase nucleation using chemical vapor condensation (CVC). The phase and particle size of TiO<sub>2</sub> nanoparticles under various processing conditions have been characterized using x-ray diffraction and transmission electron microscopy. Chamber temperature and pressure were found to be two key parameters affecting particle phase and size. Pure anatase phase was observed at temperature as low as 600 °C with chamber pressure varying from 50 torr to 20 torr. When the furnace temperature was increased to 1000 °C at a pressure of 50 torr, a mixture of anatase and rutile phase was observed, with the predominant phase being anatase. The average particle size under all the experimental conditions is less than 20 nm. The chemistry and thermodynamics of the formation of nanocrystalline TiO<sub>2</sub> particles will be discussed in this poster.

#### **Z7.13**

**Synthesis of GaS Nanoparticles using [Ga(S<sub>2</sub>CNET<sub>2</sub>)<sub>3</sub>] as a Single-Source Precursor.** Mohammad Azad Malik<sup>1</sup>, Paul O'Brien<sup>1</sup>, Neerish Revaprasadu<sup>2</sup> and Sibusiso N. Mlondo<sup>2</sup>; <sup>1</sup>School of Chemistry, University of Manchester, Manchester, United Kingdom; <sup>2</sup>Department of Chemistry, University of Zululand, Empangeni, Kwazulu-Natal Province, South Africa.

The thermolysis of single-molecule precursors in high boiling point co-ordinating solvents is an established route to high quality surface passivated nanoparticles. We report synthesis of GaS nanoparticles in 4-ethylpyridine at 160 °C using a stable single source precursor [Ga(S<sub>2</sub>CNET<sub>2</sub>)<sub>3</sub>]. The as-prepared nanoparticles show size-dependant

properties such as a blue shift in the UV/Vis spectrum. Other techniques used to investigate the properties of the nanoparticles include PL, XRD and TEM. The results of this study are presented and discussed. References 1. T. Trindade, P.O'Brien and N. Pickett, Chem. Mater., 2001, 13, 3843.

#### **Z7.14**

**Synthesis of Monodisperse, Submicron-Sized Spherical V<sub>2</sub>O<sub>5</sub> Particles.** Shinpei Yamamoto, Mikio Takano and Yuchi Shimakawa; Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan.

Monodisperse, submicron-sized spherical metal oxide particles attract much interest in many areas of science and technology, e.g., pigments, catalysts, raw materials of advanced ceramics, and photonic crystals. Among a number of preparing methods, hydrolysis of metal alkoxide in homogeneous solution is one of the most effective methods to prepare high purity spherical metal oxide particles. However, application of this method for preparing small particles has been limited to less reactive metal alkoxides. In this study, we have succeeded in synthesizing monodisperse, submicron-sized spherical V<sub>2</sub>O<sub>5</sub> particles with narrow size distribution via hydrolysis of a reactive vanadium isopropoxide (VO(OiPr)<sub>3</sub>) in acetone/pyridine mixed solution. Transmission electron microscopic observations revealed that the formed particles had almost perfect spherical shape and were non-agglomerated. Their sizes are 200 to 800 nm with narrow size distribution of less than 7%. In addition, the particle size can be easily controlled by changing the concentration of pyridine. Another important feature of our method is the extremely fast formation of the monodisperse spherical particles. They formed at most within 30 sec, or possibly much faster. The obtained particles have layered structure and have a composition of V<sub>2</sub>O<sub>5</sub> xPy yH<sub>2</sub>O (x = 0.8, y = 0.9) independent of their size. X-ray diffraction studies also revealed that our V<sub>2</sub>O<sub>5</sub> particles have an interlayer spacing of ca. 1.05 nm, indicating intercalation of H<sub>2</sub>O and pyridine between the V<sub>2</sub>O<sub>5</sub> sheets. V<sub>2</sub>O<sub>5</sub> particles are possibly used in catalysis, lithium ion battery, electrochromic device, sensors and actuators. The monodisperse spherical V<sub>2</sub>O<sub>5</sub> particles obtained by our developed method will greatly improve the performance in such applications.

#### **Z7.15**

**Self-peeling of Porous Nickel Foam from the Electrochemically Etched Porous Silicon.** Xi Zhang and King-Ning Tu; Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California.

A moderately doped p-type silicon wafer was wet-etched to form macro-size pores in a straight high aspect ratio manner along the Si (100) direction. It was then plated in a concentrated ammonium fluoride (NH<sub>4</sub>F) aqueous solution containing Ni<sup>2+</sup>. Metallic Ni was rapidly deposited into the macro-pores without using a reducing agent or any activation treatment at a slightly elevated temperature. After being extended for a long immersion duration, the initially single crystalline Si sidewall on the pores was almost completely replaced by a polycrystalline Ni film while the original one-dimensional deep micron-size pore structure was still maintained. Newly generated voids or nanopores were found inside the nickel metallized sidewalls of the straight pores. When nickel became the dominant phase in the entire porous part, the porous Ni metallic film more than 200 micrometers thick was discovered to be able to peel off very easily from the silicon substrate beneath. In this way, a nickel foam with straight pores of very high aspect ratio is self-formed and self-peeled.

#### **Z7.16**

**The Photophysics of Si Nanowires Grown via Chemical Vapor Deposition.** Alex Richard Guichard<sup>1</sup>, David Nicholas Barsic<sup>1</sup>, Mark L. Brongersma<sup>1</sup>, Ted I. Kamins<sup>2</sup> and Shashank Sharma<sup>2</sup>; <sup>1</sup>Materials Science & Engineering, Stanford University, Stanford, California; <sup>2</sup>Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

Since the initial discovery of efficient, visible photoluminescence from highly porous Si by Canham et al, much effort has been devoted to integration of Si nanostructures into photonic devices. Si nanowires with diameters less than 10 nm are model systems for studying the effects of quantum confinement on the optical properties of Si nanostructures. We have grown Si nanowires using Ti-catalyzed chemical vapor deposition with diameters ranging from 8 nm to 35 nm. In subsequent processing steps, the wire diameter was reduced by oxidizing the nanowire, followed by removing the oxide by etching; the surface was then passivated before optical measurements. We have observed photoluminescence (PL) from the nanowires with an emission wavelength that is substantially shifted from that corresponding to the bandgap of bulk Si and long luminescence decay lifetimes on the order of 10 μs. Both of these observations are in agreement with the quantum-confined exciton model for light emission. We will present transmission electron microscopy and PL studies that provide information on the size-dependent optical

properties of the wires. Proper surface passivation of the nanowires is essential to obtain efficient light emission, and we will discuss different passivation strategies. The result of this work may have implications for the design and fabrication of future CMOS-compatible light sources and photonic devices.

#### **Z7.17**

**Ferromagnetism Above the Room Temperature of ZnO Doped with Mn Thin Film and Nanowires Electrodeposited.** Mohamed Abid and Jean-Phillipe Ansermet; Physics, EPFL, Lausanne, Switzerland.

Integrating spin functionality into otherwise nonmagnetic solids has become a highly desirable goal in the context of the rapidly developing field of spintronics<sup>1,2</sup>. DMSs are semiconductor solid solutions, where a small percentage of cations are replaced by magnetic impurities such as Mn. Due to the host sp-Mn d interactions in these DMSs, unusual magnetotransport and magneto-optical phenomena like large Faraday rotations, giant negative magnetoresistances and magnetic field induced metal-insulator transitions have been observed. Recently, it was reported that Mn doped ZnO thin films as well as in bulk exhibit ferromagnetism at room temperature<sup>3</sup>. Here, we present the formation of ZnO doped with Mn thin film and nanowires by electrodeposition from a single bath. The electrodeposition was made in an aqueous bath solution of low concentrations of zinc chloride and manganese chloride at pH = 6.2. The one-phase zinc manganese oxide is deposited in a classic three-electrode potentiostatic configuration at -0.8V to -1.0V. With the right deposition parameters the evidence of 1-5% wt Mn within ZnO crystals were confirmed by using X-Ray photoelectron spectroscopy (depth profile) and XRD to confirm the presence only of one phase (Zincite). SQUID measurements show that the film and nanowires prepared by this way leads to ferromagnetism with a Curie temperature as high as T<sub>c</sub> = 500 K and still retaining its optical transparency and semiconductivity properties. 1. H. Ohno, Science 281, 951 (1998) 2. G. A. Prinz, Science 282, 1660 (1998) 3. Sharma, Parmanand; Gupta, Amita; Rao, K. V.; Owens, Frank J.; Sharma, Renu; Ahuja, Rajeev; Guillen, J. M. Osorio; Johansson, Boerje; Gehring, G. A. Nature materials 2 (10) , 673 (2003)

#### **Z7.18**

**Preparation of Nanostructured Metals using Conducting Polymers.** Hsing-Lin Wang, Wenguang Li and Quanxi Jia; Los Alamos National Laboratory, Los Alamos, New Mexico.

We report here a simple method to synthesize single-crystalline Ag, Au, and Pt nanoparticles with a good size dispersity using water-dispersible conducting polymer colloids composed of polyaniline (PANI) and polyacrylic acid. The process involves incrementally adding a metal ion solution to aqueous conducting polymer colloids and does not require other reducing agents. The reduction of metal ions takes place either within the colloidal particles or on the surface of the nanoparticles. PANI colloids actually act as tiny reactors. With the tunable oxidation states of conducting polymers, we expect this synthetic platform can be used in preparing a wide range of nanostructured metals with specific size, shape and property.

#### **Z7.19**

**High Yield Synthesis of Few-Walled Carbon Nanotube.** Hang Qi, Cheng Qian and Jie Liu; Chemistry, Duke University, Durham, North Carolina.

Carbon nanotube (CNT) has attracted extensive attention due to its unique electrical and mechanical properties and potential applications since the discovery in 1991. Most of the research work till now has focused on two kinds of CNT, single-walled carbon nanotube (SWNT) that consists of only one layer of graphite sheet, and multi-walled carbon nanotube (MWNT) that consists of tens of or more layers. Recently a new kind of CNT, Few-Walled carbon nanotube (FWNT) has attracted more and more attention. FWNT can be considered as the intermediate between SWNT and MWNT, which consists of several layers of graphite sheets but has a very small diameter, thus may have special properties due to its unique structure. For example, FWNT shows excellent field emission effect, which is much better than any other kind of CNT. Some potential applications require large amounts of FWNT. In order to cater to such a requirement, we explored Chemical Vapor Deposition (CVD) method. We employed cobalt/molybdenum-doped magnesium oxide as the catalyst and ethanol as the carbon source. To optimize the reaction condition, we explored several parameters such as the composition of the catalyst and carrier gas, reaction temperature and reaction time. Three gram of raw product with a 400% carbon yield (catalyst = 100%) can be produced per day at present by the optimum reaction condition. Next step we will try to apply this method to larger reactor and produce more raw materials in unit time.

#### **Z7.20**

**Preparation of Copper Nanowire/Polymer Nanocomposites**

by Melt Mixing and Solution Processing. Joel A. Haber<sup>1</sup>, Utandaraman Sundararaj<sup>2</sup>, Orna Breuer<sup>2</sup>, Genaro A. Gelves<sup>1</sup>, Matthew Krantz<sup>2,1</sup> and Zakari T. M. Murakami<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada; <sup>2</sup>Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

A scalable synthesis of metal nanowires has been developed using an electrodepositon into the pores of porous aluminum oxide (PAO) templates, through the resistive barrier layer. Gram quantities of high aspect-ratio Cu nanowires (25 nm in diameter by ~20,000 nm in length) were produced by an electrodepositon into PAO templates. The nanowires were liberated by dissolving the PAO film with phosphoric acid or sodium hydroxide solution. The surface chemistry of copper nanowires is controlled by the liberation method and by post-liberation derivatization with molecular monolayers. The agglomerated nanowires were dispersed in methanol by ultrasonication, collected by centrifugation or filtration, and blended into amorphous polyamide, Nylon 6-6, Polycarbonate, Polyethylene, Polystyrene, or EVA by melt processing, solution casting, and/or spin casting. The dispersion and percolation of the nanowires in these polymers was investigated by electron microscopy and conductivity measurements as a function of wire loading, polymer chemistry, and processing route. In well-dispersed composites percolation was achieved with ~2 vol % of copper nanowires dispersed in the polymer matrix. Mechanical properties were evaluated by tensile testing of miniature (25 x 1 mm) dog bones.

#### Z7.21

**One-Pot Synthesis Of Amphiphilic Dendritic Molecular Nanocarriers By Chain Walking Polymerization.** Guanghui Chen and Zhibin Guan; Chemistry, University of California, Irvine, California.

Amphiphilic core-shell structured molecular nanocarriers have attracted much attention recently because of their many potential applications including controlled drug delivery and release, phase transfer, preparation of nanomaterials, and catalysis. As one example, dendrimers having amphiphilic core-shell structures were shown to have interesting unimolecular micelle properties. Whereas perfect dendrimers offer precise structural control and uniformity, the multistep synthesis involved in their preparations limits their general applicability. Developing efficient synthesis of this type of soft nanoparticles is challenging and highly needed. Using a methodology developed in our laboratory based on a special chain walking catalyst, copolymerization of ethylene and a comonomer with a polyethylene glycol (PEG) tail afforded, in one step, amphiphilic copolymer having hydrophobic core and hydrophilic shell (J. Am. Chem. Soc. 2004, 126, 2662). In a similar manner, copolymerization of ethylene and a fluorinated alpha-olefin comonomer afforded, again in one step, an amphiphilic copolymer having a CO<sub>2</sub>-phobic core and a CO<sub>2</sub>-philic shell. Light scattering, fluorescence and UV/Vis spectroscopic studies with Nile Red revealed unimolecular micellar properties for the copolymers in aqueous or CO<sub>2</sub> solutions. The unimolecular micellar properties coupled with the good water solubility and biocompatibility of the PEG moieties make these molecular nanocarriers promising candidates for a variety of biomedical applications. We are currently investigating these amphiphilic dendritic nanoparticles as nanocarriers for drug delivery and encapsulation of quantum dots, and as scaffolds for presenting multivalent ligands and proteins for biological applications.

#### Z7.22

**Novel Liquid Metal Cathode for Prussian Blue Nanowire Synthesis.** Cengiz Sinan Ozkan<sup>1</sup> and Sathyajith Ravindran<sup>2</sup>;

<sup>1</sup>Mechanical Engineering, University of California at Riverside, Riverside, California; <sup>2</sup>Chemical and Environmental Engineering, University of California, Riverside, Riverside, California.

We report a novel technique utilizing a liquid metal (Hg) cathode with porous alumina to make nanorods. This technique eliminates the many steps involved in the conventional technique. With this new technique Prussian blue nanowires were fabricated and characterized using SEM, TEM and EDS. The technique was also demonstrated for the synthesis of metallic gold nanowires. Detailed SEM, TEM, EDS and diffraction analysis are presented for the same. Hg contamination on the nanorods was removed by boiling mercury at 370C in vacuum. EDAX data before and after heating clearly indicates the elimination of Hg from the nanorods.

#### Z7.23

**A Large Scale One-Pot Synthesis of Highly Luminescent CdSe-ZnS Core-Shell Semiconductor Quantum Dots.** Jae Il Kim and Jin-Kyu Lee; School of Chemistry, Seoul National University, Seoul, South Korea.

We have developed a simple and efficient one-pot process to produce

CdSe-ZnS core-shell quantum dots (QDs) in multi-gram quantity by a deliberate modification of pyrolysis method. The obtained QDs are highly luminescent (PL QY > 50%) and have nearly monodisperse size distribution. Appropriate surface ligand exchange also produced water-soluble QDs having high PL quantum yield (PL QY > 20%) in multi-gram scale. All the prepared QDs are characterized by UV, PL, TEM, XPS, and ICP-AES. This multi-gram synthetic technique is expected to be easily applied to similar pyrolytic synthetic methods of semiconductor quantum dots, and to accelerate the related researches in QD applications.

#### Z7.24

**Size-Dependent Electrochemical Behavior of Thiol-Capped Nanocrystals in Aqueous Solution.** Nikolai Gaponik<sup>1</sup>, Sergey Poznyak<sup>2</sup>, Nikolai Osipovich<sup>2</sup>, Alexey Shavel<sup>1</sup>, Dmitri Talapin<sup>1</sup>, Mingyuan Gao<sup>3</sup> and Alexander Eychmuller<sup>1</sup>; <sup>1</sup>Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany; <sup>2</sup>Physico-Chemical Research Institute, Belarussian State University, Minsk, Belarus; <sup>3</sup>Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Science, Beijing, China.

Electrochemical studies of thiol-capped CdTe nanocrystals in aqueous solution have demonstrated several distinct oxidation and reduction peaks in the voltammograms, with the peak positions being dependent on the size of the nanocrystals. While the size-dependence of the reduction and one of the oxidation potentials can be attributed to altering the energetic band positions owing to the quantum size effect, an extraordinary behavior was found for the oxidation peak observed at less positive potentials. In contrast to a prediction based on the quantum size effect, this peak moves to more negative potentials as the nanocrystals size decreases. Moreover, the contribution of the charge associated with this peak compared to the total charge passed during the nanocrystals oxidation correlates well with the PL efficiency of individual fractions of the CdTe nanocrystals. These experimental observations allow to assign this peak to the oxidation of Te-related surface traps. The intra-band-gap energy level assigned to these Te-related trap states shifts towards the top of the valence band as the nanocrystal size increases, thus allowing to explain the higher photostability of the larger nanocrystals. At a certain nanocrystal size the trap level even can move out of band gap. The applicability of the method to the probing of surface states as well as the prediction of luminescence properties of other thiol-capped nanocrystals (ZnSe, CdS) is demonstrated.

#### Z7.25

**Synthesis of Silicon Nanowires and their Heterostructures by Thermal Chemical Vapor Deposition.** WooSung Jang, Seung Yong Bae and Jeunghee Park; Korea University, Seoul, South Korea.

The Si nanowires were synthesized using a novel catalytic thermal reaction under Ar flow. The average diameter is in the range of 50 ~ 100 nm. They consist of defect-free single-crystalline cubic structure with the [111] growth direction. The thickness of amorphous oxide outer layers was controllable by growth conditions or surface treatment. In order to protect the oxidation, the Si nanowires were coated with boron nitride layer by the reaction of boron oxide mixture with NH<sub>3</sub>.

#### Z7.26

**Preparation of Chitosan-Poly(acrylic Acid) Nanofiber and Nanofibrous Structure via Self-Assembling.** Chin-i Chen<sup>1</sup>, Jian-Wen Wang<sup>2</sup> and Ming-Hsiun Hong<sup>1</sup>; <sup>1</sup>Material Science and Engineering, National Chen Kung University, Tainan City, Taiwan; <sup>2</sup>Department of Environmental and Safety Engineering, Chung Hwa College of Medical Technology, Tainan City, Taiwan.

Nanofibers appear several amazing characteristics, especially very large surface area to volume ratio. This property makes the polymer nanofibers be useful for many applications. In this study, Chitosan(CS)-Poly (acrylic Acid) (PAA) nanofibers have been synthesized by a modified dropping method successfully. By selecting proper carboxyl acid to dissolve CS and adjusting the reaction solution pH value, CS-PAA nanofibers whose diameter ranging from 50 to 400nm can be formed in suspension solution. Also, a nanofibrous structure can be formed after freeze-drying process. The CS-PAA nanofibrous structure has a great potential in gas sensor which needs large surface area.

#### Z7.27

**Short-Period Superlattice Structure of In<sub>2</sub>O<sub>3</sub>(ZnO)<sub>x</sub> Nanowires.** Chan Woong Na, Seung Yong Bae, Doo Suk Han, Woo Sung Jang and Jeunghee Park; Korea University, Seoul, South Korea.

The In<sub>2</sub>O<sub>3</sub>(ZnO)<sub>x</sub> (x=4 or 5) nanowires with short-period superlattice structure have been successfully synthesized by evaporating a mixture of ZnO, In, and Sn powders. The superlattice

structure and optical properties were investigated by high-resolution transmission electron microscopy and X-ray diffraction (XRD), X-ray photoelectron spectroscopy, and photoluminescence (PL). They consist of Sn-doped In-O and Zn-O layers stacked alternately perpendicular to the long axis, with a modulation period of 1.6 or 1.9 nm. XRD reveals the wurtzite structure with significantly expanded lattice constants. As the In content increases, the NBE peak of PL becomes broader with a lower energy shift. The electrical properties of individual nanowire have also been measured by four probe method.

#### **Z7.28**

**Covalent Linking of CdTe Nanocrystals to Amino-Functionalized Surfaces.** Alexey Shavel, Alexander Eychemueller and Nikolai Gaponik; Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

A new method for modifying substrate surfaces has been developed: preliminarily aminated substrates of various compositions and shapes are linked with water soluble high luminescing CdTe nanocrystals through the formation of an amide bond between the carboxylic groups of mercaptoacid-capped nanocrystals and the amino groups of the substrates. Carbodiimide compounds are used for the formation of an amide bond between the amino groups of the substrate surface (i.e. of "aminated" surfaces) and the carboxylic groups of the stabilizers of the CdTe NCs. In order to apply this chemistry to the fabrication of conjugates with CdTe NCs the substrate surface was pre-treated with amino-functionalized silanes. The method described is not limited to flat substrates but is of more generality as seen by our successful attempts to coat glass spheres of micron size and silica beads by CdTe NCs. For the generation of these conjugates CdTe NCs of two different sizes were used, namely 3 - 4 nm in diameter and 6-8 nm in diameter, respectively. It is mentioned that the larger particles exhibit an emission at around 800 nm which, thus, occurs at lower energies than all CdTe-NC-emissions reported before opening the path to the near-infrared spectral region hardly accessible with other materials. The absorption spectra of the conjugates possess well pronounced first electronic transitions and strong emissions. The position of the absorption and luminescence maxima relate well to the sizes of the NCs in accord with the size quantization effect. This luminescence is not altered for at least 3 months. The <sup>1</sup>H NMR spectra of conjugated silica particles exhibit obvious differences to those of the pure silica particles. The conjugated materials show additional peaks which are attributed to the amide bond (7.81 ppm) and to the protons of the NCs stabilizer molecules (2.75 and 2.90 ppm). Thus, also with NMR the conjugation between the amino groups of the modified substrate surface and the carboxylic groups of the NCs' stabilizers leading to the formation of an amide bond is detected.

#### **Z7.29**

**Blue Luminescent Semiconductor Nanocrystals and Their Application to Light Emitting Diode.** Eunjoo Jang, Shinae Jun, Seong Jae Choi and Miyang Kim; Samsung Advanced Institute of Technology, Yongin-Si, Gyeonggi-do, South Korea.

II-VI group colloidal semiconductor nanocrystals, showing size-dependent optical properties in visible range, have been extensively investigated in recent years for the application including light emitting device (LED), biological fluorescent labels and lasers. However, the preparation of high quality blue emitting semiconductor nanocrystal is difficult because crystal size should decrease below ~2nm to emit blue light and the resulting small crystal has unstable surface trap to decrease the quantum efficiency. Therefore, proper treatment of the nanocrystal surface to reduce defect sites is needed to achieve high quantum yield. In this work, highly blue luminescent nanocrystals were prepared by simple surface treatment at room temperature with reducing agent like NaBH<sub>4</sub>. The quantum efficiency of CdS nanocrystal was remarkably enhanced up to 75% at blue region, about 50 times improvement after surface treatment maintaining original photoluminescence peak position and narrow line width. The TGA and XPS data revealed that some of the surfactants on the nanocrystal surface were removed by reacting with NaBH<sub>4</sub> and that the exposed cadmium on the surface was converted to cadmium oxide under air condition. The oxide layer functioned as a passivation layer on the CdS surface and donated more electron density toward the inside of the CdS core to enhance exciton recombination. The surface treatment was generally effective in improving the quantum efficiency of II-VI compound semiconductors including CdS, CdSe and CdTe and other mixture type nano-sized materials. We also prepared highly luminescent multi-component semiconductor nanocrystals exhibiting high quantum efficiency in blue region by the design of new structures. The resulting nanocrystals were embedded in the light emitting diode as an active material, and the external quantum efficiency of the pure nanocrystal electroluminescence was 1.5Cd/A at 470nm. The detailed results will be further discussed in the presentation.

#### **Z7.30**

**Controlled Synthesis of Chrysotile-Based Nanotubes Under Hydrothermal Conditions.** Bostjan Jancar and Danilo Suvorov; Advanced Materials, Jozef Stefan Institute, Ljubljana, Slovenia.

In order to study the mechanisms that lead to the formation of nanotubes from layered structures we chose chrysotile, which is a naturally occurring nanotubular serpentine group mineral, as a model system. We used hydrothermal conditions to follow the curling process that leads to the formation of chrysotile. The curling of the layered serpentine structures is believed to occur as one of the possible mechanisms that overcomes the mismatch between the lateral dimensions of the Mg-containing octahedral and Si-containing tetrahedral components of the bilayer. In the case of several different combinations of precursors involving crystalline Mg(OH)<sub>2</sub>, MgO and various types of amorphous SiO<sub>2</sub>, we found that among several varied parameters the pH exerts the strongest influence on the curling of the serpentine layers. Under acidic conditions the curling process seems to be hindered and other types of mechanisms for overcoming the structural mismatch are favored, which leads to the preferential formation of the antigorite and lizardite phases of the serpentine mineral group. In a highly basic environment, however, curling occurs readily and leads to the formation of multiwall chiral chrysotile nanotubes. The temperature, on the other hand, does not affect the curling process but strongly influences the growth rate of the thus formed nanotubes. Further experiments involved the intercalation of long-chain primary amines between the serpentine layers in order to control the diameter and chirality of the chrysotile nanotubes.

#### **Z7.31**

**Development and Control of Nano-Agglomerated Units in the Protein Thin Films prepared by Pulsed Laser Deposition and via a Colloid Chemical Route.** Mamoru Senna<sup>1</sup>, Sayuri Nakayama<sup>2,1</sup>, Ichiro Taketani<sup>1</sup>, Jo Sagawa<sup>1</sup> and Sanshiro Nagare<sup>2,1</sup>; <sup>1</sup>Faculty of Science and Technology, Keio University, Yokohama, Japan; <sup>2</sup>Technical Development, Nara Machinery Co., Ltd., Tokyo, Japan.

Formation and microstructure of nano-agglomerated units (NAU) with their external size ranging from 2nm to more than 100nm in the protein thin films were examined. Silk fibroin (SF) with and without preliminary degumming and bovine serum albumin (BSA) were deposited on the Si(100) substrate either by laser deposition (PLD) or via a colloid chemical route (CCR). Properties of NAU were examined mainly by microscopic observation with TEM and AFM and chemical analyses, IR spectra in particular, together with conventional characterization, e.g. contact angle, QCM and ellipsometry. Size, frequency and degree of ordering of NAU were discussed in terms of the laser fluence, species and concentration of the background gas for PLD and the deposition conditions from various colloidal solutions for CCR. Smoother films with suppressed NAU development were obtained at smaller laser fluence close to the threshold (PLD) or dilution of the colloidal solution (CCR). Post rinsing revealed particular geometries without NAU, reflecting smaller units, i.e. protein secondary structure (PSS). Relationship between PSS and NAU was discussed in terms of the dispersed state in the deposition chamber (PLD) or in the colloidal solution (CCR) and nuclei-growth processes therefrom.

#### **Z7.32**

**White-Light Emitting Ge Nanoparticles by Ultrasound-Induced Solution Route.** Soojin Lee, Woon Jo Cho, Il Ki Han, Won Jun Choi and Jung Il Lee; Korea Institute of Science and Technology, Seoul, South Korea.

There has been growing interests in nanoparticles of indirect band gap, elemental semiconductors, such as Si and Ge, especially since these show useful levels of photoluminescence in the visible region and suggest possible applications in optoelectronics and microelectronics. Compared to Si, Ge nanoparticles are of particular interest, because the Bohr radius is larger in Ge (17.7 nm) than in Si (~ 4.9 nm). The quantum size effects will be more prominent in Ge nanoparticles even for larger sizes of the crystallites. Ge nanoparticles are more likely to undergo a transition to a direct band gap semiconductor since Ge is nearly a direct band gap semiconductor in the bulk and the lowest direct band gap for Ge is 0.8 eV, which is only about 0.1 eV above the indirect band gap, thus making it an interesting material for the photonic applications in the near IR region, too. We report here white-light emitting Ge nanoparticles prepared through a sonochemical approach. The Ge nanoparticles were synthesized by sonicating NaGe in glyme solvent (ethylene glycol dimethyl ether) under the condition of below 100 °C and ambient pressure. The surface of nanoparticles was modified with hydroxyl group. The nanoparticles were characterized by high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS) and FTIR spectroscopy. The average size of Ge nanoparticles emitting white-light was approximately 5 nm. The room temperature

photoluminescence typically ranged from 350 nm to 700 nm with the peak center around 490 nm. The practical route presented herein demonstrated that Ge nanoparticles could be produced at an accelerated rate due to the high energy generated by ultrasonic waves. In addition, we could achieve the white-light using only a single-step process, i.e., by controlling only size distribution without adding any fluorescent ions. Due to its wide and continuous luminescence over the whole visible spectrum, our method might be useful for white light emitting diodes using Ge nanoparticles as nanophosphor layer, providing light-illuminating applications.

### **Z7.33**

**Abstract Withdrawn**

### **Z7.34**

**Catalyst-Free Growth of Single Crystalline Ge and Core-Shell Ge/Si-C-N Nanowires.** Sanjay Mathur, Hao Shen, Vladimir Sivakov and Ulf Werner; Leibniz Institute of New Materials, Saarbruecken, Germany.

Semiconductor materials (Ge, Si) in confined 1D (nano)geometries display interesting electronic and optical properties due to the partial quantization of electronic states. We have prepared single crystalline Ge and Ge/Si-C-N nanowires in high yields by the chemical vapour deposition (CVD) of molecular precursors [Ge(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (1) and [Ge{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (2). Whereas the decomposition of 1 provides single crystal Ge nanowires with crystalline plane up to the surface, a core-shell morphology is formed in the case of 2 in which a crystalline Ge core is wrapped in a Si-C-N amorphous overlayer. Given the inherent advantages of metal-organic precursors, the nanowire morphology is achieved at relatively lower temperature (1: < 300 oC; 2: < 600 oC) and the axial and radial dimensions of the 1D structures can be precisely adjusted by changing the precursor flux and deposition temperature. The nanowires could be grown on different substrates (Al<sub>2</sub>O<sub>3</sub>, Si, Fe, MgO, MgAl<sub>2</sub>O<sub>4</sub>) without any surface treatment or catalysts. In contrary to the VLS technique, which is a popular growth mechanism for nanowires, nanowires in our case form through a defect-assisted solid state diffusion. The model can be supported by following observations: (i) preferable growth on artificial defects created by nano-indenting a sapphire substrate and (ii) cross-sectional HR-TEM of a single nanowire to reveal the bonding of nanowires to the substrate. The microstructure, morphology and chemical composition of the deposits have been characterized by XRD, SEM, TEM and XPS techniques. The wires were several tens of micrometers in length with diameter in the range 10-100 nm. In the case of Ge/Si-C-N system, an EDX line scan on a single wire revealed a Ge-enriched crystalline core whereas Si is distributed locally in the shell. A comparison of Si 2p binding energy proved that Si exists in the Si-C-N composition and not in the elemental form. In comparison to bulk Ge (~ 300 cm<sup>-1</sup>), the micro-Raman spectra of both systems revealed a low field shift (< 300 cm<sup>-1</sup>) which excluded the possible formation of GeSi alloy in the CVD of 2 and indicated the quantum confinement in 1D geometries.

### **Z7.35**

**Interaction Control of Protein-Drug in the Nanocomposites Prepared by Pulsed Laser Deposition from Mechanically Conjugated Mixtures.** Sanshiro Nagare<sup>1,2</sup>, Jo Sagawa<sup>2</sup> and Mamoru Senna<sup>2</sup>; <sup>1</sup>Technical Development Division, Nara Machinery Co. Ltd, Tokyo, Japan; <sup>2</sup>Faculty of Science and Technology, Keio University, Yokohama, Japan.

In an attempt to develop a concept of nanopharmacy, composites of bovine serum albumin (BSA) and indomethacin (IM) were prepared by pulsed laser deposition (PLD) using the targets of various compositions under varying operational conditions of PLD. BSA and IM were preliminarily conjugated with widely varying compositions by mechanical co-milling in a solid state, as well as from colloidal mixtures to optimize properties of the targets for laser ablation. Morphological studies were carried out by FE-SEM, TEM and AFM. Interactions between BSA and IM were examined in detail from FT-IR and XRD. Effects of preconjugation on the deposition rate, morphology of the nanostructures, and protein-drug interactions in the nanocomposites were examined. Laser wavelength and fluence were varied systematically to further control the structures of the nanocomposites. Focus is laid on the breakage of the intramolecular hydrogen bonds predominating IM-IM or BSA-BSA interactions, and the subsequent reorganization of intermolecular hydrogen bond between BSA and IM.

### **Z7.36**

**Formation of Germanium Nanostructures from Molecular Precursors Containing Labile Ge-Ligand Fragments.** Sanjay Mathur, Hao Shen, Vladimir Sivakov and Ulf Werner; Leibniz Institute of New Materials, Saarbruecken, Germany.

Nanostructured semiconductor materials are receiving increasing

attention due to the unique physical properties. Germanium is an important semiconductor, however, synthesis of pure Ge nanostructures is difficult due to the easy formation of native oxide and incorporation of heteroatoms. We report here a general molecular approach to obtain various Ge nanostructures by chemical vapour deposition (CVD) of appropriate precursors (1: Ge(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>; 2: Ge(OiPr)<sub>4</sub>; 3: Ge{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>; 4: GeI<sub>2</sub>). We are exploring low-temperature routes for the controlled synthesis of nanoscopic structures (particles, films and 1D morphologies) by employing precursors with labile metal-ligand bonding in the CVD process. In comparison to conventional physical methods, the chemical vapour deposition of metal-organic precursors is a viable low-temperature route for the fabrication of Ge nanostructures. The labile Ge-L (L = ligand atom) bonds in precursors 1-4 resulted in the formation of GeO clusters and various volatile organic fragments. The Ge nanostructures are achieved at relatively lower temperatures (1: < 300 oC; 2: < 600 oC; 3: < 650 oC and 4: < 600 oC). The presence of Ge native oxide and incorporation of heteroatoms were ruled out by detailed XRD and XPS studies. The HR-TEM investigation on single wires exhibits single crystalline domains of Ge with no dislocations and stacking faults and a preferred growth orientation (<111>). A brief review focusing on the fabrication of Ge nanostructures from chemically designed precursors will be discussed.

SESSION Z8: Applications and Devices of  
Nanomaterials I

Chairs: Christopher Murray and Younan Xia  
Thursday Morning, March 31, 2005  
Room 3016 (Moscone West)

### **8:30 AM Z8.1**

**Wafer-scale Nanopatterning and Nanomaterials Synthesis for Functional Nanodevices and Nanosensors.** Qi Ye, Alan M. Cassell and M. Meyyappan; Center For Nanotechnology, NASA Ames Research Center, Mountain View, California.

The key hurdle in nanoscience and nanotechnology is the large-scale integration of nanoscale materials with micron scale electronics and structures to form functional devices and sensors. We have developed an innovative bottom-up wafer scale fabrication method that combines nanopatterning and nanomaterials synthesis with traditional silicon micromachining technologies. We have achieved nano-micro integration through catalyst nanopatterning and registration at wafer scale and through effective nanocatalyst protection and release before and after microfabrication. In this paper, we will address our device and sensor design and fabrication considerations in detail, and present our recent results on large-scale controlled patterning and synthesis. We will demonstrate an example of our wafer-scale nanopatterning and nanomaterials synthesis approach by presenting our recent achievements on integrating carbon nanotubes (CNTs) with silicon cantilevers for reliable fabrication of CNT based probe tips for atomic force microscopy (AFM) critical dimension imaging applications. CNT tip locations and diameters are defined by e-beam lithography. CNT length, orientation, and crystalline quality are controlled by the plasma enhanced chemical vapor deposition (PECVD) method. In PECVD, an electric field is present in the plasma discharge to direct the nanotubes to grow and align parallel to the electric field. With effective catalyst protection schemes, this fabrication process is very similar to the conventional approach for fabricating wafer-scale silicon AFM probe tips. Process control is therefore feasible and the overall yield is greatly improved. This is a truly bottom-up wafer-scale CNT AFM probe fabrication approach. Our method and technology can be easily adapted to many other nanomaterials (nanotubes and nanowires) synthesis and processes for their rational design, fabrication, and integration in their applications.

### **8:45 AM Z8.2**

**Integration of Multiple Functions into Nanoscale Building Blocks.** Yue Wu<sup>1</sup>, Jie Xiang<sup>1</sup>, Hao Yan<sup>1</sup>, Wei Lu<sup>1</sup> and Charles M. Lieber<sup>1,2</sup>; <sup>1</sup>Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Nanoscale building blocks, such as nanowires and nanotubes, have been demonstrated as functional units for nanoelectronic and nanophotonic devices. Yet, the ultimate realization of large scale nanoscale device arrays and integrated nanosystems will require integration of multiple functions into these single nanowire building blocks. To this end, we have developed new approaches to the controlled synthesis of compositionally modulated nanostructures, including axial superlattice and radial core/shell nanowire heterostructures. First, we demonstrate the controlled preparation of metal/semiconductor nanowire superlattices through solid state transformation of silicon nanowires to single crystal metallic nickel silicide. Second, rational synthesis of semiconductor/oxide insulator

core/shell structures using vapor-phase atomic layer deposition will be described. Electrical transport properties of the nickel silicide nanowires, nickel silicide/silicon and silicon/oxide insulator nanowire heterostructures demonstrate unique potential of the multifunctional materials for integrated device arrays. Potential applications of these nanowire building blocks for nanoscale computing will be discussed.

**9:00 AM Z8.3**

**Nanoparticle Assembly Strategies for the Development of Functional Mesoporous Materials.** Jaya L. Mohanan, Indika Arachige and Stephanie L. Brock; Chemistry; Wayne State University, Detroit, Michigan.

An important hurdle for the incorporation of nanoparticles into device architectures is the development of methodologies that assemble nanoparticles together for functionality while retaining the intrinsic, size dependent properties of the individual components. A method has been developed for the assembly of nanoparticles into porous architectures using controlled surface decomplexation reactions accompanied by sol-gel processing and supercritical drying. The exploitation of this methodology for the preparation of porous materials based on quantum confined metal chalcogenide nanoparticles, and the physical characteristics of these materials, will be presented. The generality of this approach for the synthesis of functional nanostructures based on a variety of different chemical systems will be discussed.

**9:15 AM \*Z8.4**

**Environmental and Health Impacts of Engineered Nanoparticles.** Vicki L. Colvin, Chemistry, MS60, Rice University, Houston, Texas.

Traditionally, nanotechnology has been motivated by the growing importance of very small ( $d < 50\text{nm}$ ) computational and optical elements in diverse technologies. However, this length scale is also an important and powerful one for living systems. At Rice University, we believe that the interface between the "dry" side of inorganic nanostructures and the "wet" side of biology offers enormous opportunities for medicine, environmental technologies, as well as entirely new types of nanomaterials. As a part of our work on the potential biological applications, we also consider the unintended environmental implications of water soluble nanomaterials. Given the breadth of nanomaterial systems, we use a carefully selected group of model nanoparticles in our studies and focus on natural processes that occur in aqueous systems. We characterize the size and surface-dependent transport, fate and facilitated contaminant transport of these engineered nanomaterials. Models from larger colloidal particles can be extended into the nanometer size regime in some cases, while in others entirely new phenomena present themselves. We also consider biological interactions of nanoparticles and specifically address the interactions of a classic nanomaterial, C60, with cellular systems.

**9:45 AM \*Z8.5**

**Metal and Semiconductor Nanocrystals as Precursors for Printed Electronics.** Joerg Rockenberger, Kovio, Sunnyvale, California.

Printed Electronics presents the promise of fabricating electronic devices at greatly reduced costs, on cheap flexible substrates, and over large areas. However, many commercially interesting applications require device performances and stabilities close to the ones provided by conventional semiconductor technology. Using metal and semiconductor nanocrystals as precursors for printed electronics combines the performance, stability, and integration schemes of materials well-known from conventional processing with the low cost and flexibility of printing technologies. In this presentation, we will discuss Kovio's approach to the production and application of Silver and Silicon nanocrystals and inks.

**10:30 AM \*Z8.6**

**Molecular Wiring of Spin Coherence Between Semiconductor Nanostructures.** Min Ouyang, Jesse Berezovsky, Florian Meier, Dwight Seferos, Guillermo Bazan and David D. Awschalom; Center for Spintronics and Quantum Computation, University of California, Santa Barbara, California.

Semiconductor quantum dots are attractive candidates for scalable solid state implementations of quantum information processing based on electron spin states, where a crucial requirement for practical devices is to have efficient and tunable spin coupling between them. We focus on femtosecond time-resolved Faraday rotation studies of self-assembled multilayer spintronic devices based on colloidal quantum dots bridged by conjugated molecules [1,2]. The data reveal the instantaneous transfer of spin coherence through conjugated molecular bridges spanning quantum dots of different size over a broad range of temperature. The room temperature spin transfer

efficiency exceeds 20%, which approximately doubles the value measured at  $T=4.5\text{K}$ . A molecular pi-orbital mediated spin coherence transfer mechanism is proposed to provide a qualitative insight into the experimental observations, suggesting a correlation between the stereochemistry of molecules and the transfer process. The results show that conjugated molecules can be used not only as physical links for the assembly of functional networks, but also as efficient channels for shuttling quantum information. This class of structures may be useful as two-spin quantum devices operating at ambient temperatures and may offer promising opportunities for future molecule-based spintronic technologies. Work supported in part by DARPA, ARO, and NSF. [1] M. Ouyang et al., Science 301, 1074 (2003). [2] F. Meier et al., Phys. Rev. B, in press (2004).

**11:00 AM \*Z8.7**

**Synthesis and Characterization of Metal-Oxide and Chalcogenide Nanostructures.** Hongkun Park, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

In this presentation, I will discuss the syntheses and characterizations of various transition-metal-oxide and chalcogenide nanostructures performed in my laboratory. The examples that will be discussed include (1) the synthesis of  $\text{BaTiO}_3$  nanowires and the characterization of finite-size scaling of their ferroelectricity, (2) the synthesis of  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$  nanocubes and the investigation of their magneto-transport property, (3) the synthesis of  $\text{VO}_2$  nanowires and the characterization of their Mott metal-insulator transition, and (4) the synthesis of  $\text{NbSe}_x$  nanobelts and the investigation of charge-density-wave transport.

**11:30 AM Z8.8**

**1-D Semiconducting Nanowires: Chemical Synthesis and Transistor for Logic Application.** Bin Yu, Laura Ye and Meyya Meyyappan; NASA Ames Center for Nanotechnology, Moffett Field, California.

Following Moore's Law for nearly three decades, silicon CMOS technology will eventually reach its fundamental technological limits in roughly 15 years. In the effort to fight with the transistor physical limits to scaling, the state-of-the-art nano-device architecture features multiple gate control over a Si nanowire fabricated by extremely aggressive photolithography and anisotropic plasma etching. Though this type of device was proved to be scalable down to 10nm physical gate length, labor- and cost-intensive integration effort is needed to fabricate the nano-scale Si nanowires. The bottom-up nanotechnology, in which the critical device structures or components are self-assembled by specifically-designed chemical route, provides a promising solution to produce Si or Ge nanowire-based field-effect transistor for sub-10nm gate length CMOS technology. In this paper we will report the chemical synthesis and nanomaterials engineering approach of one-dimensional Si and Ge nanowires with appropriate pre-treatment, gas-phase transport, chemical/physical vapor deposition, and metal-mediated vapor-liquid-solid (VLS) growth. Materials characterization of both compositional and mesoscopic structural features of these 1-D semiconducting nanowires will be reported. Next, 4-inch wafer-scale very large arrays of MOSFET transistor were fabricated with a cost-effective nanofabrication integration process. Detailed device physics study will be presented, focusing on ambipolar channel conducting, subthreshold behavior, parasitic resistance, carrier mobility, gate leakage, nanowire interface quality, and low-barrier metal-semiconductor Schottky junctions. The feasibility of extending the bottom-up fabricated Si or Ge nanowire transistors into sub-10nm CMOS logic technology, from nanomaterial synthesis, device integration, and device performance perspectives, will be analyzed and predicted.

**11:45 AM Z8.9**

**High Performance Oxide Logic Devices based on Single Crystalline Transparent Semiconducting Oxide Nanorods.** Won Il Park, Jin Suk Kim, Je-Pil Yun and Gyu-Chul Yi; POSTECH, Gyeongbuk, South Korea.

Metal oxide nanostructures are potentially ideal functional components for nanometer-scale electrical, optical, magnetic, and superconducting device applications, thanks to a wide variety of crystal structures and metal ions that constitute oxides, along with their great natural abundance and excellent environmental compatibility. In particular, metal oxide semiconductors exhibit an air-stable surface without formation of an insulating native oxide layer, which can realize clean and abrupt metal/semiconductor interfaces without any specific oxide etching process. Nevertheless, nanodevice applications using metal oxide nanostructures have rarely been reported. Their applications into real electronic circuit level have been limited even for metal oxide bulk materials. This results from a lack of high quality epitaxial or single-crystalline films and difficulty in controlling metal/oxide junction characteristics. However, single

crystalline oxide nanostructures may solve these problems as they have already facilitated fabrication of high quality ZnO nanorod metal oxide semiconductor field-effect transistors (MOSFETs) exhibiting field effect electron mobility as high as 1000 cm<sup>2</sup>/Vs. Meanwhile, further control of the metal/oxide junction characteristics to either good ohmic or Schottky contacts on oxide nanomaterials would readily enable creation of many oxide-based electronic nanodevices. Here we report on fabrications of high performance metal oxide nanodevices including Schottky diodes, MOSFETs, metal semiconductor field-effect transistors, and logic gate devices. These sophisticated oxide electronic devices would greatly increase the versatility and power of the building blocks for fabrication of numerous nanodevices based on metal oxides.

SESSION Z9: Nanocrystals and Nanoparticles II  
Chairs: Vicki Colvin and Jun Liu  
Thursday Afternoon, March 31, 2005  
Room 3016 (Moscone West)

**1:30 PM \*Z9.1**

**Excitons and Multiexcitons in Semiconductor Nanocrystal Quantum Dots: Single Dots, Many Dots, Applications.**

Moungi G. Bawendi, MIT, Cambridge, Massachusetts.

Nanocrystals of semiconductors access the regime of strong exciton confinement where exciton and multiexciton energetics and time scales differ markedly from the bulk and quantum wells. In this talk we will review recent work probing the energetics and dynamics of multiexcitons at both the single dot and the ensemble regime. We show at the single dot level that a photon cascade can be generated with ordered photons from the triexciton, biexciton, and finally the exciton. We discuss optically pumped stimulated emission and lasing from biexcitons and triexcitons. We also present recent results where emission from nanocrystal quantum dots is used in hybrid organic/inorganic light emitting devices and in biomedical imaging.

**2:00 PM \*Z9.2**

**A Facile Route to Surface Terminated Si and Ge Nanocrystals.** Jing Zou, Hsiang Wei Chiu, Philip Sanelle and Susan M. Kauzlarich; Chemistry, UC Davis, Davis, California.

Silicon and germanium nanocrystals have been of interest for a large number of applications, from optoelectronics to biological tags. There are a large number of methods for synthesizing these nanoparticles, however; they all have drawback such as requiring a specialized apparatus such as high pressure vessel, specialized reagents such as Zintl salts, or low yields. We have recently presented a room temperature route to Si and Ge nanocrystals. This route allows for surface termination with alkyl groups and enough product to characterize by powder X-ray diffraction. There are two methods that we have developed to terminate the surface, using alkyl Grignards and silanization. Recent results from this synthetic route will be presented. X-ray powder diffraction, TEM, FTIR, NMR, UV-vis and photoluminescence data will be presented and compared with other synthetic routes.

**2:30 PM Z9.3**

**Synthesis of Ge Nanocrystals in a High Temperature Supercritical Solvent.** Xianmao Lu, Keith P. Johnston and Brain A. Korgel; Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas.

Germanium (Ge) nanocrystals passivated with capping ligands have been synthesized in supercritical organic solvent from diphenylgermane or tetraethylgermane at 400-500°C and ~3000psi. Group IV nanocrystals, such as Si and Ge, have been particularly challenging to synthesize by solution-phase methods, primarily due to their strong covalent bonding and the need for high temperatures to promote crystallization. At high temperatures, supercritical fluids may be used to solvate capping ligands and to thus stabilize nanocrystals. Octanol is added to control particle growth, which appears to serve as a capping ligand that binds to the particle surface through an alkoxide linkage. The nanocrystals were characterized by high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS), FTIR spectroscopy and X-ray diffraction (XRD). The Ge nanocrystals with diameters of 3-4 nm exhibit blue-shifted optical absorbance and photoluminescence spectra relative to bulk Ge. Under the high reaction temperature, however, the degradation of the solvent and capping ligand is significant, and the removal of the by-products is challenging. Variations in the organic solvent and germanium precursor are used to minimize solvent and capping ligand degradation and organic contamination, while increasing the reaction yield and selectivity.

**2:45 PM Z9.4**

**Metal Sulfide Nanocrystals with Predictable Shapes and Sizes.** Wen Pei Lim<sup>1,2</sup>, Zhihua Zhang<sup>1</sup>, Hong Yee Low<sup>2</sup> and Wee Shong Chin<sup>1</sup>; <sup>1</sup>Chemistry, National University of Singapore, Singapore, Singapore; <sup>2</sup>Institute of Materials Research and Engineering (IMRE), Singapore, Singapore.

Architectural control of nanomaterials holds tremendous potential in the synthesis and design of various advanced materials. The "bottom-up" preparation of nanocrystals with uniform shapes and sizes is emerging as one of the promising approaches in the development of new nanodevices and the realization of novel nanoscale properties. A general method, using an air-stable precursor, was developed for the preparation of metal sulfide nanocrystals under mild conditions in solution. Recent systematic investigation of various critical reaction parameters clearly demonstrated that both the shape and size of the nanomaterials can be controlled in a predictable manner. Well-defined shapes of metal sulfide nanocrystals such as Ag<sub>2</sub>S and Cu<sub>x</sub>S, from nanocubes, nanorods, nanodisks, faceted or spherical nanocrystals, to dendrites can be readily produced and illustrated in this presentation.

**3:00 PM Z9.5**

**Synthesis of Germanium Nanocrystals and Nanowires via Ge(II) Precursors.** Henry Gerung<sup>1</sup>, Scott D. Bunge<sup>3</sup>, Timothy J. Boyle<sup>2</sup>, C. Jeffrey Brinker<sup>1,2</sup> and Sang M. Han<sup>1</sup>; <sup>1</sup>Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; <sup>2</sup>Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; <sup>3</sup>Chemistry, Kent State University, Kent, Ohio.

We have developed a new synthesis route for Ge nanocrystals (Ge NCs) via reduction of Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> at 300°C and 1 atm. Literature reports on Ge NC syntheses have focused mainly on direct reduction of Ge(IV) to Ge(0), which requires a combination of high temperature (>400°C), high pressure (>1 atm), and strong reduction agents. We have developed a simple synthetic route that does not require strong reducing agents or special additives (e.g., detergents) wherein no salts or undesirable byproducts are formed. Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> is chosen as the Ge(II) precursor due to the ease of its synthesis in high yield, the absence of potential halide contamination, and the labile amido ligand sets. The synthesis involves the injection of Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> dissolved in oleylamine into octadecene/oleylamine solvent at 300°C and 1 atm Ar. The resulting Ge NCs form quickly and show a high degree of crystallinity with no oxide formation. The washed Ge NCs display the characteristic infrared absorption peaks of NH<sub>2</sub> and CN vibrational modes, indicating that the oleylamines encapsulate the Ge NCs. An alternative Ge(II) precursor, Ge[DBP]<sub>2</sub> (DBP = 2, 6-di-tert-butylphenoxide) is isolated from an amide alcohol metathesis reaction between Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and 2 equivalents of DBP-H. The use of Ge[DBP]<sub>2</sub> under identical reaction conditions as discussed above yields Ge nanowires (Ge NWs) instead of Ge NCs. These Ge NWs display a strong emission at 360 nm when excited by a 325-nm HeCd laser line and appear to be air stable.

**3:30 PM \*Z9.6**

**Chemical Transformations of Nanocrystals.** Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

Chemical transformation of nanocrystals from one composition to another can proceed rapidly and with remarkably simplified kinetics compared to bulk solid state transformations. Two recent examples we have investigated are the formation of hollow nanocrystals via addition reactions and cation exchange reactions. Hollow nanocrystals of many transition metal oxides and sulfides have been studied, and from these we are learning how to predict the shell thickness. Cation exchange from CdSe to Ag<sub>2</sub>Se proceeds completely, but is reversible, and the number of anions per nanocrystal remains invariant. Above a critical size, the nanocrystals retain non-equilibrium shapes over multiple cycles of cation exchange.

**4:00 PM \*Z9.7**

**Generalized Synthesis of Monodisperse Nanoparticles and Uniform-sized Nanorods.** Jaeghwan Hyeon, School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We developed a new generalized synthetic procedure to produce monodisperse nanocrystals of many transition metals, metal oxides, and metal sulfides without a size selection process. Highly-crystalline and monodisperse nanocrystals of magnetite, MnFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, MnO, Ni, NiO, CeO<sub>2</sub>, and Pd were synthesized from the thermal decomposition of metal-surfactant complexes. Very recently, we were able to synthesize 40 gram of monodisperse magnetite nanoparticles using inexpensive and environmentally-friendly reagents such as metal chlorides. By controlling the nucleation and growth processes, we were able to synthesize monodisperse magnetite nanoparticles with particle sizes of 6, 7, 8, 9, 10, 11, 12, 13, and 14 nm. We developed a new

generalized synthetic procedure to produce various nanorods. Diameter-controlled synthesis of magnetic iron phosphide (Fe<sub>2</sub>P) nanorods was achieved from the controlled thermal decomposition of iron-triethylphosphine complex delivered using a syringe pump. By controlling the injection rate of syringe pump, we were able to control the length of the nanorods with keeping diameter nearly unchanged. Using a similar procedure, we synthesized nanorods of iron phosphide (FeP), cobalt phosphide, manganese phosphide, nickel phosphide, ZnO, and ZnS. Using a non-hydrolytic sol-gel processes, we were able to synthesize various anisotropic nanocrystals of ZnO and TiO<sub>2</sub>.

#### 4:30 PM Z9.8

**Nonaqueous Routes to Crystalline Metal Oxide Nanoparticles: Formation Mechanisms and Applications.** Markus Niederberger, Georg Garnweitner, Nicola Pinna and Markus Antonietti; Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The unique characteristics of transition metal oxides make them the most diverse class of materials, with properties covering almost all aspects of materials science and solid state physics. The general trend to further miniaturization of functional devices in emerging technologies such as sensing, pigmentation, energy storage and conversion and electroceramics demands for the production of these materials with the highest possible purities, small crystallite sizes, well-defined particle morphologies and small particle size distributions. In the last few months, we developed novel reaction approaches using nonaqueous and halide-free procedures to synthesize a wide variety of different metal oxide nanoparticles including the binary metal oxides of group IV and V, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and perovskites such as BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and LiNbO<sub>3</sub> [1]. The routes involve the solvothermal reaction of metal oxide precursors such as metal alkoxides or metal acetylacetonates with oxygen supplying agents such as alcohols, aldehydes and ketones. The careful characterization of the organic species in the final reaction mixtures provides information about possible condensation mechanisms. In the case of BaTiO<sub>3</sub>, the formation of the Ti-O-Ti bond most probably occurs via a novel mechanism involving a C-C bond formation between the isopropoxy ligand and the solvent benzyl alcohol [2]. The use of oxidizing solvents instead of alcohols allows the preparation of lead-based metal oxides such as PbTiO<sub>3</sub>, Pb(Ti,Zr)O<sub>3</sub> and PbZrO<sub>3</sub>. Depending on the metal oxide precursor and on the solvent, different formation mechanisms were found. In this presentation, we will give an overview of the various nanoparticles synthesized via the nonaqueous sol-gel approach, the particle formation mechanisms found in these systems, and first examples of applications in gas sensing devices [3], catalysis and electroceramics. [1] M. Niederberger, N. Pinna, J. Polleux, M. Antonietti, *Angew. Chem. Int. Ed.* 2004, 43, 2270 [2] M. Niederberger, G. Garnweitner, N. Pinna, M. Antonietti, *J. Am. Chem. Soc.* 2004, 126, 9120 [3] N. Pinna, G. Neri, M. Antonietti, M. Niederberger, *Angew. Chem. Int. Ed.* 2004, 43, 4345

#### 4:45 PM Z9.9

**Synthesis of Stable Near- to Mid-Infrared Emitting PbSe Nanocrystals in High Yield.** Jeffrey M. Pietryga<sup>1</sup>, Richard D. Schaller<sup>1</sup>, Jagjit Nanda<sup>1</sup>, Kenneth V. Salazar<sup>2</sup>, Joanna L. Casson<sup>1</sup>, Victor I. Klimov<sup>1</sup> and Jennifer A. Hollingsworth<sup>1</sup>; <sup>1</sup>Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

We recently reported the synthesis of the first colloidal PbSe nanocrystal quantum dots (NQDs) exhibiting mid-infrared (mid-IR) photoluminescence (JACS, 2004). Including these results, size-specific syntheses of PbSe NQDs with room-temperature emission over the range of just above 1  $\mu\text{m}$  to 3.5  $\mu\text{m}$  (NQD diameters of 2 to 17 nm) have been reported. While these syntheses succeed in producing predictable sizes and small size distributions, two important shortcomings remain that prevent full application of these NQDs: low chemical yield and poor stability in air. This talk presents our recent studies and developments towards addressing these problems. The synthesis of highly emissive near-IR PbSe NQDs is inefficient (~4% yield for NQDs emitting  $\lambda \approx 1.5\mu\text{m}$ ), as much of the precursor compounds remain unreacted when the target size is reached. Recent experiments with new precursors have raised yield as much as 20-fold. Both near-IR and mid-IR NQDs show marked changes in emission on storing in air. Synchrotron XPS studies reveal evidence that selenium on the surface of these particles is prone to oxidation, especially in the larger, less-thoroughly passivated and less-brightly emitting mid-IR NQDs. Through application of post-preparative treatments, we have been able to reduce spectral "blue-shifting" in near-IR dots, and enhance emission intensity and stability in mid-IR dots.

SESSION Z10: Poster Session: Synthesis,  
Characterization, and Applications of Nanostructures  
Chair: Shawn Feng  
Thursday Evening, March 31, 2005  
8:00 PM  
Salons 8-15 (Marriott)

#### Z10.1

**Abstract Withdrawn**

#### Z10.2

**Self Seeded ZnO Nanowire Growth by Ultrasonic Spray Assisted Chemical Vapour Deposition.** Ming Wei, Dan Zhi and Juidith L. MacManus-Driscoll; Material Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

ZnO, which exhibits a direct bandgap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV, is of considerable technological importance because of its potential use in short-wavelength devices, such as ultraviolet (UV) light-emitting diodes and laser diodes. The fabrication and application of 1-D ZnO nanostructures has attracted considerable interest in recent years. In this work, we produced single crystal nanowires of zinc oxide using a novel self-seeded growth using ultrasonic spray assisted chemical vapour deposition, in which a nanocrystalline seed layer was first deposited onto a glass substrate and the nanowires subsequently grown using a different precursor concentration and substrate temperature. The diameter of the nanowires is in the range of 20-80 nm and the length of the wires is as long as 10  $\mu\text{m}$ . The single crystal nature of the nanowires was revealed by high resolution transmission electron microscopy. The formation of liquid droplets due to the reducing atmosphere and the higher temperature during the nanowire growth was found to be the key step of the ZnO nanowire formation.

#### Z10.3

**Chemical Vapor Synthesis of Complex Nanocrystalline Oxides.** Markus Winterer<sup>1,2</sup> and Vladimir V. Srdic<sup>3,2</sup>; <sup>1</sup>Department of Engineering, University of Duisburg-Essen, Duisburg, NRW, Germany; <sup>2</sup>Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Hessen, Germany; <sup>3</sup>Department of Materials Engineering, University of Novi Sad, Novi Sad, Serbia, Yugoslavia.

Functional materials such as ferroelectrics are often based on complex materials. The synthesis of such multinary, nanocrystalline oxides is highly demanding because it requires the control of composition / stoichiometry on the level of a few thousand atoms per particle. The challenge is especially difficult in case of chemical vapor synthesis (CVS) of compounds such as perovskites where often only solid precursors with low volatilities are available. We will discuss several approaches to solve this problem and report on a novel flash evaporating method to produce stoichiometric, nanocrystalline strontium zirconate from tetramethylheptanedionates. This precursor delivery method may also be applied to the chemical vapor deposition (CVD) of thin films.

#### Z10.4

**All Inorganic Light Emitting Diodes based on Active Layers of CdSe Nanocrystals.** Alexander H. Mueller<sup>1</sup>, Elshan A. Akhadov<sup>1</sup>, Melissa A. Petruska<sup>2</sup>, Marc Achermann<sup>2</sup>, Daniel D. Koleske<sup>3</sup>, Victor I. Klimov<sup>2</sup> and Mark A. Hoffbauer<sup>1</sup>; <sup>1</sup>C-ADI, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>C-PCS, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>3</sup>Sandia National Laboratory, Albuquerque, New Mexico.

Encapsulation of colloidal nanocrystals (NCs) in an inorganic semiconductor matrix is difficult owing to the harsh conditions typically needed for the deposition of semiconductor films. Conventional III-nitride growth techniques require high substrate temperatures and reactive organometallic precursors to achieve growth, leading to the decomposition of the NCs during the encapsulation process. If the deposition parameters are adjusted to more benign conditions, the resulting films are of low semiconducting quality, limiting their usefulness in electronic devices. The use of reactive nitrogen atoms with kinetic energies between 1 and 5 eV and an evaporated metal flux permits the deposition of semiconducting nitride films at significantly lower temperatures than conventional methods (e.g. CVD, sputtering, laser ablation, etc.). Films grown by energetic neutral atom beam lithography/epitaxy (ENABLE), a unique thin film deposition technique developed at LANL, allow the growth of high-quality semiconducting nitride films on thermally unstable and non-epitaxial substrates. Successful encapsulation of CdSe NCs by GaN layers using ENABLE allows NC light emission by direct carrier injection from the semiconducting layers into the NCs<sup>1</sup>. Light emitting devices based on a combination of non-contact energy transfer<sup>2</sup> and direct carrier injection may be fabricated using this deposition technique, allowing for improved efficiencies in the electrical pumping of CdSe nanocrystals. 1. Mueller et al., submitted



#### Z10.5

##### **Electroless Synthesis of Gold Nanoparticles in SBA-15.**

Tewodros Asefa and R. Bruce Lennox; Chemistry, McGill University, Montreal, Quebec, Canada.

The chemical synthesis of nanostructured materials is a very important area of research for the development of nanoscale devices. In this talk, the synthesis of Au/SBA-15 nanocomposite materials via electroless deposition in the nanometer confined channels of mesoporous SBA-15 will be discussed. Subsequent etching of the silica from the composite materials with HF in the presence of alkane thiol resulted in mg quantity of stable monodisperse gold nanoparticles. Both the Au/SBA-15 nanocomposite material and the extracted gold nanoparticles were characterized by XRD, TEM, EDX, and UV-Vis spectroscopy. This novel synthetic route is shown to be more advantageous compared to traditional thermal and chemical routes as it offers higher loading of aligned nanoparticles in the channels to form and synthesis of mg quantity of monodisperse alkane thiol capped possible. Furthermore, the extracted gold nanoparticles were obtained to be stable in various solvents for months and form unique aggregates when deposited on substrates.

#### Z10.6

##### **Carboxylic Acids as Solvent for the Preparation of Metal Sulphides Nanoparticles.** Lidia Armelao<sup>1,2</sup>, Helmut Bertagnolli<sup>3</sup>, Daniele Camozzo<sup>1,2</sup>, Silvia Gross<sup>1,2</sup>, Dieter Holzinger<sup>4</sup>, Guido Kickelbick<sup>4</sup>, Venkata Krishnan<sup>3</sup> and Eugenio Tondello<sup>1,2</sup>;

<sup>1</sup>Department of Chemical Sciences, ISTM-CNR and University of Padova, Padova, Italy; <sup>2</sup>Consorzio Interuniversitario per la Scienza e la Tecnologia dei Materiali, ISTM, Firenze, Italy; <sup>3</sup>Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany; <sup>4</sup>Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

Dispersions of transition metal sulphide nanoparticles into polymerisable solvents can find wide applications as fillers for polymeric materials, as UV-Vis filters, nanopigments and to improve and tailor optical and mechanical properties of the final materials in which they are embedded. A novel method to prepare copper sulphide nanoparticles has been developed, which is based on the fast nucleation of the sulphide by using carboxylic acids as solvents. The particles have been synthesized by reaction of thioacetic acid with copper carboxylates (acrylate, methacrylate, propionate, isobutyrate), in presence of a small amount of water, using the correspondent carboxylic acid (acrylic, methacrylic, propionic, isobutyric) as solvents. The use of a carboxylic acid as solvent gives several advantages. First, the acid environment catalyzes the hydrolysis of carbon-sulphur bond, producing a fast CuS supersaturation and a high nucleation rate. Secondly, especially in heavier solvents (methacrylic and isobutyric acid) the reduced mobility of the precursor molecules favours the nucleation events against particle growth. Finally, the low dielectric constant stabilises the dispersion by reducing the critical coagulation concentration. The prepared nanoparticles were investigated by UV-Vis spectroscopy and by light scattering. The nanoparticle suspensions are clear and are characterized by an adsorption edge which is blue-shifted with respect to that of the bulk semiconductor. Light scattering measurements evidence the formation of monodispersed nanoparticles with average diameters of ca.10 nm.

#### Z10.7

##### **Wurtzite ZnO, ZnCoO, and CoO Nanomaterials.** Aditi Risbud, Ram Seshadri and Lauren Snedeker; Materials, UCSB, Santa Barbara, California.

Wide bandgap materials in the wurtzite structure are currently of interest due to their potential in numerous applications, ranging from bulk materials to the nanoscale: ZnO is a well-known piezoelectric material; Co-substituted ZnO is a candidate dilute magnetic semiconductor for spintronic applications, and ZnO nanoparticles are useful when ultraviolet absorption along with a high degree of optical transparency is required. The synthesis of ZnO nanoparticles was performed via thermal decomposition of zinc acetylacetonate, [Zn(acac)<sub>2</sub>] in benzyl ether solvent at 300°C to form ZnO nanoparticles. While maintaining the wurtzite structure, nanoscale Zn<sub>1-x</sub>Co<sub>x</sub>O particles with x= 0.05, 0.10, and 0.15 were formed by decomposing [Co(acac)<sub>2</sub>] and [Zn(acac)<sub>2</sub>] in the appropriate ratios, with Co<sup>2+</sup> substituting for Zn<sup>2+</sup> in the wurtzite lattice. The synthesis of nanosized ZnO and Zn<sub>1-x</sub>Co<sub>x</sub>O from bulk powders of the respective oxides will also be presented. Additionally, the end-member of this system, novel wurtzite CoO was synthesized using a similar thermolysis route. Characterization of these materials is performed via x-ray diffraction, neutron diffraction, transmission electron microscopy, and DC magnetization measurements.

#### Z10.8

Abstract Withdrawn

#### Z10.9

##### **Synthesis, Characterization, and Growth Mechanism of Silicon Oxide Nanowires.** Lifeng Dong<sup>1</sup>, Michael Coulter<sup>2</sup>, Neil

Ford<sup>3</sup> and Jun Jiao<sup>1</sup>; <sup>1</sup>Department of Physics, Portland State University, Portland, Oregon; <sup>2</sup>Harvard University, Cambridge, Massachusetts; <sup>3</sup>Department of Chemical Engineering, Oregon State University, Corvallis, Oregon.

In this study, two methods have been investigated to synthesize silicon oxide nanowires. One was catalytic thermal evaporation method in which silicon monoxide was used as the precursor and Au particles served as the catalysts. Our study suggests that the growth position of silicon oxide nanowires could be controlled by catalyst locations. For the second method, we explored the procedures for growing silicon oxide nanowires directly from the silicon substrate, which means without the silicon monoxide as the precursor and without the aid of Au catalyst. We have also carried out a series of experiments to study effects of reaction time, temperature, and hydrogen on the growth of nanowires. Experimental results show that hydrogen plays an important role in the formation of oxide nanowires along the <110> direction of the silicon substrate. Without the introduction of hydrogen, there was no growth of silicon oxide nanowires. Scanning electron microscope (SEM), transmission electron microscope (TEM), and energy dispersive x-ray spectrometer (EDX) were used to characterize morphologies and internal structures of the silicon oxide nanowires and to analyze their compositional distributions, respectively. In this report, the characterization results of different silicon oxide nanowires and their formation mechanisms in relation to both preparation methods will be discussed.

#### Z10.10

##### **Low Temperature Synthesis of Silicon Nanowires.**

Rezina Siddique, George Sirinakis and Michael A. Carpenter; College of Nanoscale Science and Engineering, University at Albany, Albany, New York.

Silicon Nanowires (SiNWs) have many potential applications that include diodes, transistors, logic gates, circuitry, and sensors. SiNWs also open the possibility for integrating optoelectronics with microelectronics, since silicon has semiconducting properties and amorphous silicon nanowires have been shown to emit blue light. It has also been demonstrated that SiNWs have tunable electrical properties, depending on the dopant used. With such a range of applications, the ability to mass-produce silicon nanowires simply and easily with no other source of silicon needed other than the substrate itself, will prove very useful. Such methods have previously been reported, but we report a methodology that produces SiNWs at a lower temperature than those widely observed. A (100) silicon substrate was cleaned for five minutes each in ethanol followed by acetone. Films with thicknesses of less than 20nm of either Gold, Palladium, or 60/40 Gold/Palladium were deposited on the substrate through physical vapor deposition to serve as the growth center for the SiNWs. The samples were placed in a furnace and annealed to 900°C, under a 1500 sccm flow of Argon at atmospheric pressure. SEM and TEM were used for characterization of the SiNWs. The resulting SiNWs were amorphous in structure and very convoluted, with lengths on the order of tens of microns, diameters of 40nm and a bed thickness of approximately 10 μm. The effect of varying gold concentration, annealing time, temperature, and gas flow rate were then investigated. The results, which will be discussed in further detail, indicate that adjusting these parameters allows for control over the length, thickness, density, and morphology of the nanowires.

#### Z10.11

Abstract Withdrawn

#### Z10.12

##### **Synthesis and Applications of the Hollow Nanocrystals.**

Yadong Yin<sup>1,3</sup>, Can Erdonmez<sup>2,3</sup>, Andreu Cabot<sup>2</sup>, Justine A. Shaw<sup>2,3</sup> and A. Paul Alivisatos<sup>2,1,3</sup>; <sup>1</sup>The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California; <sup>2</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>3</sup>Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

We demonstrate the successful synthesis of hollow nanocrystals of various materials based on the concept of nanoscale Kirkendall Effect. Cobalt sulfide is used as a typical example to discuss the mechanism for forming the hollow morphology. Carefully studies show that the pore size and shell thickness depend on the size of the original nanocrystals, and the relative concentration of the two species in the diffusion couple. We will discuss the feasibility to extend the same method to the synthesis of hollow nanocrystals of other materials,

such as semiconductors and metals. We will also discuss the potential applications of these new materials.

#### **Z10.13**

**One-Step Synthesis and Assembly of Gold Nanoparticles by Direct Reduction through Termini of Self Assembled Molecular Assemblies.** Ashavani Kumar, Pethuraja Gopal Ganesan and Ganapathiraman Ramanath; Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Metallizing organized molecular assemblies and porous structures with nanoparticles is of interest to exploit the unique properties of nanoparticles for addressing molecular devices, obtaining high-loading of nanoparticle catalysts, and templating for further functionalization. Conventional protocols of synthesis and assembly of nanoparticles require multiple steps and reagents for synthesis, surface modification, phase transfer, and subsequent assembly in predefined geometries. Here we demonstrate a simple and versatile room-temperature method to synthesize and assemble nanoparticles in two dimensional or three dimensional structures such zeolites, and molecular assemblies directly from metal ions without external reducing agents. The main premise of the strategy involves the reduction of metal ion directly by using terminal moieties of molecular layers that form assemblies, or functionalize pores and external surfaces. We illustrate the flexibility of the direct reduction strategy through by demonstrating it on three example of surfaces, namely, (a) tubular assemblies of octadec-9-enoic acid (6-amino-pyridine-2-yl)-amide, (b) pores of 4-aminophenyl trymethoxy silane (APTMS)-terminated MCM 41 zeolites, and (c) APTMS-modified planar silica. In all three cases, nanoparticles form via migration and coalescence metal ions reduced by the amine termini of the surfaces. The particle size can be precisely controlled from 3 to 5 nm, with a very narrow distribution (e.g., +1 nm), by varying the functionalization process parameters. Other key features include uniform surface coverage on planar surfaces, high loading fractions (e.g., ~20 wt %) in porous channels, and electrically addressable metallization nodes on surfaces of molecular assemblies. We also demonstrate selectively nanoparticle formation on amine-terminated patterns on planar surfaces generated by surface probe-induced chemical modification and photolithography. Finally, we describe a mechanistic model of the direct reduction based on transmission electron microscopy, X-ray photoelectron spectroscopy, Infrared Spectroscopy, and UV-visible Spectroscopy measurements.

#### **Z10.14**

**Synthesis of Silica Films with Orthogonally Aligned Ordered Nanopore Arrays by Controlling Surface Chemistry.** Venkat R. Koganti and Stephen E. Rankin; Chemical & Materials Engineering, University of Kentucky, Lexington, Kentucky.

Mesoporous thin films can find many applications in membrane based separations, model surfaces for heterogeneous catalysis, low dielectric constant materials, etc. A popular way to prepare these films is by surfactant templation of dip coated sol-gel solutions. However, interactions with the substrate align the 2-D hexagonal close-packed (HCP) cylindrical channels in these films parallel to the substrate when the films are coated onto normal hydrophilic glass substrates, thus making these channels inaccessible. Even hydrophobic surfaces like graphite align these channels parallel to the substrate. Prior efforts to control the orientation using electric, magnetic and flow fields were effective, but could not achieve perfect orthogonal orientation. Molecular simulations and block copolymer literature suggest that perfect orthogonal orientation of anisotropic mesophases should be promoted by chemically neutral surfaces. To test this approach for mesoporous ceramic films, we have modified normal hydrophilic glass surface in several ways create chemically neutral surfaces. We modified the surfaces by cross linking (a) random polyethylene oxide (PEO)-polypropylene oxide (PPO) copolymers (b) triblock PEO-PPO copolymers, or by (c) partially replacing the terminal hydroxyl groups with methyl groups by silylation. We have used Brij-56 and (PEO)-(PPO) triblock (P123) surfactants as templating agents. Brij-56 was used as the templating agent on silylated slides, and P123 was used in conjunction with cross-linked copolymers. X-ray diffraction supplemented by TEM shows that sandwiching freshly deposited films between two modified slides completely aligns the pores orthogonal to the substrate. The pores in films cast onto unmodified slides align completely parallel to the substrate. The pores in films cast onto modified slides, but which are exposed to air, partially align parallel to the substrate. Thus, we report a simple and effective method to prepare completely orthogonally aligned mesoporous ceramic films.

#### **Z10.15**

**Solution-Phase Synthesis of GaN Nanoparticles.** Jifa Qi<sup>1</sup> and Angela M. Belcher<sup>1,2</sup>; <sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Bioengineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The synthesis of GaN nanocrystals is of importance for understanding the fundamental properties of a wide band gap semiconductor and for developing optoelectronic devices operated in the ultraviolet and blue ranges. GaN and the related III-V nitride compound semiconductors have attracted intense attention due to recent successes in commercial production of blue/green light emitting diodes, lasers, and other devices. Although, significant progress has been made in forming some semiconductor nanocrystals, e.g. CdSe and CdS, there are no good chemical methods to produce homogeneous GaN nanoparticles in solution so far. We are interested in the synthesis of GaN nanoparticles in solution, since free standing solution phase nanoparticles are easy to manipulation, especially through the biological method that developed in our laboratory. Here, we report a solution phase synthetic method of colloidal GaN nanocrystals that using the commercial available precursors and through the reaction and nucleation process in solution at moderate temperatures. The purification method of the products was investigated, and the nanocrystals were characterized by transmission electron microscope and x-ray diffraction. TEM observations revealed that the size of GaN nanoparticles ranged from 2 to 17 nm depending on the synthesis process. The optical absorption band exhibits size dependent blue shifts comparing with that of bulk GaN. Further, GaN nanoparticles synthesized by this method have high fluorescent efficiency in blue or green color ranges. The emission band in violet regime is observed, which may originate from the quantum confined excitonic transition in GaN nanoparticles. The GaN nanocrystal surfaces can be coated with a variety of organic and biological molecules, giving them functionality that that enables self-assembly, patterning biocompatibility and cell labeling.

#### **Z10.16**

**How Cationic Fluorinated Surfactant Structure Influences Mesoporous Silica Particle Architecture.** Stephen E. Rankin<sup>1</sup>, Bing Tan<sup>1</sup>, Sandhya M. Vyas<sup>2</sup>, Hans-Joachim Lehmler<sup>2</sup> and Barbara L. Knutson<sup>1</sup>; <sup>1</sup>Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky; <sup>2</sup>Department of Occupational and Environmental Health, University of Iowa, Iowa City, Iowa.

Fluorinated surfactants are a special class of surfactants that assemble into aggregates and form novel "intermediate" mesophases more easily than hydrocarbon surfactants. These properties should allow co-assembly with ceramic precursors to create materials with a wider range of pore sizes, shapes, and orientations than are available from hydrocarbon surfactants. Fluorinated surfactants also possess processing advantages for organic functionalization and supercritical carbon dioxide processing. We report a comprehensive investigation of the use of cationic fluorinated surfactants as templates for ordered nanoporous silica. A homologous series of perfluoroalkylpyridinium chloride surfactants with tail lengths between 4 and 12 carbons is synthesized. Using these surfactants, materials are synthesized by precipitation from either aqueous or ethanol-water solutions. Pore structures obtained include worm-like pores, 2D close-packed hexagonal cylindrical pores, pillared layers of silica with a random mesh phase structure, and porous sheets of silica. Particle morphologies include irregular particles, solid spheres, hollow spheres / vesicles, and foam-like structures. The 4-carbon straight chain surfactant produces materials with unusually small (~1.6 nm diameter) pores. The layers of the mesh phase structure prepared with the 10-carbon surfactant align orthogonal to the main axis of the particles, to give rod-like particles rather than platelets. Ethanol promotes the formation of ceramic aggregates with long-chain fluorinated surfactants, and promotes spherical particle formation. Interestingly, the pores in the spherical particles are usually oriented radially, whether the pores are cylindrical or slit-shaped. The variety of pore architectures found in this study is much greater than would be found for a homologous series of hydrocarbon surfactants. We relate this structural variety to the known variety of micelle aggregates and mesophases formed by fluorinated surfactants

#### **Z10.17**

**One-Dimensional Nanostructure of Polycyclic Aromatic Hydrocarbon Molecule Fabricated by Low-Temperature Vacuum Evaporation.** Shich-Chang Suen<sup>1,2</sup>, Wha-Tzong Whang<sup>2</sup>, Kuo-Rong Huang<sup>2</sup>, Tsung-Che Tsai<sup>2</sup> and Bau-Tong Dai<sup>1</sup>; <sup>1</sup>National Nano Device Lab., Hsinchu, Taiwan; <sup>2</sup>Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

The synthesis of one-dimensional (1D) nanomaterials has attracted intensive research recently owing to their unusual physical properties and unique applications in nanoscale devices. Most of studies concern inorganic materials. However, the organic 1D nanomaterials, which possess amazing electronic and optical properties, remains poorly studied, and only a few successful examples have been reported. In this study, we successfully fabricate 1D nanostructure of coronene, one of polycyclic aromatic hydrocarbon (PAH) molecules, whose bulk form is normally used as a dye for the organic light emitting diode or

a semiconductor layer of organic thin film transistor. With the vacuum evaporation method, coronene nanofibers (CNFs) with diameter ca. 66nm have been synthesized at room temperature without the aid of catalyst that are normally needed for growing carbon nanotubes (CNTs). The novel method mainly makes use of the intermolecular  $\pi$ - $\pi$  interaction of PAH molecules, which can self-assemble into columnar aggregates. Besides, the surface energy of substrate, which relates to the unsaturated surface bond, also strongly affects the geometry of PAH-CNFs. The nanofibers exhibit excellent field emission characteristics when biased under vacuum. Moreover, the high aspect ratio morphology provides a lotus effect that greatly enhances hydrophobic property of a film. This relative easier process provides a broad range of applications in nanoscience and technology.

#### **Z10.18**

**Dynamics of Silicon Nanoparticle Synthesis by Pulsed Laser Ablation.** Terry Murray<sup>2,1</sup> and Larry Grazulis<sup>2</sup>; <sup>1</sup>Graduate Materials Engineering, University of Dayton, Dayton, Ohio; <sup>2</sup>Research Institute, University of Dayton, Dayton, Ohio.

Si nanoparticles have been synthesized by pulsed laser ablation in an Ar atmosphere, and the size distribution was determined by AFM and by time of flight mass spectrometry. The mean particle size determined by both techniques was 3 nm at an Ar pressure of 133 Pa, and this shifted to a slightly larger size at 266 Pa. The kinetic energy distribution of the nanoparticles was determined by varying the delay time between ablation and photoionization lasers; the results indicated the nanoparticles had a kinetic energy on the order of 5 eV at the end of the growth process. The implications for Si thin film growth from Si nanoparticles will be discussed. Finally, the photoionization dynamics of the nanoparticles were investigated. The results indicated that some multiply charged nanoparticle ions underwent Coulomb explosion upon photoionization as indicated by broadening in the  $\text{Si}^+$ ,  $\text{Si}^{+2}$ , and  $\text{Si}^{+3}$  peaks. This was modeled by the liquid drop model.

#### **Z10.19**

**Preparation of Free-Standing Nanoparticles.**

Rabindra Nath Das<sup>1,2</sup> and Panchanan Pramanik<sup>1</sup>; <sup>1</sup>Chemistry, IIT Kharagpur, Kharagpur, West-Bengal, India; <sup>2</sup>Materials Science, Cornell University, Ithaca, New York.

With the growing interest in building advanced materials using nanoscale building blocks, there is a need for general approaches to controlling the sizes of nanoparticles. Size controlled free-standing nanoparticles are crucial for addressing some important fundamental issues such as the finite size effect on electronic properties. Here we demonstrate relatively simple synthetic strategies for preparing free-standing nanoparticles that can be translated from one system to another. Nanoparticles with free-standing form have been prepared by solution evaporation process. The process involves the preparation of metal ion ligand (tartarate, citrate, oxalate, EDTA etc.) complex solution followed by evaporation. Complete evaporation results in fluffy dried precursor mass. Calcination of precursor mass at low to moderate temperatures produce phase pure nano sized powders. TEM studies clearly show free-standing individual nanoparticles. Metal ion complex routes play a crucial role in preparing the nanoparticles having good physical properties. In complex process precursor mass originates from a homogeneous mixture of metal ions, and careful control of the removal of the organic ligands permits the production of free standing nanoparticles without agglomeration. The examples discussed include perovskites, i.e. lead zirconate titanate ( $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ), lead magnesium niobate ( $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ ) and lead iron niobate ( $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ).

#### **Z10.20**

**Cobalt-Nickel Nanoparticles with Hybrid Shapes Synthesized by Heterogeneous Nucleation in Liquid Polyols.** Diane Ung, Guillaume Viau and Fernand Fievet; ITODYS, University Paris 7, Paris, France.

Magnetic nanoparticles with anisotropic shape are desired for various applications such as magnetic recording or electromagnetic absorbers. In our laboratory we study the synthesis of cobalt and cobalt-nickel particles by reduction of acetate salts in liquid polyols. By acting upon the experimental conditions (heterogeneous nucleation with ruthenium and basicity) we obtained recently Co and  $\text{CoNi}(1-x)$  particles ( $x = 1 - 0.3$ ) with anisotropic shapes, such as wires or platelets. The formation of the hexagonal close-packed phase was found to be the driving force for the anisotropic growth of the particles. The shape was controlled by the sodium hydroxide concentration in solution: growth occurs preferentially along the c axis or perpendicular to it for low and high hydroxide concentrations, respectively, giving either wires or platelets. Particularly interesting are the intermediate hydroxide concentrations for which  $\text{CoNi}(1-x)$  particles ( $x = 0.8 - 0.3$ ) with shapes like nails, dumbbells and diabolos, are obtained. All these shapes are hybrid shapes between wire and platelet: the central part of the particles is a wire with

diameter of 10 nm and length varying from a hundred to a few nanometers depending on the sodium hydroxide concentration and on the CoNi composition, and the edges are hexagonal platelets with a diameter in the range 20-30 nm. High resolution electronic microscopy showed nearly monocrystalline particles with the crystallographic c-axis parallel to the wires but did not show any hexagonal-cubic structural segregation within the particles. In contrast local energy dispersive X-ray analysis showed a chemical composition gradient: the Ni content of the platelet edges is higher with respect to the global composition. These hybrid shape particles are thus complex nanocrystals that can be qualified as a new class of bimetallic particles, neither solid solution, nor core-shell particles. The study of growth mechanism showed that a high number of ruthenium seeds allows complete separation between the nucleation and growth steps. The hydroxide concentration controls the supersaturation concentration by acting upon the equilibrium between the solution and the unreduced solid phase in which are involved the Co(II) and Ni(II) species when the reduction takes place. Moreover the unreduced solid phase depends on the metal cations, a Co(II) alkoxide and a Ni(II) hydroxy-acetate were evidenced. Difference in the coordination chemistry of the two metal ions may be responsible of the segregation within the final metal particles. Magnetic measurements showed a ferromagnetic behaviour at room temperature with saturation magnetization close to the bulk and coercivity in the range 1500-2000 Oe, for the wires and the hybrid shape particles. The coercivity is mainly governed by the shape anisotropy of the particles but increasing density of stacking faults density as inferred from X-ray diffraction studies is found to lower the coercivity.

#### **Z10.21**

**Ab Initio Analysis of the First Elementary Processes of BN and BCN Nanotubes Formation.** Vladimir Makarov, Brad Weiner and Gerardo Morell; University of Puerto Rico, San Juan, PR, Puerto Rico.

Ab initio analysis of the BN and BCN nanotube structure, spectroscopy and physical properties are available in the open scientific literature. In the present study, we have undertaken the investigation of the first elementary processes of the BN and BCN nano species growth. Experimentally, the process is induced by focusing laser radiation on the bulk sample surface. We propose that the initial intermediates induced by the laser radiation are BN, BNB and NBN. The first step of our analysis includes calculation of enthalpy of the elementary processes: 1.  $\text{BN} + \text{BN} \rightarrow \text{BNBN}$ ; 2.  $\text{BNB} + \text{NBN} \rightarrow ?$ ; 3.  $\text{BNBN} + \text{BN} \rightarrow ?$ ; 4. and so on. The next step being undertaken is to calculate potential surfaces for the listed processes and their transition state configuration. Both the first and second steps will allow to estimate the rate constant of the relevant processes, and to further carry out modeling of the BN and BCN nanotube formation process.

#### **Z10.22**

**Process Control of Nanocrystalline Grain Size in Gold-Copper Electrodeposits.** Alan Jankowski, Lawrence Livermore National Laboratory, Livermore, California.

The enhancement of mechanical properties and structural stability are attributes sought for metal alloys used in the form of thick coatings for high-strength capsules. Grain refinement is a known microstructural path to increase the hardness and flow stress of many metal alloys. In this study, the growth of ten to thirty micron-thick foils is pursued using the method of pulsed electrodeposition from an aqueous potassium-cyanide solution of gold and copper. The process parameters of current and potential affect both the structure and composition of the foils. The alloy foils are found to have an equiaxed nanocrystalline structure as revealed by electron and x-ray diffraction. The crystallite size is quantified using the Debye-Scherrer formulation for peak-broadening of the Bragg reflections in the x-ray diffraction scans. The composition of the gold-copper foils is determined by analysis of energy dispersive x-ray spectra. A decrease in the current density and cathode voltage favors deposition of the more noble metal species. A short current pulse favors nanocrystalline grain sizes. The mechanism for nucleation and growth as determined from current transients yield relationships for nucleus density and nucleation rate. However, to develop a greater understanding of the role of process variables on grain size (as a design structural parameter to control strength), a formulation is developed to model the effect of the electrodeposition energetics on grain size. The relationship between the aqueous process variables with the resultant grain size is presented using an equation-of-state analogy to grain growth phenomena in the solid-state. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

#### **Z10.23**

**Dispersion of Polymer-Stabilized Gold Nanoparticles in High Molecular Weight Polymer Matrices.** Muriel K. Corbierre<sup>1</sup>, Neil

S. Cameron<sup>2</sup> and R. Bruce Lennox<sup>1</sup>; <sup>1</sup>Chemistry, McGill University, Montreal, Quebec, Canada; <sup>2</sup>IMI-CNRC, Boucherville, Quebec, Canada.

We studied the dispersion of small (< 10 nm) polymer-covered gold nanoparticles (PS<sub>19</sub>-Au and PS<sub>125</sub>-Au, where the subscript number indicates the number of polystyrene repeat units) in high molecular weight polymer matrices in the preparation of nanocomposite materials. The dispersions were assessed by transmission electron microscopy, UV-visible spectroscopy and small angle X-ray scattering. The dispersions are interpreted in terms of wetting of the polymer brushes bound on the gold core by the polymer matrix. PS<sub>19</sub>-Au exhibits complete dispersion in a low molecular weight PS matrix (2000 g/mol) and partial dispersion in higher molecular weight matrices up to 80000 g/mol. Because the theoretical limit for wetting of a dense brush is reached when the molecular weights of both the polymer brush and the polymer matrix are the same, the partial dispersion of the PS<sub>19</sub>-Au nanoparticles in matrices of molecular weight higher than the brush molecular weight is attributable to the existence of a high volume fraction of voids within the brush. These voids arise from the geometry of the gold core. Conversely, complete dispersion was nevertheless achieved in the case of PS<sub>125</sub>-Au in all polystyrene matrices up to 80000 g/mol. This is probably due to the PS<sub>125</sub>-Au lower grafting density on the gold core and/or the high fraction of void volumes caused by the facets on the gold cores. This allows for their dispersion when the matrix molecular weight is greater than that of the brush.

#### Z10.24

**Nucleation and Growth of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> Films Prepared by Atomic Layer Deposition for Catalytic Membrane Fabrication.** Piotr W. Klamut<sup>1,4</sup>, Jeffrey W. Elam<sup>2</sup>, Guang Xiong<sup>3</sup>, Catherine Y. Han<sup>1</sup>, Hsien-Hau Wang<sup>1</sup>, John N. Hryn<sup>2</sup> and Michael J. Pellin<sup>1</sup>; <sup>1</sup>Material Sciences Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Energy Systems Division, Argonne National Laboratory, Argonne, Illinois; <sup>3</sup>Chemistry Division, Argonne National Laboratory, Argonne, Illinois; <sup>4</sup>Department of Physics, Northern Illinois University, DeKalb, Illinois.

Atomic layer deposition (ALD) is a thin film growth technique allowing precise, conformal oxide layers to be deposited on a variety of nanoporous media including membranes, nanotubes and powders. Characteristics of the ALD growth make it an ideal method for developing new nanocatalysts. We have recently fabricated novel nanostructured catalytic membranes by depositing Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> layers onto anodic aluminum oxide (AAO) scaffolds. To fabricate these membranes effectively, it is necessary to understand the chemistry underlying the nucleation and growth of the different ALD layers. In this study, the nucleation and growth of ALD Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> on each other were studied by depositing ALD films on planar substrates and then analyzing the films using spectroscopic ellipsometry and x-ray photoelectron spectroscopy. It was found that by varying the underlying oxide layer, the growth rate of the subsequent overlayers could be enhanced or suppressed. In addition to these ex situ analyses, in situ quartz crystal microbalance (QCM) measurements were performed during the nucleation and growth of the ALD Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> containing bilayers. These QCM measurements reveal details regarding the interfacial chemistry during the nucleation of the mixed oxide layers. Using the growth rates determined for the various ALD layer on the planar substrates, ALD films were deposited on the inside surfaces of AAO to fabricate nanostructured catalytic membranes. These nanostructured catalytic membranes synthesized using ALD showed enhanced selectivity for oxidative dehydrogenation when compared with conventional powder catalysts.

#### Z10.25

**Synthesis of Complex Metal Carbides using Biological Templates.** Yongsoon Shin, Xiaohong S. Li, Chongmin Wang, William D. Samuels, Yong Wang, Larry R. Pederson and Greg J. Exarhos; Materials Department, Pacific Northwest National Lab, Richland, Washington.

Biological structures are distinguished by the extremely high precision of their self-assembly, replication, and functionality. Diatoms, bacteria, cornstarch, pollen and wood have been used for the biomimetic synthesis of a range of organized inorganic architectures with potential applications in catalysis, magnetism, separation science, electronics and photonics. In this presentation, we describe a facile method for replicating the complex surface structures of wood, tree and grass pollen grains, and rice hull, which in the case of metal carbide produces complex hierarchical cellular structures morphology with surface areas high than 250m<sup>2</sup>/g. Such materials show highly nanocrystalline (100-500nm) in particle sizes and extreme thermal stability up to 1500°C in air. Cellulose is a critical component to maintain the original structures due to its crystalline network, while lignin helps the metal carbides nanocrystalline. The synthetic

procedures and surface characterizations including microscopic measurements will be presented in detail.

#### Z10.26

**One-Dimensional Boron-Based Nanostructures: Synthesis and Characterization.** Terry Xu<sup>1</sup> and Rod Ruoff<sup>2</sup>; <sup>1</sup>Department of Mechanical Engineering & Engineering Science, The University of North Carolina at Charlotte, Charlotte, North Carolina; <sup>2</sup>Department of Mechanical Engineering, Northwestern University, Evanston, Illinois.

Catalyst-assisted growth of one-dimensional (1D) boron-based nanostructures was achieved by pyrolysis of diborane (B<sub>2</sub>H<sub>6</sub>) at 850-900 °C and ~200mtorr. Gold (Au) or platinum/palladium (Pt/Pd) alloy are effective catalysts. The as-synthesized nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. In addition to the crystalline  $\alpha$ -tetragonal boron nanowires, novel tube-catalyst-wire hybrid nanostructures were discovered. Increasing tube length by post-annealing was also realized. By tuning the size of catalyst particles, boron nanotube-catalyst-nanowire hybrid structures with smaller diameter ~8nm were synthesized. Possible mechanisms for the growth of these crystalline boron nanowires and nanowires-catalyst-nanotubes hybrid structures will be presented. The 1D boron-based nanostructures will find applications in nanoelectronics, nanocomposites and thermoelectric energy conversion devices. We appreciate the support of the National Science Foundation (grant EEC-0210120), and the Office of Naval Research grant (No. N000140210870).

#### Z10.27

**New Gold Nanoparticle Preparation from Soluble Gold(I)-Thiolate Materials.** Muriel K. Corbierre and R. Bruce Lennox; Chemistry, McGill University, Montreal, Quebec, Canada.

A novel preparation method of thiol-stabilized gold nanoparticles is introduced. Soluble Au(I)-thiolate complexes with bulky thiol ligands were prepared from Au(III) salts and isolated in order to study the reductive transition to Au<sup>0</sup>. These isolated and stable intermediates were chemically reduced in suitable inert solvents. The resulting gold nanoparticles were compared with those prepared using conventional methods (i.e. that use a mixture of Au(III) salts and thiols as the initial reagents). The stepwise synthetic technique permitted the examination of the effect of adding ions during the synthesis process on the gold nanoparticle sizes. The diameters and dispersities of the thiol-capped gold nanoparticles synthesized here are typically comparable to those prepared by the conventional methods used. This preliminary work lends support to our hypothesis that further study of the effect of reaction conditions on the controlled reduction of Au(I)-thiolate salts will shed light on the tailored preparation of gold nanoparticles.

#### Z10.28

**Synthesis and Consolidation of Microemulsion-Derived Zirconia Nanopowders.** Olivia A. Graeve and Harpreet Singh; Metallurgical and Materials Engineering, University of Nevada, Reno, Reno, Nevada.

Nanocrystalline powders of yttria-stabilized zirconia and pure zirconia were synthesized using a reverse micelle synthesis procedure using zirconium oxychloride, Na-AOT, and iso-octane as precursors. X-ray diffraction, surface area analysis, differential thermal analysis, dynamic light scattering, scanning electron microscopy, fourier transform infrared spectroscopy, and transmission electron microscopy studies were performed to fully characterize the as-synthesized and heat treated powders. The pure zirconia powders exhibited a crystallite size of 2-5 nm in the as-synthesized state. Upon heat-treatment, metastable tetragonal phase was stabilized at heat treatment temperatures below 500 degrees C. Above 500 degrees C, the powders started changing to the stable monoclinic phase. Synthesis of 3 mol% and 8 mol% yttria-stabilized zirconia produced pure tetragonal and cubic phases, respectively, with a crystallite size smaller than 6 nm. The use of a novel wash media allowed the synthesis of ultrapure powders with no measurable organic or inorganic impurities. Reaction parameters such as precursor concentration, aging time, and water-to-surfactant ratio were varied to optimize the synthesis process. The nanoparticles were further sintered using a spark plasma sintering (SPS) method. Dense compacts of >98% density were obtained in 20 minutes. The grain size of the compacts was around 50 nm.

#### Z10.29

**Melting of Alkyl-Terminated Ge Nanoparticles.** Hsiang Wei Chiu<sup>1</sup>, Christopher Chervin<sup>1,2</sup> and Susan Mary Kauzlarich<sup>1</sup>; <sup>1</sup>Chemistry, University of California Davis, Davis, California; <sup>2</sup>University Outreach, Lawrence Livermore National Laboratory, Livermore, California.

Crystalline Ge is an ideal surface for growing GaAs for high efficiency photovoltaics. In order to grow a crystalline Ge film on a flexible substrate, we are exploring the use of Ge nanoparticles. Ge nanoparticles have been synthesized by solution routes. In here, we concentrated on a high yield reduction synthesis that gives good surface passivation. The room temperature as-prepared Ge nanoparticles are crystalline. The transmission electron microscopy (TEM) showed crystalline Ge and the average size is 5-8nm depending on synthetic conditions. The typical size distribution of the Ge nanoparticles is 5.0 (1.0) nm. Heat treatment at 300C produces amorphous alkyl terminated Ge that is still soluble in nonpolar organic solvent. Further heating up to 420C shows that most carbon is removed and the product contains both crystalline and amorphous, non aggregated Ge nanoparticles. X-ray powder diffraction (XRD), Raman spectroscopy, TGA/DTA and TEM data will be presented.

#### **Z10.30**

**Energetics of ZnS Semiconductor Quantum Dots in Zinc Phosphate Glasses.** Riham M. Morcos, Alexandra Navrotsky and Subhash Risbud; Thermochemistry Facility and NEAT ORU, University of California at Davis, Davis, California.

The goal of this research is to investigate the energetics of zinc sulfide quantum dots doped in a zinc phosphate glass matrix using high temperature solution calorimetry and differential scanning calorimetry. Nucleation and coarsening processes play a major role in the synthesis of nanocrystals in glasses. ZnS is a well-studied II-VI semiconductor material having a bandgap in the visible and just into the ultraviolet. The following questions will be addressed. When the glass is initially doped with several percent ZnS, and no quantum dots are detected, is the ZnS truly dissolved or is it present as nanoclusters? As the particles coarsen, how does their enthalpy depend on size? At what size is their enthalpy the same as that of bulk ZnS? A combination of thermodynamic and structural tools will be used. The techniques used are drop solution calorimetry into a molten oxide solvent at 700 or 800 oC, differential scanning calorimetry, transmission electron microscopy, x-ray diffraction, and nuclear magnetic resonance. Each provide information on specific aspects of the structure or dynamics of complex disordered materials such as glasses. The DSC analysis of ZnS doped glass matrix [(P2O5)0.5 (ZnO)0.5] detected a glass transition (Tg) temperature of 480 oC for glasses containing 20 % ZnS quantum dots, compared with 500 oC for glass with nominally dissolved ZnS and 450oC for glass with no ZnS at all. Drop solution calorimetry, which obtains the heat of formation of the system, is in progress.

#### **Z10.31**

**Doping Kinetics in Semiconductor Nanocrystals.** Lijun Zu<sup>1</sup>, David J. Norris<sup>1</sup>, Steven C. Erwin<sup>2</sup>, Michael Haftel<sup>2</sup>, Thomas A. Kennedy<sup>2</sup> and Alexander L. Efros<sup>2</sup>; <sup>1</sup>Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; <sup>2</sup>Naval Research Laboratory, Washington, District of Columbia.

Growth kinetics has recently been studied in the context of the shape control of semiconductor nanocrystals. For example, quantum rods and other more exotic shapes (e.g., tetrapods) have been fabricated from CdSe by varying the precursor and surfactant concentrations during growth. It has been proposed that these shapes arise in CdSe when extremely high precursor concentrations (i.e., high monomer) exist. With high monomer concentration, strongly non-equilibrium, diffusion-controlled growth combines with the anisotropic hexagonal crystal structure of wurtzitic CdSe. Further, if the precursors are subsequently depleted, the shape of the quantum rods can revert to a more isotropic shape during continued growth. This occurs due to diffusion of material between facets on the same nanocrystal ("intraparticle ripening"). Here, we will utilize this knowledge of the kinetics of shape control to explore similar issues in the kinetics of doping of semiconductor nanocrystals. We have recently observed many parallels between these two subjects during our studies of Mn-doped ZnSe nanocrystals. For example, we have observed strong ripening effects of Mn incorporation if the precursor concentrations are allowed to fall during continued growth. The implications of this and other observed phenomena on the doping process will be discussed.

#### **Z10.32**

Transferred to Z3.37

#### **Z10.33**

Abstract Withdrawn

#### **Z10.34**

**Influence of Linker Molecules on Charge Transport through Self-Assembled Single-Nanoparticle Devices.** Al-Amin Dhirani, Amir Zabet and Yoshinori Suganuma; University of Toronto, Toronto, Ontario, Canada.

We investigate electrical characteristics of single-electron electrode/nano-island/electrode devices formed by alkanedithiol assisted self-assembly. Measurements of single electron charging energies determined by Coulomb blockade (CB) voltage thresholds exhibit a significant discrepancy with the Orthodox model. The energies do, however, scale with particle sizes, consistent with single electron charging phenomena. We propose that the discrepancy is caused by a multi-barrier junction potential that leads to a voltage divider effect. Temperature and voltage dependent conductance measurements performed outside the blockade region probe the junctions directly and are consistent with this picture. We simulated our data using a suitably modified Orthodox model.

#### **Z10.35**

**Synthesis and Characterization of Cuprous Oxide Nanodots, Nanorods and Thin Films.** Haitao Zhang<sup>1</sup>, Zigeng Yin<sup>2</sup>, Duane M. Goodner<sup>1</sup>, Michael J. Bedzyk<sup>1</sup>, Tobin J. Marks<sup>3</sup>, John B. Ketterson<sup>2</sup> and Robert P. H. Chang<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Department of Physics and Astronomy, Northwestern University, Evanston, Illinois; <sup>3</sup>Department of Chemistry, Northwestern University, Evanston, Illinois.

Cuprous oxide (Cu<sub>2</sub>O) is an important p-type oxide semiconductor. It is a promising candidate for observing Bose-Einstein condensation of excitons, and also a potential material in applications as solar cell, photocatalysis and chemical sensor. We have fabricated different Cu<sub>2</sub>O structures, such as nanodots, nanorods and thin films. Using metalorganic chemical vapor deposition (MOCVD), Cu<sub>2</sub>O nanodots have been grown on LaAlO<sub>3</sub> (001) substrates. X-ray diffraction reveals that the nanodots are fully relaxed, and grow epitaxially with a Cu<sub>2</sub>O (001)——LaAlO<sub>3</sub> (001) and Cu<sub>2</sub>O [100]——LaAlO<sub>3</sub> [100] epitaxial relationship despite the large lattice mismatch of 12.7% between Cu<sub>2</sub>O and LaAlO<sub>3</sub>. The dots are pyramid-shaped islands with {111} side facets which have a steep slope of 54.7° with respect to the (001) surface plane. Kinetics study indicates that restrained Ostwald ripening plays an important role in the formation of the dislocated nanodots. A non-catalyst growth of Cu<sub>2</sub>O nanorods on silicon substrates has been achieved using a two-step MOCVD process. After the initial seeding step, Cu<sub>2</sub>O nanorods are grown laterally only on the sidewalls of silicon substrates. The nanorods are single crystal Cu<sub>2</sub>O with a diameter of 100-250 nm, a length up to 3 μm, and a growth direction of <110>. The formation of nanorods is explained using a vapor-solid growth mechanism. To our knowledge, this is the first report on the synthesis of single crystal Cu<sub>2</sub>O 1D nanostructures directly on the substrates using a non-solution approach. Continuous epitaxial Cu<sub>2</sub>O films on MgO (011) have been synthesized using DC magnetron sputtering. Scanning electron microscopy images reveal that surfaces of the films are flat and continuous, and a closer examination by atomic force microscopy on the films shows terrace structures on the surface, which is characteristic of two-dimensional (2D) growth. The 2D growth is contributed to the bombardment effect of energetic particles in the sputtering growth. Optical properties and excitonic structures in these materials are studied and will be reported.

#### **Z10.36**

**Combined UHV and Liquid Phase (CULP) Processing of Self-Assembled Nanostructures.** Samir Emre Ogun and Raymond T. Tung; Dept. Physics, Brooklyn College, Brooklyn, New York.

Self-assembled nanostructures are important for a wide range of applications. Present techniques employed for the self-assembly of quantum dots use surface/interface energies and/or limited reaction kinetics to achieve nanometer characteristic size, and are in general limited to specific material systems. Here we present results from an entirely novel, "combined UHV and liquid-phase processing" (CULP) method for the fabrication of quantum dots from a wide range of materials. This novel approach makes use of an inert liquid film, to mediate the growth of physically deposited thin films and to accommodate the self-assembly of nanoparticles. The intended material is co-adsorbed, along with a chemically inert gas species as a mixture at an appropriate (cryogenic) temperature onto a substrate in ultrahigh vacuum (UHV). Because of the high-vacuum and low-temperature conditions employed, co-adsorbed films are in the "solid" phase. The mixed film is then pressurized, without exposure to air, with cold high-purity helium gas to above the triple-point pressure of the gas species before the temperature is also raised to above the triple-point temperature. This sequence brings the thin film to the liquid phase and uses the high diffusivity in the liquid film (> 1x10<sup>-5</sup> cm<sup>2</sup>/s) to allow atoms to self-assemble into particles. Nano-particles of semiconductors (Si, Ge), metals (Co, Ni, Mo, Ti), alloys (NiSi<sub>3</sub>, TiNi), and oxides (TiO<sub>x</sub>, SiO<sub>x</sub>), with diameters of 5 - 50 nm, have been fabricated using the CULP technique operated at ~100K, using molecules of sulfur hexafluoride (SF<sub>6</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>)

as co-adsorbates. The pressurization was typically carried out at 50-200 kPa. The size and density of nanodots were found to depend sensitively on the concentration of the starting solid film, the film thickness, the surface condition of the substrate, and the pressurizing and drying conditions. Results of "selective deposition" of nanoparticles with partially dried liquids on pre-patterned substrates and the use of freeze-drying for a uniform deposition of particles are also presented. Essentially, this technique combines the cleanliness and fine control associated with UHV deposition with the favorable kinetic (physical) processes available in the liquid phase for self-assembly. Results obtained from scanning probe microscopy, scanning electron microscopy, and optical methods will be discussed. Electrical characteristics of junctions containing CULP-grown nanoparticles are also presented. We also comment on the soft-landing contact formation capability offered by the present scheme, which has important bearings for delicate materials and interface control. This work is supported by an NER grant from NSF-DMR.

#### **Z10.37**

##### **Solution Approaches to Organizing One-Dimensional Nanostructures on Substrates.** Z. Ryan Tian<sup>1</sup> and J. Liu,<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas; <sup>2</sup>Sandia National Laboratories, Albuquerque, New Mexico.

Large arrays of highly oriented one-dimensional nanomaterials (1DNMs) have many important technological applications. Here we report generalized solution approaches to direct syntheses of oriented nanowires, nanorods, and nanotubes. Results from the structural analyses suggest that a variety of 1DNMs (e.g. TiO<sub>2</sub>, ZnO, conducting polyaniline, etc.) can be organized on nearly any substrates under the help of nanoseeds and self-assembled monolayers (SAMs). Due to their unique physical and chemical properties, these oriented arrays of 1DNMs are expected to have novel potential applications in catalysis, filtration, sensing, and photovoltaics.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

#### SESSION Z11: Applications and Devices of Nanomaterials II

Chairs: Shawn Feng and Dongyun Zhao  
Friday Morning, April 1, 2005  
Room 2010 (Moscone West)

#### **8:00 AM Z11.1**

##### **Solution-Phase Methods for Synthesis of Complex Hybrid Nanostructures.** Erik David Spoecker<sup>1</sup>, Julia Hsu<sup>2</sup> and James A.

Voigt<sup>1</sup>; <sup>1</sup>Chemical Synthesis and Nanomaterials, Sandia National Laboratories, Albuquerque, New Mexico; <sup>2</sup>Surface and Interface Sciences, Sandia National Laboratories, Albuquerque, New Mexico.

We have investigated the synthesis and characterization of multicomponent nanocrystalline hybrid materials and films. Nanoscale materials present unique optical, electrical, and structural properties with significant technological implications. Such unique properties are strongly dependent on the chemical and structural composition of these materials. We have explored synthetic strategies to create hybrid materials whose chemical and structural composition may be controlled on multiple organizational levels. By applying micropatterning techniques, we have created organized surface modifications on various metal and oxide surfaces. Utilizing these selective patterns we have explored solution-phase growth of complex hybrid materials with multiple levels of organization. The solution phase nature of these crystal growth processes allows for the use of organic crystal modifiers, such as functional peptides. These organic tools facilitate the controlled, directed nanostructure formation, interfacing functional materials such as cadmium sulfide nanoparticles and zinc oxide nanorods. Using multiple levels of organizational control allows for the creation of intricate nanomaterials with varied chemical and structural characteristics. These methods for the growth of complex nanostructures represent powerful tools for the synthesis of new material systems. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-ACO4-94AL85000.

#### **8:15 AM Z11.2**

##### **Optical Applications and Characterization of Mesoporous Fluorocarbon-Modified Titania.** Shannon Wachter Boettcher<sup>1</sup>,

Michael H. Bartl<sup>1,3</sup>, Jerry G. Hu<sup>2</sup> and Galen D. Stucky<sup>1,2</sup>;  
<sup>1</sup>Chemistry, University of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Materials Science, University of California, Santa Barbara, California; <sup>3</sup>California NanoSystems Institute, University of California, Santa Barbara, California.

We have developed a new inorganic/organic mesostructured composite consisting of a fluorocarbon-modified titania precursor and block copolymer phase segregated into hexagonal or cubic nanoscale architectures. This approach enables facile processing of the titania/block copolymer surfactant precursor solution into optically activated, transparent, and crack-free fibers, planar waveguides, and micropatterns. These dye-activated, high refractive index, TiO<sub>2</sub>-based composites show efficient waveguiding and mirrorless lasing at low thresholds without the need of an ultralow refractive index support layer such as mesoporous SiO<sub>2</sub>. The waveguiding properties and lasing thresholds for these materials are investigated for different mesostructures and surface morphologies. Structural characterization is realized by 2D SAXS and TEM combined with IR and modern solid state NMR spectroscopic techniques.

#### **8:30 AM Z11.3**

##### **Nanocrystalline Mixed Metal Oxides and their use as Novel Photocatalysts.** Blake Simmons<sup>1</sup>, Tom Zifer<sup>1</sup>, Heather Gardea<sup>1</sup>, Tim Boyle<sup>2</sup>, Gene Lucadamo<sup>1</sup>, Daniel Morse<sup>1</sup>, Sherrika Daniel<sup>2</sup>, Richard Kemp<sup>2</sup> and Kevin McCarty<sup>1</sup>; <sup>1</sup>Sandia National Laboratories, Livermore, California; <sup>2</sup>Sandia National Laboratories, Albuquerque, New Mexico.

Titanium dioxide (TiO<sub>2</sub>) has long been a research focus in many research groups since it is a highly stable, nontoxic, and highly reactive photocatalyst that can be used to effectively deactivate chemical and biological agents in either air or water. The mechanism of photochemical oxidation produced by anatase TiO<sub>2</sub>, after illumination by light of the appropriate wavelength, is a universal mechanism for biological and chemical deactivation. The multitude of processes by which TiO<sub>2</sub> powders have been previously synthesized have led to extreme variations in its photoactivity and overall efficiency. We are developing a science-based engineering approach to synthesizing photoactive nanoparticles for decontamination applications. Nanocrystalline photocatalysts are of increased interest due to the surface dominated characteristics that are expected to exist at these confined length scales. Certain types of doped nanocrystalline TiO<sub>2</sub> have been shown to possess an altered and decreased band-gap energy requirement for activation, thus making them more desirable as photocatalysts. Our initial work was focused on two alternative schemes for the doping of TiO<sub>2</sub>: (i) coating TiO<sub>2</sub> nanoparticles with metals and (ii) coating metal nanoparticles with TiO<sub>2</sub>. We have recently employed a co-hydrolysis route to produce nanocrystalline mixed metal oxides comprised of TiO<sub>2</sub> and rare earth metal oxides that show improved photocatalytic efficiency when compared to undoped nanocrystalline TiO<sub>2</sub>. We will present results that demonstrate that these doped nanocrystalline photocatalysts are efficient in the deactivation of both chemical and biological agent simulants. The chemical simulant is a dye that has been shown to be susceptible to photocatalyzed deactivation in the scientific literature. Monitoring of biological activity, as measured by ATP production, is the metric by which rate of biological deactivation is measured. In both cases, the doped mixed metal oxides produce superior deactivation rates when compared to commercially available nanocrystalline TiO<sub>2</sub>.

#### **8:45 AM \*Z11.4**

##### **Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles.**

Richard M. Crooks, Robert W. J. Scott, Orla M. Wilson and Joaquin C. Garcia-Martinez; Department of Chemistry, Texas A&M University, College Station, Texas.

In this talk we show that dendrimers can be used as both templates and stabilizers for preparing nearly monodisperse transition-metal nanoclusters suitable for fundamental studies and for use in catalysis. These interesting new materials are prepared by sorbing metal ions (Cu, Pt, Pd, Au, Ru, etc.) into poly(amidoamine) (PAMAM) dendrimers where they complex with interior tertiary amine groups. Subsequent chemical reduction of the metal ions yields dendrimer-encapsulated metal nanoparticles, ranging in size from 1-3 nm, that contain the same number of atoms as were initially preloaded into the dendrimer. By preloading the dendrimer templates with two different types of metal ions it is possible to prepare nanoparticle alloys. Likewise, core/shell nanoparticles can be synthesized by loading the dendrimer with metal ions, reducing them to yield a metal nanoparticle seed, reloading the dendrimer with a different type of metal ion, and reducing a second time. Using these approaches, we have prepared PdPt, PdAu, and AuAg alloys, as well as Au/Ag and Pd/Au core/shell nanoparticles. UV-vis spectroscopy, TEM, EDS, SAXS, and selective extraction experiments confirm the properties of these materials. The homogeneous and heterogeneous catalytic properties of these materials depend on their size, composition, and structure.

#### **9:15 AM \*Z11.5**

##### **Synthesis of Ordered Mesoporous Materials for**

**Bio-Applications.** Dongyuan Zhao, Chemistry, Fudan University, Shanghai, China.

Supramolecular templated mesoporous materials have drawn more attention since the discovery of ordered silica or aluminosilicate mesoporous materials one decade ago. The strategy should be extended to the synthesis of mesoporous materials with new structure that exhibit marvelous properties for bio-applications such as separation and analysis of protein since the size of their pore channels is similar to the size of the proteins. Here, we report the synthesis of ordered mesoporous materials with new cubic (Fm3m) structures. We take the advantages of their unique structural properties to introduce new type of nano-reacting devices for sensitive and efficient proteolysis. Highly ordered mesoporous bioactive glasses (MBGs) with compositions of CaO-P2O5-SiO2 have also been synthesized and shown superior bone-forming bioactivities. A large cavity (10 ~ 27 nm) cubic (Fm3m) mesoporous silica (FDU-12) has been synthesized by using triblock copolymer F127 as a template. The entrance sizes of FDU-12 are quite large and can be adjusted in the range of 4 ~ 16 nm. The immobilization measurements of proteins such as lysozyme (with an average spherical diameter of ~ 3.2 nm) within FDU-12 are revealed that the entrance size of FDU-12 is much more facilitated for the proteins or enzymes transportations and diffusions. We use FDU-12 as a nano-reactor for sensitive, complete, and efficient proteolysis. With its unique 3D nanopore cavities, FDU-12 is capable of facilitating simultaneously multiple steps of protein capture/enrichment, structural unfolding/denaturation, and rapid in situ proteolytic digestion. In less than 15 min, the peptides derived from complete digestion of a protein mixture at the low-femtomole level are detected with very high sequence coverage of digests of 84% (MOWSE scores 170). Highly ordered MBGs with 15%CaO-5%P2O5-80%SiO2 compositions have been synthesized by block copolymer P123 templating. XRD pattern of the calcined MBG shows a well-ordered 2D hexagonal mesostructure with a cell parameter of 8.50 nm. The surface area, pore size, and pore volume is 351 m2g-1, 4.7 nm, and 0.49 cm3g-1, respectively. The in vitro bone-forming activity of MBGs is tested by immersing MBGs in simulated body fluid (SBF) to monitor the hydroxycarbonate apatite (HA) formation at different time periods. It is surprising to note that after soaking for 8 h, exclusively rod-like morphology of crystalline HA (~ 100 nm in length) is observed. Further growth leads to an increasing in the Ca/P molar ratio while the rod-like morphology of crystalline HA similar to that in the human bone retains. For comparison, bioactive glass (BG) with the same components synthesized in the absence of templates shows much slower HA formation behavior than MBG, moreover, the rod-like HA materials cannot be observed even after 4 days. Obviously, MBG leads to superior bone-forming bioactivities than conventional BG.

**10:00 AM \*Z11.6**

**Polyoxometalate Based Multifunctional Nanoarrays and Crystalline Nanoporous Materials.** Craig L. Hill, Wade A.

Neiwert, Huadong Zeng, Jong Woo Han, Travis M. Anderson, Rui Cao and Xikui Fang; Chemistry, Emory University, Atlanta, Georgia.

The design, preparation, characterization and use of two new types of nanomaterials based on polyoxometalates will be described. Condensation of labile polyvanadates with trifunctional organic linking groups leads to hexavanadate containing materials that trap, detect and catalytically remove target molecules (e.g. pollutants, toxic agents). One well characterized example involves condensation of a tris(tri-ol) linker molecule with decavanadate to form an ensemble of nanoarrays comprised of esterified hexavanadate units. Five independent lines of experimental evidence: small angle X-ray scattering, solid state NMR, single crystal X-ray diffraction of a model compound, atomic force microscopy and elemental analysis, indicate that the dominant species is a nanoarray comprised of 72 esterified hexavanadate units. This material entraps and gels many target liquids. The entrained molecules are then detected by reduction of the polyvanadate units or by electron donor acceptor interactions. The former involve intervalence charge transfer transitions with naturally high extinction coefficients. Finally, the entrained and detected molecules are removed by catalytic O2 oxidation. A second new class of materials from when carboxylate terminated bis(triester)hexavanadate precursor units react with lanthanide complexes under appropriate conditions. The resulting crystalline nanoporous or microporous materials have been characterized by single crystal X-ray diffraction and several other methods and are also multifunctional. Namely they associate key molecules and catalyze their oxidation without need of energy sources or reagents. We thank the U.S. National Science Foundation and Department of Defense for funding this work.

**10:30 AM \*Z11.7**

**Syntheses and Applications of Chalcogenide Tetrahedral Clusters and their Superlattices.** Pingyun Feng<sup>1</sup>, Nanfeng Zheng<sup>1</sup> and Xianhui Bu<sup>2</sup>; <sup>1</sup>Chemistry, University of California at Riverside,

Riverside, California; <sup>2</sup>California State University of Long Beach, Long Beach, California.

Open framework based on chalcogenide tetrahedral clusters represents an interesting class of materials that combines uniform porosity with high electrical conductivity and tunable optical properties. They consist of single-sized tetrahedral clusters that act as molecular building blocks in the formation of well-ordered superlattices from zero to three dimensions. Tetrahedral clusters can be joined directly to produce purely inorganic frameworks or by multidentate organic ligands to form inorganic-organic hybrid frameworks. A number of main-group and transition metals have been incorporated into clusters to allow the modification of structural and physical properties. The structural analysis based on single crystals reveals detailed information that could help the structural elucidation of larger colloidal nanostructures. The syntheses, structures, and various properties such as porosity, photoluminescence, photocatalytic property, and fast ion conductivity will be discussed.

**11:00 AM Z11.8**

**Nano-scale Ordered Structure in Nonoxide Ceramics.**

Julin Wan, Patrick Malenfant, Seth T. Taylor, Azar Alizadeh, Sergio M. Loureiro and Mohan Manoharan; Ceramic and Metal Technologies, GE Global Research, Niskayuna, New York.

Inspired by the observation of excellent mechanical properties in natural ceramics such as seashells, a bottom-up approach was explored in an effort to build nanometer scale structures with long-range order in the high temperature ceramic system Si-C-N. Using block copolymer as structure-directing agent, polymer precursor which can lead to desired non-oxide ceramic composition was self-assembled into various types of ordered structures. Nano-scale ordered structure in block copolymer/precursor hybrid can be maintained throughout the ceramization process, thereby leading to ordered structure in the pyrolysis product. Structural and compositional evolution during this templated synthesis was analyzed by TEM and SAXS.

**11:15 AM Z11.9**

**AC Electrodeposition of Uniform High Aspect-Ratio Metal Nanowires in Porous Aluminum Oxide Templates.**

Nathan Gerein, Shazma Mithani and Joel Haber; Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

Nanotechnology requires new fabrication methods that are cost effective, easily executed, and industrially scalable. One such promising route to nanostructured materials is via porous aluminum oxide (PAO) templates and AC electrodeposition. The use of AC electrodeposition permits deposition through the resistive Al<sub>2</sub>O<sub>3</sub> barrier layer, enabling the use of the as-grown PAO template. This results in a process that is cost effective, simple, and scalable. However, achieving uniform filling of deep pores using this technique is challenging. The non-uniform nature of the insulating barrier layer makes it difficult to achieve consistent growth conditions in all pores, leading to variations in growth rates and erratic pore filling. For AC electrodeposition to be used to its full potential, a more detailed understanding of the complex system is required. We have carried out a systematic study of the effect of multiple variables (barrier layer thickness, AC frequency, AC voltage, continuous or pulsed electrodeposition, and deposition bath composition) on the AC electrodeposition of copper nanowires with large aspect-ratios (wire length to diameter) using a fractional factorial design of experiment (FFDOE). These experiments led to the identification of template damage that occurs when continuous wave AC deposition conditions are employed, as well as to effective pulsed wave AC electrodeposition conditions. Further rational examination of the effects of pulse polarity (the order in which oxidative and reductive components of the pulse are applied), and wave shape (sine wave vs. square wave) was carried out based on current transients collected during the deposition process, and characterization of the quality and extent of pore filling. These experiments have led to a more detailed understanding of the behavior of the Al<sub>2</sub>O<sub>3</sub> barrier layer and the effect of electrodeposition conditions on wire growth and uniformity, resulting in the identification of pulsed AC electrodeposition conditions that produce more uniform wire growth than has previously been reported using similar techniques. Results obtained on the deposition of copper nanowires have also been extended to the deposition of iron nanowires with similar results. Pore filling of PAO templates was quantified using scanning electron microscopy (SEM) of pore cross-sections and of as-deposited and ion-milled surfaces of the templates. Wire characterization has been carried out using in-situ X-ray diffraction (XRD) and transmission electron microscopy (TEM) of wires liberated from the PAO template.