SYMPOSIUM M

Nanoparticles and Nanowire Building Blocks-Synthesis, Processing, Characterization, and Theory

April 12 - 16, 2004

Chairs

Guilia Galli
Lawrence Livermore National Laboratory
L-415
7000 East Ave.
Livermore, CA 94550
925-423-4223

Christopher B. Murray
IBM T. J. Watson Research Center
P.O. Box 218
1101 Kitchawan Rd., Rte. 134
Yorktown Heights, NY 10598
914-945-3021

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 818
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

SESSION M1: Magnetic Nanostructures I
Chair: Christopher B Murray
Monday Morning, April 12, 2004
Room 3001 (Moscone West)

8:30 AM *M1.1

Control of Magnetic Spinel Ferrite Nanoparticles and their Biomedical Applications. Z. John Zhang, School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Understand and control of the unique superparamagnetic properties in nanoparticles is of great importance to the fundamentals in magnetism and to the rational design of magnetic nanoparticles for biomedical applications. The high compositional flexibility of spinel ferrites, MFe2O4 (M = Mn, Mg, Zn, Co, Fe etc.) offers great opportunities for designing and fine-tuning the size and magnetic properties of nanoparticles. By manipulating the quantum couplings at the atomic level, the magnetic anisotropy energy barrier EA can be controlled. Consequently, the blocking temperature for superparamagnetic transition can be tuned in the nanoparticles. The saturation magnetization can also be enhanced through fine tuning magnetic interactions. In addition, surface chemistry is crucial to the biomedical applications of magnetic nanoparticles. We will discuss the surface chemical modification of spinel ferrite nanoparticles and the correlation between the magnetic properties of nanoparticles and their surface chemistry. The interactions between magnetic nanoparticles and biological entities such as antibodies and cells will also be discussed.

9:00 AM *M1.2

One Nanometer-level Controlled Synthesis of Monodisperse Nanoparticles. Taeghwan Hyeon[1], Jongnam Park[1], Eunae Kang[1], Eunwoong Lee[1], Kwang-Jin An[1] and Nong-Moon Hwang[2]; [1]School of Chemical Engineering, Seoul National University, Seoul, South Korea; [2]School of materials science and engineering, Seoul national university, Seoul, South Korea.

In a continuation of our research on the synthesis of monodisperse nanoparticles, herein we report on the direct synthesis of monodisperse iron nanoparticles from the thermal decomposition of iron-surfactant complexes. By controlling the nucleation and growth processes, we were able to synthesize monodisperse iron nanoparticles with particle sizes of 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 16 nm. The subsequent oxidation of these nanoparticles using a mild chemical oxidant produced monodisperse maghemite nanoparticles. In the current synthesis, no size-selection process is involved, and monodisperse nanoparticles were obtained directly from a single reaction. As far as we know, this is the first report on the direct and nanometer-level controlled synthesis of monodisperse nanoparticles. We are currently working on the generalization of this procedure to synthesize many other nanoparticles. The diameter-controlled synthesis of iron nanorods and nanowires will be also presented. Thermal decomposition of iron-surfactant complexes in the presence of suitable surfactants produced iron nanorods with uniform diameters. The diameters were controlled from 2 nm to 10 nanometers by changing the reaction conditions.

9:30 AM M1.3

Magnetic and Structural Characterization of Fe-Pt Superlattices. Keir Foster[1], Joerg Weissmueller[1,2], Branko Stahl[3], Jens Ellrich[3], Viswanath Raghavan[1], Andreas Michels[4] and Horst Hahn[3]; [1]Institute for Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany; [2]Technische Physik, University of Saarlande, Saarbruecken, Germany; [3]Institute of Materials Science, Technical University of Darmstadt, Darmstadt, Germany; [4]Paul Scherrer Institute, Villigen, Switzerland.

A detailed magnetic and structural characterization of Fe-Pt superlattices will be presented. Fe-Pt alloy particles of 4.5 nm and 2.7 nm average diameters with chemical compositions of $Fe_{0.48}Pt_{0.52}$ have been synthesized primarily via the wet-chemical route proposed by Sun *et.al.*[1] Particles with compositions of $Fe_{0.33}Pt_{0.67}$ were also synthesized. It should be stressed that the particles studied were of the 'as-prepared' low-anisotropy solid-solution (fcc) phase. Experiments focused primarily on colloidal crystals, but complimentary measurements on dilute samples, where particles were dispersed in a solvent, were also performed. Average particle sizes and size-distributions were determined from Transmission Electron Microscopy (TEM), Small-Angle X-ray Scattering (SAXS) and Wide-Angle X-ray Scattering (WAXS). Particle-size distributions were derived, via a maximum entropy method, from SAXS data for dilute samples of Fe-Pt particles dispersed in n-hexane. The self-assembly of the monodisperse particles into 2-D and 3-D superlattices was investigated by TEM and SAXS. From the SAXS data 5-6 of the lower order Bragg peaks were observed, enabling the crystallographic symmetry and lattice constants of the superlattice to be derived. For example, it was found that the 4.5 nm $Fe_{0.33}Pt_{0.67}$ particles formed a 3-D hcp lattice of lattice parameters; a = 6.7 nm, and c = 10.9 nm. The SAXS data revealed the polycrystalline nature of the colloidal samples with the dimension of the ordered superlattice regions estimated at 15-25 mono-layers. Magnetic characterization was performed by Vibrating Sample Magnetometry (VSM) and AC Susceptibility methods. It should be highlighted that the magnetization and SAXS measurements were performed on the same samples, so that the magnetic properties could be directly correlated to the inter-particle spacing and / or order of the superlattice. Superparamagnetic (SP) blocking temperatures were determined from field-cooled and zero-field cooled measurements and showed a strong concentration dependence and did not scale simply with volume. The magnetization loops showed an unusual but consistent form for all samples studied: displaying a strongly temperature-dependent rapid switching of the magnetization at low applied fields and a rapid increase in the coercivity for temperatures below the SP blocking temperature. The real and imaginary components of the initial AC susceptibility data showed frequency dependent maxima for measurement frequencies of 0.1-10 kHz and were analysed in terms of the Neel-Brown theory of superparamagnetism. To investigate the nature of the total anisotropy of the magnetic nanoparticles, the magnetic viscosity, a Langevin-analysis of the magnetization loops and the magnetic field dependence of the AC susceptibility were investigated. [1]S.Sun, C.B.Murray, D.Weller, L.Folks and A.Moser, Science **287** (2000), 1989.

9:45 AM M1.4

The effects of interacting deposition parameters on the magnetic properties of Co and Co/Cu multilayered nanowires. Ryan K. Cobian, Nahyoung Kim and Bethanie Stadler; Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Recently, magnetic nanoparticles have been generating a lot of interest for applications such as biological tagging and magnetic sensors. In many applications it would be useful to have tunable magnetic elements that could provide various levels of magnetic biasing on the nanoscale depending on the processing conditions. This study focuses on tuning the magnetic properties of Co and Co/Cu multilayered nanowires fabricated by electrochemical deposition into nanoporous aluminum oxide templates. Cobalt nanowires are of interest because hcp Co has a large uniaxial magnetocrystalline anisotropy (K_1=4.1x10^6 erg/cm^3) along its c-axis that is comparable to the shape anisotropy of the nanowires ($2\pi M_s{}^2$=1.3x10^7 erg/cm^3). Thus, the relative orientation of these two anisotropy axes determine whether the nanowire array behaved as a hard or soft magnetic material. VSM data showed that the coercivity increased from 180 Oe to 630 Oe and the remnant magnetization (M_r/M_s) increased from 0.06 to 0.34 when the crystalline and shape anisotropy axes went from perpendicular to parallel. In the past, the composition of the electrolyte and an applied magnetic field during deposition have been used separately to control the crystallographic texture of Co nanowires. This study revealed significant interactions between these deposition parameters that must also be considered. XRD and TEM data showed that in unbuffered electrolytes with a low concentration of Co ions the texture of Co nanowires was influenced by the presence of an applied magnetic field during deposition. In this case, the uniaxial crystalline anisotropy axis favored the direction of the applied field. The effect diminished as the electrolyte became increasingly buffered or concentrated. A single optimized electrolytic solution produced nanowire arrays with varying crystalline alignment simply by varying an applied magnetic field during deposition. Multilayered Co/Cu nanowires were also fabricated using the same processes to control the magnetic properties of the Co layers. TEM and electron diffraction data showed that the individual Co layers were mostly single crystal hcp with the c-axis orientated according to the deposition parameters as discussed above. Scanning TEM (STEM) with XEDS was used for chemical characterization and to verify that the individual layers were 400nm thick. These multilayered nanowires are promising candidates for nano-GMR (giant magneto-resistance) magnetic sensors.

10:30 AM M1.5

Orbital Magnetism in Monodisperse Co/CoO nanoparticles. Ulf Wiedwald[1], Marina Spasova[1], Kai Fauth[2], Markus Hessler[2], Hans-Gerd Boyen[3] and Michael Farle[1]; [1]Institute of Physics, University of Duisburg-Essen, Duisburg, Germany; [2]Experimental Physics IV, University of Wuerzburg, Wuerzburg, Germany; [3]Solid State Physics, University of Ulm, Ulm, Germany.

The orbital contribution to the total magnetic moment is measured via ferro-/paramagnetic resonance (FMR/EPR) and x-ray magnetic circular dichroism (XMCD) which have strongly different sampling depths. The magnetism of self-assembled Co/CoO particles (diameter 10 and 12 nm with a 2 nm CoO shell) will be discussed [1,2,3]. FMR reveals a small MAE in comparison to hcp Co and a bulk-like g factor g = 2.15 of fcc Co, while XMCD yields a 300 % enhanced ratio of orbital-to-spin moment [4]. A quantitative comparison taking into account the different sampling depths of both techniques reveals the presence of uncompensated large magnetic Co moments at the interface of the antiferromagnetic CoO shell to the ferromagnetic Co core. By the exposure to mild hydrogen plasma we succeeded in a complete reduction of the CoO shell and the formation of pure and isolated metallic nanoparticles. In the metallic state the orbital and the spin magnetic moment are bulk-like. These "magnetic" results will be correlated with atomically resolved and element specific transmission electron microscopy studies [4] which show that the crystalline structure of the metallic Co core and the CoO shell is fcc. Supported by European Community HPRN-CT- 1999-00150 and Deutsche Forschungsgemeinschaft. 1. M. Spasova, M. Farle, Magnetism of Monodisperse Core/Shell Particles, in Low-Dimensional Systems: Theory, Preparation, and some Applications, eds. Liz-Marzan and M. Giersig, NATO Science Series II, (2003) Vol 91, 173 2. U. Wiedwald, M. Spasova, M. Farle, M. Hilgendorff and M. Giersig, Ferromagnetic Resonance of monodisperse Co Particles, J. Vac. Sci. Technol. 19 (2001) 173 3. M. Spasova, U. Wiedwald, R. Ramchal, M. Farle, M. Hilgendorff, M. Giersig, Magnetic properties of arrays of interacting Co nanocrystals, J. Magn. Magn. Mater. 240 (2002) 40 4. M. Spasova, et al., Structure and Magnetism of Co and CoAg Nanocrystals, Mat. Res. Soc. Symp. Proc. 721 (2002) 195; U. Wiedwald et al., Ratio of orbital-to-spin magnetic moment in Co core-shell nanoparticles, Phys. Rev. B 68 (2003) 064424

10:45 AM M1.6

Nanomagnets: from Nanodots to Nanorings. vitali metlushko[1], U. Welp[2], V. Vlasko-Vlasov[2], G. Crabtree[2], M. Grimsditch[2], V. Novosad[2], N. Zaluzec[2], J. Bekaert[3], V. Moshchalkov[3], Y. Bruynseraede[3], P. Vavassori[4], B. Ilic[5], Xiaobin Zhu[6], A. Imre[7], G. Bernstein[7] and W. Porod[7]; [1]University of Illinois at Chicago, Chicago, Illinois; [2]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [3]Katholieke Universiteit Leuven, Leuven, Belgium; [4]Dipartimento di Fisica, Universita' di Ferrara, Ferrara, Italy; [5]Cornell University, Ithaca, New York; [6]University of Alberta, Edmonton, Alberta, Canada; [7]University of Notre Dame, Notre Dame, Indiana.

The magnetic properties of submicron magnetic rings have attracted considerable attention since they show unique properties that may hold great potential for technological applications such as high-density storage or magnetic random access memory (MRAM) [1]. Recent studies on Co and permalloy rings have shown that a totally flux-closed magnetic vortex state can be stable at remanence. The two chiralities of the vortex, clockwise and anticlockwise, have been proposed as the carriers for the stored information that could be read in a magnetoresistance-based device. The results of systematic characterization of arrays of small Co and permalloy ring elements of different symmetry (circular, square, rectangular) and with zero separation between elements (chains of touching rings) with SQUID magnetization to determine the magnetic moment, magnetic force microscopy (MFM), scanning Hall microscopy and Lorentz STEM to determine the magnetic patterns inside the rings, and with magneto optical imaging to visualize the reversal process during a magnetization cycle, will be presented. [1] J.-G. Zhu, Y. Zheng, G. A. Prinz, J. Appl. Phys. 87, 6668 (2000). Supported by the US NSF under contracts ECS-0202780 and DMR-0210519. Work at ANL was supported by US Department of Energy, BES Materials Sciences under contract W-31-109-ENG-38.

11:00 AM M1.7

Self-catalysis process and structure of catalyst particles in formation of nanobelts. Zhonglin Wang[1], Xiang Yang Kong[1], Yong Ding[1] and Jianmin Zuo[2]; [1]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois.

Ionic crystals that consist of alternating layers of oppositely charged ions, stacked parallel to the polar surfaces, produce an accumulating normal dipole moment, resulting in divergence in surface energy. Structurally, the wurtzite structured ZnO crystal is described schematically as a number of alternating planes composed of fourfold tetrahedral-coordinated O2- and Zn2+ ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces. In this paper, we demonstrate that the surface polarization and surface termination are important factors for determining the growth of ZnO nanostructures. The polar +-(0001) surfaces of ZnO result in anisotropic growth along +-[0001]. This growth is attributed to a self-catalysis process for formation of nanobelts. Vapor-liquid-solid (VLS) is a well-established process in catalyst-guided growth of nanowires. The catalyst particle is generally believed in liquid state during the growth, and it is the site for adsorbing incoming molecules. In this paper, using tin particle guided growth of ZnO nanostructures as a model system, we show that the interface between the tin particle and the ZnO nanowire/nanobelt could be crystalline during the VLS growth, and the crystallographic structure at the neck-interface between the catalyst particle and the oxide is important in defining the structural characteristics of the grown nanowires/nanobelts. The interface prefers to take the least lattice mismatch, thus, the crystalline orientation of the tin particle may determine the growth direction and the side surfaces of the nanowires/nanobelts. This result may have important impact to the physical chemical process involved in the VLS growth. [1] Pan, Z.W., Dai, Z.R., Wang, Z.L., Nanobelts of semiconducting oxides, Science 291, 1947-1949 (2001)

11:15 AM M1.8

Nanochemistry of ceria abrasive particles. Shelley Gilliss[1], Jim Bentley[2] and C. Barry Carter[1]; [1]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [2]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cerium oxide (ceria: CeO_2) is one of the most widely used abrasives for the planarization of silicate glasses. Extensive work has been carried out on the characterization of ceria abrasives with inductively coupled plasma chemical analysis, surface-area analysis, and zeta-potential characterization. Typically, chemical analysis of ceria abrasives involved bulk sampling of the material without a spatially related understanding of the composition. Ceria abrasives have been investigated using electron energy-loss spectroscopy (EELS) in a field-emission-gun transmission electron microscope. By using EELS in a TEM the specimen can be imaged and the chemical information collected at specific points with nanometer spatial resolution. Analysis shows that abrasive particles from different batches can vary significantly in homogeneity and composition. One abrasive may be composed of individual oxide particles containing just La or just Ce, whereas another abrasive may be homogeneous in its distribution of cerium, but can vary in F content and the amount of impurities such as Pr in each individual particle. Individual particles of silica and alumina (which may be intentionally added as fillers) are also detectable by this technique. Line profiles across the ceria particles show enrichment of impurities (or dopants) at the surface of the nanoparticles. The oxidation state of the cerium cation can be monitored by the ratio of the Ce $M_{4,5}$ white lines. The presence of fluorine is associated with a reduction of the Ce cation. The surfaces of all the CeO_2 particles that were analyzed, regardless of impurity levels, were found to be reduced relative to the interior of the particles.

11:30 AM M1.9

Nanocrystalline Colloidal Transition Metal Doped TiO_2: Precursors to Diluted Magnetic Semiconductor Spintronic Materials. J. Daniel Bryan and Daniel R. Gamelin; Chemistry, University of Washington, Seattle, Washington.

Manipulation and control of the electron spin in microelectronics has been the goal of the field of research known as spintronics. In effort to reach this goal new magnetic-ion doped semiconducting materials are being developed that exhibit ferromagnetism well above room temperature. Transition metal doped TiO_2 (TM:TiO_2) thin films, grown by vacuum deposition techniques, have shown the potential to achieve these goals and are the currently the subject of intensive investigations. Small spin-dependent devices constructed at the nanoscale such as Spin-based LEDs show great promise. We present an alternative approach to these materials using wet-chemical colloidal techniques. This nanoscale approach provides opportunities to use solution chemical processing to control both the oxidation state and chemical homogeneity of the dopant ion in the host semiconductor lattice. By using doped nanocrystals as spintronics material precursors, different assemblies and length-scale dependent magnetic properties can be investigated. Controlling the assembly of the nanocrystals changes the magnetic properties of the material from paramagnetic, in the case of the isolated TM:TiO_2 nanocrystals, to ferromagnetic when allowed to aggregate in the form of thin films. The synthetic procedure is presented along with magnetic susceptibility, X-ray diffraction, optical and magneto-optical measurements. Optical measurements were used to verify dopant incorporation into the TiO_2 nanocrystals and gain information concerning the dopant ions crystallographic site.

11:45 AM M1.10

Structure of Cobalt Nanosphere Superlattice Films by Small Angle X-ray Scattering. Michael Beerman[1], Masato Ohnuma[2], Yuping Bao[1], Kannan M. Krishnan[1] and Kazuhiro Hono[2]; [1]Materials Science and Engineering, University of Washington, Seattle, Washington; [2]National Institute for Materials Science, Tsukuba, Ibaraki-ken, Japan.

Recently synthesized Co nanocrystals [1], with narrow size distributions and controlled shapes, organize in a wide range of arrays as a function of shape, size and interparticle interactions [2]. The nanocrystals (NCs) consist of a cobalt metal core with a nominal diameter of 10 nm, and an organic surfactant surface layer with a chain length of 1.7 nm. For the simplest case (epsilon-Co nanospheres, super-paramagnetic at room temperature) a hexagonal arrangement of NCs is observed in TEM micrographs when precipitated from solution onto holey carbon grids. For practical applications and for further understanding of the self-assembly process large areas and a variety of substrates need to be investigated. Hence, small angle x-ray scattering (SAXS) measurements were performed on superlattice films of cobalt nanospheres assembled on three different substrates (glass, carbon and mica, all about 12 mm in diameters). SAXS measurements provide particle size distribution, interparticle spacing and structural symmetry information averaged over the entire substrate [3]. The intensity (I) distribution as a function of the scattering vector (k) and a Guinnier plot of the linear region (I vs. k²) gave an average particle size of 9.5 ± 0.75 nm for all three samples. The interparticle separation between the NCs was 14.5 nm for the mica sample and 15.6 nm for both carbon and glass. The intensity of the SAXS peaks, corresponding to interparticle separation and structure factor were greatest for the glass substrate. This suggests that glass provides a better host for more uniform self-assembly; however, it remains to be determined whether this is due to surface energy or surface roughness. The SAXS data is compared to a Gibbs free energy model that governs the self-assembly of the nanoparticle system. The model includes van der Waals attraction between metal particles in a solvent, the steric repulsion from interpenetration of linear surfactants and thermal energy [4]. [1] V. F. Puntes, K. M. Krishnan, A. P. Alivisatos, Science, 291, 2115-2117 (2001). [2] Y. Bao, M. Beerman and Kannan Krishnan, JMMM (in press). [3] K. Kajiwara, M. Ohnuma, D.H. Ping, O. Haruyama, K. Hono, Intermetallics, 10, 1053-1060, (2002). [4] This work was supported in part by the National Science Foundation under DMR grant # 6079771, by a JSPS Fellowship and by the Campbell Endowment at UW.

SESSION M2: Magnetic Nanostructures II
Chair: Charles Black
Monday Afternoon, April 12, 2004
Room 3001 (Moscone West)

1:30 PM *M2.1
Electronic Conduction in Self Assembled Magnetic-nanocrystal Thin Film Devices. C.T. Black, T. J. Watson Research Center, IBM, Yorktown Heights, New York.

Self-assembled nanocrystal arrays provide tunable model systems for understanding charge transport in granular thin films produced by more conventional methods. Electronic conduction through arrays of uniformly-sized nanocrystals occurs predominantly by sequential electron tunneling between neighboring grains, and thus gives rise to single-electron charging effects at sufficiently-low temperatures, and in the case of magnetic nanocrystals, tunneling magnetoresistance. We will present and discuss experimental data from two different device geometries utilizing both cobalt and iron oxide nanocrystals. We will also describe processes for depositing and patterning nanocrystal films of uniform thickness which combine Langmuir-Blodgett films with either standard polymer resist techniques or elastomeric stamp lithography.

2:00 PM *M2.2
Atomistic Strain Computations for Epitaxial Nanostructures. Russel Caflisch and Youri Bae; Mathematics, UCLA, Los Angeles, California.

We present computations of the strain energy in epitaxial nanostructures, including nanocrystals and quantum wires. Computations for layered nanocrystals, consisting of a core of one material and a shell of a different material in 2D and 3D, show that there is a critical shell thickness at which the strain energy density is maximal. Computations for quantum wires, consisting of a single material, show that surface stress drives step bunching for a 3D quantum wire. The resulting effects of strain on growth of nanostructures are discussed.

2:30 PM M2.3
Fabrication and Assembly of Monodisperse FePd Nanoparticles. Yanglong Hou, Horishi Kondoh and Toshiaki Ohta; Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan.

FePd alloys are a kind of important materials for magnetic applications because of their high chemical stability and large magnetocrystalline anisotropy. However, there have been few reports on monodisperse FePd nanoparticles so far. We have prepared monodisperse FePd nanoparticles by the polyol reduction of palladium acetylacetonate and thermally decomposition of iron pentacarbonyl in the presence of 1-adamantanecarboxylic acid and tri-alkylphosphine. The composition of iron and palladium in the particles depends on the amounts of their precursors charged to the reaction. The mean particle size can be varied from 5 to 16 nm by controlling the concentration and type of stabilizers and the reaction conditions. High monodispersity of the FePd nanoparticles leads to the formation of two-dimensional superlattices consisting of hexagonal close-packed particles on carbon-coated copper grids. Power x-ray diffraction, high-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS) were used for characterization of the FePd nanoparticles.

3:15 PM M2.4
Controlled growth of ultralong Pt-containing SiO_2 nanotubes. Lirong Ren and Michael Wark; Institute of Physical Chemistry and Electrochemistry, Hannover, Germany.

We present an efficient and elegant way to prepare SiO_2 NTs with high aspect ratio and simultaneously realized metal filling of the tubes. The method bases on the use of structure-directing agents and self-assembly. With an intrinsically anisotropic crystallographic morphology, $Pt(NH_3)_4(HCO_3)_2$ tends to grow in solution to one-dimensional nanofibers (NFs). The formation mechanism of NFs from this Pt salt solution by solvent modification, i.e. by increasing the ethanol/water ratio, was investigated in detail and decoded as nucleation, anisotropic growth, aggregation and aging successively. Based on this mechanism, pre-hydrolyzed tetraethyl orthosilicate (TEOS) was employed as capping agent forming a monolayer around the nuclei of the Pt salt. With continuous providing of building blocks, subsequent anisotropic growth of NFs was promoted while aggregation among NFs was effectively prohibited by the capping agent. After stirring for 12 h in a sol-gel process, monodisperse (100-200 nm) and ultralong (10 30 μm) SiO_2 nanotubes (NTs) filled with Pt salt were achieved. Hollow Pt metal-contained SiO_2 NTs resulted by subsequent calcination at 500°C for 5 h. The Pt content inside the SiO_2 NTs prepared by this template method could be up to 25 wt-%. Inside NTs with diameters less than 50nm, very often continuous nanowires of Pt could be observed. Their high metal content and anisotropic structure renders this kind of NTs prospective for nanoelectronics.

3:30 PM M2.5
Magnetic nanowires and Y-junctions. Nahyoung Kim, Ryan Cobian and Bethanie Stadler; Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

As nanoelectronics develop, devices to increase overall circuit functionality are becoming increasingly important. This work focuses on the fabrication of magnetic nanowires with magneto-electronic potential and of Y-junction nanowires. First, anodic alumina nanopores were grown with diameters of 20-250nm and lengths up to tens of microns. These pores were removed from their Al substrates and the barrier oxide was removed. Co nanowires were initially grown inside the pores by electrochemical deposition. It was shown that the coercivity and remnant magnetizations could be tripled in (100) oriented Co by shrinking the pore diameter from 150nm to 40nm. These properties were further enhanced by fabricating (002) oriented Co using the proper pH and applying a magnetic field during growth, as we reported at the last MRS meeting. The ability to connect two or more nanostructures is critical to the long term success of nanoelectronics and circuits. Here, Y-junctions were grown by subsequent growth of 40nm then 20nm pores such that two smaller pores extended from the bottom of each larger pore. These pores were then filled with Co in order to produce Y-junctions in our magnetic nanowires. Scanning electron microscopy was used to verify the shape of the nanowires, both inside the alumina matrix and removed from the matrix. Next, magnetic nanowires were fabricated with alternating layers of Cu and Co in order to obtain a layer of 'soft' Co in series with a layer of 'hard' Co. These materials promise to extend magnetoelectronic functionality to the field of nanoelectronics.

3:45 PM M2.6
Synthesis of Fe3O4/MgO core-shell nanowires by pulsed laser deposition. zuqin liu, Daihua Zhang, Song Han, Chao Li and Chongwu Zhou; School of Engineering, University of Southern California, LA, California.

We report that Fe3O4/MgO core-shell nanowire arrays have been successfully grown by pulsed laser deposition method. The diameter of MgO core was precisely controlled by using monodispersed gold clusters as the catalyst. Different thickness of epitexial layers of Fe3O4 could be obtained by tuning the laser ablation time and power. Detailed material analysis such as transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to confirm the crystal structure of the core-shell nanocompsite. The results showed Fe3O4 coated layer was uniformly epitaxial single crystal. The axial direction of both MgO and Fe3O4 are [100] oriented.

SESSION M3: Metallic Nanoparticles
Chairs: Heinrich Jaeger and Campell Scott
Tuesday Morning, April 13, 2004
Room 3001 (Moscone West)

8:30 AM *M3.1
Self-Assembly and Electronic Transport Properties of Metal Nanocrystal Superlattices. Heinrich Jaeger[1], Terry Bigioni[1], Klara Elteto[1], Thu Tran[1] and Xiao-Min Lin[2,1]; [1]James Franck Institute, University of Chicago, Chicago, Illinois; [2]Materials Science Division and Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

Using a simple technique based on the drying of a drop of metal nanocrystal solution, monolayer particle arrays can be produced that extend over millimeters and exhibit near-perfect long-range order over fields of view of tens of square microns, containing 100,000 to 1,000,000 particles in a single crystalline domain. The superlattices initially self-assemble at the liquid-air interface and, during solvent evaporation, drape themselves over the underlying substrate, including any prefabricated electrode structures, without requiring transfer or further processing. The nanocrystals are 5.5-7.5nm in diameter, with size dispersion less than 5 percent, capped with alkanethiol ligands and dissolved in toluene. The particle spacing in the assembled lattices is below 2nm, with sub-nanometer control. This allows for electron tunneling between neighboring particles. The talk will cover two aspects: the mechanisms underlying the superlattice formation and its control, and the resulting electronic transport properties. Arrays have been assembled on silicon nitride membrane window substrates, making it possible to image with high resolution transmission electron microscopy the particle arrangement in each of the samples after the transport measurements have been completed. Strong Coulomb blockade effects in the presence of quenched charge disorder give rise to robust, highly nonlinear current-voltage characteristics. We show that below some characteristic temperature T* the threshold voltage for conduction decreases only weakly (linearly, rather than exponentially) with temperature. A model is presented that predicts T* as well as the collapse of data from arrays with different lengths and charging energies onto a universal curve. We also discuss an electron beam "cutting" method that allows for the fabrication of arbitrary two-dimensional shapes from the self-assembled monolayers, with a resolution approaching a single particle diameter.

9:00 AM M3.2
Metallic Nanoparticles as Charge Storage Centers in Organic Memory Elements. J. Campbell Scott, Luisa D Bozano, Kenneth R Carter and Philip M Rice; IBM Research Division, Almaden Research Center, San Jose, California.

There is a growing interest in developing new solid-state non-volatile memory technologies. One candidate is based on a crosspoint element consisting of metallic nanoparticles dispersed in an amorphous semiconducting medium. With proper choice of materials for the electrodes, nanoparticles and semiconductor, such devices exhibit bi- or multi-stable resistance states at low voltage (< 2 V), and may be switched between these states by applying higher voltage pulses. Retention times of more than one year have been demonstrated. We present experimental evidence that the bistability is due to charging of the nanoparticles. When they are uncharged, space-charge effects are minimal and current injection occurs at one of the electrodes, leading to the low resistance state. When they are charged, the resulting space-charge field inhibits injection and raises the resistance by several orders of magnitude.

9:15 AM M3.3
Templated Formation of Ordered Metallic Nano-particle Arrays. Amanda L Giermann[1], Carl V Thompson[1] and Henry I Smith[2]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nano-particles prepared through interruption of Volmer-Weber film growth in the pre-coalescence stage and through solid phase agglomeration or dewetting of continuous films have been used as catalysts for nano-tube and nano-wire growth on flat substrates. However, both the interrupt and agglomeration techniques lead to nano-particle catalysts with broadly distributed sizes and spacings. We have used interference lithography to create surfaces with 200 nm mono- and di-periodic topography and formed nano-particle arrays on these substrates by both the interrupt and agglomeration techniques. The resulting particles have significantly improved order, with more uniform sizes and spacings. Under appropriate conditions, we have found that agglomeration of metal films on di-periodic arrays of {111}-bound pits in silicon leads to *periodic* arrays of particles with very narrow size distributions. Both the results and mechanisms of topographic control of nano-particle formation will be discussed.

9:30 AM M3.4
Syntheses and Optical Properties of Gold Nanocubes, Nanoprisms, and Icosahedrons. Franklin Kim, Stephen Connor, Hyunjoon Song, Tev Kuykendall, Andrea Tao and Yang Peidong; Dept. of Chemistry, University of California, Berkeley, Berkeley, California.

Nanoparticles of noble metals such as gold and platinum have been of great interest due to their unique optical, electrical, and catalytic properties. The strong electromagnetic field enhancement associated with the plasmon resonance of the metal particles plays an important role in applications such as surface enhanced Raman spectroscopy (SERS) and near field optical microscopy. The properties of the particles are highly dependant on the size and shape of the particles. In order to fully utilize the metal nanoparticles, it is important to study particles with arbitrary shapes. Much work has already been done on spherical nanoparticles, but it is still a challenge to prepare uniform metal particles of non-spherical shapes. Here, we present a simple synthesis of gold nanoparticles of various shapes prepared via polyol process. By slightly changing the conditions, we were able to control the shapes from cubes, prisms, and icosahedrons with good uniformity. The self-assembly behavior and the optical properties of the particles changes drastically with the different shaped particles, as expected. We have also expanded this synthesis to other metals, such as platinum, and were able to produce platinum nanocubes and octahedrons. The control over the shape of the metal nanoparticles will ultimately lead us to the application of the particles, such as optoelectric devices and sensors.

9:45 AM M3.5
Biotemplate Synthesis of Ag Nanoparticles and Nanowires. Silke Behrens[1], Eberhard Unger[2], Jin Wu[1], Wilhelm Habicht[1] and Eckhard Dinjus[1]; [1]Institut fuer Technische Chemie, Forschungszentrum Karlsruhe, Karlsruhe, Germany; [2]Institut fuer Molekulare Biotechnologie, Jena, Germany.

Biological systems exhibit typical size dimensions from the lower nanometre size range up to several micrometers, well-defined surface functionalities, and molecular recognition capabilities. However, often they do not posses the desired physical properties, e.g., many among them display poor electric conductivities, others are insulators. Recently, the unique features of biological systems have been explored as building blocks for bottom-up assembly or controlled deposition of novel inorganic materials and devices with advanced structures and functionalities. Among bulk phase metals, silver exhibits a very high electric conductivity, and, thus, has been broadly applied in modern electronic industry. The fabrication of silver nanowires has a large potential application in nanoelectronics for wiring individual nanoelectronic devices. Inspired by the unique physical and chemical properties, a lot of effort has been made to tailor defined one, two, or three-dimensional nanostructures. We address the template-directed deposition of metals on microtubule supports for generating metal nanostructures with different morphologies. Microtubules are highly ordered protein assemblies of tubular structure with a high aspect ratio. In this approach, the biostructure serves as a functionalised scaffold where the metal is generated in situ and shaped into a nanostructure with its morphology complementary to that of the biotemplate. When the biotemplate is coupled to an appropriate chemical reaction, different Ag / protein structures are produced, from microtubules densely covered by small Ag nanoparticles, 5 nm in size, to continuous Ag nanowires which were as narrow as 40 nm.

10:30 AM M3.6
Metal Nanoparticle Decorated Polyaniline Nanofibers. Jiaxing Huang and Richard B. Kaner; Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California.

We have recently developed a room temperature chemical synthesis to make conducting polymer polyaniline nanofibers with diameters controllable from 30 to 120 nm. This synthesis is template-free and readily scalable. The success of the polyaniline nanofiber synthesis enables us to employ polyaniline nanofibers as the active component to make a number of nanocomposites. For example, metal-polyaniline nanocomposites can be readily made by direct reaction between polyaniline and oxidative metal ions. With polyaniline nanofibers the size of the metal particles and their distribution in the polymer matrix is controllable. This is very difficult, if not impossible in conventional metal-polyaniline composites. Using polyaniline nanofibers, metal nanoparticles including Au, Ag, Pt and Pd can be grown along the nanofibers uniformly with diameters between 5 and 100 nm. By finely tuning the reaction conditions, two distinct nanocomposites can be created. In the first case, metal nanoparticles grown on the surface of the nanofibers decorate them in a "nanoparticle-ON-nanofiber" structure. The size of the metal nanoparticles can be controlled between 10 and 100 nanometers kinetically by varying the reaction time. In the second case, 3 to 6 nm size metal nanoparticles are embedded inside the nanofiber forming a "nanoparticle-IN-nanofiber" nanocomposite.

10:45 AM M3.7

Nucleation and growth of gold nanoparticles deposited by RF-sputtering: an experimental study. Davide Barreca[1], Alberto Gasparotto[2], Elisabetta Pierangelo[2] and Eugenio Tondello[2]; [1]Department of Chemistry, ISTM-CNR and INSTM, Padova, Italy; [2]Department of Chemistry, Padova University and INSTM, Padova, Italy.

Gold nanoparticles supported on various substrates have received a wide attention for both fundamental and applicative purposes. In the former case, many research activities have been aimed at understanding the processes involved in the transition from free atoms to bulk metal. In the latter, a great interest has mainly been devoted to heterogeneous catalysis and microelectronics. As a general rule, the chemico-physical properties of these composite materials are strongly dependent on size and shape of gold nanoparticles and both metal-metal and metal-substrate interactions. These characteristics can be easily controlled by plasma-assisted techniques such as RF-sputtering, due to the *soft* preparative conditions and to the competition between deposition/ablation processes characterizing glow-discharges. In the present work, Au nanoparticles were deposited on SiO_2, Si(100) and HOPG (Highly Ordered Pyrolitic Graphite) by RF-sputtering in Ar plasmas. Experiments were carried out at a substrate temperature of 60°C, in order to minimize thermally activated processes thus allowing a better insight on plasma-dependent phenomena. In particular, the role of different process parameters such as applied RF power, total pressure and deposition time on system composition, nanostructure and morphology was investigated. To this aim, both $in-situ$ and $ex-situ$ characterization techniques were employed. While LRI (Laser Reflection Interferometry) was used for a real-time monitoring of growth processes, XPS (X-ray Photoelectron Spectroscopy) and GIXRD (Glancing Incidence X-ray Diffraction) yielded precious information concerning the dependence of gold overall amount and crystallite size on synthesis conditions. Moreover, AFM (Atomic Force Microscopy) and UV-Vis spectroscopy provided additional results regarding surface topography and optical properties respectively. Finally, complementary information were obtained by STM (Scanning Tunneling Microscopy) on Au/HOPG nanocomposites. As a general rule, a careful modulation of the substrate coverage and gold nanocrystal size could be obtained by controlled variations of the experimental parameters and the used substrate, resulting in different nanocomposite properties.

11:00 AM M3.8

Synthesis and Optical Properties of Anisotropic Metal Nanoparticles. encai hao, Joseph T. Hupp and George C. Schatz; Chemistry, Norhwestern University, Evanston, Illinois.

The synthesis of inorganic nanocrystals with controllable shape is an important goal of modern materials chemistry and one that has been characterized by rapid progress. An extraordinary synthesis of nanostructures, including, rods, triangular prisms, disks, and even branched tetra-pods, can now be generated often in high yield. Beyond their aesthetic appeal, these new structures are compelling for multiple fundamental and practical technological reasons. Herein, we report the wet-chemical synthesis of several anisotropic nanostructures and systemically study the intrinsic shape-dependent properties by comparison of experimental observations and theoretical simulations. In addition, we show that these structures are desirable for emerging applications entailing bio-labels, chemical sensing, and surface enhanced Raman scattering (SERS).

11:15 AM M3.9

Controlled Synthesis of 2-D and 3-D Dendritic Platinum Nanostructures. Yujiang Song[1,2], Craig J. Medforth[1], Eulalia Pereira[3], Anup K. Singh[1], Frank van Swol[1,2] and John A. Shelnutt[1,4]; [1]Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; [2]Department of Chemistry, Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; [3]CEQUP/Departamento de Quimica, Faculdade de Ciencias, Universidade do Porto, Porto, Portugal; [4]Department of Chemistry, University of Georgia, Athens, Georgia.

Seeding and autocatalytic reduction of platinum salts in aqueous surfactant solution using ascorbic acid as the reductant leads to remarkable dendritic metal nanostructures. In micellar surfactant solutions, spherical dendritic metal nanostructures are obtained, and the smallest of these nanodendrites resemble assemblies of joined nanoparticles and the nanodendrites are single crystals. With liposomes as the template, dendritic platinum sheets in the form of thin circular disks or solid foam-like nanomaterials can be made. Synthetic control over the morphology of these platinum circular nanosheets and nanostructured foams is realized by using a tin-porphyrin photocatalyst to conveniently and effectively produce a large initial population of catalytic growth centers. The concentration of these seed particles determines the ultimate average size and uniformity of these novel two- and three-dimensional platinum nanostructures.

SESSION M4: Metallic Nanowires
Chairs: Taeghwan Hyeon and Catherine Murphy
Tuesday Afternoon, April 13, 2004
Room 3001 (Moscone West)

1:30 PM *M4.1

Synthesis, Assembly, and Reactivity of Metallic Nanorods. Catherine J. Murphy, Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina.

We have developed seed-mediated growth procedures in aqueous solution to synthesize gold and silver nanorods of controlled aspect ratio. Insight into the mechanism of nanorod growth has been gained from high resolution microscopy and electron diffraction experiments. The nature of the surfactant in solution that directs nanorod growth is a key parameter. Gold nanorods coated with the principle surfactant we use can self-assemble into liquid crystalline arrays. Biological molecules can also be used to link nanorods up with some degree of selectivity. Finally, experiments in which the chemical reactivity of metallic nanorods is compared to nanospheres will be discussed.

2:00 PM M4.2

Observing the Impact of Charge Transport in Metal Nanowires by In-situ Transmission Electron Microscopy. Vidyut Gopal[1], Eric A Stach[1] and Peidong Yang[2]; [1]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Chemistry, University of California, Berkeley, California.

Metallic nanowires have great potential as building blocks for several applications, including nanoelectronics and sensors. In order to realize this potential, it is critical to study the impact of sustained charge transport on the structural stability of the nanowires. We have developed a novel method for imaging one-dimensional nanostructures in a transmission electron microscope (TEM) during biasing. A four probe setup was incorporated into a TEM specimen holder for this purpose. The challenges of fabricating nanoscale circuitry on a fragile electron transparent substrate will be discussed. We have developed a single step direct-write metallization scheme to interconnect solution-dispersed nanowires with macroscale electrodes. Decomposition of a metal organic precursor gas injected in the path of a focused ion/ electron beam resulted in localized deposition of conductive platinum. Thus, the process complexity and wet chemistry steps inherent to electron beam lithography were avoided. Observations of current-induced degradation, such as localized melting due to Joule heating, electromigration behavior, and conduction pathways in core-sheath nanowires will be presented using silver nanowires as a model system.

2:15 PM M4.3

Self-assembled nanostructure templates: synthesis, characterization and control!. Regina Ragan[1], Sehun Kim[1], Yong Chen[3,1], Chengxiang Ji[2], D.A.A. Ohlberg[1], Y. Austin Chang[2] and R. Stanley Williams[1]; [1]Quantum Science Research, Hewlett Packard, Palo Alto, California; [2]Material Science and Engineering, University of Wisconsin, Madison, Madison, Wisconsin; [3]Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California.

Research in semiconductor physics is undergoing a paradigm shift. A bottoms up or self-assembly approach is being investigated as an alternative to the current top down lithographic approach. Most significantly, the shift from the exclusive use of lithography for device fabrication opens the field to not only novel fabrication schemes but to the incorporation of diverse material systems. Self-assembly of nanostructures has been demonstrated in many systems. Yet, the exploitation of self-assembly for device fabrication is contingent on the ability to control the size and shape of these quantum structures and thereby engineer the desired nanoscale device structure. Understanding thermodynamic driving forces and kinetics of nanostructure assembly will enable the use of these as templates for further nanostructures formation. I will discuss synthesis, characterization and the thermodynamic and kinetic driving forces for the experimental system, rare earth disilicides on Si(001), that self assemble into nanowire arrays during physical vapour deposition.

Rare earth disilicide nanowires exhibit high aspect ratios having lengths exceeding 1 micron and widths less than 5 nm. Total energy minimization drives the system to form one-dimensional nanostructures along Si[110]. The length of coherently strained nanowires is dependent on surface kinetics while the wire width is thermodynamically controlled via strain energy. The alignment of rare earth disilicide nanowires has been achieved along a single direction by growth on vicinal Si(001) substrates with a density of 10Î1/cm2̂. In bulk form and in thin films, rare earth disilicides are good conductors, ρ 0.1 $\mu\Omega$ cm, with a low Schottky barrier to n-type silicon. Yet, a highly reactive surface limits applications for rare earth disilicide nanowires. I will discuss the use of these nanowire arrays as an etch mask for Si nanowire formation. Semiconducting nanowires are candidates as highly sensitive chemical and biological sensors. In addition, I will also present experimental results in which noble metal monolayers passivate the rare earth disilicide nanowire surface. The achievement of a high density, 10Î1/cm2̂, of self-assembled metal nanowires coupled with self assembled molecular monolayers is an important precursor to forming molecular sensing, memory and logic devices using chemical self assembly with density and features sizes not attainable using conventional lithography.

2:30 PM M4.4

Tellurium nanotubes and -rods synthesized by Physical Vapor Deposition. Bernard Grobety and Cedric Metraux; Dep. of Geosciences, University of Fribourg, Fribourg, Fribourg, Switzerland.

Tellurium nanorods and -tubes were synthesized by PVD placing elemental tellurium powder on a graphite rod, which was heated by magnetic induction. The deposition targets were silicon wafers cut parallel to (111) and polycrystalline aluminum foils. The growth morphologies depended on the substrate type and the atmosphere in the furnace. Deposition was performed under argon atmosphere (1atm) as well as under vacuum (1.0 E-7 bar) and 3 different temperatures 140, 200 and 240 deg C. The PVD products have been analyzed by Scanning and Transmission Electron Microscopy. For a temperature of 140 deg C, on silicon wafers and under argon atmosphere, tellurium has been deposited as rounded particles 50 to 100 nm in diameter and as hexagonal, tube like crystals with the c-axis parallel to the tube-axis. Selected Area Electron Diffraction indicated, that tellurium had trigonal crystal structure, space group P3121. At higher temperatures (200, 240 deg C), the number of tellurium tubes increases. Small tubes ($<$ 200 nm) grew preferentially with their c-axis perpendicular to the substrate, whereas large tubes had arbitrary orientation. The (111) surface structure of silicon has dimensions, which fit the (001) plane of tellurium and may explain the oriented nucleation of tellurium. The inner diameter of the tubes varies from 50 nm to 2 micrometers. Under vacuum, the tellurium was deposited in form of blades and tubes with missing walls. Under vacuum and with polycrystalline aluminum as substrate, tellurium crystallized in form of rods with diameters between 50 and 100 nm forming dense carpets. The oriented growth of rods makes tellurium a candidate for electron emitter applications and a possible precursor for tellurium compounds with rod morphology. Emission current measurements and PVD experiments depositing tellurium and selenium simultaneously are currently undertaken.

3:15 PM M4.5

TEM 3D Tomography of Noble Metal Nanowires Growth inside SiO2 Mesoporous Aggregates. Jordi Arbiol, Emma Rossinyol, Andreu Cabot, Francesca Peiro, Albert Cornet and Joan Ramon Morante; Electronica, Universitat de Barcelona, Barcelona, Catalonia, Spain.

Development of new catalytic systems by using nanostructured mesoporous materials is nowadays having much attention [1]. Noble metal addition in order to modify these mesoporous materials has improved their physical and chemical properties [2]. One of the most used mesoporous molecular sieves (MMS) is the well-known SBA-15 matrix family, with hexagonal pores. In the present work we use SBA-15 mesoporous silica due to its long range order, large monodispersed mesopores and thicker walls, which make it more thermally and hydrothermally stable than other mesoporous materials. By selecting the growth conditions, we can control the mesoporous aggregates pore size (from 3 to 10 nm). Therefore, the final width of the noble metal nanowires synthesized inside the pores is also under control, as we use the mesoporous materials as controllable nanotemplates. Once this nanowires have been synthesized, we would like to know whether the nanowires growth has occurred inside the pores or on the aggregates external walls. At this point, it is not enough to study the 2-D morphology of these nanostructures (e.g. using conventional TEM images) in order to demonstrate that the metal nanowires grow inside the pores. We need some extra 3D information about our materials. To solve this problem, we have used a technique rarely used in materials science such as TEM 3D Tomographic Reconstruction. In the present work, we present those 3D reconstructions demonstrating how, effectively, metal nanowires grow inside mesoporous nanotemplates. References [1] S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, Nature, 412 (2001) 169. [2] J. Arbiol, A. Cabot, J. R. Morante, F. Chen, M. Liu, Appl. Phys. Lett., 81 (2002) 3449.

3:30 PM M4.6

Nanolithogrpahy Manipulation of Length of Aligned Metal Oxide Nanowires. Lesley Jane Campbell, Yuxi Chen and Weilie Zhou; AMRI/Chemistry, Advanced Materials Research Institute/UNO, New Orleans, Louisiana.

Controlling the characteristics of nanowires in order to later construct nanoarchitecture and nanocomponents for nanodevice and nanosensor applications is essential. Metal oxide nanowires are aligned using the Langmuir-Blodgett technique to uniaxially compress the nanowires. A surfactant monolayer of metal oxide nanowires is fabricated, and then compressed on an aqueous subphase. The compression yields an array of aligned nanowires with controlled spacing, which is transferred to a planar substrate. The lengths of the nanowires are defined by electron beam nanolithography. After an etching process, it is shown that the metal oxide nanowires have been successfully sliced into controlled sizes. The nanowires can then be suspended in solution and used to construct basic building blocks of nanodevices and nanosensors.

SESSION M5: Poster Session: Magnetic and Metallic Nanostructures

Chair: Christopher B Murray
Tuesday Evening, April 13, 2004
8:00 PM
Salons 8-9 (Marriott)

M5.1

Selective synthesis of silver nanowires: the first steps toward large scale synthesis of nanoscaled electronic components. Emil Avier Hernandez[2,1], Bertina Posada[2,1], Sorelis Nieto[2,1], Roberto Irizarry[3] and Miguel E. Castro[2,1]; [1]Chemistry, University of Puerto Rico at Mayaguez, Mayaguez, USA, Puerto Rico; [2]Chemical Imaging Center and Center for Chemical Sensor Development and Department of Chemistry, The University of Puerto Rico at Mayaguez, Mayaguez, USA, Puerto Rico; [3]Dupont Microelectronics, Dupont Microelectronics, Manati.

The synthesis of silver nanowires has received significant attention in recent years due to the central role they are to play in a number of nanoscaled devices. Large aspect ratio nanowires can be used in a number of nanoscaled circuits requiring long length electrical connections. Short aspect ratio nanowires, on the other hand, are suitable for the fabrication of antennas for wireless and remote communication applications. The presence of the longitudinal plasmon band makes silver nanowires attractive substrates for surface enhanced Raman scattering (SERS) measurements. Selective methods that can be used for mass scale production of nanowires is, with little doubt, an important step in the commercialization of nanoscaled electronics. Wet chemical approaches based on silver ion reduction in basic solution are known to result in the formation nanoscaled spheres, rods and wires mixtures, requiring the employment of separation methods for the isolation of pure nanowire samples. We will present ne methods for the syntehsis of silver nanowires with a 100 % selectivity over nanospheres. THe nanowires are characterized with a number of analytical techniques that includes Raman amd FTIR microscopy, scanning electron microscopy, atomic force microscopy and near field optical microscopy. The nanowires aspect ratio is found to be sensitive function of the ratio of reactants concentration.

M5.2

Methods of Solid Phase Synthesis for the Preparation of Gold Nanoparticles with a Single Surface Functional Group. James G Worden and Qun Huo; Polymers and Coatings, North Dakota State University, Fargo, North Dakota.

Nanotechnology is an emerging area of science that will have a major impact on the development of new materials. Potential applications include: chemical and biological sensors, computer and electronic devices, drug delivery systems, and others. Colloidal gold nanoparticles with their unique optical and electrical properties and relative ease of preparation have received much attention for potential device and sensor applications. Gold nanoparticles have been traditionally prepared using the Schiffrin reaction and/or the place-exchange reaction. However, these techniques only allow for the synthesis of nanoparticles with an unknown number and distribution of surface functional groups and thus limit their uses as individual molecules. To use gold nanoparticles as individual molecules, they must contain only a single or limited number of surface functional groups. Previous results in our laboratory have demonstrated that through solid phase synthesis on Wang resin gold nanoparticles with a single surface functional group may be obtained. In this presentation the results of using additional support materials including cotton and filter paper will be discussed.

M5.3

Patterned Ferromagnetic Ceramics Containing Fe/Co Alloy Nanoparticles Using Electron-Beam Lithography and Highly Metallized Metallopolymer Resists. Scott B. Clendenning and Ian Manners; Chemistry, University of Toronto, Toronto, Ontario, Canada.

The use of lithographic techniques to pattern functionality into a material is well established but generally involves multiple steps. Organometallic polymers are excellent candidates for the direct introduction of metals into nanostructures using lithographic techniques due to their inherently high and uniform metal loadings and processibility. Soluble, high molecular weight polyferrocenylsilanes (PFS) are readily available via thermal, transition metal catalyzed and anionic ring-opening polymerization (ROP) of strained ferrocenophane monomers. Polyferrocenylsilanes possess unique redox, semiconductive and magnetic properties and function as excellent ceramic precursors. The highly metallized, soluble, air stable cobalt-clusterized polyferrocenylsilane (Co-PFS) with three metal atoms per repeat unit is available via the treatment of an acetylene-substituted PFS with dicobalt octacarbonyl. Patterned arrays of ceramics have been fabricated using electron-beam lithography (EBL) and a Co-PFS resist. Highly ordered arrays of features such as dots, bars and curved lines rich in Fe and Co direct-written using EBL will be presented. Subsequent pyrolysis of the patterned arrays leads to the formation of ferromagnetic ceramics containing Fe/Co alloy nanoparticles with tunable properties.

M5.4

Formation of High-Spin Molecular Clusters Mn$_6$and Mn$_{12}$ in Monocrystal Silicon Matrix and the Related Positive Magnetoresistance. Eshkuvat Ulashevich Arzikulov and Jalol T. Ruzimuradov; Physics, Samarkand State University, Samarkand, Samarkand, Uzbekistan.

Over last two decades the nano-technology and related nano-electronics were intensively developed. Ultra-small particles, which consist of 10-10000, play the leading role in nano-technology. Such formations are called in different ways: nanoparticles, nanocrystals, quantum dots, but more frequently - nanoclusters. Interest to study their properties is related first of all with their properties, which are different from those of bulk materials of the same composition. That is why nanoclusters are considered to be "large blocks" for creation of new materials and devices. Magnetic nanoclusters are of special interest since the presence of additional internal degree of freedom - magnetic moment - provides great variety of their properties, as well as possibility to operate their state by application of external magnetic field. By the present time a lot of molecule-magnets are known, such as Fe$_{10}$, Mn$_6$, Mn$_{12}$, Fe$_8$ etc. These high-spin metalloorganic molecules are built, principally, with participation of ions of transition elements. Such molecules are frequently called magnetic clusters. These magnetic clusters usually posses ferromagnetic and antiferromagnetic properties. In this work we present results of experimental study of magnetoresistance of silicon samples doped by manganese ions. At sufficiently high dose of ions the concentration of the doped ions exceeds significantly the solubility concentration of manganese in silicon. Actually, in the bulk (or on the surface) of sample there appears strongly non-equilibrium state of manganese atoms. These atoms (or ions) of manganese due to self-organization processes form magnetic clusters (or quantum dots) of Mn$_6$ or Mn$_{12}$ type in monocrystalline semiconductor matrix of silicon. Presence of summary spin (for Mn$_6$ $S = 12$, for Mn$_{12}$ $S = 10$) of such quantum dots affects the properties of semiconductor matrix. We have revealed large positive magnetoresistance (up to 20%), anomalously large photoionozation cross-section (10^{-13} cm^2) that is characteristic for quantum dots. On the base of the obtained results one may assert that implantation manganese ions into monocrystalline matrix of silicon stimulates formation of quantum dots due to the self-organization processes.

M5.5

Co nanocluster deposition on 6H-SiC(0001)-6*sqrt*3x6*sqrt*3R30° templates. Wei Chen[1], Kian-Ping Loh[1], Hai Xu[2] and Andrew Thye-Shen Wee[2]; [1]Chemistry, National University of Singapore, Singapore, Singapore; [2]Physics, National University of Singapore, Singapore, Singapore.

We demonstrate that the carbon-rich 6H-SiC(0001)-6*sqrt*3x6*sqrt*3R30° honeycomb-like reconstructed surface can be used as an effective template for the growth of high density, monodispersed and uniform-sized nanoclusters. In-situ UHV (ultrahigh vacumm) STM (scanning tunneling microscopy) is used to systematically study the nucleation of cobalt (Co) nanoclusters on this SiC honeycomb template. During the initial stages of Co cluster growth, the boundaries between neighboring honeycomb structures serve as active sites for Co cluster adsorption. After 2Å thick Co deposition at room temperature, high density, monodispersed and regular-sized (3-4 nm) Co nanoclusters are formed on this reconstructed 6H-SiC(0001) surface without the nucleation of Co single crystal 3D islands due to restricted adatom surface diffusion on the underlying honeycomb template. The regeneration of the honeycomb template is achieved by annealing the as-deposited 2ÅCo/SiC sample to higher than 800K. It is found that this carbon-rich SiC honeycomb template is chemically inert to Co and thermally stable, and acts as a diffusion barrier preventing Co from reacting with underlying Si atoms to form cobalt silicide during annealing. A narrow size distribution of Co nanoclusters (~6.8nm in diameter) is achieved by annealing the as-deposited 2ÅCo/SiC sample at 800K for 20 minutes. Deposition of Co on the SiC honeycomb template at different temperatures is also presented and discussed.

M5.6

Core/Shell-Reversing and Hollowing of Noble-Metal Nanospheres Using Laser Pulses. Seol Ji Kim, Chil Seong Ah and Du-Jeon Jang; School of Chemistry(NS60), Seoul National University, Seoul, Sillim-Dong, South Korea.

Core/shell-reversed hollow Pt$_{core}$Ag$_{shell}$nanospheres as well as core/shell-reversed Pt$_{core}$Au$_{shell}$ nanospheres were fabricated by irradiating the platinum-topped gold and silver nanoparticles with laser pulses. Energy dispersive X-ray analysis and transmission electron microscopy images show that the cores and shells of Au$_{core}$Pt$_{shell}$ nanoparticles are reversed to form Pt$_{core}$Au$_{shell}$ nanospheres. Furthermore, Ag$_{core}$Pt$_{shell}$nanoparticles transform into core/shell-reversed hollow Pt$_{core}$Ag$_{shell}$ nanospheres. Core/shell-reversed nanospheres form because the core metals having lower boiling temperature than the shell platinum metal boil out with irradiation.

M5.7

Synthesis of Superparamagnetic Magnesium Ferrite Nanoparticles by Microwave-Hydrothermal Method. Seema Verma, Hari S Potdar, Sadgopal K Date and Pattayil Alias Joy; Physical & Materials Chemistry Division, National Chemical Laboratory, Pune, India.

Magnesium ferrite, $MgFe_2O_4$, is one of the important magnetic oxides with spinel structure. Apart from its magnetic applications, magnesium ferrite can be used as catalysts, humidity sensors and recently it is found to be highly suitable in achieving local hyperthermia for treating cancerous cells. Therefore, synthesis of nanosized $MgFe_2O_4$ ferrite powder is extremely important for many applications. Among all the wet chemical synthetic routes, microwave hydrothermal (MH) method is a rapidly developing novel method for the synthesis of oxide nanoparticles. In the present investigation MH method is used for synthesizing $MgFe_2O_4$ nanoparticles. Nanoparticles with mean particle size of 3 nm and a narrow particle size distribution is obtained. Zero-field-cooled magnetization studies indicated a superparamagnetic blocking temperature (T_B) of 38 K. As a typical superparamagnetic behavior, the zero-field-cooled and the field-cooled magnetizations diverge below T_B. Magnetic field dependent behavior of nanosized $MgFe_2O_4$ particles show typical magnetic hysteresis behavior below T_B, with a high coercivity of 185 Oe at 12 K, and magnetic hysteresis behavior disappears when measured above T_B. The results indicate that MH method is highly suitable for the synthesis of ferrite nanoparticles of uniform particle size distribution and offers convenience for fine tuning of magnetic properties of nanoparticles for specific applications.

M5.8

Segregation in Pt-Ni and Pt-Re Catalyst Nanoparticles. Guofeng Wang[1], Michel A Van Hove[1,2,3], Philip N Ross[1] and Michael I Baskes[4]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Department of Physics, University of California, Davis, California; [4]MST-8 Structure and Property Relations Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have investigated the segregation of Pt atoms on the surfaces of Pt-Ni and Pt-Re nanoparticles, using Embedded Atom Method (or Modified Embedded Atom Method) potentials and the Monte Carlo method. (1) Pt-Ni. The nanoparticles are assumed to have disordered fcc configurations at two fixed overall concentrations (Pt75Ni25 and Pt50Ni50). We use four kinds of nanoparticle shapes [cube, tetrahedron, octahedron, and cubo-octahedron] terminated by {111} and {100} facets to examine the extent of the Pt segregation to (or from) the nanoparticle surfaces, and to (or from) surface atomic sites with different coordination numbers at the facets, edges, and vertices. We find that the facet segregation profiles of nanoparticles (especially for those with more than 2000 atoms) agree well with the segregation profiles calculated for extended low index surfaces [{100} and {111}]. Regardless of the shape and composition, the Pt atoms segregate preferentially to the facet sites, less to edge sites, and least to vertex sites in the outermost atomic layer of nanoparticles. (2) Pt-Re. The Pt75Re25 nanoparticles are assumed to have disordered fcc configurations and cubo-octahedral shapes, while the Pt25Re75 nanoparticles are assumed to have disordered hcp configurations and truncated hexagonal bipyramidal shapes (terminated by {0001} and {10-11} facets). We also find that the facet segregation profiles of nanoparticles agree with the segregation profiles calculated for extended low index surfaces. However, in contrast to the Pt-Ni nanoparticles, the Pt atoms segregate preferentially to the vertex sites, less to edge sites, and least to facet sites in the outermost atomic layer of Pt-Re nanoparticles.

M5.9

Covalent Coupling of Gold Nanoparticles to Multwalled Carbon Nanotubes for Electronic Device Applications.

Xicheng Ma[1,2], Ning Lun[3], Xia Li[3] and Shulin Wen[3]; [1]Deparment of Material Science and Engineering, Shandong Institute of Architecture and Engineering, Jinan, Shandong, China; [2]School of Chemistry and Chemical Engineeing, Shandong University, Jinan, Shandong, China; [3]Characterization and Analysis Center for Materials,School of Material Science and Engineering, Shandong University, Jinan, Shandong, China.

Carbon nanotubes (CNTs) have remarkable electronic properties owing to their unique molecular structure and are attractive building blocks for creating next generation electronic devices and networks. Examples of nanotube-based devices include single-electron transistors, molecular diodes, memory elements, and logic gates. There is a great deal of interest in devising strategies to individually address each molecular unit, and interconnect them, without adversely affecting the local electronic structure. One approach to enable this is to attach metal- or semiconductor nanoclusters to nanotubes. This approach is also attractive for creating molecular-lever hybrid units and will allow the exploration of new properties and effects that arise from electronic-structure-level interactions between the constituent molecular units and applications such as active nanodevices and heterogeneous nanocatalysts. In this distribution, we report a simple electroless plating approach to couple gold nanoparticles to CNTs via relatively strong covalent interactions. There appears to have been no reports to date on the using of eletroless plating technique to deposit Au nanoparticles onto the outside surface of CNTs. However, due to the highly hydrophobic nature and very regular structure of CNTs it may not be an easy exercise; activating their surfaces is an essential prerequisite for linking nanoclusters to them. In our work, activated CNTs were obtained by oxidizing the purified CNTs in a H2SO4-HNO3 blend acid and followed by activating the oxidized CNTs via a single-step activation approach. Both high-resolution transmission electron microscope (HRTEM) and diffusion reflectance infrared fourier transform spectroscope (DRIFT) were used to investigate the surface states of the pretreated CNTs. Both HRTEM and energy-dispersive X-ray spectroscopy (EDS) microanalysis techniques were used to provide information about the composition and microstructure of the samples after electroless plating, the dispersion and the particle size of the supported phase. Experimental results showed that pretreatment with H2SO4-HNO3 can create high-dense active defects and various functional groups such as hydroxyl and carboxyl groups on CNTs, which can act as specific sites for tethering metal ions to the tubse. HRTEM micrographs evidenced the very high-dense and homogeneous dispersion of spherical gold nanoparticles on the outer surface of the carbon nanotubes after electroless plating, with a sharp particle size distribution centered at around 3-4 nm of diameter. The influences of the experimental parameters on the final disposition, i.e. the dispersion and the particle size of the supported phase, were also discussed. Such molecularly interlinked hybrid nanoblocks presented in this work are attractive for building next generation electronic nanodevices.

M5.10

Extraction of Metal Nanoparticles from Dendrimer Templates.

Joaquin C Garcia-Martinez and Richard M Crooks; Chemistry, Texas A&M University, College Station, Texas.

We report that size-monodisperse metal nanoparticles can be extracted intact from dendrimer templates using n-alkanethiols. This is a significant discovery for several reasons. First, it demonstrates that nanometer-scale materials prepared within a molecular template can be removed leaving both the replica and template undamaged. Second, it provides a straightforward approach for preparing highly monodisperse metallic and bimetallic monolayer-protected clusters (MPCs)[1] without need for subsequent purification. Third, it is possible to recycle the expensive dendrimer template after preparation and extraction of the nanoparticle. Finally, it demonstrates that multiple, fairly complex operations, including formation of covalent bonds, electron-transfer, molecular transport, heterogeneous self assembly, and nanoparticle transport, can all be executed within the interior of a dendrimer. These points are demonstrated by templating the formation of diverse metals nanoparticles within poly(amidoamine) dendrimers,[2] and then extracting them into a toluene phase while leaving the dendrimer in the aqueous phase. This new strategy[3] is versatile, because it provides a means for controlling the kind of metal, particle size, and type of cluster stabilizer ligand for MPCs. In addition, extraction experiments can also be used as a tool to fully study the physical properties of these nanoparticles that not be possible while they remained in the dendrimer. (1) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc.Chem.Res.* **2000**, *33*, 27-36. (2) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc.Chem.Res.* **2001**, *34*, 181-190. (3) Garcia-Martinez, J. C.; Scott, R. W. J.; Crooks, R. M. *J.Am.Chem.Soc.* **2003**, *125*, 11190-11191.

M5.11

MoO$_{3-x}$ One Dimensional Structures.

Alejandra Camacho Bragado[1], Mario Miki-Yoshida[1] and Miguel Jose Yacaman[2,1]; [1]Texas Materials Institute and Center for Nano and Molecular Science and Technology, University of Texas-Austin, Austin, Texas; [2]Department of Chemical Engineering, University of Texas-Austin, Austin, Texas.

A wide variety of building blocks with nanoscopic dimensions have been recently investigated because of their novel electronic, optical, magnetic and catalytic properties. In this work we present particularly one dimensional building blocks, such as nanowires, nanorods and nanobelts. Transition metal oxides present already interesting catalytic and electronic properties, these are expected to be enhanced by the decrease in dimensionality. There were synthesized different 1-dimensional structures of this layered oxide using a vapour transport process. We started from molybdenum oxide synthesized from ammonium molybdate and treat it at temperatures close to the melting point. We found that the appearance of the product depends on the atmosphere used and the temperature of the substrate where the recrystallized oxide would condense. Different morphologies, from nanorods to nanobelts, were obtained depending on the synthesis conditions. The structures were characterized by electron microscopy techniques (scanning electron microscopy, high resolution electron microscopy, nanobeam diffraction, X-ray energy dispersive spectroscopy and EELS) to determine their crystallographic orientation, elemental composition and bonding. Preliminary results demonstrate that morphology depends strongly on the atmosphere used in the process. Belt-shaped crystals mostly in the micron size are obtained in inert atmosphere. In contrast, samples prepared in air recrystallize in form of nanorods about hundred nanometers long, and diameters in the 25-40 nm range. It is been also observed that freshly prepared samples present smaller rods, compared to the samples that were analyzed several days after were longer rods were found.

M5.12

Defect-Related Optical Behavior in Surface Modified TiO$_2$ Nanostructures.

S M Prokes[1], W E Carlos[1] and James L Gole[2]; [1]Code 6876, NRL, Washington DC, District of Columbia; [2]Dept. of Physics, Georgia Institute of Technology, Atlanta, Georgia.

The surface modification of TiO$_2$ nanostructures to form the visible light absorbing TiO$_{2-x}$N$_x$ oxynitride has been studied. Anatase TiO$_2$ structures in the 3-20 nm range formed by a wet chemical technique and nitridation of the highly reactive TiO$_2$ nanocolloid surface was achieved by a quick and simple treatment in alkyl ammonium compounds. The resulting TiO$_{2-x}$N$_x$ product was then introduced into a Ni, Au or Ag electroless plating solution to metallize the nanostructure surfaces. The samples were then examined by photoluminescence spectroscopy (PL), Raman spectroscopy, and electron spin resonance (ESR). Results indicate that the surface modified TiO$_{2-x}$N$_x$ nanostructures remained anatase and the freshly prepared samples exhibited a strong photoluminescence near 560nm (2.21 eV), which red shifted to 660 nm (1.88 eV) and dropped in intensity with aging in the atmosphere. This behavior was also evident in some of the combined nitridized and metalized TiO$_2$ nanocolloids. Electron Spin Resonance performed on these samples identified a resonance at g = 2.0035, which increased significantly with nitridation. This resonance is attributed to an oxygen hole center created near the surface of the nanocolloid, which correlates well with the observed optical activity.

M5.13

Single Crystal Mn$_3$O$_4$ Nanowires Prepared by One-Step Solid-State Reaction at Room Temperature.

Guanghou Wang and Wenzhong Wang; Department of Physics and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing, China.

Mn$_3$O$_3$ is known to be an active and catalyst for several processes, such as the oxidation of methane and carbon monoxide, or the selective reduction of nitrobenzene. Moreover, different polymorphs of

Mn_3O_4 (hausmannite) can be active and stable catalysts for the combustion of organic compounds at temperatures of 373-773K, which limits the emission of NO_x and volatile organic compounds from waste gases of different origins. Nanowires will be even more effective in electrochromic for anodic coloration and catalytic for combustion process, thus reducing air-pollution. Here we report a novel and simple approach to syntheses of single-crystal Mn_3O_3 nanowires by means of one-step solid-state reaction to prepare nanometer-sized precursors at ambient temperature and then deposit them in NaCl flux. This technique needs no complex apparatus and sophisticated procedure nor metal catalysts and/or template. The Mn_3O_4 nanowires have diameters of 40-80nm and lengths of 150 micrometers and show smooth surfaces and crystal structure of tetragonal cell with lattice parameters of a = 0.5762 and c = 0.9469nm. Fourier transform infrared (FTIR) spectrum of the as-prepared nanowires exhibits two absorption bands at 609 and 509cm^{-1} in the region of 650-500cm^{-1}. These bands may be associated with the coupling modes between the Mn-O stretching modes of tetrahedral and octachedral sites. Two other bands at 478 and 418 cm^{-1} are also observed and assigned as the band stretching modes of the octahedral sites while negating displacement of the Mn^{2+} ions in tetrahedral sites. Comparative studies have been carried out in order to reveal the growth mechanism and the effects of the NaCl flux and surfactant nonylphenyl ether (NP-9). We find that the nanowires by this technique grow not during cooling process, which is different from that in the usual "flux method", but instead during the soaking of the melt. Furthermore, no spherical droplets are observed. Therefore, it is suggested that the Mn_3O_4 nanowires do not grow by VLS or SLS mechanisms, but by an Ostwald ripening, namely, the dissolution of fine particles and their redeposition on larger particles. Adding NaCl significantly decreases the viscosity of the melt, and thus the mobility of components in the flux becomes easier. Therefore, NaCl provides a favorable liquid environment for nanowire growth. The surfactant NP-9 aids the formation of fine particles during the grinding process of the precursor. Consequently, ground precursor powders have high specific surfaces and are metastable in the thermal decomposition process. At the same time, NP-9 can decrease the eutectic temperature of the system, which is favorable for the formation of the nanowires.

M5.14

Synthesis of Indium Tin Oxide Nanoparticles and Application to IR-Reflective Film. Ja Eun Song and Young Soo Kang; Department of Chemistry, Pukyong National University, Pusan, South Korea.

ITO nanoparticles were synthesized by chemical coprecipitation method in an aqueous solution and autoclave method in an alcohol solution. The coprecipitate prepared at room temperature showed the crystal structure of indium oxide in X-ray diffraction when it was annealed at the temperature above 300 °C. In autoclave method, the nanoparticles have two phase crystal structure of indium oxide hydroxide (InOOH) and indium hydroxide ($In(OH)_3$). Annealing at the temperature above 300 °C, it shows the rhombohedral crystal structure of indium oxide (In_2O_3). IR-reflective film was prepared by spin coating method using ITO sol solution. X-ray power diffraction (XRD), Diffractional Scanning Calorimeter (DSC), Transmission Electron Microsopy (TEM) and Energy Dispersive X-ray Spectrometer (EDS) were used to characterize the structure and morphology of ITO nanoparticles. UV-vis and Near-IR spectrophotometers were used to determine transparency in the visible and reflection in the IR-radiation.

M5.15

Ultrasonic Spray Pyrolysis of Ultra fine Metal Oxides. Kai Yau[1] and Kwang-Leong Choy[2]; [1]Materials, Imperial College London, London, United Kingdom; [2]School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, Nottingham, United Kingdom.

Ultrafine particles of various metal oxides (ZnO, Fe2O3 and TiO2) were produced via the Ultrasonic Spray Pyrolysis method over a range of processing temperatures using metal-organic precursors. The physical properties of the powders such as particle size, morphology and crystallinity were obtained using a variety of characterization techniques including Transmission electron microscopy (TEM) and X-ray diffraction (XRD). The oxides of the different metals were then analyzed for their Ultraviolet (UV) light absorption qualities and the results compared.

M5.16

Magnetism of uniaxial ultra-high density Co cluster lattices on Au(788). stefano rusponi[1], Nicolas Weiss[1], Tristan Cren[1], Maximilian Epple[1], gregory Baudot[2], vincent Repain[2], Sylvie Rousset[2] and harald Brune[1]; [1]IPN, EPFL, Lausanne, Switzerland; [2]Groupe de physique des solids, CNRS, Paris, France.

The potential of magnetic monodomain particles for industrial applications has widely been recognized. However, exploitation of this potential needs fundamental knowledge of the origins of magnetic properties. A particular challenge is the fabrication of nanostructures with homogeneous magnetic properties (i.e. narrow MAE distribution, common easy magnetization axis) organized in periodic lattices. We report on the magnetism of long-range ordered arrays of 2D monodomain Co nanoparticles with a density of 26 Tdots/in2 grown by self-assembly on Au(788). In contrast to superlattices of 3D nanoparticles, our particles have uniaxial out-of-plane anisotropy. In addition, they have an unprecedented narrow distribution of the magnetic anisotropy energy of 17% half width at half maximum, narrower than the size distribution. Our data exclude particle interactions. Co/Au(788) is thus a model system for ultra-high density magnetic recording with so far unattended properties.

M5.17

Comparison of the Properties of γ-Fe_2O_3 Nanoparticles Synthesized Inside of Ferritin Protein Cages to the Native Iron Oxy-hydroxide Cores. Keith Gilmore[1], Johnathon Holroyd[1], Joseph Dvorak[1,3], Yves U. Idzerda[1], Michael Klem[2] and Trevor Douglas[2]; [1]Department of Physics, Montana State University, Bozeman, Montana; [2]Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana; [3]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York.

The structural and magnetic properties of native iron oxy-hydroxide in ferritin and γ-Fe_2O_3 artificially mineralized inside of horse spleen ferritin have been compared. While the native material has been studied in detail, little work has been done on artificially mineralized materials. Such synthetic materials can form highly uniform, self assembling systems which can be used in magnetic recording and other applications. We show that the mineralized iron oxide has more favorable magnetic properties for these applications than the native material. Specifically, through XAS and XAFS spectra, we conclude that the native cores are highly disordered and non-uniform while the mineralized sample is uniform and ordered γ-Fe_2O_3. γ-Fe_2O_3 is ferrimagnetic while it has been shown that the native material is antiferromagnetic. Alternating current susceptibility measurements reveal that, relative to the native material, the mineralized sample has a higher blocking temperature by a factor of two, is about 20 times more susceptible to magnetization, and has a larger anisotropy energy by 150%. Particle size distributions have also been extracted from the AC data indicating a mean diameter of 5 nm for the native cores and 6 nm for the mineralized cores. DC magnetic measurements provide supporting evidence of the magnetic structure, blocking temperatures, and crystalline disorder of the two samples. This study demonstrates the feasibility of using of biological containers as reaction vessels to synthesize uniform ensembles of novel magnetic nanoparticles. Future work will explore a variety of magnetic materials grown inside cages of several sizes and shapes.

M5.18

Synthesis of Co@Au core-shell nanoparticles in non-aqueous solution and characterization. Zhihui Ban and Charles J O'Connor; AMRI, New Orleans, Louisiana.

A homogeneous non-aqueous solution reactions method has been developed to prepare gold-coated cobalt (Co@Au) nanoparticles. After the sample was washed with 8% HCl, TGA, XRD, TEM, and magnetic measurements SQUID are utilized to characterize the nanocomposites. TGA shows the weight change in atmosphere of air and hydrogen. XRD shows the pattern of sample. TEM results show that the average size of Co@Au nanoparticles is about 10 nm and we can find core-shell structure of the sample. SQUID results show that the particles are ferromagnetic materials at 300K. So the gold-coated cobalt nanoparticles (Co@Au) can be successfully prepared by the homogeneous non-aqueous approach. This kind of core-shell materials are stable in acid condition, which would give many opportunities for bio- application.

M5.19

Surface Plasmon Resonance Enhanced Phosphorescent Emission From PtOEP. shanlin pan, Zhengjia Wang and Lewis J. Rothberg; chemistry, university of rochester, rochester, New York.

We demonstrated enhanced phosphorescent emission by PtOEP (2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphyrin platinum II) adsorbed near silver 'mirror films' prepared by the Tollens reaction. These result in a clean and fractally organized nanotextured silver surface that supports giant surface-plasmon resonance enhanced electromagnetic fields. Higher phosphorescent enhancement for excitation at 535nm (S0-S1 transition) than for 380nm (S0-S2 transition) excitation reflects larger surface plasmon enhancement of the field at longer wavelengths on these silver nanoparticle assemblies. Time resolved luminescence decay indicates a shorter excited state lifetime even though apparent quantum yields are increased by as much as a factor of 50. We estimate the relative importance of 'absorption enhancement', 'emission enhancement' and quenching to the total phosphorescent enhancement. We have also studied the dependence of the phosphorescent emission enhancement on distance between the PtOEP and the silver surface and conclude that optimal distances are around 5 nm.

M5.20

Preparation and characterization of Tin Oxide Nanowires for gas sensing. Daihua Zhang, zuqin liu, Chao Li and Chongwu Zhou; School of Engineering, University of Southern California, LA, California.

Efficient and reliable laser-ablation approaches for large-scale synthesis of SnO2 nanowires are reported. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to confirm the crystal structure of the nanowires. The results show that these nanowires had uniform diameters around 20 nm and lengths in the order of 10 ?m. In addition, field effect transistors have been constructed based on individual SnO2 nanowires. Excellent n-type transistor characteristics have been observed for SnO2 nanowire transistors. Detailed analysis revealed threshold voltages -50V with on/off ratios as high as 103 at room temperature. These nanowire transistors were further demonstrated to work as sensitive UV detectors and gas sensors.

M5.21

Fabrication and Modification of Silver Nanowires with Multi-structure by Pulse-potential Electroplating. chung kuang chou[1], Yu-Hung Cheng[2], Syh-Yuh Cheng[2] and Chih Chen[1]; [1]Department of Materials Science and Engineering, National Chiao Tung University, Hsin-Chu, Taiwan; [2]Material Research Laboratories, Industrial Technology Research Institute, Hsin-Chu, Taiwan.

Nanomaterials of noble metals are a very attractive research area due to their potential applications in microelectronics and their optical, electronic, and catalytic properties. Many methods for fabricating nanowires have been reported, including thermal decomposition, surfactant-assisted hydrothermal process, and vapor-liquid-solid (VLS), template synthesis. The processes of the crystal growth of nanowire by template with differently pore sizes have been extensively examined. Also, numerous studies have also addressed to modify nanowires after they are grown. In this study, we used anodic aluminum oxide (AAO) as a template and controlled silver nanowires surface by pulse-potential electroplating. Silver nanowire arrays have been synthesized successfully by DC electrodeposition within AAO template in an aqueous solution of AgNO3 and CH3COONH4. The morphology of the Ag nanowire arrays were characterized by scanning electron microscopy (SEM) and transmission electron after removed AAO template. The SEM results indicate that the highly aligned and uniform silver nanowires can be obtained. Their dimension is about 200 nm in diameter, and 10 μm or more in length , which corresponds to the pore sizes of the template used. Furthermore, silver nanowires with smooth and rough periodic surface were grown. The multi-structure was realized by electroplating at low potential in the beginning, pausing electroplating for a while, and then changing to a higher potential to grow rough surface. The above process was repeated to obtain multi-structure silver nanowires with smooth and rough periodic surface. The TEM results show that the silver nanowires possessed many twin boundaries on the rough surface area and were single crystalline on the smooth surface.

M5.22

Synthesis of Copper Oxide Nanowires. Hong-Ying Chen[1], Sheng Han[3] and Han C. Shih[2]; [1]Department of Materials Engineering, National Chung Hsing University, Taichung, Taiwan; [2]Department of Materials Science and Engineering, National Tsing Hua University, HsinChu, Taiwan; [3]National Taichung Institute of Technology, Taichung, Taiwan.

Copper oxide nanowires have been synthesized by the combination of electrodeposition and thermal annealing. The Cu metal was firstly embedded into anodic aluminum oxide templates with the diameter of 80 nm by electrodeposition technique. The Cu nanowires were then annealed in air at 250°C to 900°C for 12 h. The Cu_2O nanowire was appeared above 250°C with the grain size of 20 nm and the Cu_2O would further transformed into CuO at 900°C with the diameter of 80 nm. The correlation between the size effect and the phase transformation will be also discussed.

M5.23

Electrochemical synthesis of Ag/Co multi-layer structure nano-wires. Chih-Yung Wang[1], T.S. Chin[1,2], S.Y. Cheng[3] and R.J. Lin[3]; [1]Material science and engineering, National Tsing Hua University, Hsinchu, Taiwan; [2]National United University, Miaoli, Taiwan; [3]Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan; [4]Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan.

Ag/Co multi-layer nano-wires up to a length 60 micrometer were prepared using anodized aluminum oxide (AAO) with pore diameters 100 200 nm as templates by electro- chemical deposition with a program-controlled source-meter in a single-bath electrolyte containing silver nitrate and cobalt sulfuric. Cyclic Voltammetry was used to determine the electro-deposition potentials of Ag and Co, respectively. On the other hand, the competition between deposition rates of Ag and Co was studied by an analysis of deposits coming from altering electro-deposition conditions on the Si substrate. As a result, a 98wt% Co-rich nanowire could be obtained at -1.1V and a pure Ag nanowire could be obtained below -0.6V vs. Ag/AgCl standard electrode as verified after dissolving the AAO template with 5wt% sodium hydroxide. Furthermore, electric redissolution under lower applied voltages and interface reduction problems in fact seriously affect the structure quality of nano-wires. With the combination of designed electrochemical processes, including the use of a rest time between electric pulses for deposition to balance the ion concentration of electrolyte within pores, and with outside and step voltages applied to avoid bubbles, it was successful to fabricate Co99.43/Ag80 multi-layer nano-wires. The electrolyte concentrations were: CH3COONH4:0.4M, AgNO3: 0.5mM, CoSO4E7H2O: 0.15M. The settings of applied voltage and time segments were Ag 0.65V, 200 sec; Co 0.9V, 100 sec; off time 20sec. The contrast in TEM micrographs and TEM-EDS analyses showed a clear composition modulation along the longitudinal axis of the nano-wires. The magnetic measurements of nano-wires 200nmCo/20nmAg demonstrate a magnetic anisotropy behavior that higher saturations, lower remnant magnetization by applying the field parallel to the longitude axis of the nano-wires, as compared with those perpendicular.

M5.24

Coating of BaTiO3 Nano-layer on Spherical Ni Particles for highly integrated Multilayer Ceramic Capacitors. Yong-kyun Lee, [1]MD Lab, Samsung Advanced Institute of Technology, Su-Won, South Korea; [2]Samsung Advanced Institute of Technology, Su-Won, South Korea.

The nano-thin BaTiO3 layer were uniformly coated on spherical Ni particles for multilayer ceramic capacitor application via the controlled hydrolysis using Ba(OH)2 *8H2O, TiCl4, (C3H7)2NH, (C2H5)2NH (iso-propylamine, diethylamine), and C4H7OH as Ba-source, Ti-source, gradual (OH)- former and solvent, and the subsequent hydrothermal conversion of the Ti-hydroxide coating layer into BaTiO3 layer. At the constant [DEA]/[TiCl4]=10.6, the Ti-hydroxide could be coated uniformly using the dilute source solution ([TiCl4]<0.2M) while the Ti-hydroxide powder in a separated form was frequently observed at [TiCl4>0.4M]. The uniform coating for Ti-hydroxide layer was attained at the slower precipitation and the kinetics of precipitation could be controlled by tuning trace amount of water in the solution. The BaTiO3-coating not only prevented the Ni oxidation but also retarded the sintering between Ni particles to a large extent.

M5.25

Synthesis of Barium Titanate Nanowires and Particles. Sung-Oong Kang, Hyung-Ju Park, Wan-Joong Kim, Chil Seong Ah, Jinhee Kim and Wan Soo Yun; Electronic Device Group, Korea Reseach Institute of Standards and Science, Daejeon, South Korea.

Barium titanate (BaTiO3) nanowires and particles were synthesized by thermal decomposition of metal alkoxide/hydroxide precursors. The shape of the BaTiO3 was found to be strongly dependent upon the molar ratio of precursor to surfactant, which could be used to control the shape of BaTiO3. The diameters of the nanoparticles and wires are in the range of 50 - 150 nm, while the length of the nanowires exceeds several micrometers. Field emission scanning electron microscopy, X-ray diffraction, energy dispersive spectroscopy, and transmission electron microscopy were used to characterize the synthesized BaTiO3. Both nanowires and particles are ferroelectric, which was verified by electrostatic force microscopy.

M5.26

Capping layer controlled magnetic coupling between Fe nanoislands. E. Navarro[1], Y. Huttel[2,3], C. Clavero[2], G. Armelles[2] and A. Cebollada[2]; [1]Fisica Aplicada I, Ftad de Veterinaria, Universidad Complutense de Madrid, Madrid, Spain; [2]Instituto de Microelectronica de Madrid, IMM (CNM-CSIC), Madrid, Spain; [3]Instituto de Ciencia de Materiales, ICMM-CSIC, Madrid, Spain.

The magnetic properties of ultrathin continuous films can be tuned by deposition of adequate metal overlayers. For example, Kisilievski et al [1] have recently reported a silver overlayer thickness-driven magnetic reorientation transition in Co ultrathin films. In this work we report on the effect of magnetically polarizable capping layers such as Pt and Pd on the intergrain correlation in granular Fe (110) thin films grown by triode sputtering on Al_2O_3(0001). The deposition temperature (700 ° C) favors the growth of 3D Fe nano-islands. Both, the size of the islands and the physical contact between them can be monitored with the deposition time. In-situ and ex-situ magneto-optical experiments show that, before capping layer deposition, isolated islands (10 nm diameter) exhibit superparamagnetic behavior while a ferromagnetic phase is developed for islands size above 12 nm. This behavior is unaltered upon deposition of either Al or MgO capping layers. Nevertheless, Pd and Pt capping layers give rise to a superperamagnetic-ferromagnetic transition in the sample formed by small islands and a stronger inter-island coupling in samples formed by larger ferromagnetic islands. No evidence of perpendicular magnetic anisotropy is observed, regardless the nature of the capping layer. The exchange transmitter capability found for Pt and Pd is attributed to their magnetic polarizability at the interface with Fe, as confirmed by polar Kerr spectroscopy measurements and simulations. These results exemplify the importance of the in-situ characterization of magnetic nanostructures and open new methods to tailor magnetic systems with novel properties just by changing the capping material. [1] Kisielewski et al., PRL 89, 087203 (2002).

M5.27

Surface Monolayer Modification of Metal Oxide Nanoparticles to Control Interfacial Properties. Seiichi Takami, Takahiro Yamaguchi, Tahereh Mousavand, Satoshi Ohara, Mitsuo Umetsu and Tadafumi Adschiri; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan.

We report surface monolayer modification of metal oxide nanoparticles to control various interfacial properties including the interaction with other particles/bio-molecules and dispersibility in solvents. These interfacial properties of noble metal nanoparticles are commonly controlled by thiols using the affinity between noble metals and SH groups. Our method relies on the chemical reaction between hydroxyl groups on metal oxide nanoparticles and surface modifiers including aldehydes, carboxylic acids, etc. The modification is performed either in situ or ex situ. We have established hydrothermal synthesis of metal oxide nanoparticles in supercritical water. For in situ modification, we simply add the surface modifier in reactants, namely, aqueous solutions of metal salt and raise the temperature and pressure (typically supercritical conditions) to produce and modify nanoparticles simultaneously. We stress that the use of supercritical phase is necessary to modify nanoparticles with longer hydrocarbon chains that is not miscible with water. We examined surface modification of TiO2 by hexanal and hexylamine. Obtained nanoparticles were hydrophobic and dispersed in an organic phase instead of water, indicating that the surface was modified and terminated with CH3 groups. We confirmed that the similar approach is effective for various metal oxides including SiO2, ZnO, CeO2, NiO, Al2O3, and SnO2. Our method provides the way to use metal oxides as building blocks that exhibits various functions.

M5.28

Synthesis and Characterization of Indium Oxide nano-crystals by Thermal Chemical Vapor Deposition. Yen-Chih Chen and Chuan-Pu Liu; Material Science and Engineering, National Cheng Kung University, Tainan, Taiwan.

Due to its direct energy band gap of 3.6ev and excellent conductive properties while doping, Indium oxide is one of the technologically important materials in the fields of optoelectronic and transparent conductive devices. In this paper, we fabricate single crystalline indium oxide crystals by thermal chemical vapor deposition. Scanning electron microscopy images show that these crystals have different morphologies ranging from thin film to nanoparticle array with shape in cube and hexahedron as well as other shapes depending on the growth temperature and gas flux. The materials are subsequently characterized by transmission electron microspcopy and x-ray diffraction, which show that the structure of these crystals is single-crystalline cubic bixbyite indium oxide with various types of defects. The optical properties are measured by micro-photoluminescence. The results show that the characteristics of PL spectra are largely influenced by the size and shape of the crystals and differ from the bulk indium oxide. The growth mechanisms of indium oxide nanocrystals with and without catalysts are discussed.

M5.29

A Novel Fabrication Method for Metal/Oxide Nano Tubules. Daekyun Jeong[1], Nohheon Park[1], Hyunjeong Shin[1], Jaegab Lee[1], Myungmo Sung[2] and Jiyoung Kim[1]; [1]Advanced materials engineering, Kookmin University, Seoul, South Korea; [2]Chemistry, Kookmin University, Seoul, South Korea.

Recently, nanotubules have attracted lots of attention as 1-dimensional nano-structure for nanotechnology applications. Various techniques, such as sol-gel and nano-template methods have been introduced to fabricate nanotubules. However, few papers have reported method for multi-layered nanotubules even though hybrid nanotubules have various potential applications. In this presentation, we will demonstrate novel fabrication routes of metal/oxide multi-wall nanotubules using nano-template and atomic layer deposition (ALD). ALD has several excellent features such as excellent conformal deposition and easy nano-laminate film formation. We successfully deposited oxide and metal thin films in extremely high aspect ratio holes of nanotemplates. We used commercially available polycarbonate (PC) filters as nanotemplates, which have various hole sizes from 30nm to several hundred nm. We performed surface treatment on the nanotemplate using SAM (Octadesyl-tetrachlorosilane) in order to prevent undesirable formation of metal and oxide layers on the nanotemplate surfaces. We deposited conformal and uniform thin ZrO2 oxide layer inside of the holes in order to form walls of nanotubules. Zr-tert-butoxide and H2O were used as precursor and oxidant, respectively. And then, we deposited Cu thin layer using ALD using Cu metal organic precursors ((hexafluoroacetylacetonate) Cu(I) DMB (3,3-dimethyl-1-butene))and H2. All deposition temperatures were suppressed lower than 200°C in order to avoid thermal damage on PC templates. Finally, we obtained oxide/metal multi-wall nanotubules up to 10μm of length, after the organic nanotemplates were dissolved by organic solvents. We also fabricated various nanotubules with different layer walls, as we changed deposition sequence and materials using ALD. We found that wall deposition rate depends on radius of nanotubules. We will also report lattice images and crystallinity of tubewalls using HRTEM. And, AFM and SEM images will show overall geometric features of various nanotubes. This research was performed with the financial support of the Center for Nanostructured Materials Technology under the 21st Century Frontier R&D Program of the Ministry of Science and Technology, Korea

M5.30

Effect of Template Materials on the Surface Morphologies of Copper Nanowires. Ran-Jin Lin and Lu-Huy Wu; Microsystems Technology Division, Industrial Technology Research Institute, Chutung Hsinchu, Taiwan.

High purity and good crystalline copper (Cu) has the best electrical conductivity among the commonly-used metals. It become the main material for application of current leads in the sub-micron IC fabrication. Therefore, the fabrication and characterization of the Cu nanowires (diameter $<$ 100 nm) have great interest in electronics. Several papers have reported the fabrication of Cu nanowires using the template methods, such as porous alumina, mica or polymeric ion track membranes. But, no one presented the difference of morphology as the wires reach the upper surface of the templates. The Cu nanowires were grown in a nanoporous template of anodic aluminum and ion track etched polycarbonate (PC) membranes (6 um thick) by the DC electrodeposition of CuSO4-based electrolyte at a room temperature and applied voltage of 0.2 volt. For growth of porous alumina , the gold seed layer (100 nm thick) and aluminum film (400 nm thick) were sequentially grown on the 4-inch silicon wafer by the magnetron sputtering method. Then the Al film was anodized in 0.3 M oxalic acid at 0 degree C and applied voltage of 30 V. After removing the barrier oxide layer by 5 wt% H3PO4 solution, the partially ordered nanopores with diameter of 40-50 nm were uniformly formed. For PC membranes, the Au layer (100 nm thick) was first deposited on the one side of membrane. Then the Cu nanowires were grown from the bottom of nanopores with diameter of 50 nm. There are marked difference in surface morphologies of Cu nanowires, grown from alumina and PC template. The typical feature of Cu nanowires, grown from the former template, is spherical Cu agglomerates with diameter of about 10 micro-m, although the template thickness is only 0.5 micro-m. No tips of Cu nanowires are found between the Cu agglomerates. On the contrary, no Cu agglomerates were found as the growth of Cu nanowires reached the upper surface of the PC template. The tips of Cu nanowire can be clearly identified before the continuous film is formed. This morphology difference is mainly caused by the value of interface energy between the Cu and the templates. There is a lower value of interface energy between Cu and anodic alumina than that between Cu and PC membranes. The detailed morphologies of the Cu nanowires with deposition time will be presented.

M5.31

Production method for aligned Nanowires on arbitrary materials. Rainer Kunz and Rainer Adelung; Faculty of Engineering, University of Kiel, Kiel, Germany.

We present a method that allows us to produce aligned metallic nanowires on almost any material. This method recently enabled us to produce interconnected platin nanowire networks on Nafion-polymer or gold nanowires on Teflon AF. We will explain the principle of this method by means of a reference material, so called layered transition metal dichalcogenides (TMDC) crystals. The method is based on producing cracks in thin films as templates, using large sticking coefficient differences and long diffusion length. The underlying mechanism that forms the template cracks is mechanical stress. In the case of the TMDC crystals this stress is introduced in the substrate by an electronic interaction between the metal used for the nanowires and the TMDC-crystal. The large difference in condensation coefficient is an immanent property of layered crystals for many different adsorbates. Obtained by cleavage along a so called "Van-der-Waals-gap", surfaces of such crystals are atomically flat over hundreds of microns. As a consequence of their layered character the surfaces have no reconstruction and almost no step edges or other defects, which is the basis for long diffusion length. In contrast, the rare defects have a very high sticking coefficient and act as excellent nucleation centers. Therefore, after metal evaporation on such surfaces in UHV, various structures can be formed in a self organized processes. We observed, e.g., clusters in fractal or geometric arrangements or large nanowire networks on the surfaces [1]. In order to understand, why the different structures occur, a systematic study of the growth parameters, (nucleation, diffusion length, evaporated metal, influence of the substrate-crystal), is necessary. Therefore, we first carried out diffusion studies on these surfaces. We could show that in extreme cases (Cu on metallic TaS2) diffusion length of more than $50\mu m$ could be observed combined with a nucleation probability of almost zero. This is evident from a growth mode, showing similarities with the DLA (Diffusion Limited Aggregation) growth process. In contrast, metal diffusion (Cu) on the geometrically similar surfaces on the semiconducting (WSe2) surface show much shorter diffusion length and no DLA growth. We suggest a model to explain the different diffusion behavior as a key to understand the different self organized structures. Learning from the TMDC crystals, we show the application on technological more important materials. [1] see, e.g., review and citations in: R. Adelung, R. Kunz, F. Ernst, L. Kipp, M. Skibowski, Self-Organized Structures on Flat Crystals: Nanowire Networks Formed by Metal Evaporation, in: Advances in Solid State Physics 43 (Ed. B. Kramer), Springer, Heidelberg, 463-476 (2003)

M5.32

Assembly of alumina based nanoparticles doped with Ag clusters and their optical, mechanical and electrical properties. Phani Ratna Ayalasomayajula[1], Christian Hinderling[1], Henry Haefke[1], Sandro Santucci[2] and Maurizio Passacantando[2]; [1]Nanotechnology and Life Sciences Division, CSEM, Swiss Center for Electronics and Microtechnology, Inc.,, CH-2007 Nuchatel, Switzerland; [2]Department of Physics, University of L'Aquila, L'Aquila, Italy.

Nanometer-sized ultrafine particles of metals and semiconductors display many intriguing properties including optical nonlinearity properties, which are quantitatively and qualitatively different from respective bulk materials. It is a challenging task to deposit such films on to plastic substrates (polycarbonate, polyacrylic etc.,) at low temperature and cost effective technique such as sol-gel. In the present investigation, alumina has been chosen as matrix because of its high hardness, chemical resistance, and scratch resistance. Nanostructured Al_2O_3 as well as boehmite AlOOH (on plastic substrates) thin films with 10-12 nm size have been prepared by sol-gel process and subsequently the films were doped with different concentrations of Ag nanoclusters. The alumina based thin films have been deposited on quartz, polycarbonate and polyacrylic substrates at room temperature and then subjected to annealing at different temperatures ranging from 100^oC (plastic substrates) to 400^oC (quartz) for 30 minutes. The reduction of AgO to Ag has been performed by two processes, one during the formation of nanoclusters by treating with $NaBH_4$ reducing agent and other by treating in H_2 atmosphere. The structure formation and chemical composition of these films were examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) technique respectively. The size of the nanoclusters of Ag in the alumina based matrix was examined with high-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) techniques. It has been observed that there was no aggregation of Ag clusters by this new method of deposition. Ag nanoclusters grown within the alumina based matrix were very small with less than 5 nm size, and were isolated and dispersed from each other with very narrow size distributions. With increasing Ag content and additional annealing, shift in the optical absorption measurements was observed. Adhesion strength failure as well as hardness of the deposited films were measured by microscratch resistance test and nanohardness indentor techniques, respectively. Electrical conductivitiy of the films with various concentrations of Ag were also measured with four-probe sheet resistance technique.

M5.33

Self-assembled Nanostructures in the Au-Si System. Aditi Chandra and Bruce M Clemens; Materials Science and Engineering, Stanford University, Stanford, California.

This talk will describe a novel method for fabricating both gold-rich nanoparticles and silicon nanowires in sputtered thin films. The thermal decomposition of amorphous AuSi/Si multilayers results in the formation of Au-rich nanoparticles. Via metal-induced-crystallization, these nanoparticles diffuse through amorphous silicon, leaving trails of crystalline silicon nanowires along the diffusion track. High resolution electron microscopy studies reveal organized lines of nanoparticles that are approximately 2nm in diameter, and neighboring silicon nanowires that are also 2nm in diameter and 24nm long. Once both nanostructures are formed, further annealing has little effect on either nanostructures' size. The ability to tailor the unique physical properties of nanostructures requires an understanding of the forces that drive nanostructure assembly. Therefore, thermodynamic models are provided to explain the origin of the size-selection, as well as other uniformities observed in the multilayer system.

M5.34

Self-Assembly and Integration of Ordered, Robust, Three-Dimensional Gold Nanocrystal/Silica Arrays. Hongyou Fan[1,2], Kai Yang[2], Kevin Malloy[2], Thomas Sigmon[2] and Jeff Brinker[1,2]; [1]Sandia National Laboratories, Albuquerque, New Mexico; [2]Univeristy of New Mexico, Albuquerque, New Mexico.

Metal and semiconductor nanocrystals exhibit a wide range of size-dependent properties, motivating a large amount of work concerned with the preparation, characterization and dispersion of the nanocrystals. While controlling the size of individual nanocrystals, recent developments have concentrated on directing the self-assembly of nanocrystals into two- and three-dimensional arrays with precisely controlled spatial interparticle arrangement. Such nanocrystal arrays provide exciting opportunities for optimizing properties of materials and for producing new collective physical phenomena. The work reported to date employed nanocrystals stabilized by alkanethiols from nonpolar solvent-phase and gas-phase. These nanocrystals are only soluble in nonpolar organic solvents. The fabrication of ordered nanocrystals is limited to the usage of organic solvents. The resulting ordered nanocrystal arrays exhibit weak thermal and mechanical stabilities impeding their integration into device. Here we report a new method for producing water-soluble high quality nanocrystals and for further organizing these nanocrystals into highly ordered, robust inorganic matrices enabling fabrication of useful devices. The detailed synthesis and microstructural characterization of water-soluble nanocrystals and ordered nanocrystal/silica nanostructures will be presented along with their electronic performance as determined by C-V and I-V measurements. Sandia National Laboratory is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

M5.35

Strain driven nucleation by interfacial misfit dislocations. Yong-Won Lee, Mats I. Larsson and Bruce M. Clemens; Materials Science and Engineering, Stanford University, Stanford, California.

Control of the spatial distribution of nucleation sites offers one approach for tuning the growth mode of a thin film. Our recent kinetic Monte Carlo simulations indicate that films grown with a high density of uniformly distributed nucleation sites have a greater tendency to grow by layer-by-layer growth. Here we investigate the effect of an array of buried misfit dislocations on thin film growth. The strain field of the dislocations strongly moderates the adatom energy and mobility, leading to control over the spatial distribution of nucleation sites. We present experimental results of a metal thin film system which indicate that dislocation strain fields lead to smoother films, consistent with layer-by-layer growth induced by a dense array uniformly distributed nucleation sites. The misfit dislocation array was formed under ultrathin, epitaxial films of Pt (001) grown by UHV sputter deposition on single crystal MgO (001) substrates. Transmission electron microscopy (TEM) revealed orthogonal dislocation arrays with an average spacing between dislocations of 5.9 nm, which was slightly larger than the value calculated from bulk lattice parameters. To investigate the effect of the strain field on nucleation and growth, 1 nm thick Co films were grown on Pt underlayers with the thicknesses 2, 5, and 10 nm. The growth mode of the Co films was characterized by electron microscopy and magnetic property measurements, including the delta-m technique, whereby intergranular interactions are deduced by comparing the isothermal remanent magnetization and DC-demagnetization curves. These measurements indicate that the films grown on the thinner Pt underlayer, where the stress field of the dislocation array is larger, are smoother, consistent with a high density of nucleation sites.

M5.36

SnO2 Fishbone-Like Nanoarchitectures Fabricated by Sn Nanocatalysts. Yuxi Chen, Lesley Jane Campbell and Weilie Zhou; AMRI/Chemistry, Advanced Materials Research Institute/UNO, New

Orleans, Louisiana.

We report microstructure fabrication and growth mechanism of SnO2 fishbone-like nanostructures synthesized through a vapor transport deposition process using SnO powder as a source material. Microstructural investigation indicated that Sn nanoparticles formed by a decomposition of SnO acted as catalysts for controlling the growth of SnO2 fishbone-like nanostructures. High temperature orthorhombic SnO2 phase remained at ambient temperature and was the dominant phase of such fishbone-like nanoarchitectures. Growth directions of the stem and branches in the SnO2 fishbone-like nanocomponents were identified as orthorhombic <110> directions by transmission electron microscopy. A two-step self-catalytic vapor-liquid-solid growth model was proposed to describe the growth of the SnO2 fishbone-like nanoarchitectures. The growth of semiconductor metal oxide nanoarchitectures has potential application for nanoelectronic devices and sensors.

M5.37

Large-scale, Solution-phase Synthesis of 1-D Transparent Conducting Oxide (TCO) Nanostructures. Bin Cheng[1], Wensheng Shi[1], Lei Zhang[2] and Edward T Samulski[1,2]; [1]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; [2]Curriculum in Applied Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

One-dimensional (1-D), transparent conducting oxide (e.g., ZnO, SnO2) nanostructures with different aspect ratios were prepared in solution. The aspect ratio of these novel 1-D nanostructues can be controlled by delicately-selected experimental conditions. The detailed structures of the as-prepared nanostructures were characterized by TEM, XRD, SAED and HRTEM, and the optical properties of these novel nanostructues are reported.

M5.38

Characterization of Nanocrystalline Al2O3 Aerogels Containing Fe and Co. Anna Corrias, Maria F. Casula, Andrea Falqui and Giorgio Paschina Dept Scienze Chimiche, University of Cagliari, 09042 Monserrato, ITALY. Maria Francesca Casula, Anna Corrias, Andrea Falqui and Giorgio Paschina; Scienze Chimiche, University of Cagliari, MONSERRATO, Italy.

The sol-gel technique has been succesfully adopted for the preparation of composites in that it allows a homogeneous distribution of the dispersed phase thanks to the mixing of the precursors at a molecular level. In this work, we used the sol-gel method to prepare Al2O3 containing Fe and Co using aluminum tri-sec-butoxide, iron nitrate and cobalt nitrates as precursors. High temperature supercritical drying was performed in order to obtain an aerogel. Pure Al2O3 aerogels were also prepared as a reference. The crystal structure of the aerogel samples was characterized by X-Ray powder diffraction (XRD), selected area electron diffraction and X-Rays absorption spectroscopy (XAFS). The texture was studied by N2 physisorption and TEM. Thermogravimetric analysis (TGA and DTA) and calcination treatments were performed in order to study the evolution of the porous texture, the particle size and the crystal phase as a function of the heat treatment. The Al2O3 aerogel sample after the supercritical drying has a pseudobohemite-like structure, i.e. a layered structure typical of the hydrated aluminum hydroxyoxide, but the interlayer distance is larger than in pseudobohemite due to the presence of OR instead of OH terminal groups. The layered structure gives rise to a diffraction peak at low Bragg angle, whose position is related to the interlayer spacing and therefore to the size of the OR terminal group. When Fe and Co are also present, the overall XRD pattern is similar to te one recorded for Al2O3, but the diffraction peak at low angle is not present, indicating a more disordered structure. Both the pure alumina and the Fe and Co-containing aerogels are mesoporous and have surface areas around 500 m2/g-1. Bright field TEM observations show the presence of needle-like particles. Dark field TEM observations indicate that the needles are not single crystals, but are made out of spherical nanocrystals arranged into chains. After calcination, the aerogels retain a mesoporous texture and exhibit a significant surface area even after heat treatment at 900'C. In pure alumina aerogels, the calcination gives rise to the formation of g-Al2O3 which is stable up to 1000'C. When Fe and Co are also present, a cubic nanocrystalline phase is formed which has a structure similar to g-Al2O3 with the Fe and Co ions located in the vacancies of the spinel structure. Structural details are obtained by XAFS and Mossbauer spectroscopy. On the other hand, thermal treatments in reducing atmosphere give rise to the formation of phase separation resulting in FeCo alloy-Al2O3 nanocomposite formation .

M5.39

Deposition of Mono-dispersed TiC Nanoparticle Coatings by a Laser-assisted Pyrolysis Process. Gayan Dedigamuwa, Pritish Mukherjee and Sarath Witanachchi; Laboratory for Advanced Materials Science and Technology, Department of Physics, University of South Florida, Tampa, Florida.

The enhanced hardness associated with nanoparticle coatings and nanocomposites of TiC make them attractive for applications in tribology. In this paper, we present a laser-assisted pyrolysis technique for the deposition on a substrate of a coating of TiC nanoparticles, having a narrow particle size distribution. In this process, a titanium containing organometallic compound, cyclopentadienyltitanium trichoride ($C_5H_5TiCl_3$) is dissolved in toluene and atomized to droplet sizes of the order of 5μm by using a nebulizer with SF_6 as the carrier gas. The tip of the nebulizer is placed inside a chamber that contains argon gas at a pressure of about 10 Torr. A 15W CO_2 laser beam at 10.6 μm wavelength is tightly focused onto a point just above the nebulizer tip where a spray of the chemical is injected into the chamber. The laser radiation at this wavelength is strongly absorbed by SF_6, and thus increases the temperature of the droplets to about 500^{o}C. At this temperature the droplets decompose to form TiC particles. The size of the particles is determined by the droplet size and the concentration of the organometallic compound. Particles of sizes less than 100 nm are generated by reducing the concentration of the organometallic compound in the solvent. The particles are deposited on a heated substrate, and the morphology and size distribution is studied by AFM, while the crystallinity of the nanocoating is analyzed by x-ray diffraction. The results of a systematic study of the particle size dependence on the concentration of the organometallic compound will be presented.

M5.40

The Use of Polypyrrole to Control Magnetic and Conductive Properties of a Nanocomposite. Silvia Liong[1], Alexa W. Harter[2], Rick L. Moore[2] and William S. Rees[1]; [1]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; [2]GTRI-Signature Technology Laboratory, Georgia Institute of Technology, Atlanta, Georgia.

In recent years, there has been significant interest in composites made of magnetic nanoparticles. One potential application is magnetic material with controllable resistivity. However, the tendency for these nanoparticles to agglomerate has presented a challenge to the experimentalists. In this work, magnetite (Fe3O4) nanoparticles (diameter is app. 10nm) are coated with a layer of conductive polymer, such as polypyrrole, and then embedded in a polymer matrix. This layer of polypyrrole can improve the dispersion of magnetite nanoparticles in a polymer matrix and impart surface conductivity on these particles. The process of coating magnetite nanoparticles with polypyrrole was adapted from a process to make conductive textiles. To produce a coating of polypyrrole, the particles are stirred in a solution of oxidizing agent. A solution containing monomer and dopant is added into the mixture and then stirred to allow polymerization to take place on the surface of the particles. The coating thickness and conductivity of polypyrrole are dependent on several variables: reaction time, temperature, pH, solvent, monomer, dopant, oxidizing agent, and their respective concentrations. There are a few benefits for using magnetite nanoparticles coated with polypyrrole in composites. The polypyrrole coating provides the magnetite nanoparticles with surface conductivity, so these particles may be used to fabricate a composite that has controllable magnetic and conductive properties. The most important variable for adjusting the functional properties of a composite is usually the concentration of the particles. By modifying the coating thickness and conductivity of polypyrrole coating, conductivity (or resistivity) of a composite may be controlled without changing concentration of particles and magnetic properties of the composite. Lastly, the polypyrrole coating was observed to improve the dispersion of magnetite nanoparticles. The scope of this work is to determine the effect of polypyrrole coating on the dispersion of magnetite nanoparticles in a polymer matrix and to study the conductive and magnetic properties of the composites. Firstly, the magnetite nanoparticles (with and without polypyrrole coating) is characterized. To qualitatively analyze the surface of the nanoparticles, FTIR and SEM are used. Thermal analyses such as TGA and DSC are used to analyze the polypyrrole coating. The conductivity and isoelectric point of the particles are measured. Secondly, composite samples are analyzed at different levels of particle loading. To determine the dispersion of magnetite nanoparticles, microstructures of composites are studied using SEM, TEM, and MFM. Conductivity of composites is measured using 4-probe method and the critical particle loading to achieve percolation is determined. Electromagnetic properties of composites are measured as functions of temperature, DC magnetic field, and frequency.

M5.41

The synethsis of magnetic nanoparticles into nanochannel templates. Liu Jingjing, South China University of Technology, Guangzhou, China.

We used a new method to synthesis magnetic particles in uniform nanochannel of a template. Using mesoporous silica as the template, magnetic particles can be incorporated and grew up in the nanochannel. In this processing,how to realize and control magnetic particles anchored into the nanochannel are the keys. In this talk,different methods of disposing the template and inducing of the magnetic particles into the pore were investigated. By controlling conditions and steps of synthesis, magnetic nanoparticles interpenetrating nanochannel silicas can be synthesized . Further more, this processing can be done under the mild temperature. This article focus on studying the synthesis and processing of magnetic particles with smaller and more narrow disperse of size than from other methods. The diameters of magnetic nanoparticles are confined to pores of the template about 10-30nm range. The effect of conditions on the structure and properties of magnetic nanoparticles was also discussed.

M5.42

Finite-Size Effects and Surface-Enhanced Raman Scattering in Noble-Metal Nanoparticles. Vitaliy N. Pustovit, Kendrik M. Walker and Tigran V. Shahbazyan; Department of Physics, Jackson State University, Jackson, Mississippi.

Surface-enhanced Raman scattering (SERS) from molecules adsorbed on small metal particles has attracted increasing interest during past two decades. The main SERS mechanism has electromagnetic (EM) origin and is due to the strong surface plasmon local field near the surface[1] (see also [2] for review of all SERS mechanisms). Recent observations of strong enhancement of single-molecule Raman scattering [3] as well as emerging possibilities of nanoparticle-based Raman sensors [4] have prompted a new interest in single particle SERS and, in particular, in the role of finite nanoparticle size. Although classical EM enhancement is size-independent, quantum corrections due to the discreteness of the electron spectrum result in a weaker enhancement in small nanoparticles. Here we describe a novel finite-size quantum-mechanical mechanism that leads to therelative increase of SERS in small noble-metal particles. This mechanism stems from different effect that confining potential has on s-band and d-band electrons. Namely, the spillout of delocalized sp-electrons beyond the classical nanoparticle boundary results in an incomplete embedding of s-electron distribution in the background of localized d-electrons, whose density profile follows more closely the classical shape [5]. In the absence of d-electron population in the nanoparticle surface layer, the effective dielectric constant is reduced as compared to the bulk. We demonstrate that SERS in small noble-metal nanoparticles is strongly affected by the interplay of electron confinement and screening. Indeed, a reduction of d-electron screening in the surface layer leads to the stronger surface plasmon local field acting on a molecule located in a close proximity to metal surface. This results in the additional enhancement of the Raman signal which becomes more pronounced for small nanoparticle sizes due to the larger ratio of surface layer to radius. We have developed a theory for SERS that includes the surface layer effect and performed numerical calculations of the Raman enhancement factor for Ag nanoparticles with radii in the range from 1.0 to 4.0 nm. This work was supported by ARO under grant DAAD19-01-2-0014 and by NSF under grants DMR-0304036 and DMR-0305557. [1] G. C. Schatz and R. P. Van Duyne, in Handbook of Vibrational Spectroscopy, edited by J. J. Chalmers and P. R. Griffiths (Wiley, 2002). [2] K. Kneipp et al., Chem. Rev. 99, 2957 (1999). [3] S. Nie and S. R. Emory, Science 275, 1102 (1997). [4] Y.C. Cao, R. Jin, and C. A. Mirkin, Science 297, 1536 (2002). [5] A. Liebsch, Phys. Rev. B 48, 11317 (1993).

M5.43

Synthesis of Hollow Cobalt Chalcogenides Nanostructures. Yadong Yin and Paul Alivisatos; Lawrence Berkeley National Laboratory, Berkeley, California.

Hollow cobalt chalcogenides nanostructures were synthesized in organic solvent by starting with monodispersed cobalt nanocrystals. The size and shape of the hollow structures could be readily controlled. In this paper the possible formation mechanism of the hollow structures will be discussed. We will also explore the interesting applications of these novel materials.

M5.44

A New Template Method of Fabricating Nickel Wires. Jiye Fang[1,2], Weigang Lu[2] and Eun Young Shin[2]; [1]Chem, Univ of New Orleans, New Orleans, Louisiana; [2]Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

The properties of low dimensional nanomaterials have attracted extensive interest. One of the successful methods to achieve the shape control is using the static template to enhance the growth rate of one crystallographic face over another. In this work, we created a new approach and fabricated nickel wires through a high temperature wet chemical solution in which a polar organic solvent system consisting of hydroquinone and diethylene glycol acts as static template medium to form desirable structure. The as-reduced Ni wires range 80-120 nano meter in width and 2-15 micro meter in length. XRD analysis confirmed the cubic phase, and HRTEM revealed the crystalline structure of the wires. It is proposed that the interaction of hydrogen-bonding between hydroquinone and diethylene glycol plays a significant role in the formation of the Ni wires.

M5.45

Synthesis and Characterization of Novel Au(core)-Au/Pt alloy(shell) Nano Bimetals. Ru-Shi Liu[1], Hau-Ming Chen[1] and Shu-Fen Hu[2]; [1]Department of Chemistry, National Taiwan University, Taipei, Taiwan; [2]National Nano Devices Laboratories, Hsinchu, Taiwan.

We have developd a new method that mixture the metal ions at the same time to fabricate the core (Au)-shell (Au/Pt alloy) structure nanoparticles. The surface plasmon absorption band of Au shifts to 410 nm at the Au/Pt bimetallic nanoparticles. On the other hand, the significant difference in lattice parameter between the individual Pt and the bimetallic Pt was observed. The lattice parameter of Pt increased about 4%. The Au atoms inserted into the lattice of Pt resulted in an increase in the lattice parameter of Pt in the bimetallic system. This result suggests that a new phase involved with Au and Pt was formed in the shell. Moreover, we report on studies of alloy formation of Au-core Au/Pt alloy-shell nanoparticles in solution at ambient temperature using extended X-ray absorption fine structure spectroscopy. Various thickness of the Au/Pt shell with different amount of Pt and constant amount of Au was synthesized using chemical wet reduction. The equilibrium structures (alloy versus core-shell) of these nanoparticles were determined in solution. We observed remarkable interdiffusion of the Au and Pt metals. These results indicate that formation of a novel structure with Au-core and Au/Pt alloy-shell.

SESSION M6: Semiconductor Quantum Dots
Chairs: Geoff Strouse and Alex Zunger
Wednesday Morning, April 14, 2004
Room 3001 (Moscone West)

8:30 AM *M6.1

Theory of Spectra and Entanglment in Quantum Dot Molecules. Alex Zunger, National; Renewal Energy Laboratory, Golden, Colorado.

Abstract Not Available.

9:00 AM *M6.2

Magnetism in Quantum Dot Alloys: From paramagnetism to ferromagnetism. G. Strouse, Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California.

From the earliest studies on molecular magnets, nanoscale semi-magnetic semiconductors, and magnetic nanoparticles, scientists have been fascinated by the potential to systematically study the unique magnetic phases achievable in these materials, particularly as a function of size, shape, and confinement within a host matrix. Intentionally incorporating a defect ion by random ion displacement of the cation site in the core of II-VI and III-V nanoparticles offers a convenient platform to probe the influence of quantum confinement on the interplay of magnetic and electronic degrees of freedom. Research efforts into these semi-magnetic semiconductors or diluted magnetic semiconductors at the nanoscale have resulted in a wide range of magnetic phases observable in MBE prepared materials. Unfortunately, chemical prepared nanomaterials tend to anneal the defect ions out of the core of the particles. Using a single source synthetic strategy, we have prepared a series of core doped II-VI and III-V nanomaterials that exhibit paramagentism, antiferromagnetism, or ferromagnetism dependning on the dopant ion type, lattice type and carrier concentrations. Insight into the effect of size, lattice, and onset of the magnetic phases will be presented.

9:30 AM M6.3

Reversible, surface-controlled structure transformation in nanoparticles induced by aggregation state. Benjamin Gilbert, Feng Huang, Hengzhong Zhang and Jillian F Banfield; Earth & Planetary Sciences, University of California - Berkeley, Berkeley, California.

Complex three-dimensional structures can be obtained by assembly of individual nanoparticles. While nanoparticles are generally considered to be stable building blocks we demonstrate that the interparticle contacts formed during the aggregation of uncoated nanoparticles can cause profound reversible structural modifications within the nanoparticles at room temperature. Wide-angle x-ray scattering measurements show that the structure of 3 nm ZnS nanoparticles differs from that of bulk ZnS and varies with particle aggregation state. Loosely packed nanoparticles have a more distorted internal structure than highly aggregated nanoparticles of the same size. Nanoparticles have a crystalline structure when they aggregate slowly during drying. Their structure becomes more distorted when the same particles are resuspended in methanol, ultrasonically dispersed, then rapidly aggregated by quick drying. It is possible to switch reversibly between the two structural states by cycling between different aggregation states. The powder formed by rapid drying has a higher fractal dimension than that formed by slow drying. Reversible switching occurs at room temperature, implying a low activation energy for the transformation. UV absorption spectroscopy shows that the structure switching between nanoparticles dispersed and aggregated in methanol is accompanied by a reversible change in electronic structure. Molecular modeling illustrates a mechanism with a low activation barrier in which interparticle interactions drive a low energy structural transformation. The reversible nature of the transformation indicates that nanoparticles are not trapped in a metastable state and are responsive to changes in their surface environments. These results suggest the use of nanoparticles as acousto-optic sensors and are relevant to methods of nanostructure formantion via self-assembly because interparticle contact may lead to unexpected modification of the materials properties of individual nanoparticles.

9:45 AM M6.4

A Continuous Flow Microcapillary Reactor for the Preparation of a Size Series of CdSe Quantum Dots.

Brian K.H. Yen[1], Nathan E Stott[1], Klavs F Jensen[2,3] and Moungi G Bawendi[1]; [1]Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have used a simple, capillary flow reactor to prepare colloidal CdSe quantum dots (QDs). The reactor produced samples with emission profiles (as narrow as 27 nm FWHM) and quantum yields (as high as 51%) comparable to those prepared in conventional batch processes. The continuous flow system made it possible to rapidly and systematically screen through important reaction parameters such as reaction temperature, time (flow rate), and precursor concentration. Such experiments provided insight into the kinetics of QD nucleation and growth. As a result, we were able to rationally tune the effective band gap of the QDs continuously over a wide spectral range while maintaining excellent size distributions and high quantum yields.

10:30 AM M6.5

Direct observation of highly polarized non-linear absorption dipole of single semiconductor quantum rods.

Eli Rothenberg[1,2], Yuval Ebenstein[1,2], Miri Kazes[1,2] and Uri Banin[1,2]; [1]Institute of Chemistry, the Farkas Center for Light Induced Processes, The Hebrew University of Jerusalem, Jerusalem, Israel; [2]the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel.

Polarization fluorescence microscopy was used to study the nature of the emission and nonlinear absorption dipole of single CdSe/ZnS quantum rods. Rods, with aspect ratio ranging from 2.75 to 15, showed strongly polarized emission consistent with previous one-photon studies. Non-linear excitation showed a sharp angular dependence fully consistent with the predicted two-photon absorption process. Two-photon absorption probes different transitions than linear absorption due to modified parity and angular momentum selection rules. The two-photon absorption dipole was found to be parallel to the emission polarization, and allows achieving highly orientation selective excitation of quantum rods. This is yet a further demonstration of single molecule measurements in unraveling basic principles of light-matter interaction that are otherwise masked by ensemble averaging.

10:45 AM M6.6

Low-Loss Electron Energy-Loss Spectroscopy of CdSe Quantum Dots in a Scanning Transmission Electron Microscope.

Rolf Erni[1], Nigel Browning[1,2], Delia J Milliron[3,4], Steve Hughes[3,4] and A Paul Alivisatos[3,4]; [1]Department of Chemical Engineering and Materials Science, University of California Davis, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Department of Chemistry, University of California Berkeley, Berkeley, California; [4]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

By changing the size of CdSe quantum dots, the electronic structure of these semi-conducting nanoparticles can be tuned over a wide range. Starting with a value of 1.7 eV for bulk CdSe, the direct band gap can be increased, up to about 3.5 eV, when decreasing the particle size down to 1 nm. This variability of the optical gap, which is due to quantum confinement for CdSe particles smaller than about 10 nm, makes CdSe quantum dots interesting for optical applications. So far, the electronic structure of individual CdSe quantum dots has been calculated and reported in the literature. These calculations match well with optical measurements, which average the electronic structure of a multitude of similar particles. Owing to their size, measurements on individual nanoparticles are rare. However, such measurements are crucial to decide if either electronic properties emerge from interacting particles arranged in agglomerates or if the fundamental electronic properties can solely be attributed to individual quantum dots. Using a focused electron probe in scanning transmission electron microscopy, Z-contrast imaging in combination with low-loss electron energy-loss spectroscopy (EELS) is used to locally probe the electronic structure of individual CdSe quantum dots. A Kramers-Kronig transform of the energy-loss function (ELF), which is basically given by the electron energy-loss spectrum, yields the real part of the dielectric function. Combined with the imaginary part of the dielectric function given in the ELF, the complex dielectric function is known and the interband transition strength can be calculated and compared with optical measurements as well as with calculations. Z-contrast imaging and EELS was carried out in a Tecnai F20 UT microscope equipped with a double-focusing Wien filter optionally acting as a monochromator directly below the field-emission gun. Low-loss electron energy-loss spectra with an energy resolution of 0.2 eV were acquired using a monochromated electron probe of about 2 nm diameter. High energy resolution in EEL spectra not only sharpens and resolves more clearly spectral features, it also enhances the signal to background ratio close to the zero-loss peak. With an energy resolution of 0.2 eV, spectrum information can unambiguously be accessed down to about 0.5 eV electron energy loss. Measurements of optical gaps are thus possible. Considering the zero-loss peak, an asymmetric Pearson VII function was fitted to the experimental zero-loss peak and subtracted from the spectra. The spectra were further corrected for multiple scattering. Processing of the spectra was done using the electronic structure tools (EST) running on GRAMS software.

11:00 AM M6.7

Power Spectrum of Blinking Quantum Dots.

Matthew Pelton, David Grier and Philippe Guyot-Sionnest; James Franck Institute, University of Chicago, Chicago, Illinois.

The potential of colloidal semiconductor nanocrystals, or quantum dots (QDs), for optical applications is currently limited by intermittency, or "blinking" in their fluorescence. In order to characterize this blinking, we measured the power spectral density of the fluorescence from single QDs. The dots were seen to exhibit 1/f-type noise. This is consistent with previously reported autocorrelation functions and probability distributions of fluorescing and non-fluorescing periods, but is more straightforward to calculate and interpret. The power spectrum also has the advantage of being independent of the number of particles investigated, meaning that it can be measured on ensembles of dots. This allows blinking to be observed in cases where microscopy is impractical, such as measurements of QDs suspended in solution. We have observed similar power spectra for dots in solution and dots on a glass slide, indicating that the blinking behavior is insensitive to the QD environment.

11:15 AM M6.8

EELS study of Colloidal II-VI Semiconductor Quantum Dots.

Zhiheng Yu[1], Hui Du[2], Li Guo[2], Todd Krauss[2] and John Silcox[3]; [1]Physics Department, Cornell University, Ithaca, New York; [2]Chemistry Department, Rochester University, Rochester, New York; [3]School of Applied and Engineering Physics, Cornell University, Ithaca, New York.

Electron energy loss spectroscopy (EELS) is an important tool for the study of the electronic structure and chemical composition of materials. Colloidal II-VI semiconductor quantum dots (QDs) have been a strong research focus due to their interesting electronic and optical properties and potential for a wide range of applications. We have used EELS to study interactions between colloidal PbSe QDs and the shell structure of core-shell CdSe/ZnS QDs. It is widely known that QDs can be self assembled into organized superlattices. In this case, interactions between neighboring QDs should exist. Colloidal PbSe QDs stored in hexane were deposited onto a thin carbon film covered copper grid and studied with a VG HB501 100kV UHV STEM. Regions of a well-patterned hexagonal superlattice formed by a single monolayer of QDs (clustered QDs) and regions of well-separated QDs (single QDs) were found. EELS spectra in the low-loss region (0-60 eV) are obtained from both clustered QDs and single QDs. In both cases the two strongest peaks that were observed are the bulk plasmon peak (a collective response of valence electrons in the QDs to the incident electron beam) at 15 eV and the Pb O4,5 edge at 23 eV. However, for the two cases the relative intensity of these two peaks is very different. For single QDs the plasmon peak is much stronger than the Pb O4,5 edge, whereas the reverse is seen in the clustered QDs. Due to superior surface passivation, core-shell CdSe/ZnS QDs have shown increased quantum efficiency of photoluminescence by an order of magnitude over core CdSe QDs. EELS was employed to check the distribution of the shell material (ZnS) in the QDs. Localized spectra with sub-nm spatial resolution from various positions of individual QDs show the existence of sulfur in the QDs, and allow for a determination of the ZnS shell uniformity and thickness.

11:30 AM M6.9
Temperature Effects on Quantum Dots for Solid State Lighting Applications. Billie L. Abrams, Lauren Rohwer, Jess Wilcoxon and Steven Thoma; Sandia National Labs, Albuquerque, New Mexico.

Thermal quenching behavior of CdS and CdSe quantum dots (QD) in solution was compared to QDs embedded in polymer matrices. Due to the fact that light emitting material in close proximity to an LED die will experience a temperature rise on the order of 50-150oC, it is important to understand the effects of temperature on light emission. It is also important that the quantum efficiency of the quantum dots be maintained at these elevated operating temperatures. The photoluminescent (PL) emission of CdS and CdSe quantum dots can be tuned by controlling the surface properties. A series of CdS and CdSe quantum dots (2-3 nm in size) with different surface properties were first studied in solution. These QDs were then embedded in polymers, e.g., epoxy, silicone. The QDs in solution form and in the polymer matrix form were subjected to temperature cycling from room temperature to 100oC. Thermal quenching temperatures (defined as the temperature at which the PL is 50% of the original PL) ranging from 75oC to 100oC were measured. The thermal quenching temperatures was highly dependent upon what type of surfactant was used to pacify the surface of the QD (i.e., AOT vs. TOPSe). Upon cooling back to room temperature the PL intensity and position was fully recovered for both the quantum dots in solution and in the polymer matrix. PL and PLE (PL excitation) were taken during the heating and cooling cycles in a SPEX Fluorolog II spectrometer using a Xe arc lamp as a light source. Theoretically, QDs should not exhibit thermal quenching since the vibrational lattice modes are not present. However, since the emission of the quantum dots depends upon the surrounding surface chemistry, a new path of thermal degradation becomes apparent. The bonds between the quantum dots and the surrounding organic ligands may be adversely affected by increased temperature leading to thermal quenching of PL. This suggests that ligand bond strength plays an important role. The effects of prolonged temperature exposure inducing ligand bond breaking and QD aggregation are also presented. Possible ways to decrease thermal effects on the PL of these quantum dots will be discussed. Acknowledgments: 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.

11:45 AM M6.10
Polymer/tetrapod Photovoltaic Devices. Baoquan Sun, Henry J. Snaith, Anoop S. Dhoot, Sebastian Westenhoff, Carlos Silva and Neil C. Greenham; Department of Physics, University of Cambridge, Cambridge, United Kingdom.

Blends of conjugated polymers and semiconductor nanoparticles are attractive for use in solution-processed thin-film photovoltaic devices, since nanoparticles act as excellent electron acceptors from photoexcited conjugated polymers. Efficient photovoltaic operation requires not only efficient charge separation, but also effective transport of charges to the appropriate electrodes. The use of nanorods has significantly improved efficiencies, but these rods are able to lie parallel to the plane of the film, leading to non-optimal charge transport to the electrodes. Here, we use CdSe tetrapods as electron acceptors, since these three-dimensional particles are unable to lie flat within the plane of the film and hence can allow electron transport over large distances perpendicular to the plane. We use spectroscopic techniques to study the dynamics of charge separation and recombination in these systems, and we also control the deposition conditions in order to optimize the photovoltaic performance. Using a slow-evaporating solvent we obtain vertical phase separation in the films, which improves the power conversion efficiency. Using a poly(*p*-phenylenevinylene) derivative as the polymer component, we achieve solar power conversion efficiencies in excess of 3% under AM1.5 1 sun conditions,
comparable with the best reported polymer-based photovoltaic devices.

SESSION M7: Semiconductor Quantum Dots II
Chairs: Nickolas Kotov and David J. Norris

Wednesday Afternoon, April 14, 2004
Room 3001 (Moscone West)

1:30 PM *M7.1
In Vivo Imaging with Quantum Dots. David J. Norris, Dept. of Chemical Engineering & Materials Science, University of Minnesota, Duluth, Minnesota.

While fluorescent semiconductor quantum dots (nanocrystals) promise to revolutionize biological imaging, their use has been limited by difficulties in obtaining quantum dots that are bio-compatible. Recently there have been several new strategies that try to address this problem. Here, I will discuss our approach. We found that, by encapsulating individual quantum dots in phospholipid block-copolymers, bio-compatibility could be obtained. We then demonstrated both in vitro and in vivo fluorescent imaging with such quantum dots. When conjugated to DNA, the quantum dots act as in vitro fluorescent probes to hybridize to specific complementary sequences. More importantly, when injected into Xenopus (frog) embryos, the quantum dots are stable, non-toxic (below 5x109 nanocrystals per cell), cell autonomous, and slow to photobleach. The quantum dot fluorescence can also be followed to the tadpole stage, allowing lineage tracing experiments in embryogenesis. Our experiments demonstrate that very simple approaches to producing bio-compatible dots are possible and that the resulting nanomaterials should have a high impact in biological imaging.

2:00 PM *M7.2
A Quantum Dot Nanoconjugate Toolbox. Sandy Rosenthal, Vanderbilt Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

We have developed fluorescent quantum dot probes based on small molecule, peptide, and antibody conjugates for labelling specific cell surface receptors which are significant in neuroscience, infectious disease, and cancer. Physical and biological characterization of the probes will be discussed in the context of designing highly fluorescent, selective, and active nanoconjugates. Several examples of cell surface receptor labelling will be presented.

2:30 PM M7.3
Organizing Colloidal Nanostructures at Multiple Length Scales. Yi Cui[1], Alexander Liddle[2] and Paul Alivisatos[1,2]; [1]Chemistry, University of California, Berkeley, Berkeley, California; [2]Materials Science Division, Lawrence Berkeley National Lab, Berkeley, California.

Controlled organization of colloidal nanostructures in multiple length scales is critical in developing nanotechnology for nano-electronics and photonics although it remains a big challenge. Here we demonstrate a facile method utilizing the capillary interaction at the nanostructure suspension-air-substrate contact interface. Nanostructures were organized selectively into lithographically defined templates, showing the ordering at nm to mm length scale. The number and geometry of nanostructures in the single template under equilibrium assembly are determined by the size of nanostructures and templates. Significantly, this approach was successfully applied to extremely small particle sizes - down to 2 nm diameter, complex shape nanostructures such as nanotetrapods and nanostructures of any materials. This assembly method offers large advantages over electric or magnetic field assembly which relies upon specific susceptibilities. In addition, electronic and plasmonic devices fabricated by this method are demonstrated. This approach offers a facile and general way for integrating wet chemical nanostructures with lithographically prepared devices and could be scaled up to wafer-size process for a large scope of functional nanoelectronics and nanophotonics applications.

3:15 PM M7.4
New Synthetic Strategies for Nanosized Phosphors Based Upon Semiconductor Quantum Dots. Jess Patrick Wilcoxon, Stephen Woessner, Billie Abrams, Stephen Thoma and Lauren Rohwer-Shea; 1122, Sandia National Laboratories, Albuquerque, New Mexico.

A defining aspect of nanosize materials is the presence of an enormous fraction of surface atoms. These surface species and their chemical interactions with surface passivating agents affect properties like absorbance, photoluminescence, (PL) and magnetic response. Concepts employed in solid state physics which assume significant translational symmetry (e.g. direct vs. indirect bandgaps) become less relevant and inorganic clusters behave more like large molecules, with discrete densities of states. For this reason, the optical properties of even dilute dispersions of nanoclusters are strongly affected by the embedding medium. We discuss experimental studies of the effect of organic passivating agents and coordinating solvents on the absorbance and PL properties of semiconductor nanoparticles such as CdS, CdSe, and Si. Among the interesting results reported is a large

dependence of the PL efficiency and energy on solvent, organic passivator, and also inorganic ions (e.g. Cd(II)). Perhaps, even more interesting is the significant effect of these interface factors on the absorbance excitonic features (e.g. linewidth), demonstrating that such features cannot be predicted just from the known the mass (size) of the cluster. Chemically specific chromatographic separation is used to demonstrate that even clusters with identical band-gaps, can have distinct chemical properties and absorbance features.
Acknowledgment: This work was supported by the Division of Materials Scientce and Engineering, Office of Science, US Department of Energy under contract DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

3:30 PM M7.5

Self-Assembling PbSe Nanocrystal Superlattices on an Organic Semiconductor Contact. Jonathan Stephen Steckel[1], Seth Coe-Sullivan[2], Vladimir Bulovic[2] and Moungi Bawendi[1]; [1]Chemistry, MIT, Cambridge, Massachusetts; [2]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

Control of the placement of nanocrystal quantum dot (QD) monolayers over large areas is essential to the development of QD-based optical and electronic devices. We previously demonstrated that large area (cm^2) and well defined layered structures of semiconductor QDs enabled the creation of efficient hybrid organic/inorganic QD light emitting devices (LED). This was achieved by isolating the role of the QDs in the LED luminescence processes from their participation in charge conduction. The monolayer formation is governed by phase segregation between the QDs, which are functionalized with aliphatic capping groups, and the aromatic organic molecules, during a single spin-casting step. In contrast to these first studies where the crystalline QD domains were only $0.09\mu m^2$, we now demonstrate domains as large as $4\mu m^2$. This enhanced order is primarily enabled by advances in the colloidal synthesis of PbSe nanocrystal QDs which yield samples with size distributions narrower than $\sigma = 5\%$. Additionally, the use of slower drying solvents contributes to larger grains. Grain boundaries and defects (ie line dislocations, vacancies, interstitial defects) similar to those found in atomic and molecular crystals are observed in these two-dimensional superlattices. Near infrared emitting PbSe QD-LEDs are fabricated using this new material synthesis and device assembly process.

3:45 PM M7.6

Boron-based Nanostructures: Synthesis and Characterization. Terry T Xu[1], Jianguo Zheng[2], Nianqiang Wu[2], Alan W Nicholls[3], John R Roth[3], Dmitriy A Dikin[1] and Rodney S Ruoff[1]; [1]Mechanical Engineering, Northwestern University, Evanston, Illinois; [2]NUANCE Center, Northwestern University, Evanston, Illinois; [3]Research Resource Center, University of Illinois at Chicago, Chicago, Illinois.

Boron-based nanostructures were synthesized by pyrolysis of diborane (B_2H_6) at elevated temperature and low pressure. Boron-based nanostructures having different morphology were obtained, depending on whether catalysts were used in the experiment or not. Catalyst-free growth of single crystal α-tetragonal boron nanoribbons was observed at 600-750°C and 200 mtorr pressure, with 2.5 vol % diborane in argon. Amorphous tube-like boron nanostructures were synthesized by using Au or Pt/Pd alloys as catalysts. The as-synthesized nanostructures were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), secondary ion mass spectrometry (SIMS), and FT-IR. The elemental composition of these B nanostructures will be presented, as small percentages of C and O have been observed by several of these analytical techniques. Possible mechanisms for the growth of these nanoribbon or nanowire/nanotubes, will also be presented. We appreciate the support of the National Science Foundation (grant EEC-0210120), and the Office of Naval Research grant (No. N000140210870).

4:00 PM *M7.7

Nanoparticle Self-Assembly: A New Synthetic Approach to Semiconductor Nanowires. N. Kotov, Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Nanoparticles of CdTe were found to spontaneously reorganize into crystalline nanowires upon controlled removal of the protective shell of organic stabilizer. The intermediate step in the nanowire formation was the formation of pearl-necklace aggregates, in which the nanoparticles were aligned due to the strong dipole-dipole interaction. These linear aggregates subsequently recrystalized into nanowires whose diameter was determined by the diameter of the nanoparticles. The produced nanowires have high aspect ratio, uniformity, and optical activity. It was demonstrated that the similar nanoparticle-to-nanowire assembly procedure can be observed for different materials such as Ag, CdSe, and ZnO. The luminescence images of the single nanowires of different diameters had been obtained. These findings demonstrate (1) the collective behavior of nanoparticles and (2) a convenient simple technique for production of one-dimensional semiconductor colloids suitable for subsequent processing into quantum-confined superstructures, materials and devices. The formation of nanowires was modeled by Monte-Carlo simulation approach taking advantage of the mathematical description of the force field around proteins and large colloidal particles. The formation of the nanoparticle chains from the colloid was demonstrated. At the same time, the dipole-dipole interaction alone appears to be insufficient to induce the formation of long (100s of nanoparticles) long pearl necklace agglomerates. The produced nanowires were subsequently modified by different techniques and simple elements of electronic circuits were produced. The potential of organization of nanowires into assemblies for nanolelectronics and photonics will be discussed.

SOMIYA AWARD TALK

4:30 PM *M7.8

Carbon-Assisted Synthesis of Inorganic Nanowires. C.N.R. Rao, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India; A. K. Cheetham, Materials Research Laboratory, University of California, Santa Barbara, CA.

Nanowires of a variety of inorganic materials such as metal oxides, sulfides, nitrides and carbides have been synthesized and characterized in the last three to four years. Among the several strategies developed for the synthesis of these materials, the carbothermal route is noteworthy since it provides a general method for preparing crystalline nanowires of many of these materials, which include oxides such as ZnO, Al_2O_3 and Ga_2O_3, nitrides such as AlN and Si_3N_4, and carbides such as SiC [1]. The method involves heating a mixture of an oxide with carbon in an appropriate atmosphere. This approach has enabled the synthesis of crystalline nanowires of both silica and silicon. In the case of GaN, it has been possible to dope it with Mn, Mg and Si to bestow useful optical and magnetic properties. In this short talk, highlights of the recent results on the carbon-assisted synthesis of inorganic nanowires are presented. [1] C.N.R. Rao, G. Gundiah, F.L. Deepak, A. Govindaraj, and A.K. Cheetham, J. Mater. Chem. 14, 440 (2004).

SESSION M8: Poster Session: Semiconductor Dots and Wires

Chair: Gullia Galli
Wednesday Evening, April 14, 2004
8:00 PM
Salons 8-9 (Marriott)

M8.1

Optical Properties of Polaronic Excitons in Quantum Dots. Jozef T. Devreese, TFVS, Departement Natuurkunde, Universiteit Antwerpen, Antwerpen, Belgium.

Numerous experiments on photoluminescence and Raman scattering reveal a surprisingly high probability of phonon-assisted optical transitions in quantum dots. For some cases, attempts to interpret these experiments on the basis of the adiabatic theory meet considerable difficulties. Namely, the calculated values of the Huang-Rhys factor often appear to be significantly (by one or two orders of magnitude) smaller than those derived from experiment. Moreover, some experimental spectra cannot be described by a Franck-Condon progression, predicted by the adiabatic theory. In this context, we introduced a theory of optical transitions in semiconductor quantum dots, which relies on two key building stones. First, we emphasize, that the exciton-phonon system in a quantum dot can be essentially non-adiabatic [1]. The interaction of an exciton in a degenerate state with phonons results in internal non-adiabaticity, while the existence of exciton levels separated by an energy smaller than or comparable with the LO-phonon energy leads to external non-adiabaticity. Starting with the Feynman ordered-operator calculus, we have developed an approach to calculate the absorption coefficient taking non-adiabaticity into account [1]. Using a diagrammatic technique, we have obtained for the matrix elements of the evolution operator a closed set of algebraic equations [2], which describe the effect of non-adiabaticity both on positions and intensities of absorption peaks. Calculations of the absorption spectra provide useful data for analysing the photoluminescence spectra of polaronic excitons in quantum dots [1,2]. Within our approach, we are able to take into account the interaction of an exciton with phonon modes of different frequency, which are present in quantum-dot structures. These phonon modes and the Hamiltonian of the electron-phonon interaction are obtained using the multimode dielectric continuum model [3], which constitutes the second key ingredient of our theory. Taking into account the effects of non-adiabaticity, it is possible to interpret quantitatively experiments on photoluminescence and Raman scattering in numerous quantum-dot structures: spherical CdSe and PbS nanocrystals [1,3], self-assembled InAs/GaAs and CdSe/ZnSe quantum dots. This work has been performed in collaboration with V. M. Fomin, E. P. Pokatilov, V. N. Gladilin, S. N. Klimin and S. N. Balaban. It has been supported by the IUAP, GOA BOF UA 2000, FWO-V projects No. G.0274.01 and the WOG WO.025.99 (Belgium), and the European Commission GROWTH Programme, NANOMAT project, contract No. G5RD- CT-2001-00545. [1] V. M. Fomin, V. N. Gladilin, J. T. Devreese, E. P. Pokatilov, S. N. Balaban, and S. N. Klimin, Phys. Rev. B 57, 2415 (1998). [2] V. N. Gladilin, S. N. Klimin, V. M. Fomin, and J. T. Devreese, to be published. [3] E. P. Pokatilov, S. N. Klimin, V. M. Fomin, J. T. Devreese, and F. W. Wise, Phys. Rev. B 65, 075316 (2002).

M8.2

Optical Properties of Wurtzite GaN and ZnO Quantum Dots. Vladimir Fonoberov and Alexander Balandin; Nano-Device Laboratory, Department of Electrical Engineering, University of California - Riverside, Riverside, California.

Wurtzite GaN/AlN and ZnO quantum dots have recently attracted attention as promising nanostructured materials for optoelectronic applications. Optical properties of quantum dots strongly depend on the dot size. Although the band gap energy for GaN and ZnO is nearly the same (about 3.5 eV), the optical properties of GaN/AlN and ZnO quantum dots are different. The main difference in optical properties of these quantum dots comes from the presence of strong strain and piezoelectric fields in GaN/AlN quantum dots and absence of those fields in ZnO quantum dots. Using a theoretical approach developed by us in Ref. [1], we investigate exciton states in wurtzite GaN/AlN and ZnO quantum dots. A strong piezoelectric field in GaN/AlN quantum dots tilts conduction and valence bands, thus pushing the electron to the top and the hole to the bottom of the GaN/AlN quantum dot. As a result, the exciton ground state energy in GaN/AlN quantum dots with heights larger than 3 nm exhibits a red shift with respect to bulk GaN energy gap. The radiative decay time of the red-shifted transitions is large and increases almost exponentially from 6.6 ns for quantum dots with height 3 nm to 1100 ns for the quantum dots with height 4.5 nm. On the contrary, the electron and the hole are not separated in ZnO quantum dots. The latter fact leads to a very large exciton and biexciton binding energies as well as strongly different size dependence of the radiative decay time in ZnO quantum dots. The results of our multiband calculations are in good agreement with available experimental data and can be used to optimize parameters of wurtzite quantum dots for the optoelectronic applications. This work is supported in part by the NSF-NATO 2003 award to V. A. F. and by the ONR Young Investigator Award N00014-02-1-0352 to A. A. B. [1] V. A. Fonoberov, E. P. Pokatilov, and A. A. Balandin, J. Nanosci. Nanotech. 3, 253 (2003); V. A. Fonoberov and A. A. Balandin, J. Appl. Phys. 94, to appear (2003).

M8.3

In Situ Oriented Grain Growth of SnO2 Nanoparticles Into SnO2 Nanoribbons. Caue Ribeiro, Eduardo Jian Hua Lee, Tania Regina Giraldi, Rosiana Aguiar, Edson Roberto Leite and Elson Longo; Chemistry Dep, Federal University, Sao Carlos, Sao Carlos, Brazil.

The use of nanostructures as building blocks for the preparation of devices is a topic of great interest, due to the possibility of manufacturing materials with potential for novel applications in several fields. In this work we show the oriented grain growth of SnO2 nanoparticles and the attachment of these nanoparticles into SnO2 nanoribbons. Tin dioxide is a well-known material with applications in varistors, gas sensors, catalysts, etc. The SnO2 nanoparticles (with mean particle radius of approximately 2 nm) were prepared by the hydrolysis reaction of dihydrate tin chloride (II) at room temperature. The nanoribbons were synthesized by the condensation of carbothermal-evaporated tin dioxide powders. The morphology characterization and growth experiments were done by means of high resolution transmission electron microscopy (HRTEM). First of all, the nanoparticles and nanoribbons were characterized separately, in order to gather morphological information. Afterwards the nanoparticles and nanoribbons were mixed and irradiated by the electron beam to induce the oriented attachment of the particles into the surface of the nanoribbons. It could be observed that the electron beam induced the growth of the nanoparticles. The morphological changes were relatively fast and resulted in elongated oriented particles with a higher mean particle radius. The oriented attachment of the particles into the nanoribbons was also observed, and the resulting morphology differed a lot from the pure nanoribbons. Defects related to imperfect oriented attachment, such as dislocations and twin boundaries, were present at the nanoparticle-nanoribbon interface. The results of the experiments indicated that the electron beam irradiation induced grain growth by the oriented attachment between particles of similar orientation. This is a very interesting result since it shows the feasibility of assembling oriented nanoparticles into substrates.

M8.4

Observation of small-angle Rotation in individual colloidal CdSe Quantum Rods. Zhiheng Yu[1], Megan Hahn[2], Jack Calcines[2], Todd Krauss[2] and John Silcox[3]; [1]Physics Department, Cornell University, Ithaca, New York; [2]Chemistry Department, University of Rochester, Rochester, New York; [3]School of Applied and Engineering Physics, Cornell University, Ithaca, New York.

Due to their unique optical and electronic properties, colloidal CdSe quantum rods (QRs) are highly promising novel materials that are poised to have a technological impact. The optical and electronic properties of an individual QR depends strongly on its size, shape and internal structure. Therefore, investigations of the internal crystalline structure of individual QRs hold significant importance. CdSe QRs with diameters of 5-6 nm and aspect ratios from 1:10 to 1:16 were imaged with a Cornell VG HB501 100kV UHV STEM. A small probe with a FWHM of 0.2 nm and a convergent angle of 10 mrad was used to obtain high-resolution lattice images. A broad probe with a FWHM of 2 nm was employed to get localized nanodiffraction patterns on certain places of individual QRs. The high-resolution images of some QRs show changes of the lattice patterns along their long axes with some portions appearing as two-dimensional lattice and some portions as a one-dimensional lattice. This is a sign of orientation or lattice structure changes along those rods. Nanodiffraction patterns from various portions of individual QRs clearly show that the QRs have wurtzite structure all the way along their long axes. The relative intensities in the nanodiffraction patterns along a single QR often change from place to place. The nanodiffraction pattern associated with the two-dimensional lattice portion is symmetric indicating that portion is aligned close to a zone axis. The nanodiffraction pattern associated with the one-dimensional lattice is asymmetric suggesting that portion is tilted off the zone axis. The direction of the tilt axis and the magnitude of the tilt was obtained using a multislice simulation. A simulated QR can be rotated about an arbitrary axis for an arbitrary angle and the resultant nanodiffraction pattern at each position can be simulated. By matching the simulated nanodiffraction patterns with the experimental ones, we find some relative rotations exist from point to point on individual QRs. The rotation angle is basically small (only 2-3 degrees) and the rotation axis may have a substantial angle with the long axis of the rod. That means there exists small angle twisting as well as bending in individual QRs.

M8.5

Multiscale modeling of a 3-dimensional superlattice of quantum dots. Vinod K. Tewary, Materials Reliability Division, NIST, Boulder, Colorado.

Currently there is a strong scientific and technological interest in the self assembly of 3-dimensional arrays of nanoparticles such as quantum dots that are the nanoscale building blocks for fabrication of devices. The self assembly is largely determined by elastic interaction energy between the nanoparticles, which is a collective property of the extended structure formed by the assembly of nanoparticles. The elastic interaction is usually calculated by using the continuum model which is not exactly valid for nanoparticles because the discrete lattice effects are significant at the nanoscale. In this paper, a fully discrete lattice calculation at the atomistic scale is presented for the lattice distortion caused by a quantum dot in a semiconductor, its elastic interaction with another quantum dot, and the total elastic energy of a 3-dimensional array of quantum dots. A block lattice model is described in which the crystal lattice is divided into blocks, each consisting of a finite number of lattice sites. The interaction between the blocks is calculated by summing over the interatomic potential between all the atoms in the blocks. The summation is carried out by using an efficient algorithm in the reciprocal lattice space. A quantum dot is created by replacing a block of the host lattice by a block of foreign atoms constituting the quantum dot. The defect-lattice Green's function is then calculated by solving the discrete lattice Dyson equation which gives the lattice distortion due to a single quantum dot and the elastic interaction between two dots. The elastic energy of the entire array is then calculated by summing over all the quantum dots forming the array by using the summation algorithm in the reciprocal space. The minimum of the energy gives the equilibrium spacing between the quantum dots. Numerical results will be presented for cuboidal Ge dots in Si using the modified embedded atom potential.

M8.6

Piezoelectric characterization on individual zinc oxide nanobelt under atomic force microscope. Minhua Zhao[1], Zhong Lin Wang[2] and Scott X. Mao[1]; [1]Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Individual zinc oxide nanobelt that grows along a-axis, with the dimension of hundreds of nanometer in width, tens to hundreds of nanometer in height and tens of micron meter in length, is a promising piezoelectric material for nano-sensor and nano-actuator application due to its perfect single crystalline structure and free of dislocation. An atomic force microscope(AFM) is used to measure the effective piezoelectric coefficient (d_{33}) of individual zinc oxide nanobelt lying on conductive surface. Measurements on x-cut single-crystal quartz(as a piezoelectric standard), (0001) bulk ZnO and individual zinc oxide nanobelt are performed with a conducting AFM tip in contact mode using function generator and lock-in amplifier. The measured piezoelectric coefficients of x-cut quartz and (0001) ZnO bulk are in a reasonable range, while piezoelectric constants measurement on ZnO nanobelt is frequency dependent and varies from 14.3pm/V to 26.7pm/V, which is much larger than the bulk single crystalline ZnO of 12.4pm/V. The results support the application of ZnO nanobelts as nano-scale sensors and actuators.

M8.7

Synthesis of one-dimensional cadmium sulfide by a novel hydrothermal process. Deren Yang, Hui Zhang, Yujie Ji, Xiangyang Ma, Shengzhong Li and Duanlin Que; State Key lab of Silicon Materials, Zhejiang University, Hangzhou, China.

Over the past decade, one-dimensional (1D) nanostructured materials have sparked a worldwide interest because of their unique electronic, optical, and mechanical properties and their potential applications in nanodevices and functional materials. Many methods have been employed to prepare one-dimensional nanostructure materials. Among them, chemical methods, i.e. bottom to up approach, provide a more promising direction to the synthesis of nanostructures due to the low cost, high effective and potential for large-scale production. Recently, Qian et al. has reported a solvothermal synthesis of CdS nanorods using enthylenediamine as the solvent [1]. However, it is inevitable to use toxic, dangerous and expensive solvent in the solvothermal process. Therefore, we have presented a thioglyeolic acid (TGA) assisted hydrothermal method to prepare one-dimensional chalcogenides including CdS nanorods, Bi2S3 nanowires, SnS2 nanobelts, and PbS nanorods, which is milder, simpler, more practical, and more environmentally friendly in comparison with the solvothermal method [2-3]. As we know, many growth conditions in the hydrothermal process can affect the morphology and structure of CdS. Herein, we will mainly investigate the effect of sulfur source on the morphology and structure of CdS. Scanning electron microscopy (SEM) and transmission electron microscopy image (TEM) indicate that the morphology of CdS with nanorods, wiskers, and nanobelts have been observed using Na2S, TGA, and thiourea as sulfur source, respectively. Moreover, X-ray diffraction pattern (XRD) reveals that CdS nanostructures with different phases have been prepared by TGA-assisted hydrothermal process using different sulphur source. Furthermore, the effect of temperature and complexing agents on the morphology and structure of CdS have also been investigated. Finally, we discuss the mechanism of the TGA assisted hydrothermal process synthesis of CdS nanostructures. Reference (1) Xie, Y. Huang, J. Li, B. Liu, Y. Qian, Y. Advanced Materials 2000, 12, 1523. (2) Hui Zhang, Xiangyang Ma, Yujie Ji, Jin Xu, Deren Yang, Chemical Physics Letters 377 (2003) 654 (3) Hui Zhang, Yujie Ji, Xiangyang Ma, Jin Xu and Deren Yang, Nanotechnology 14 (2003) 974

M8.8

Abstract Withdrawn

M8.9

Electrical Behavior and Surface Chemistry of Semiconductor Nanoparticles: In situ FTIR Spectroscopy as a Dual-purpose Characterization Technique. Marie-Isabelle Baraton[1] and Lhadi Merhari[2]; [1]SPCTS UMR CNRS 6638, University of Limoges, Limoges, France; [2]CERAMEC, Limoges, France.

At the nanometer scale, the electronic properties of semiconductor materials are no longer determined by bulk effects but essentially by surface effects, that is by the nature of surface adsorbates and contaminants. It has indeed been shown that the electrical conductivity at the nanometer scale is dependent on surface inhomogeneities, surface impurities, surrounding media, etc. The dependence of the electrical properties upon surface chemical composition can be taken advantage of to tailor the conductivity of semiconductor nanoparticles by surface functionalization. As a consequence, surface control becomes a critical issue to ensure the reproducibility and thus the commercial viability of any device based on semiconductor nanomaterials. In this work, we explain how Fourier transform infrared spectroscopy can help taking up the challenge by allowing the characterization of the surface chemical species and surface chemical reactivity simultaneously with the evaluation of the electrical conductivity of semiconductor nanoparticles. Comparative results obtained on SnO2, In2O3 and WO3 nanoparticles are presented and, as examples, applications of the technique in the field of chemical gas sensors are described. This work has been partly funded by the European Commission under the "Information Society Technologies" programme (contract number IST-12615).

M8.10

The influence of core capping interaction on the luminescence of II-IV quantum dots. Sander Wuister, Arie van Houselt, Celso de Mello Donega, Andries Meijerink; Chemistry, Utrecht University, Utrecht, Netherlands.

For the preparation of efficiently luminescing quantum dots a good surface passivation is crucial. The choice of the capping molecules determines not only the kinetics of the quantum dot formation, but also passivates dangling bonds at the surface of the quantum dot. The temperature dependent efficiency and decay curves of efficiently luminescing CdSe quantum dots were measured. A gradual quenching the luminescence was observed above 20K and a surprising recovery of the luminescence around 250K. The original TOP/TOPO/HDA capping of the efficiently luminescing CdSe quantum dots was replaced by various alkylamines with chain lengths. The recovery of the luminescence and luminescence decay time is observed to depend systematically on the chain length of the alkylamine capping molecules: for shorter chains the recovery happens at a lower temperature then for longer chains. This indicates that a phase transition in the capping is responsible for the recovery of the luminescence. A comparison is made to the temperature dependent phase behaviour of bulk and self assembled monolayers of alkylamines. In addition, our results show how chemical exchange of the capping provides control over the temperature-dependent optical properties of QDs.

M8.11

Local-field effects on the spontaneous emission rate of CdTe quantum dots in dielectric media. Sander Wuister, Celso de Mello Donega, Andries Meijerink; Chemistry, Utrecht University, Utrecht, Netherlands.

The dependence of the solvent refractive index on the spontaneous emission rate is a important fundamental issue that has already gain at lot of attention from both theoreticians and experimentalists. Different models have proposed to describe the dependence of the solvent refractive index on the radiative lifetime. A lot of insightful work has been done where Eu3+ complexes were used as luminescent species. Here, nanocrystalline CdTe quantum dots (QD's) are used to probe the influence of the solvent refractive index on the radiative decay rate. Due to quantum confinement effects, discrete levels arise at the band edges and as a result semiconductor QD's are also known as artificial atoms. By placing these artificial atoms in media with different refractive indices, an ideal test case is obtained to determine the relation between the radiative decay rate and the refractive solvent index if the QD luminescence is dominated by radiative decay. An important advantage of QD's over Eu3+ is the insensitivity of the radiative decay rate of the exciton emission to changes in the local symmetry since the exciton emission of QD's is a fully allowed electric dipole transition. Highly luminescent CdTe quantum dots with a mono-exponential decay have been used to study systematically the influence of the organic solvent on the radiative decay rate. The experimentally observed influence of non the radiative lifetime is smaller than previously observed for Eu3+ complexes. The results are however in good agreement with a recently developed fully microscopic model for the local-field enhancement of the spontaneous emission rate.

M8.12

Growth mechanism of ZnS nanowires and -structures. Carsten Ronning[1], Christopher Ma[2], Daniel Moore[2], Yolande Berta[2], William Hughes[2] and Zhong Lin Wang[2]; [1]II. Institute of Physics, University of Goettingen, Goettingen, Germany; [2]Dept. of Materials Science & Eng., Georgia Institute of Technology, Atlanta, Georgia.

A variety of different zinc sulfide (ZnS) nanostructures could be grown via thermal evaporation of ZnS powders in a tube furnace. The as-deposited material shows either belt-, saw-, wire-, comb-, or plate-like structures in a nanometer scale depended on the growth parameters. We investigated the morphology and composition by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS) as a function of these parameters, and evaluated the basic growth mechanism. Both will be presented and discussed in this poster. Further, we will demonstrate that using a catalyst (sputtered Au, Au nanoparticles, or tin) has a much more influence on the morphology compared to the above described growth parameters.

M8.13

Synthesis and Characterization of ZnO Nanowires. Chia Ying Lee[1], Tseung-Yuen Tseng[1], Seu Yi Li[2] and Pang Lin[2]; [1]Dept. of Electronics Eng. and Inst. of Electronics, National Chiao-Tung University, Hsinchu, Taiwan; [2]Inst. of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

The ZnO nanowires synthesized by vapor-liquid-solid (VLS) growth mechanism with Cu and Au as the catalyst were investigated. Large differences in morphology between Cu and Au catalyzed ZnO nanowires are observed and lead to significant differences in their field emission and photo fluorescence characteristics. The Cu catalyzed ZnO nanowires with a high-quality wurtzite structure were grown vertically on p-type Si(100) substrate along [0002] direction. A strong ultraviolet (UV) emission at 381 nm is observed. These ZnO nanowires show excellent field emission properties with turn-on field of 0.83 V/μm and corresponding current density of 25 μA/cm^2. The emitted current density of the ZnO nanowires is 1.52 mA/cm^2 at a bias field of 8.5 V/μm. The large field emission area factor, β arising from the morphology of the nanowire field emitter, is partly responsible for the good emission characteristics. The ZnO nanowires with high emission current density and low turn-on field are expected to be used in field emission flat panel display. Furthermore, the tin doped ZnO nanowires were fabricated to study its optical characteristics. The fabrication temperatures ranged from 800 to 920°C depend on the mole ratio of Zn/Sn in the mixture of SnO^2 and ZnO starting powders. The tin doped ZnO nanowires have single crystal structure. A red shift at ultra violet band from 380 to 396 nm was observed for tin-doped ZnO nanowires by the photoluminescence spectra. The green light emissions located at 461 and 502 nm were also observed. The tin plays an important role on the effect of the energy band and the lattice structure of the ZnO single crystal nanowires.

M8.14

Atomistic simulation of fabrication of a single-atom chain from a helical nanowire. S. Kameoka and K. Shintani; Dept of ME & Intelligent Sys, Univ of Electro-Comm, Chofu, Tokyo, Japan.

Metallic nanowires have drawn much attention of researchers since a single-atom chain of gold atoms at a nanocontact between a scanning tunneling microscopic probe and a metal surface was observed. They have some unique properties at nanoscale such as quantized conductance and long bond-length that are not observed for materials at macroscopic scale. Nanowires are probably applicable to wiring and atomic switches in nanocircuits. Understanding their mechanical properties is essential to realization of such applications. Suspended Au nanowires were produced with the electron beam thinning technique in an ultra-high-vacuum (UHV) transmission electron microscope (TEM). It was revealed by high-resolution TEM that these nanowires have multi-shell helical structures. It is well known that carbon nanotubes also have such helical structures and that they are metallic or semiconducting depending on the chirality. Similarly, metallic nanowires are expected to have interesting physical properties owing to their helicity. Although atomistic simulations using the ab initio scheme and tight-binding potential were performed in the literature to investigate the formation mechanism and bond-lenghts of single-atom chains, the nanowire models in these computations have no helical structures, and the effect of helicity on the mechanical properties of nanowires remains unknown. In the present molecular-dynamics study using the modified embedded-atom method potential, model Au nanowires with helical structures are constructed, and their equilibrium structures are addressed first. Next, elongation of the nanowires is simulated to investigate how their helicity affects the formation of single-atom chains.

M8.15

'Ball and Stick' Resolution Imaging: Application of Spherical Aberration Corrected Z-STEM for Characterization of CdSe Nanocrystals. James McBride[1,2], Tadd C. Kippeny[1], Stephen J. Pennycook[2] and Sandra J. Rosenthal[1]; [1]Chemistry, Vanderbilt University, Nashville, Tennessee; [2]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Precise control of nanocrystal morphology is necessary for success in the design of nanocrystal-based structures and devices. For example, desirable characteristics such as a high quantum yield or the ability to spontaneously form long ordered arrays can be adversely affected by very small deviations in structure. One technique, abberation corrected (C_s) Atomic Number Contrast Scanning Electron Microscopy (Z-STEM) has recently demonstrated an amazing ability not only to obtain sub-angstrom levels of detail but also to yeild chemical information at that level. With an optimal probe size of 0.8 Å, extremely detailed images of CdSe nanocrystals were obtained showing lattice structure and surface morphology with 'ball and stick' clarity. As an example of the usefulness of this technique, a sample of CdSe nanocrystals prepared using TOPO as the surfactant was compared to a sample of CdSe prepared using a mixture of TOPO/HDA as the surfactant. The TOPO/HDA nanocrystals exhibit a narrower size distribution and fluorescence that is greater by several orders of magnitude compared to that of the TOPO-only nanocrystals. Interestingly, the Z-STEM images show a striking difference in nanocrystal morphology as the result of the addition of HDA to the reaction mixture. Additionally, C corrected Z-STEM reveals surface morphology differences between the two samples which are undetectable through conventional HRTEM. This result suggests that surface morphology can be tuned through judicious choice of surfactant. A second example of Z-STEM imaging involves the characterization of CdSe/ZnS core/shell nanocrystals. The mass contrast afforded by Z-STEM can easily distinguish between core and shell. Shelling anomalies were seen and attributed to the lattice mismatch between CdSe and ZnS, leading to a modified shelling process to produce uniform, epitaxial shells.

M8.16

Abstract Withdrawn

M8.17

Template-assisted fabrication of dense, ordered nanowire and nanotube arrays on substrates. Melissa S. Sander[1], Matthew J. Cote[2], Le-Shon Tan[1], Han Gao[1], Wei Gu[3] and Carl P. Tripp[3]; [1]Inst. of Materials Research and Engineering, Singapore, Singapore; [2]Chemistry, Bates College, Lewiston, Maine; [3]LASST, Univ. of Maine, Orono, Maine.

Using nanoporous anodic alumina films as templates for deposition, we have produced highly dense arrays of nanoparticles with controllable dimensions directly on substrates. The templates are made by anodizing aluminum films that have been evaporated onto the substrates and can be fabricated on various metal, semiconducting and insulating substrates.[1] To create hexagonally ordered arrays of nanopores, we employ a simple imprinting technique to pre-pattern the Al films before anodization. The resulting nanopores have uniform diameters ranging from 25-90nm, aspect ratios from 1-50, and densities $>10^{10}$/cm^2. Because the nanoparticle dimensions are determined by the pore dimensions in the templates, a variety of deposition methods may be employed to create the nanoparticle arrays. For example, we have used electrodeposition to fabricate gold nanowire arrays with controllable grain structures. In addition, oxide nanotube arrays have been created by atomic layer deposition, which permits sub-nanometer control over the thickness of the nanotube walls. These arrayed nanostructures are aligned perpendicular to the substrate surface and can be fabricated over large areas, which will enable straightforward integration of the arrays into device configurations. [1]M.S. Sander and L.S. Tan, Adv. Funct. Mater. 13, 393 (2003).

M8.18

The control of the crystal growth orientation in GaN nanaowires using different substrates. Yun-Mo Sung, Dae-Hee Kim and Jung-Chul Lee; Materials Sci. & Eng., Daejin University, Kyunggi-do, South Korea.

As a noble III-V semiconductor having a wurzite structure and a wide band gap GaN has been extensively studied for various applications such as laser diodes (LD), light emitting diodes (LED), and photo detectors (PD). Recently, GaN in nanowire forms has brought much attention due to its superior light-emitting and light-detecting properties compared to thin films. However, the crystallographic study for this material has mostly been concentrated on thin film forms. In this study Ni-catalysts were used for the vapor-liquid-solid (VLS) growth of GaN nanowires and substrates of Si(111), AlN/Si(111), and GaN/AlN/Si(111) were used to investigate the effect of substrates on the crystal growth orientation of GaN nanowires. Scanning electron microscopy (SEM) analyses on the GaN nanowires grown on AlN/Si(111) and GaN/AlN/Si(111) substrates showed formation of straight nanowires with 30-80 nm diameter. Transmission electron microscopy (TEM) analyses on the GaN nanowires grown on GaN/AlN/Si(111) showed high crystallinity with low defect concentration. The crystal growth direction of the GaN nanowires grown on GaN/AlN/Si(111) was [1 0 -1] and (101) crystal planes parallel to the nanaowire direction were formed in the nanowires. The (101)-GaN nanaowire arrays grown on GaN/AlN/Si(111) showed strong photoluminescence (PL) emission at the wavelength of 367.2 nm and almost negligible intensity for the yellow luminescence. By introducing buffer layer into Si(111) substrates the crystal growth orientation of GaN nanowires was able to be controlled and the enhanced PL properties were successfully achieved.

M8.19

ZnO nanostructures prepared by different methods. Yu Hang Leung[1], Aleksandra B. Djurisic[1], Wallace C. H. Choy[2], Wai Kin Chan[3] and Kok Wai Cheah[4]; [1]Dept. of Physics, the University of Hong Kong, Hong Kong, Hong Kong; [2]Dept. of Electrical and Electronic Engineering, University of Hong Kong, Hong Kong, Hong

Kong; [3]Dept. of Chemistry, University of Hong Kong, Hong Kong, Hong Kong; [4]Dept. of Physics, Hong Kong Baptist University, Hong Kong, Hong Kong.

ZnO is of great interest for photonic applications due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV). Variety of preparation methods and obtained morphologies (such as nanorods, tetrapod nanorods, nanowires, nanoribbons, hierarchical structures, nanobridges, and nanonails) were reported for this material. In this work, the morphology and optical properties of ZnO nanostructures prepared by three different methods were studied. ZnO nanostructures were prepared by oxidation of Zn (no catalyst) at 950^{o}C, heating of a mixture of ZnO:graphite (1:1) at 1100^{o}C, and chemical method (from solution of zinc nitrate hydrate and hexamethylenetetramine at 90^{o}C). The properties of obtained products were examined using scanning electron microscopy, transmission electron microscopy, selected area electron diffraction, X-ray diffraction, room temperature photoluminescence and electron paramagnetic resonance spectroscopy. Chemical synthesis method produced different morphology compared to heating of Zn and ZnO:C. In the former case, straight rods are obtained, while in the latter case ZnO tetrapod structures are formed. The ZnO tetrapods, both from Zn and ZnO:C, exhibit similar photoluminescence spectra with UV peak and characteristic broad green emission but they have different EPR spectra. The EPR signal g 1.96 is clearly visible in ZnO tetrapods synthesized from ZnO:C, while it is at noise level in ZnO tetrapods synthesized from Zn. Therefore, it can be concluded that the type of intrinsic defects in ZnO nanostructures is strongly dependent on the fabrication conditions, and that the green photoluminescence is not necessarily related to g 1.96 EPR peak which is commonly assigned to shallow donors.

M8.20

Control of Arrayed ZnO Nanorods via Surface Tension in Aqueous Solutions. chin-ching lin and Hung-Pei Chen; Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, Taiwan.

A novel rod-like nano-structure of hexagonal ZnO has been successfully grown on polystyrene (PS)/Si and ZnO(film)/Si by soluthermal method. The arrayed PS and ZnO films were coated on the silicon substrate and used as buffer-layer in this work. Subsequently, ZnO nanorods were perpendicular to ZnO/Si substrate at 75oC in aqueous solutions. In this study, it was found that surface tension of both PS/Si and ZnO films could control the nucleation site and growth mechanism of ZnO nanorods in soluthermal method. Therefore, we presented a new growth mechanism of these ZnO nanorods in this aqueous solutions system. The ZnO nanorods were characterized using X-ray diffraction, scanning and transmission electron microscopy (TEM), and photoluminescence spectroscopy (PL). Depending on the precursor concentration and immobile time, ZnO nanorods having various morphologies and size can be developed. After surface treatment process, these nanorods show strongly UV emission and week deep-level emission on the PL spectroscopy. In addition, we can successfully pattern single crystalline ZnO nanorods on PS/Si substrate by controlling surface tension in low temperature without any catalyst. These arrayed ZnO nanorods can be further used as building blocks to assemble two- or three-dimensional assemblies.

M8.21

Lasing Characteristics of Single Zinc Sulfide Nanoribbons. J A Zapien[1], Y Jiang[1], X M Meng[1,2], Y Lifshitz[1,3] and S T Lee[1]; [1]Center of Super-Diamond and Advanced Films (COSDAF) and Physics and Materials Science, City University of Hong Kong, Hong Kong, SAR, China; [2]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China; [3]On leave from: Soreq Nuclear Research Institute, Javne, Israel.

Zinc sulfide (ZnS) is a promising material for room-temperature ultraviolet lasing applications due to its wide direct band gap (3.7 eV) and the relatively large (40 meV) exciton binding energy. We report the photoluminescence (PL) properties of ZnS nanoribbons prepared by hydrogen-assisted thermal evaporation. The as-prepared ZnS nanoribbons present a wurtzite-2H single crystalline structure, a [120] growth direction, and uniform rectangular cross section (40-100 nanometer thick, 1-5 micrometers wide) and 50-200 micrometers long. We use a single nano-object measurement methodology that enables correlation of the size/morphology/structure, as determined by TEM, with the corresponding PL characteristics of the same single nanoribbon. In particular, we measure the PL characteristics of optically pumped (266 nm, 5 ns pulsed excitation light from the 4th harmonic of a Nd:YAG laser) individual single-crystal zinc sulfide nanoribbons. We show that nanoribbons form excellent optical cavities and gain medium with record (FWHM<0.1nm) lasing modes free of PL background even for a low pumping power density of 9 kW/cm2. Our results show that single ZnS nanoribbons serve as an active medium as well as an optical resonant cavity and a waveguide with very intense, narrow modes with the spacing determined by the nanoribbon length.

M8.22

Highly Luminescent Semiconductor Nanocrystals and Their Applicability to Light Emitting Diode. Shinae Jun and Eunjoo Jang; Electronic material lab, Samsung Advanced Institute of Technology, Yongin-Si, Gyeonggi-Do, South Korea.

Since the semiconductor nanocrystals exhibit tunable luminescence properties from Infrared to UV with change of particle size, they have attracted much attention as applications to light-emitting devices (LED), lasers and biological labels. Among the various kinds of semiconductor materials, the II-VI group semiconductor nanocrystals emitting visible light have been investigated more actively in recent years. In this work, high luminescent CdSeS nanocrystals were synthesized by one-step addition of Se and S source mixture into the Cd precursor solution at elevated temperature. The narrow band edge of photoluminescence emission spectra (FWHM=34nm) of the resulting CdSeS nanocrystal was finely tuned from red to blue region not by change of particle size, but by control of the Se/S ratio in the synthetic mixture. Although used Se amount was extremely small compared to the amount of S, it had critical effect on determining optical properties of resulting products. The colloidal nanocrystals exhibited very homogeneous particle size (5 nm) so that they assembled to form a well-ordered close packed hexagonal array through simple drying. In addition, the nanocrystals showed remarkably improved room temperature photoluminescence quantum efficiency (up to 85%). The spectrally clean and narrow electroluminescence emission from these highly luminescent CdSeS nanocrystal, embedded in traditional OLED structure, was obtained at identical position to the photoluminescence spectrum. The detailed results will be further discussed in the presentation.

M8.23

Cross-linked ZnO nanoparticles by molecular wires in electrically conductive composite materials. Daniel Morel, Raphael Pugin, Syed Imad-Uddin Ahmed and Henry Haefke; Micro and Nanomaterials, CSEM Swiss Center for Electronics and Microtechnology, Inc, Neuchatel, Switzerland.

Semiconductor nanoparticles possess unique size-tunable optical properties. These characteristics make them ideal candidates as building blocks for a variety of next-generation sensor technologies. While much progress has been made in the synthesis and study of direct band gap semiconductor nanoparticles, such as ZnO, linking nanoparticles is still a challenging task. The aim of this study was to prepare a matrix array of ZnO nanoparticles with a high electron conductivity. Using both commercially available as well as in-house synthesized nanoparticles, it is shown that the absorption edge of a material can be shifted to significantly lower wavelengths in the UV range. For the in-house developed particles, by varying the diameter of the ZnO nanoparticles, the absorption wavelength could be blue-shifted from 365 to 315 nm. Commercial nanoparticles did not show shifts of this range due to their relatively large sizes (diameters approx. 20 nm) as well as their broad size distributions. A photocurrent effect of UV light on thin films prepared with nanoparticle assemblies has also been demonstrated. An important result is that in addition to the optical band-gap, the electronic band-gap also depends on the size of the ZnO nanoparticles. Nevertheless, photocurrent intensity remains quite low due to the percolation of the ZnO nanoparticles. This problem must be addressed to make the nanoparticle technology technically viable. Two approaches used in literature were combined to find a unique solution. The first is the cross-linking of gold electrodes by conductive molecular wires [1]. These molecules have a skeleton of conjugate π-electrons, generally aromatic rings and/or ethynyl groups, terminated at both ends by a thiol chemical function, which easily bond with gold. The second is the bonding of zinc oxide nanoparticles with a mono-thiol ligand [2]. This bonding was accomplished by first partially reducing the bonded zinc atoms. Using this technique it was possible to cap ZnO nanoparticles, thus stabilizing them and hindering further growth. In our work, cross-linking of ZnO nanoparticles was accomplished using a di-thiol ligand. Specifically 1,4-benzenedithiol and 4,4'-thiobisbenzenethiol have been used as coupling ligands. As a result, considerable enhancement of the photoelectrical current has now been achieved, bringing this nanoparticle technology closer to technical viability. [1] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science, 278, 252 (1997). [2] E.M. Wong, P.G. Hoertz, C.J. Liang, B.-M. Shi, G.J. Meyer, and P.C. Searson, Langmuir, 17, 8362 (2001).

M8.24

Laterally ordered magnetic EuSe quantum dots. Rainer T. Lechner[1], T. U. Schuelli[1,2], S. Dhesi[2], P. Bencok[2], J. Stangl[1], G. Springholz[1] and G. Bauer[1]; [1]Institut fuer

Halbleiterphysik, Johannes Kepler Universitaet, Linz, Austria; [2]European Synchrotron Radiation Facility, Grenoble, France.

We report on the magnetic behavior of laterally ordered EuSe quantum dots, using x-ray circular dichroism measurements in absorption and scattering geometry. As a template for the deposition of the EuSe islands we use a self organized PbSe quantum dot superlattice template consisting of a period PbSe island multilayer separated by PbEuTe spacer layers is deposited using molecular beam epitaxy. Depending on the thickness of the PbEuTe spacer layer, either a three dimensionally ordered vertically aligned hexagonal PbSe dot superlattice is formed, or a trigonal island superlattice with fcc-like dot stacking. Subsequently, 5 monolayers of EuSe are deposited. As a result two sets of samples with an EuSe island base width of about 70 nm and a height of 14 nm (sample A), and a base width of 50 nm with a height of 12 nm (sample B) are obtained. For the x-ray scattering experiments, which were carried out under UHV conditions at the ID08 beamline of the ESRF, Grenoble, the EuSe islands were capped with amorphous Se in order to prevent oxidation, which was desorbed in the UHV set-up at the beamline, immediately before the scattering experiments were performed.For resonant grazing incidence small angle x-ray scattering (GISAXS) experiments at energies tuned to the Eu-MV edge it was verified, that the lateral satellite peaks originate from the hexagonally ordered EuSe islands and not from the PbSe island template. At photon energies at the Eu-M edge of 1129 eV and at 4eV below we take advantage both of the strong Eu resonance and the extreme surface sensitivity. X-ray magnetic circular dichroism (XMCD) experiments were carried out at the Eu M edges. The resulting magnetization curves at T = 9K differ significantly for sample A and B. From fits with a Brillouin function we obtain for the sample A with the larger islands a value of the magnetic spin moment S = 8, whereas for the smaller islands of sample B a value of S = 7/2, as expected for uncoupled Eu spins is obtained. Despite the fact that the phase transition temperature to anti-or ferrimagnetic state at T < 5 K was not yet reached, we have conclusive evidence for a size dependence of the blocking temperature to superparamagnetism in these strained nanostructures.

M8.25

Controlling The Growth direction of ZnO Nanowires (NWs) on c-Plane Sapphire. Babak Nikoobakht[1], Albert Davydov[2] and Stephan Stranick[1]; [1]Chemistry, NIST, Gaithersburg, Maryland; [2]Metallurgy Division, NIST, Gaithersburg, Maryland.

In this study three types of morphologies are reported for ZnO NWs on c-plane sapphire, namely, vertical nanowires, 60° tilted NWs and vertical NWs on a 2-dimensional ZnO network. We have been able to selectively control the listed morphologies by adjusting the thickness and pre-growth annealing of the Au film. SEM, XRD and AFM have been used as characterization tools. It is found that within a certain range of Au film thicknesses, in the absence of annealing, NWs grow 60° tilted while by annealing the Au films vertical NWs grow instead. XRD for the tilted NWs shows two distinct (101) and (002) diffraction lines verifying two different growth directions while for the standing NWs the (101) line is absent. The presence of the n(002) diffraction lines is a clear evidence of unidirectional growth of NWs on c-plane sapphire which is surprising due to the 18 to 31% mismatch between ZnO and c-sapphire. In this presentation results above in addition to AFM studies on morphology of the Au films will be discussed to further explain the observed structures.

M8.26

Growth and Characterization of ZnO nano-rods on Si substrate by pulsed laser ablation. Ram S Katiyar[1], Vinay Gupta[1], Pijush Bhattacharya[1] and YU I Yuzuk[1]; [1]Department of Physics, University of Puerto Rico, San Juan, Puerto Rico; [2]Departemnt of Physics, University of puerto rico, SanJuan, PR, Puerto Rico.

ZnO nanoclusters and thin films have been shown to exhibit highly efficient ultra-violate (UV) lasing action under the optical pumping. Very recent demonstrations of novel ZnO devices include a nano-scale laser and the electrochemically gated quantum dot transistor. In the present work, the nanorods of ZnO and Zn$_{0.80}$Mg$_{0.20}$O were grown directly on Si (60-300 nm) by pulsed laser deposition technique without using any catalytic template at relatively low processing temperature (450 ^{0}C) and high oxygen pressure (5 Torr). The influence of substrate temperatures and the oxygen pressures on the formation of ZnO nanorods was studied. The diameter of the rods increased with the incorporation of Mg dopant. The only peaks corresponding to (002) and (004) planes were observed at higher substrate temperatures (>400 ^{0} C) indicating that the crystallites were oriented along the c-axis normal to the substrate. The Raman spectroscopy and SEM analysis indicated the formation of well-isolated and vertically aligned nanorods. The Raman modes at 470 and 575 cm^{-1} were observed in the ZnO nanorods and assigned to the lower and upper surface phonon modes respectively. Detailed results on polarized Raman spectra on ZnO nanorods in various configurations will be discussed. The Authors acknowledge the financial support of DOD EPSCoRE grant #F49620-01-1-1004, NASA#NCC3-1034. One of the authors (VG) is also thankful to DST, India, for BOYSCAST fellowship and financial assistance

M8.27

Early Stages of Growth of GaAs Nanowires. Rajarshi Banerjee[1], Arda Genc[1], Arnab Bhattacharya[2], Sujoy Kar[1], Brij Arora[2] and Hamish Fraser[1]; [1]Materials Science and Engineering, The Ohio State University, Columbus, Ohio; [2]Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, Maharashtra, India.

GaAs nanowires have been grown via metal-organic vapour phase epitaxy using the vapour-liquid-solid (VLS) mechanism. These nanowires typically exhibit a circular cross-section with diameters ranging from 10 nm to 50 nm. The defects in these nanowires have been investigated in detail using transmission electron microscopy. Results indicate that the wires predominantly exhibit the zinc blende type diamond cubic structure with the growth axis parallel to <111> and twins perpendicular to the growth axis. The structure of the growth-twins in these nanowires has been investigated in the detail using transmission and high-resolution electron microscopy. The interface between the nanowires and the GaAs substrate has also been investigated and the results suggest the formation of an interesting root-like structure at the early stages of growth of these nanowires. This root-like structure presumably results from defects forming on the {111} planes of the GaAs substrate. These investigations are likely to improve our understanding of the VLS growth process.

M8.28

Growth and Photoluminescent Response of AlGaAs Nanowires. Z. Wu[1], X. Y. Mei[1], M. Sun[1], H. E. Ruda[1], J. Liu[2] and K. L. Kavanagh[2]; [1]Centre for Advanced Nanotechnology, University of Toronto, Toronto, Ontario, Canada; [2]Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada.

Synthesis of semiconductor nanowires has recently attracted a great deal of interest owing to potential applications of these nanowires in electronic and photonic devices. Semiconductor nanowires have been synthesized using chemical beam epitaxy (CVD), metalorganic-CVD, and laser ablation based on the vapor-liquid-solid (VLS) mechanism [1-3]. We have used VLS with molecular beam epitaxy (MBE) to grow single crystal GaAs nanowires [4,5] and have now extended this approach to AlGaAs nanowires. Although AlGaAs is an important material for many device applications, this is the first report on the growth of free-standing, AlGaAs nanowires. The AlGaAs nanowires grew preferentially along <111> directions with uniform diameters determined by the Au dot size. There was a significant difference in the Al composition for VLS-grown AlGaAs nanowires as compared with conventional MBE grown thin films, as determined from photoluminescence (PL) and energy-dispersive x-ray spectroscopy measurements. This is likely due to differences in the growth mechanisms, which we are currently investigating. Although high resolution STEM shows that many of the nanowires have stacking faults, PL emission is easily detectable at a temperature of 4.2 K. We also report on the growth of highly-ordered, AlGaAs-nanowire arrays using nanochannel alumina template-directed VLS growth. Important issues for growing AlGaAs/GaAs multilayers in nanowires are discussed. PL from nanowires containing AlGaAs/GaAs multi-layer structures is presented and clearly shows effects of carrier confinement. References: [1] X. Duan and C.M. Lieber, Adv. Mater. 12, 298 (2000). [2] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, J. Appl. Phys. 77, 447 (1995). [3] M.T. BjÖrk, B.J. Ohlsson, T. Sass, A.I. Persson, C. Thelander, M.H. Magnusson, K. Deppert, L.R. Wallenberg, and L. Samuelson, Appl. Phys. Lett. 80, 1058 (2002). [4] Z.H. Wu, X. Mei, D. Kim, M. Blumin, H.E. Ruda, J.Q. Liu, and K.L. Kavanagh, Appl. Phys. Lett. 83, 3368 (2003). [5] Z.H. Wu, X.Y. Mei, D. Kim, M. Blumin, and H.E. Ruda, Appl. Phys. Lett. 81, 5177 (2002).

M8.29

Aerosol-Assisted Self-Assembly of Silica Particles with hierarchical pore distributions. Zhiwang Wu, J. Eric Hampsey, Jiebin Pang, Qingyuan Hu and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Mesoporous materials are of great interest for catalysis, separation, sensor, fillers and other applications. Mesoporous silica is typically synthesized through co-assembly of inorganic species and surfactant molecules. This approach usually leads to mesoporous silica with pore sizes from 2 to 30 nm. Many applications require the mesopore materials with large pores. In our work, we synthesize mesoporous silica particles with hierarchical pore structures using aerosol-assisted self-assembly technique. This was achieved by atomizing silica sols containing homogenous silicate species, surfactant, and poly (propylene glycol) (PPO). During an aerosol process, solvent evaporated from the droplets enriched the non-volatile components and promote phase separation of PPO, resulting in self-assembly of silica, surfactant, and PPO into 3-dimensional hierarchical structures. Subsequent removal of the surfactant and PPO resulted in silica particles with meso-meso or meso-macro pore structures. These particles exhibit high surface areas and high pore volumes based on nitrogen sorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) characterization. The particles are of great significance for catalyst and other applications.

M8.30

Predicting Growth Morphology of ZnO Crystals from Aqueous Solution Using Molecular Simulation.

Louise J. Criscenti[1], Randall T Cygan[1], Michael L Machesky[2] and James A Voigt[1]; [1]Sandia National Laboratories, Albuquerque, New Mexico; [2]Illinois State Water Survey, Champaign, Illinois.

The design and synthesis of oxide nanostructures for materials applications has become a research area of considerable interest in recent years. In parallel with experimental research to grow zincite (ZnO) crystals of controlled morphologies from aqueous solution, we have successfully used molecular mechanics methods to derive relative binding energies for adsorption of ions to specific ZnO surfaces. To understand how various adsorbates, including citrate, hexamethylene tetramine (HMT), and ethylene diamine, affect crystal growth and nanocrystalline morphologies, we developed representative periodic models for the primary zinc oxide growth surfaces (100), (101), and (001). Surface oxygens were protonated according to the multi-site complexation (MUSIC) model assuming an aqueous solution at 25°C and pH 7. Two-dimensional calculations were used to derive relative binding energies of each adsorbate on each of the zincite surfaces. Each zinc oxide surface was initially equilibrated to allow for surface relaxation, then optimized configurations for each adsorbate-surface system were obtained. Binding enthalpies were derived from the energy difference between the optimized configuration and one in which the adsorbate is appreciably removed from the surface. Some adsorbates like citrate exhibit dramatically different adsorption behavior for each zincite surface, while others like HMT exhibit similar adsorption behavior to all three surfaces considered. These preliminary computational results are consistent with experimental observation, and support the argument that the preferential binding of adsorbates, acting as growth inhibitors, may be used to design customized zincite morphologies. Molecular mechanics simulations to assess the effects of surface protonation as a function of solution pH and molecular dynamics simulations to examine the effects of adsorbate concentration and solvation are in progress. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy National Nuclear Security Administration under contract DE-AC04-94AL85000.

M8.31

Synthesis and Characterization of InN Nanofibers.

Alan D. Berry, Rhonda M. Stroud and Thomas Zega; Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

Recent reports in the literature have described the growth of single-crystal indium nitride nanowires using (1) ammonia and indium at 500C on gold-patterned silicon (100) substrates (APL, 81, 22, 2002) or (2) ammonia and a mixture of indium and indium oxide at 700C on alumina membranes (J.Mater. Chem. 12, 802, 2002). We report here the growth of irregularly-shaped InN fibers with diameters in the range of 100 nanometers and lengths of several microns by passing ammonia over indium at 700-750C and ambient pressure. These fibers appear as a light, fluffy, black solid that has been characterized by X-ray diffraction, SEM, and TEM.

M8.32

On comparison of Wurtzite- and Zinc blende-type CdSe Nanocrystals.

Rongfu Li[1], Jeunghoon Lee[1], Fotis Papadimitrakopoulos[1,2], Dafei Kang[3], David Horspool[3] and Mark Aindow[3]; [1]Institute of Materials Science, Polymer Program, Univ. of Conn., Storrs, Storrs, Connecticut; [2]Department of Chemistry, University of Connecticut, Storrs, Connecticut; [3]Department of Metallurgy and Materials Engineering, Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

Synthesis of CdSe nanocrystals in TOPO/TOP mixture at high temperature (300 degree C) results in monodisperse nanocrystals (< 5% rms in diameter) of wurtzite-type crystal structure. With appropriate surface passivation, highly photoluminescent (PL) CdSe NCs were obtained. The relationship between the PL peak position and the size of the nanocrystals was well established. However, room temperature synthesis of CdSe nanocrystals in water solutions produces nanocrystals of zinc blende-type crystal structure, which show no photoluminescence due to the lack of surface reconstruction and passivation. Through a controlled chemical etching process, we have successfully transformed the non-photoluminescent zinc blende-type CdSe nanocrystals into highly photoluminescent ones. Therefore, chemical etching provides an avenue to investigating the relationship between the PL properties and the crystal structure as well. It will also help provide new experimental data for theoretical studies of the quantum confinement effect in the CdSe nanocrystal system.

M8.33

Evidence of coupling in thin GaAs barrier between InAs self-assembled quantum dots.

euntae cho[1], H. D. Lee[1], J.I. Lee[2] and C. M. Lee[2]; [1]electronics, chungnam national university, Taejeon, Taejeon/Yu song, South Korea; [2]physics, korea research institute of standards & science, Taejeon, Taejeon/Yu song, South Korea.

We studied the optical properties of two layers of InAs self-organized quantum dots (QDs). The QDs were separated by the GaAs barrier with varied the thickness from 2.5 to 20nm. All samples were observed double peaks from low-temperature photoluminescence spectra. The energy difference between two peaks shows that the origin of the double peaks is different for each sample. In case of the thin barrier thickness, the couple of peaks are come from the ground states of lower QD and upper QD. In the thick thickness, the double peaks are originated from the ground and excited states because the barrier is thick enough to separate the double QDs. Also, we observed that the full width half maximum of QDs spectra reduced with decreasing the barrier thickness due to the coupling between the interdots.

M8.34

Characterization of Green Photoluminescence in ZnO Nanowires.

Han-Ho Choi, Joodong Park and Rajiv K. Singh; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Many studies in one-dimensional ZnO materials are being reported due to their importance in basic scientific research and potential applications. ZnO nanowires and nanorods have been synthesized by various methods such as the chemical vapor transport and condensation process, template-based growth method, and wet chemical synthesis and so on. Most of photoluminescence researches have been concentrated on the excitonic emission of UV region for UV device applications until now. On the other hand, the studies on the green emission of ZnO nanowires which is associated with the singly ionized oxygen vacancies have not been reported so much. In this study, ZnO nanowire samples were fabricated by evaporation of Zn metallic source using a two-step gas flow control. The green emission properties of ZnO nanowires were investigated after heat treatment in a reducing atmosphere and excimer laser irradiation method. The relation between electrical properties and green emission of ZnO nanowires was studied by measuring plasma frequency using FT-IR spectrometer. Furthermore, the stability of ZnO nanowires during heat treatment in a reducing atmosphere and excimer laser irradiation was enhanced by silica coating layer on the surface of ZnO nanowires. Research will be presented on the further analysis of silica coating layer effect and the characterization of the ZnO nanowires after heat treatment and laser irradiation.

M8.35

Material Exchange in Nano-Scale Compound Structures: A New Route to Pattern Transfer and Modification.

Rolf Koenenkamp[1,2] and Larissa Dloczik[2]; [1]Physics Department, Portland State University, Portland, Oregon; [2]Hahn-Meitner Institut, Berlin, Germany.

We report on recent experiments to produce nano-structures by material transfer between different binary semiconductors. Taking ZnO nano-wire structures as a starting-point we demonstrate that identical and modified structures can be produced in ZnS by using ion exchange techniques, i.e. by exchanging, for example, the oxygen component in ZnO by sulphur. Typical experimental conditions for this exchange are compatible with thin film technology, as the necessary gas phase reactions give sufficiently high reaction rates at intermediate temperatures. Using exchange reactions in liquid solutions, we also show that the metal ions can be exchanged. A nano-structured ZnO film can hence be converted into a completely different material, while its nano-structure is preserved. We show how to produce nano-wires of Ag_2S, Cu_2S, Sb_2S_3 and others by conversion of ZnO nano-wires. Modified structures can be obtained by limiting the exchange process to certain parts of the original structure. Thus by converting only the outer shell of nano-wires and subsequent etching of the center volume, nano-tubes can be fabricated. The wall thickness in these tubes is adjustable through the process parameters. Finally, hetero- structures can be obtained by filling the tubes again with a new material or by not removing the initial material.

M8.36
Transient photoluminescence and amplified spontaneous emission from multiexciton states in CdSe quantum dots. Jean-Michel Louis Caruge and Yin Thai Chan; Chemistry, M.I.T, Cambridge, Massachusetts.

Time resolved photoluminescence studies of CdSe colloidal quantum dots (QDs) dispersed either in hexane or incorporated into a titania matrix will be presented. We will show that, despite fast non-radiative auger relaxation, straight photoluminescence from 2 and 3 electron-hole pair states in CdSe QDs can be spectrally resolved. Ultimately, we will show that non-linear excitation of CdSe QDs incorporated into a titania matrix gives rise to simultaneous amplified spontaneous emission from two distinct multiexcitonic states.

M8.37
Effect of the Environment on the Blinking Statistics of Single CdSe Quantum Dots. Inhee Chung, Vassiliy Lubchenko, Robert Silbey and Moungi Bawendi; MIT, Cambridge, Massachusetts.

Fluorescence intermittency is a well-known phenomenon of single colloidal CdSe quantum dots. Earlier studies have shown that surface modifications of single quantum dots influence the on- and off-time statistics. We show that the host matrices and substrates in which quantum dots are also have significant effects on the blinking statistics of single colloidal quantum dots.

M8.38
Effect of Anharmonicity of Interatomic Potential on Strain Distribution in Semiconductor Nanostructures. Olga L. Lazarenkova, Paul von Allmen, Seungwon Lee, Fabiano Oyafuso and Gerhard Klimeck; Caltech, JPL, Pasadena, California.

Experiments and theory have shown that the energy spectrum of nanostructures is extremely sensitive to the built-in strain. Knowledge of the strain distribution is therefore of utmost importance for the design of optical devices with prescribed light emission spectrum. The widely used Valence-Force-Field (VFF) model developed by Keating and later Martin relies on a parabolic expansion of the inter-atomic potential. However, for the lattice mismatches present in Ge/Si and InAs/GaAs heterostructures (4PC of the equilibrium bond length in Ge/Si and 7PC in InAs/GaAs), which are materials widely used in the design of optical and electronic devices, anharmonic terms are expected to play an important role. We have developed a simple extension of the Martin-Keating two-parameter VFF model to take into account anhamonicity in the inter-atomic potential. VFF constants also determine the phonon frequencies in the crystal. We have chosen a set of anharmonicity parameters by fitting the experimental strain dependence of the phonon spectra (expressed in terms of a set of Grueneisen parameters) in GaAs, InAs, Si, and Ge. We have found that anharmonic corrections reduce the computed hydrostatic compressive strain in quantum dots by up to 20PC. To further test the impact of our model, the electronic eigen-energies of an InAs/GaAs QD array have been computed within an empirical spds* tight binding approximation, where the Hamiltonian matrix elements are dependent on the atomic positions. The modification of the strain distribution due to anharmonicity results in a shift of the lowest quantized states by up to 45 meV in the conductance band and up to 30 meV in the valence band. A valuable advantage of our simple model is that the computational cost is nearly unchanged. This work was performed while one of the authors (OLL) held a National Research Council Research Associateship Award at the Jet Propulsion Laboratory.

M8.39
TEM Characterization of Laser Induced CdTe Nanocrystals Inside Glass Microspheres. April Susan Montoya Vaverka[1], Anuranjita Tewary[3], Mark L. Brongersma[2] and Subhash H. Risbud[1]; [1]Chemical Engineering and Materials Science, University of California at Davis, Davis, California; [2]Materials Science Engineering, Stanford University, Stanford, California; [3]Applied Physics, Stanford, Stanford, California.

Glass fibers drawn from a previously synthesized bulk borosilicate glass doped with CdTe were heat treated by a CO2 laser to form microspheres at the fiber tip. The size of the microspheres varied from 50 to 300 microns. Subsequent reheating of the optically clear microspheres by the CO2 laser resulted in color changes attributed to the formation of CdTe nanocrystals inside the microspheres. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have confirmed smooth surfaces of the microspheres, which indicate high quality factors associated with whispering gallery microsphere lasers may be possible. The particle concentration and size will be characterized using transmission electron microscopy (TEM) and photoluminescence (PL). The size, chemistry, and optical properties of these CdTe quantum dots will be presented with a discussion of the applicability of these data to the fabrication of microsphere photonic structures.

M8.40
Shape control in CdSe and CdTe nanoparticles: Role of surfactants. Sandeep Kumar, Juergen Riegler and Thomas Nann; Freiburg Materials Research Center, Freiburg, Germany.

Semiconductor nanoparticles gained an increasing interest among research community because of its interesting size dependent optical properties. Recently it was observed that the shape also plays important role in property modification[1] and so it was desirable to synthesis these nanoparticles in different morphologies. Among semiconductors the shape control of CdSe and CdTe nanoparticles are well studied till date[2,3]. The driving force for the formation of various morphologies was proposed on the basis of relative reactivity of surfactant system and the monomer concentrations. However for shape modification of CdSe and CdTe nanoparticles, a mixture of surfactants with varying reactivity was invariably used. In this report we propose another parameter which controls the shape modification of CdSe and CdTe nanoparticles. We observed that the surfactant plays important role in shape modification and depending on the surfactant system we were able to stabilise various shapes viz. rods, dots and tetrapods of CdSe and CdTe nanoparticles. In contrary to earlier achieved shape modifications we were able to synthesis different morphologies in monosurfactant system. It was observed when the surfactant contains sterically uncrowded hydrocarbon chains, quantum rods were produced while on the other hand when the surfactant contained sterically voluminous groups quantum dots were obtained. The nanoparticles prepared were highly monodisperse showing narrow FWHM in photoluminescence spectra. Reference [1]. Peng X., Manna L., Yang W., Wickham J., Scher E., Kadavanich A., Alivisatos A. P., Nature, 2000, 404, 59-61. [2]. Manna, L.; Scher, E. C.; Alivisatos, A. P. J. Am. Chem. Soc. 2000, 122, 12700-12706. [3]. Peng Z.A.; Peng X., J. Am. Chem. Soc., 2002, 124, 3343-3353

SESSION M9: Semiconductor Nanowires
Chairs: W. E. Buhro and Arun Majumdar
Thursday Morning, April 15, 2004
Room 3001 (Moscone West)

8:30 AM *M9.1
Nanoparticles and Nanowire Building Blocks: Synthesis, Processing, Characterization and Theory. W.E. Buhro, Department of Chemistry, Washington University, St. Louis, Missouri.

The recent availability of soluble III-V and II-VI quantum wires having diameters in the range of 3-20 nm has afforded new opportunities to experimentally determine how quantum confinement is influenced by the geometric dimensionality of confinement. Quantum wires are ideal 2D-confinement systems, the properties of which may be compared to those of the analogous 3D-confined dots, 1D-confined wells, and anisotropically 3D-confined rods. The synthesis and spectroscopic behavior of CdSe, InP, and InAs quantum wires, grown by the solution-liquid-solid mechanism, will be described. Wire solubility was initially achieved by growth in solutions containing high concentrations of polymer stabilizers, but we have now produced soluble wires stabilized by conventional quantum-dot surfactants, such as TOPO and HDA. The absorption and emission spectra of the wires are used to analyze the band gaps, extinction coefficients, and photoluminescence quantum yields, which are compared to theory and to experimental data from rods and dots. The results confirm 2D quantum confinement in the wires, and establish quantitatively how the confinement in dots, rods, wires, and wells should compare.

9:00 AM M9.2
Crystallographic Orientation Control in Vertically Alligned GaN Nanowire Arrays. Tevye Ryan Kuykendall[1], Peter Pauzauskie[1] and Peidong Yang[1,2]; [1]Chemistry, UC Berkeley, Berkely, California; [2]Materials Science Division, Lawrence Berkeley National Labratory, Berkeley, California.

Growth of highly uniform, single crystalline GaN nanowires by metal-organic chemical vapor deposition has been achieved for the first time. Control over the crystallographic growth directions for massive, high-density arrays of gallium nitride nanowires was demonstrated, and these wires show distinct geometric and physical properties. Epitaxial growth of wurtzite gallium nitride on (100) γ-LiAlO2 and (111) MgO single crystal substrates resulted in the selective growth of nanowires with triangular and hexagonal cross sections in the orthogonal [1-10] and [001] directions, respectively. This was achieved due to the substrate-induced constraints of lattice parameter matching and symmetry registry. These arrays exhibited a systematic difference in their temperature-dependent band-edge emission resulting from the different size, shape, and anisotropic polarity of the nanostructures. Scaling of the synthetic process is entirely compatible with existing GaN thin-film technology and should enable the realization of a new generation of GaN nanowire devices and systems.

9:15 AM **M9.3**
Core-Shell Approach to Complimentary Doping of Semiconductor Nanowires. Andrew B Greytak[1], Lincoln J Lauhon[2], Mark S Gudiksen[1] and Charles M Lieber[1]; [1]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [2]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

We demonstrate a new and general approach for complimentary doping of semiconductor nanowires. In this method, dopant atoms are incorporated into the nanowire structure by growing a shell following axial elongation of intrinsic nanowire cores. This strategy allows the nanowire morphology and electronic properties to be optimized independently, and is applicable to a variety of nanowire materials. For example, germanium (Ge) nanowires were synthesized with either n-type or p-type doping steps, enabling the fabrication of high-performance complimentary Ge nanowire field-effect transistors. More elaborate designs combining core-shell nanowire heterostructures with multiple independent doping steps promise to enable a wide variety of nanoscale semiconductor device architectures to be realized at the time of synthesis in a massively parallel, bottom-up approach.

9:30 AM **M9.4**
Vapor-Liquid-Solid Epitaxy of Ge and Si Nanowires on Si. S. T. Picraux, J. W. Dailey, J. Taraci, T. Michael, D. J. Smith and J. Drucker; Arizona State University, Tempe, Arizona.

We report on a rich variety of nanostructures which can be grown by varying the pressure and temperature in Vapor-Liquid-Solid (VLS) epitaxy on Si. In these studies the CVD growth of Si and Ge nanowires and nanopillars is seeded by metallic nanodots on (111) and (100) oriented Si. Experiments are carried out for digermane and disilane in a UHV system for pressures from 10-6 to 10-2 Torr and temperatures between 400 and 800 C. Au nanodots with diameters of 10 to 50 nm are formed by heterogeneous nucleation upon vapor deposition on H-terminated Si surfaces. Selective epitaxial nanowire growth occurs at the Au nanodots. The evolution of the growth kinetics and morphology is observed to depend strongly on pressure. At lower pressures the Au seeds the growth of layered heteroepitaxial islands (referred to here as nanopillars). These structures grow both vertically and laterally and exhibit ripening by coalescing with adjacent Au nanodots. At higher pressures a transition to rapid <111> axial growth occurs resulting in the formation of nanowires. We contrast quantitative measurements of the growth kinetics for nanowires with blanket growth and the rate limiting factors in the VLS process are discussed. The growth is found to be strongly nucleation limited and a technique for controllably inducing nucleation will be presented. Strain distribution in nanowire Ge/Si heterostructures as measured by HRTEM and Fourier transform techniques will also be presented.

9:45 AM **M9.5**
Epitaxial Ge-Si core-shell nanowires as high-performance nanodevices. Wei Lu[1], Alex D Wissner-Gross[1], Brian P Timko[1], Andrew B Greytak[1] and Charles M Lieber[1,2]; [1]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

The growth of silicon-germanium (Si-Ge) heterostructures offers the opportunity to enhance the performance of transistors and other devices through materials design. In particular, holes can be driven from p-type Si to intrinsic Ge due to the valence band offset at the interface, which results in enhanced hole mobility in the Ge due to the reduction of scattering by acceptor impurities. Here we report investigations of epitaxial Ge-Si core-shell nanowires designed to exploit these ideas in nanodevices. Measurements on nanowire field-effect transistors (FETs) show device yields close to 100 percent, with on currents above $1000\mu A/\mu m$ at zero gate voltage and large hole mobilities. Investigations of transport properties as a function of channel length and temperature indicate the absence of Schottky-barriers at the metal/nanowire contacts. Both high device yield and elimination of Schottky barriers are essential to potential applications of bottom-up nanoscale FET devices. Studies addressing optimization and fundamental limits of these core-shell nanoFETs, and investigations of other nanostructures based on these nanowire materials will be discussed.

10:30 AM ***M9.6**
Transport in Nanowires and Nanotubes. Arun Majumdar, [1]Department of Mechanical Engineering, University of California, Berkeley, Berkeley, California; [2]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

The vapor-liquid-solid (VLS) technique can be used to synthesize single-crystal nanowires 5-100 nm in diameter for a wide variety of semiconducting materials. Such nanowires offer an ideal platform to study transport of energy, charge and mass in one-dimensional nanostructures. Our studies on thermal transport in Si and SiGe nanowires suggest that boundary scattering of phonons is the dominant mechanism for thermal conductivity reduction. Furthermore, for nanowires below 25 nm, the phonon spectrum seems to be modified which leads to suppression of phonon-phonon interactions. We have also shown that in alloy nanowires such as those made of SiGe, one can achieve thermal conductivities below the bulk alloy limit, which is critical in the development of thermoelectric devices made of such materials. Recently, we have been able to use single-crystal silicon nanowires as templates to form silicon dioxide nanotubes with internal diameters 5-100 nm. Such hydrophilic nanotubes are ideal to study liquid and ionic transport under confinement. Using such nanotubes we have computationally and experimentally shown it is possible to obtain unipolar ionic solutions inside the nanotubes. This type of ion separation is forming the basis for a variety of novel devices such as electrochemical batteries and ionic transistors.

11:00 AM ***M9.7**
Electron Transport and Dissipation in Nanoscale Devices. Roberto Car, Princeton, Princeton, New Jersey.

We present a quantum-kinetic scheme for the calculation of non-equilibrium transport properties in nanoscale systems. Our approach is based on a Liouville-master equation for a reduced density operator and represents a generalization of the well-known Boltzmann kinetic equation. The approach allows us, in particular, to model transport situations under high applied fields by adopting periodic boundary conditions. Applications to nanoscale devices and molecular structures are discussed.

11:30 AM ***M9.8**
Growth Kinetics of Silicon Nanowires Observed in Real Time in the Electron Microscope. F.M. Ross[1], J. B. Hannon[1], P. W. Voorhees[2], J. Tersoff[1], C.T. Black[1], and M. C. Reuter[1]; [1]IBM T.J. Watson Research Center, Yorktown Heights, New York; [2]Department of Materials Science and Engineering, Northwestern University, Evanston, IL.

Silicon-based nanowires grown by the VLS process have been suggested for a range of exciting applications in novel electronic devices, and post-growth imaging by electron microscopy has been an essential and widely used tool for understanding their structure. Dynamic microscopy, although much less widely applied, can be a powerful complementary analysis technique. By observing the entire growth process of an individual nanowire with good space and time resolution, transient phenomena can be characterised and kinetic data obtained, allowing us potentially to understand the factors controlling wire growth. In this presentation we will show real time images recorded during the controlled formation of epitaxial Si nanowires by the VLS process. Growth experiments were carried out in a UHV transmission electron microscope having gas handling facilities and a base pressure of $2x10^{-10}$ torr. Wire growth is achieved by exposing a heated, Au-covered Si (111) surface to disilane gas during imaging with an electron beam parallel to the surface. As wires grow away from the surface, their diameters and growth rates can be observed directly, as can their response to changes in pressure and temperature. Growth has been observed under a range of conditions, limited by the pumping capabilities of the microscope. Typically pressures of 10^{-7} to 10^{-5} torr of disilane or digermane are used and growth is carried out between 500 and 650°C. Under these conditions, in situ observations demonstrate that the growth kinetics of a single wire can be quite complex, with several growth regimes evident. Tapering and faceting of wires is apparent, with the Au/Si eutectic droplet size decreasing during growth, and distinctive types of droplet instability are visible. We will discuss these phenomena in the framework of a model which includes Au diffusion and changes in the chemical potential of Si and Au as the droplet shrinks, and we will compare these kinetics with wire growth observed ex situ at much higher pressures. This enables us to consider the conditions under which wires can be optimised for applications of interest to the microelectronics industry.

SESSION M10: Nano-Biological materials
Chairs: Wanda Andreoni and Naomi Halas
Thursday Afternoon, April 15, 2004
Room 3001 (Moscone West)

1:30 PM ***M10.1**
Symmetry Breaking in Synthesis and Post-synthetic

Processing of Nanoshells. Naomi Halas, Electrical and Computer Engineering, Rice University, Houston, Texas.

Nanoshells, layered spherical nanoparticles consisting of a dielectric core and a metallic shell, are a high symmetry nanostructure whose optical resonance depends critically on the nanoparticle's internal dimensions. Modifying its nanoscale geometry results in dramatic changes in how the nanoparticle interacts with light. In synthesis or post-synthesis processing, the optical signal provides sensitive macroscopic evidence that nanoscale reshaping has occurred. There are several ways in which symmetry breaking can be introduced, either during or following synthesis, which results in a systematic reshaping of the nanoshell geometry. We will discuss three such strategies: (1) performing nanoparticle growth steps on a substrate, resulting in the masking and chemical variation of specific regions of the nanoparticle surface; (2) nonequilibrium heating with femtosecond laser pulses, to modify the nanoparticles asymmetrically; and (3) the introduction of surfactant based reshaping of as-grown nanoshells to modify their geometry in unusual new ways.

2:00 PM *M10.2

Virus-Based Genetic Toolkit for the Directed Synthesis of Magnetic and Semiconducting Nanowires. Angela M. Belcher, Chuanbin Mao, Daniel J. Solis, Brian D. Reiss, Stephen T. Kottmann, Rozamond Y. Sweeney, George Georgiou, Brent Iverson, Department of Materials Science and Engineering and Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; Department of Chemistry and Biochemistry, University of Texas, Austin, Texas.

The exploitation of the self-assembly motifs employed by the M13 bacteriophage to produce a biological scaffold provides a means of generating a complex, highly ordered, and economical template for the general synthesis of single crystal nanowires. By introducing programmable genetic control over the composition, phase and assembly of nanoparticles, a generic template for the universal synthesis of a variety of materials can be realized. We report a virus-based scaffold for the synthesis of single crystal ZnS, CdS and free-standing $L1_0$ CoPt and FePt nanowires, with the means of modifying substrate specificity through standard biological methods. Peptides selected through an evolutionary screening process that exhibit control of composition, size, and phase during nanoparticle nucleation have been expressed on the highly ordered filamentous capsid of the M13 bacteriophage. The incorporation of specific, nucleating peptides into the generic scaffold of the M13 coat structure provides a viable template for the directed synthesis of semiconducting and magnetic materials. Removal of the viral template via annealing promoted oriented aggregation-based crystal growth, forming individual crystalline nanowires. The unique ability to interchange substrate specific peptides into the linear self-assembled filamentous construct of the M13 virus introduces a material tunability not seen in previous synthetic routes. Therefore this system provides a genetic tool kit for growing and organizing nanowires from semiconducting and magnetic materials.

2:30 PM M10.3

Self-Assembled DNA Nanoarrays. Angelika B Niemz[1], David J Galas[1] and Shenda M Baker[2]; [1]Keck Graduate Institute, Claremont, California; [2]Chemistry, Harvey Mudd College, Claremont, California.

We herein report a novel approach for generating DNA nanoarrays through self-assembly and immobilization of individual DNA-conjugated gold nanospheres within ordered arrays of surface nanopores. These nanoarrays can be used to direct the ordered secondary self-assembly of other nanoscopic DNA-functionalized entities, and can further be interfaced with a new DNA amplification strategy (EXPAR) to enable the detection of short oligonucleotides from genomic DNA, with the ultimate goal of developing nanoscale DNA diagnostic assays. Formation of self-assembled DNA nanoarrays relies on two key concepts; (1) the size matching between nanopores and DNA-nanoparticles and (2) selective immobilization of DNA nanoparticles at the bottom of the surface nanopores. Arrays of surface nanopores are obtained from hexagonally ordered thin poly(styrene)-b-poly(methylmethacrylate) (PS-PMMA) diblock copolymer films on silicon. Following UV irradiation and rinsing with appropriate solvents, the PMMA cylinders are removed, giving rise to nanoporous templates with pore sizes ranging from 10-40 nm. We have obtained DNA functionalized gold colloids of various diameters through reaction of thiol modified oligonucleotides with bare gold colloids. Selective immobilization can be achieved if the DNA nanoparticles do not interact with the walls, but form strong interactions with the bottom surface of the nanowells. To facilitate strong electrostatic interactions between the negatively charged DNA nanospheres and the bottom surface of the nanopores, we selectively functionalized the surface with a variety of positively charged amine-containing silanes. No non-specific interaction between the crosslinked polystyrene walls of the nanowells and DNA occurs at neutral pH. Deposition conditions have been optimized to obtain high inclusion efficiency, and the so obtained DNA nanoarrays have been characterized by a variety of surface analytical methods. To render the system useful as an actual DNA diagnostic platform, these DNA nanospheres can bind a second set of DNA colloids via short, bridging oligonucleotides. EXPAR, a new isothermal DNA amplification strategy, can rapidly amplify such short oligonucleotides from genomic DNA. We have adapted the hybridization conditions of DNA colloids to be compatible with the EXPAR amplification conditions. Self-assembly within the confined space of the surface nanopores is expected to prevent the normally observed dendritic growth of DNA nanosphere aggregates and to result in discrete 1:1 assembly, which can be detected by Atomic Force Microscopy.

3:15 PM *M10.4

Ab initio Simulations of Nanoscale Systems: from Clusters to Biomolecular Systems. Wanda Andreoni, Zurich Research Laboratory, IBM, Ruschlikon, Switzerland.

This talk will provide a brief overview of recent work done at IBM Zurich Research Laboratory, which is aimed at unraveling with ab initio methods the special structural, chemical and dielectric properties of systems in the nanoscale regime. This work includes the study of metal clusters as units of quantum dots, self-assembled monolayers on metal support, molecular electronics and biomolecular systems. Methodological aspects will be discussed and a perspective will be given on future developments.

3:45 PM M10.5

Self-organization of nanoscale building blocks into ordered assemblies. Mark A. Horsch, Zhenli Zhang and Sharon C Glotzer; Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The application of nanotechnology to areas such as photonics and electronics, chemical and biological sensors, energy storage and catalysis requires the assembly of nanoscale objects such as nanoparticles and nanowires into functional materials and devices. Currently, few demonstrated assembly approaches offer a comprehensive, predictable, and generally applicable scheme for the rational assembly of nanoparticles into one-, two-, and three-dimensional ordered structures. Inspired by recent advances in synthesis and functionalization, we seek to develop an intuitive framework for predicting the assembly of nanoparticles functionalized with organic tethers. Simulation offers a unique opportunity in this regard, provided appropriate models can be devised and the length and time scales relevant to the assembly process can be efficiently accessed. In this talk, we present new results of molecular dynamics and Brownian dynamics simulations of tethered nanocrystals and their self-assembly into complex ordered structures. We show how tuning thermodynamic parameters and architectural features of model nano building blocks can control aspects of local and global ordering of the nanoparticles. We further demonstrate that for certain categories of tethered nano building blocks the morphologies obtained may be predicted using concepts from block copolymer microphase separation and liquid crystal phase ordering, while for other categories the unique packing constraints introduced by nanoparticle geometry and by nanoparticle-tether topology lead to structures far richer than those found in conventional block copolymer, surfactant, and liquid crystal systems, including nanowires, nano-shells, and nano-cylinders.

4:00 PM M10.6

Self-Assembly of Genetically-Engineered Polypeptides for Nanowire Aplications. Christopher Kossow[1], Narender Rana[1], Autumn Carlsen[1], Seiichiro Higashiya[2], Silvana Ngo[2], Robert E Geer[1], John Welch[2], Eric Eisenbraun[1] and Alain Kaloyeros[1]; [1]School of Nanosciences, University at Albany, Albany, New York; [2]Department of Chemistry, University at Albany, Albany, New York.

Novel methodologies for controllable self-assembly are critical for the realization of functional nanomaterials including nanowires and electronic/photonic nanodevices. Here, we report the self-assembly of nanowire templates based on the spontaneous self-assembly of genetically-engineered proteins; specifically, beta-pleated sheet nanotapes. Due to the inherent flexibility of molecular biological synthesis these materials represent a new nanoscale 'toolbox' for the directed self-assembly of electronically conjugated nanostructures. The protein structure employs amino acid sequences based on alanene (Ala) and glyceine (Gly) peptides. The fundamental trellis repeat unit is {Glu(GlyAla)3GlyTyr(GlyAla)3Lys(GlyAla)3GlyHis}where anti-parallel strands of this repeat sequence form a beta-sheet structure with tyrosine (Tyr) and histidine (His) alternating as beta-turn groups along one edge of the trellis and glutamic acid (Glu, negative charge) and lysine (Lys, positive charge) alternating as beta-turn groups along the other edge of trellis. A beta-sheet structure consisting of 21 such repeats, terminated on both ends by hexahistidine (H6) groups (referred to as H6YEHKx21H6) was synthesized and deposited on metallic and dielectric substrates. Ex-situ atomic force microscopy (AFM) has been used to study the structure and assembly of these molecules and reveals the assembly of the beta-sheets into rectilinear tapes. The tape width is approximately 35 nm. The tape thickness is 0.9 nm (one molecular layer) and the length varies from 100nm to well over 1 micron. Based on molecular modeling simulations of the protein structure a preliminary analysis implies the long axis of the beta-sheet is normal to the tape axis. Thus the assembly is driven by the interaction of the beta-turn sites between proteins and exposes chemically modifiable H6 groups on the tape periphery. Such tape assembly of beta-pleated sheets has yet to be reported and opens new avenues for design and fabrication of nanowire and nanodevice structures.

4:15 PM M10.7
Biomolecule functionalized diamond nanoparticle. Hitoshi Umezawa, Guojun Zhang, Yoshikazu Nakano, Tamotsu Zako, Takashi Funatsu, Iwao Ohdomari and Hiroshi Kawarada; School of Science and Engineering, Waseda University, Tokyo, Japan.

Diamond nanoparticles are functionalized by biomolecule immobilization. Diamond nanoparticles fabricated by trinitrotoluene explosion in water have diameter of 5-35nm. Due to the surface hydrophilic group such as carboxyl and amino groups, diamond nanoparticles are water soluble. Because of the advantages in material properties such as biocompatibility and chemical/physical stability, diamond nanoparticles are expected for future biomolecule sensing and separation nano-systems. In this study, utilizing two kinds of surface modification techniques, fluorescence labeled oligonucleotides are immobilized on diamond nanoparticles. One is NHS/EDC activation method and the other is glutaraldehyde modification method. (1) Surface carboxyl group on diamond nanoparticles is activated by NHS/EDC method. Diamond nanoparticles are suspended in water solution containing N-hydrocylsulfo-succinimide (NHS) and 1-ethyl-3,3'-dimethylaminopropyl carbodiimide (EDC) overnight, washed by water (3 times). Activated particle is re-suspended in 0.01 uM solution of fluorescence labeled DNA (H2N-5'-CCACGGACTACTTCAAAACTA-3'-Cy5) in SSC buffer and incubated at 38 degree for 2 h, then washed (3 times). (2) Diamond nanoparticle is aminated by UV irradiation in ammonia gas after surface chlorination. Then, the particles are suspended in 1% glutaraldehyde in water overnight, washed by ultra-pure water (3 times). Cy5 labeled 21 mer oligonucleotides are immobilized on glutaraldehyde-modified diamond nanoparticles with the same protocol as mentioned above. Immobilization of Cy5 labeled oligonucleotides on diamond nanoparticles is observed by fluorescence microscopy. Clear fluorescence signal from oligonucleotides functionalized diamond nanoparticles is obtained from both immobilization methods.

SESSION M11: Poster Session: Group IV Nanoparticles II

Chair: Christopher B Murray
Thursday Evening, April 15, 2004
8:00 PM
Salons 8-9 (Marriott)

M11.1
Preparation of silicon carbide nano-particles using a pulsed laser deposition method. Hiroharu Kawasaki, Yoshiaki Suda, Tamiko Ohshima and Syota Nakashima; Electrical Engineering, Sasebo national college of technology, Sasebo-city, Japan.

Nano-particles, such as fullerene (C_60), have attracted a great deal of attention in the industrial production and application. Recently, silicon (Si) and/or silicon carbide (SiC) nano-particles also attract due to their small size, low power consumption, and unique functionality. Si nano-particles have been studied enthusiastically as single-electron devices, especially as a quantum dot transistor. On the other hand, as the SiC nano-particles show visible light emission property, the SiC nano-particles have been investicated as optical devices. Therefore, these particles have been prepared using several method, such as plasma CVD method, sputtering method etc. However, it is difficult to prepare stable and uniform Si and SiC nano-particles. Pulsed laser deposition (PLD) method has become a widely used technique for the deposition of thin films due to the advantages of a simple system setup, wide ranging deposition conditions, wider choice of materials and higher instantaneous deposition rates. In this paper, we have developed new PLD techniques using dual laser beam for the formation of SiC nano-particles exhibiting visible light emission. Si_nC_m particles were prepared after the reaction of Si_n and C_m nano-particles in the plasma plume generated at the same time. The behaviors of atomic species and nano-particles in the laser ablated plume were investigated by using time and special resolved spectroscopic measurement with spectrometer and ICCD camera, and two dimensional laser light scattering method.

M11.2
Structural and Electrical Properties of Boron-doped Silicon Nanowires. Kok-Keong Lew[1], Timothy E Bogart[1], Sarah M Dilts[1], Ling Pan[3], Elizabeth C Dickey[1,3], Yanfeng Wang[2], Marco Cabassi[2], Theresa S Mayer[2], Joan M Redwing[1,2,3] and Steven W Novak[4]; [1]Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [2]Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania; [3]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [4]Evans East, East Windsor, New Jersey.

The ability to controllably incorporate dopants into Si nanowires during vapor-liquid-solid growth is important for a variety of nanoscale device applications. Diborane (B_2H_6) has previously been used as a p-type dopant source for VLS-grown Si nanowires in combination with silane (SiH_4), however, gas phase pre-reactions between the two sources result in the deposition of a thick amorphous Si layer on the outer surface of the nanowire during growth. In this study, we have investigated the use of trimethylboron (TMB) as a p-type dopant source due to its higher thermal stability, and compared the resulting structural and electrical properties of the p-doped Si nanowires to those obtained using diborane. Silicon nanowires, with a nominal diameter of 85 nm, were fabricated using Au-impregnated nanoporous alumina membranes using SiH_4 (10% in H_2) and either diborane (100 ppm in H_2) or TMB (200 ppm in H_2) as the dopant source. The reactor pressure and temperature were held constant at 12 Torr and 500°C, respectively. The average boron concentration in the nanowires, as determined by secondary ion mass spectrometry measurements on a collection of wires, increased as the inlet dopant/SiH_4 gas ratio was varied from 10^{-6} to 10^{-2}. Transmission electron microscopy measurements of diborane-doped Si nanowires with a boron concentration of approximately 2 x10^{19} cm^{-3} revealed a thick amorphous Si layer (20 nm) on the outer surface of the nanowires. In contrast to this, TMB-doped Si nanowires with a boron concentration of approximately 4 x10^{19} cm^{-3} were nominally single crystal throughout. Gate-dependent current-voltage curves were used to verify that both the diborane and TMB-doped Si nanowires exhibited p-type behavior. A resistivity of approximately 0.2 ohm-cm was measured using a four-point technique for the highly doped nanowires grown using TMB. These results demonstrate that TMB can be used to obtain high p-type doping in VLS-grown Si nanowires without undesired radial growth on the wire surfaces.

M11.3
Nano-crystallography by means of transmission electron goniometry. Peter Moeck[1], Armando Acha[1], Krishnan Padmanabhan[1], Mukes Kapilashrami[4,1], Wentao Qin[2] and Phillip B Fraundorf[3]; [1]Department of Physics, Portland State University, Portland, Oregon; [2]PMCL/DDL/SPS, MD EL622,, Motorola, Tempe,, Arizona; [3]Physics and Astronomy and Center for Molecular Electronics, University of Missouri, St. Louis, Missouri; [4]Department of Materials Science, The Royal Institute of Technology, Stockholm, Sweden.

As the crystallographic phase of a material may change with the crystal size, a need arises to characterize nanoparticles individually. Transmission electron microscopy (TEM) has traditionally provided such information for micrometer-sized crystals from convergent beam electron diffraction patterns. As the sizes of nanocrystals approach the order of 10 nm, the fine structures in these reciprocal space patterns are, however, no longer available for crystallographic analyses. Direct space high-resolution phase-contrast TEM and atomic resolution Z-contrast scanning TEM combined with goniometry of direct lattice vectors offer the possibility of developing dedicated nano-crystallography characterization methods for such small nano-crystals. High tilt-angle strategies for determining the lattice parameters of individual nanocrystals from high-resolution phase contrast images [1,2] are reviewed. Wurtzite type semiconductor and copper type metal nanocrystals are employed to demonstrate the feasibility of this approach. [1] P. Fraundorf, Ultramicroscopy 22 (1987) 225 [2] W. Qin and P. Fraundorf, Ultramicroscopy 94 (2003) 245

M11.4
Synthesis of Insulator-Coated Carbon Nanotubes towards Building Blocks for Nanodevices. Takashi Ikuno[1], Kazunori Kamada[1], Tatsuro Yasuda[1], Takashi Kuzuoka[1], Kuei-Yi Lee[2], Shin-ichi Honda[1], Jung-Goo Lee[2], Hirotaro Mori[2], Mitsuhiro Katayama[1] and Kenjiro Oura[1,2]; [1]Dept. of Electronic Eng., Osaka University, Suita, Japan; [2]Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University, Ibaraki, Japan.

Although carbon nanotubes (CNTs) can be either a one-dimensional metallic or semiconductive wire, depending on its chirality and diameter, in principle, it is difficult to derive an insulating property from CNT. For applications to CNT-based nanodevices, CNT-insulator composites are required. For example, field-effect transistors (FETs)[1] and single-electron transistors (SETs)[2] have been fabricated using the combination of an insulator with a CNT. Moreover, for CNT nanoprobes including sensors and chemical detectors, insulation and passivation of the CNT are indispensable when they are used in a biochemical environment. In this aspect, the method of coating CNTs with an insulator is one of the most desirable routes to fabricating insulator-CNT composites as building blocks for nanodevices. We present a method for synthesizing insulator-coated CNTs building blocks by pulsed laser deposition (PLD)[3]. A pulsed Nd:YAG laser with a wavelength of 355 nm and a pulse duration of 5 ns was focused onto a target at a repetition rate of 10 Hz. The laser energy was fixed at 140 mJ. An isolated multi-walled CNT (MWNT) was used as specimen. The specimen was set at a tip of a specimen holder, and was placed 40 mm from the target. The angle between the axis of the holder and the normal direction of the target was 45°. The azimuth angle of the specimen was changed during PLD. In this experimental configuration, the coating of CNTs with SiO_x as an insulator was carried out at room temperature using a single-crystalline Si target under a pressure of 1×10^{-4} Torr maintained by flowing oxygen gas. Resultant insulator-coated CNTs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A SiO_x layer was found to be uniformly coated on the MWNT. The thickness of coated SiO_x can be precisely controlled to a nanometer-scale accuracy. A stoichiometric SiO_2 layer was reflected the shape of the MWNT. The thickness of the SiO_2 layer could be controlled in the range of 2-28 nm via the deposition time. The insulating property of the resultant CNTs was verified using SiO_2-coated vertically oriented CNTs (V-CNTs). The CNT coated with an insulator having well-controlled thickness and stoichiometry has high potential for versatile applications to CNT-based nanodevices. [1] S. J. Wind, J. Appenzeller, R. Martel, V. Derycke and P. Avouris: Appl. Phys. Lett. **80** (2002) 3817. [2] H. W. C. Postma, T. Teepen, Z. Yao, M. Grifoni and C. Dekker: Science **293** (2001) 76. [3] T. Ikuno, M. Katayama, K. Kamada, S. Honda, J.-G. Lee, H. Mori and K. Oura: Jpn. J. Appl. Phys. **42** (2003) L1356-L1358.

M11.5

Surface Aligned Self Assembly of CNTs: Nanotube Epitaxy. Kousik Sivakumar, Shaoxin Lu and Balaji Panchapakesan; Electrical and Computer Engineering, University of Delaware, Newark, Delaware.

Aligned growth of carbon nanotubes is a crucial factor for integrating them with nanoscale devices. Until now, nanotubes have been grown vertically and have been shown to have good field emission properties. But in order to integrate them with nano-electronic devices, alignment along the surface of the wafer is vital. In this paper, we demonstrate the self assembled growth of nanotubes along the surface of silicon wafer using thermal CVD. Extremely straight nanotubes about 10 nm in diameter and 1 micron length have been seen to grow in a direction parallel or perpendicular to the flat of an n-type <100> silicon wafer. We found that the diameter of the nanotube and that of the iron nanoparticles used to grow the nanotubes were the same (10 nm). We believe the mechanism of growth is similar to that of molecular epitaxy which occurs due to the lattice matching of the silicon and iron crystal lattices, bringing us to epitaxial growth of single wall carbon nanotubes. When the lattices are matched, the nanotubes grow either parallel or perpendicular to the <111> direction of the silicon wafer which is the most densely packed plane. The growth of nanotubes in other regions is found to be rather random as expected. Unlike other techniques such as electric field assisted growth of nanotubes and use of AFM tips to align nanotubes, this process is not cumbersome and readily compatible with bulk CMOS fabrication techniques. This brings us a step closer to realizing the idea of making large scale nanotube field effect transistors and sensors.

M11.6

Atomistic computer simulations of SiC nanoparticle condensation and growth in the gas phase. Paul Erhart and Karsten Albe; Materials Modeling Division, Institute of Materials Science, Darmstadt, Germany.

Gas phase condensation of silicon carbide nanoparticles is studied by atomic scale computer simulations. Using molecular-dynamics we investigate the fundamental processes governing growth, coagulation and agglomeration of SiC nanoparticles. In doing so, we have developed a bond-order potential which provides an accurate description of the materials behavior over a wide range of atomic configurations and coordinations. Its elastic, thermodynamic and defect properties have been carefully analyzed. A detailed analysis of the molecular reactions during the early stages of particle growth is presented which reveals an initial preference for carbon-dominated species and a sensitive dependence on the processing conditions, especially the cooling and precursor gas composition.

M11.7

Size and Structure Determination of Nanoparticles Using Synchrotron Radiation: New Techniques and Results. Christian Kumpf[1], Andreas Stahl[1], Michael Scheuermann[1], Sanjeev S. Joshi[1], Franziska Niederdraenk[1], Sulabha K. Kulkarni[3], Reinhard Neder[2], Clemens Heske[1] and Eberhard Umbach[1]; [1]Experimentelle Physik II, University of Wuerzburg, Wuerzburg, Germany; [2]Institut fuer Mineralogie und Kristallstrukturlehre, University of Wuerzburg, Wuerzburg, Germany; [3]Department of Physics, University of Pune, Pune, India.

Semiconductor nanoparticles are of increasing interest for both applied and fundamental research. Examples are the fabrication of thin film LEDs and solar cells in material science, and marker-particles in bio-sciences. Particles with a size of 1-10 nm are of particular interest in fundamental research since they represent a size scale between solid state physics and molecular or cluster physics in which quantum size effects play an important role. A precise determination of the particle size is an important issue. Often local probes like TEM or AFM are used, which cannot give representative results of the mean particle size and have additional drawbacks. Other approaches, which make use of quantum size effects, contain the risk of large systematical errors since the effective mass or tight-binding models used for data interpretation may fail for small particles. Potentially, diffraction methods are able to provide more precise structural information, provided special care is applied. We present new data obtained by x-ray diffraction methods using ZnS and CdS particles in the 1-3 nm range which were prepared using a wet-chemical route. By making use of anomalous x-ray scattering, the structural properties of core-shell particles become accessible as well. Results from ZnS nanoparticles embedded in a much larger SiO2 shell are presented. The analysis of x-ray powder diffraction patterns was performed with a forward calculation method based on the Debye formula. The presented results demonstrate the power of this technique concerning structure, size, stacking faults, and relaxation effects in the nanoparticles.

M11.8

Metallization of Multiwall Nanotubes and Subsiquent Nanocomposite Formation. Abigail Cooley, Chyi-Shan Wang and Max Dudley Alexander; Polymers, Air Force Research Lab, WPAFB, Ohio.

Multiwall nanotubes were functionalized by thin layers of various metals including silver onto their surface. The electronic properties of these materials were then characterized and correlated to the coating thickness. The functionalized tubes were then incorporated into polyurethanes to fabricate conductive elastomeric materials for inclusion into a variety of device systems. The nanotube concentration was varied to examine the percolation behavior of the treated nanotubes and compaired to the values obtained from non-treated tubes. The samples were also processed into bars for examination of the nanocomposites mechanical properties through tensile and compression testing.

M11.9

A Model for the Phase Stability of Arbitrary Nanoparticles as a Function of Size and Shape. Amanda Barnard and Peter Zapol; Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Crystal morphology has been found to affect a number of nanoscale properties, such as the phase stability of nanocarbon, and to effect number of remarkable properties such as the luminescence of Si nanoparticles. Still more often than not, nanoparticles are described as being spherical in shape. We use a thermodynamic model based on the Gibb's free energy of an arbitrary nanoparticle to make a prediction of the energetically preferred shape as a function of particle size, that may be in principle applied to any system. The surface energies and estimates of the edge and corner energies (from periodic density functional calculations) are used to determine the size regimes in which edge and corner effects become significant. The proposed model has been applied to clean and hydrogenated versions of the diamond-structured group IV semiconductors carbon, silicon and germanium; and predictions of the corresponding nanoparticle morphologies are presented. It is shown that diamond morphology at the nanoscale is more varied than Si or Ge due to higher values of surface energies, in agreement with first-principles calculations for nanoparticles.

M11.10

The effects of processing on the morphology of nanoparticles. Christopher R Perrey, Julia Deneen and C. Barry Carter; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

One of the major challenges confronting the utilization of nanoparticles in industrial and social applications is that of producing the materials. A single production process may yield nanoparticles of varying size, shape, structure, and chemistry. All of these factors can greatly impact the observed properties of such nanoparticles and determine the success of nanoparticle-based devices. Of the methods of manufacturing nanoscale materials, processes involving plasmas have been shown to be cost-effective and versatile in the production of chemically diverse material. Using transmission electron microscopy, individual nanoparticles produced by three distinctly different plasma-based production methods have been examined. The observations of these studies imply that the thermal history of the nanoparticles during formation is of great importance in the determination of the resulting nanoparticle morphology. Such a result has the potential to enable the manufacturing of nanoparticles of a specific size and shape from plasmas.

M11.11

Silicon Nanowire Growth at Relatively Low Processing Temperature. Joondong Kim, Chunhai Ji and Wayne A Anderson; Electrical Engineering, University at Buffalo, Buffalo, New York.

The Metal Induced Growth (MIG) of nanowires has the potential to alter the conventional lithographic techniques to provide an easier fabrication method. Our group has studied the MIG technique to synthesize poly-silicon and nano size structures. The work of our group in this area gave silicon nanowires of 20 200 nm diameter, 3 10 μm length and single crystal structure. Until now, the growing of silicon nanowires has been understood by two models. One is an oxide-assisted mechanism and the other is a metal catalyst assisted mechanism. Both cases need higher growing temperatures above 900 ^{o}C. We are now proposing the repeatable growth of silicon nanowires at a low processing temperature, 550 600 ^{o}C, which is the lowest silicon nanowire growing temperature without using a gas type silicon source (silane). Nickel as a catalyst metal is thermally evaporated onto SiO_2 before loading for DC magnetron sputtering. The Ni layer varied from 22 nm to 120 nm in thickness and sputtering time of a 2-inch diameter p type-Si target (ρ=0.001 0.005Ωcm) was varied to observe and confirm the growing mechanism. Silicon nanowires were grown and lengthened by control of growing temperature, gas pressure, Si/Ni composition ratio and layer thicknesses. The length of silicon nanowires was up to 10 μm and the diameter ranged from 20 nm to above 100 nm. We are proposing a NiSi mechanism instead of $NiSi_2$, which is a popular understanding in Ni assisted silicon nanowire growth at high growing temperature. This paper will cover experimental methods, optimum growth conditions, growth mechanism and experimental work.

M11.12

Lithography-Free Approach for Addressing at Nanoscale Using Assembled Modulation-Doped Silicon Nanowires. Zhaohui Zhong[1], Chen Yang[1], Ying Fang[1] and Charles M Lieber[1,2]; [1]Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Decoders, which are fundamental to microelectronics, are also expected to play an essential role in nanoscale electronics, including data communication/addressing, and importantly, to bridge between nanoscale pitch arrays and device elements, and larger scale interconnects that ultimately serve as system input/output. Building decoders for nanoscale systems requires both high performance building blocks and novel designs. Here we demonstrate that single-crystal silicon nanowires (SiNWs) are ideal candidates as nanoscale building blocks: fundamental transport studies reveal coherent single charge tunneling through SiNW over a length scales as large as 400 nm, and SiNWs exhibit room temperature hole mobilities of 400 cm2/V/s. Secondly, we describe a new concept and demonstration of a field effect transistor (FET) based decoder assembled via a lithography-free bottom-up approach using axially-modulated SiNWs. Demonstration of coding and addressing will be presented. The implications of these results for highly integrated nanoelectronics will be discussed.

M11.13

Mechanical and Electromechanical Loading of Nanosprings and Nanorods. J.P. Singh, Deli Liu, D.-X. Ye, Toh-Ming Lu, Gwo Ching Wang and Catalin Picu; Rensselaer Polytechnic Institute, Troy, New York.

The measurement of the mechanical properties of nanoscale volumes of materials is an important topic in nanotechnology. However, the fabrication of suitable nanosize test structures and the measurement of their mechanical properties are challenging. In this work, we grow isolated helical Si nanosprings and slanted straight Cu nanorods with wire diameter of about 200 nm and total length larger than 4 micrometers, which we use as test specimens. The structures, which are fabricated by the oblique angle deposition technique with substrate rotation, are fixed to the substrate at one end. The other end of the nanostructure is loaded in a purely mechanical test, using a tip-cantilever assembly attached to a conventional AFM. For the nanosprings, an electromagnetic force is induced by passing an electrical current through the structure using a conductive AFM tip. The springs tested by this method were coated with Co in order to be rendered conductive. The forces and displacements are independently measured in the mechanical test. In the electromagnetic test the deformation is measured with the AFM and the force is evaluated from a model. Appropriate modeling is used to interpret the results. The constitutive behavior of the material is derived and discussed.

M11.14

Integration of Inorganic Nanotubes into Ionic Circuits for Single Molecule Sensing. Rong Fan[1], Deyu Li[2], Min Yue[2], Arun Majumdar[2] and Peidong Yang[1]; [1]Chemistry, UC Berkeley, El Cerrito, California; [2]Mechanical Engineering, UC Berkeley, Berkeley, California.

Recently significant research work has been focused on the synthesis of inorganic nanotubes, e.g. MoS_2 and GaN nanotubes for achieving new 1D functional nanotubular structures. Silica nanotubes are of special interest because of their hydrophilic nature, easy colloidal suspension formation, and easy surface functionalization accessibility. Herein, we present a controlled synthesis of silica nanotubes from silicon nanowire templates and the first demonstration of the integration of inorganic nanotubes into nanofluidic devices which show potential application in single molecule sensing. Silicon nanowires were oxidized at high temperatures (1000 ^{o}C) to form silicon/silica core-sheath nanowires with tunable silica sheath thickness. XeF_2 vapor was utilized to selectively etch silicon cores away to leave silica nanotubular structure with inner pore size 10-200 nm. A single nanotube nanofluidic device can be fabricated by dispersing the nanotubes on the surface of quartz substrate, addressing individual nanotube and several photolithography steps to pattern metal electrodes and reservoir wall using hydrophobic polymer materials. The device has two reservoirs separated by a polymer line, under which a single silica nanotube bridges these two reservoirs. Since the silica surfaces are negatively charged which leads to a strong uni-polarity of ion distribution inside silica nanotubes, ionic current is expected to be affected by surface charge densities. A simple eletrokinetic model based on electroneutrality was proposed to simulate this interesting phenomenon. Furthermore, single biomolecule (e.g. λ-phage DNA) transpass events are being tested by tracking ionic current change, while the different molecules can be identified by blockade current and duration time. This device shows great potential for single molecule sensing.

M11.15

Complex nanotubes by template wetting. Martin Steinhart[1], Petra Goering[1], Yun Luo[1], Herbert Hofmeister[1], Andreas Greiner[2], Joachim H. Wendorff[2], Ralf B. Wehrspohn[3], Eckhard Pippel[1] and Ulrich Goesele[1]; [1]Max Planck Institute of Microstructure Physics, Halle, Germany; [2]Chemical Department, Philipps-University, Marburg, Germany; [3]Physical Department, University of Paderborn, Paderborn, Germany.

We report on the preparation of metal and metal/polymer composite nanotubes having complex wall architectures. As wall materials we have selected platinum, palladium, gold and several polymers. Nanotubes exhibiting specific porosity as well as core-shell systems are accessible. This was accomplished by wetting porous templates such as ordered porous alumina or macroporous silicon with liquid polymer/precursor mixtures (1). The precursor is transformed to the respective metal by a gentle thermal treatment, and the generated nanocrystals grow due to Ostwald ripening as long as the polymeric matrix is liquid. Since the size of the metal nanocrystallites depends on the duration of ripening, the wall morphology can be adjusted. Crystallites of group 10 metals such as Pt and Pd grow within the confinement of the walls of the metal/polymer composite nanotubes. Depending on the duration of the ripening period, they have sizes of few nm to some tens of nm. The ripening behavior of group 11 metals is significantly different. They even form plugs with lengths in the micron range. Released metal nanotubes exhibiting a specific nano-porosity are accessible by selectively removing both the polymeric component and the template, as evidenced by scanning electron microscopy as well as by transmission electron microscopy. Their walls have fine structures corresponding to the ripening stage at which the structure formation was frozen. Moreover, metal/polymer and metal/lead zirconate titanate/metal multi-layer structures can be fabricated by performing consecutive wetting steps. Such systems may be used for catalysis, and as micro-capacitors, respectively. Since the diameter of the template pores can currently be adjusted to any value from 20 nm up to few microns, template wetting represents a versatile toolbox in the fields of nano- and microtechnology that complements established fabrication methods for one-dimensional nanostructures

(2). (1) M. Steinhart, et al., Science 296, 1997 (2002). (2) C. R. Martin, Science 266, 1961 (1994).

M11.16

Growth of Si Nanowires on Self-assembled Hexagonal Au Particle Networks. Tian-Fu Chiang[1], Shao-Liang Cheng[2] and Lih-Juann Chen[1]; [1]Department of Material Science and Engineering, National Tsing Hua University, HsinChu, Taiwan; [2]Department of Chemical and Materials Engineering, National Central University, Chung-Li, Taiwan.

Novel self-assembled hexagonal networks with discrete Au particle on different substrate have been synthesized. Si nanowires, attached to single catalytic Au particle, were grown using a vapor transport deposition process. Gold particles display highly catalytic activity for the growth of the Si nanowires. Well-defined growth of the Si nanowires at the novel self-assembled hexagonal Au particle networks has been observed. The Si nanowires were characterized by scanning electron microscopy and transmission electron microscopy. The formation process of the Si nanowires is closely related to a vapor-liquid-solid (VLS) mechanism. These Si nanowires are expectedto be useful in nanoscale electronic and optoelectronic devices.

M11.17

TEM Studies of Ge Nanocrystals. Qing Xu[1,2], Ian D. Sharp[1,2], Christopher Y. Liao[1,2], Diana O. Yi[1,3], Andrew M. Minor[1], Joel W. Ager[1], Jeffrey W. Beeman[1], Zuzanna Liliental-Weber[1], Kin Man Yu[1], Dmitri N. Zakharov[1], Daryl C. Chrzan[1,2] and Eugene E. Haller[1,2]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California; [3]Applied Science and Technology Graduate Group, University of California, Berkeley, Berkeley, California.

Electron microscopy studies of ^{74}Ge and ^{70}Ge nanocrystals made by ion beam synthesis in SiO_2 are presented. Cross-sectional TEM was used to measure the size distribution. The observation of numerous twinned nanocrystals is consistent with process-induced compressive stress which was also found by Raman spectroscopy. These nanocrystals were released from the SiO_2 matrix by etching in a HF bath and examined under a Philips CM200 TEM. High-resolution micrographs confirm that the crystallinity is retained in this process and showed an amorphous shell encapsulating the released nanocrystals. Transfer of released nanocrystals was achieved through ultrasonic dispersion in methanol and deposition onto lacey carbon films via evaporation of methanol. Debye rings were obtained from these transferred nanocrystals in a JEOL 200CX microscope under selective area diffraction. In an effort to measure the melting point of Ge nanocrystals and observe the growth and evolution of nanocrystals embedded in the amorphous SiO_2 during heat treatment, as grown nanocrystals were heated in-situ up to 1007°C in a JEOL 3010 microscope. Contrast changes and fast diffusion of Ge atoms were observed. However, the size distribution remained the same after in-situ heat treatment. This work was supported in part by U.S. NSF Grant No. DMR-0109844 and by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

M11.18

Lateral and Vertical Nanotube and Nanowire Arrays for Sensor and RF Signal Processors. Eric Warren Wong[1], Michael Bronikowski[1], Choi Daniel[1], John Davis[1], Larry Epp[1], Michael Hoenk[1], Daniel Hoppe[1], Brian Hunt[1], Robert Kowalczyc[1] and Jimmy Xu[2]; [1]Jet Propulsion Laboratory, Pasadena, California; [2]Division of Engineering, Brown University, Providence, Rhode Island.

In recent years, there has been exciting progress towards the integration of nanowires into nanoscale electronic devices. We will describe important new developments in this field that have been made at the Jet Propulsion Laboratory. Single-walled carbon nanotubes and silicon nanowires have been grown in lateral device geometries for chemical sensor and high Q resonator applications. Improvements for directing growth along substrates and on electrodes will be described. Iron nanoparticles were patterned as dots down to 50 nm diameters and were used to grow single-walled nanotubes with improved reliability over other methods. Also, template based methods were used to grow multi-walled carbon nanotubes in vertical and highly ordered hexagonal arrays with nanotube diameters of 50nm, tube to tube spacings of 150 nm, and controllable lengths. These vertical arrays have been patterned into nanoscale device geometries suitable for RF Signal Processing applications. Initial RF measurements show that these array devices behave as narrow band gigahertz RF transmission filters.

M11.19

UV emitting SiC quantum dots: optical gaps and thermodynamic stability. Fernando Agustin Reboredo[1], Laurent Pizzagalli[2] and Giulia Galli[1]; [1]PAT, Lawrence Livermore National Lab, Livermore, California; [2]Universitede Poitiers, Futuroscope,, Cedex, France.

We present an extensive, ab-initio theoretical study of the quantum dots (QDs) that could be potentially synthesized from compounds containing C, Si and H. The properties of SiC QDs are compared to alkyl and H terminated Si and diamond QDs. Our first principles study of 1 to 3 nm cubic SiC nanoparticles shows that quantum confinement and surface termination effects are equally important in determining their optical gaps. Independent of size, hydrogenated, unreconstructed C terminated surfaces and (2x1)-reconstructed Si terminated surfaces give rise to the most stable SiC QDs (which, for the same diameter, have gaps differing by as much as 1 to 1.5 eV depending on the surface termination). Unreconstructed, C-terminated SiC dots with diameters smaller than 2 nm have gaps larger than those of C, Si and Ge nanoparticles. We therefore predict that SiC nanostructures could be potential candidate materials for semiconductor based UV light sources and that their band gap can be engineered as a function of their size and surface composition to obtain absorption and emission varying from the UV to the green. On the basis of the total energies obtained theoretically, we discuss the experimental conditions under which each type of dot and surface termination could be obtained near thermodynamic equilibrium.

M11.20

Direct Synthesis of Highly Porous Spherical Carbon Particles Using Aerosols. J. Eric Hampsey, Jiebin Pang, Qingyuan Hu, Zhiwang Wu, Byron McCaughey, Donghai Wang and Yunfeng Lu; Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Mesoporous carbon materials are of great interest for many applications such as electronics, catalysts, and hydrogen storage systems. One of the most cited techniques for preparing mesoporous carbons involves infiltrating a hard template such as mesoporous silica with a carbon source followed by carbonization. While this method is useful for preparing carbons with ordered pore structures, it involves multiple steps that may be difficult and tedious. Here, we report the synthesis of highly porous spherical carbon particles using a one-step aerosol process. With nitrogen as a carrier gas, aqueous solutions containing colloidal silica particles and sucrose are sent through an atomizer creating aerosol droplets. The aerosol droplets are then passed through a glass tube heated to 400 degrees C to evaporate the water and cause the formation of spherical colloidal silica/sucrose composite particles. Finally, the particles are collected, carbonized at 900 degrees C under nitrogen, and the colloidal silica is removed using a NaOH solution. The porous carbon particles show very high porosity with large pore volumes greater than 4 cm3/g. The pore size distributions are narrow and the pore diameters are controlled by the size of the colloidal silica. The porous carbon particles are characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), nitrogen sorption, thermal gravimetric analysis (TGA), and other techniques. These highly porous carbon particles have potential applications as catalysts and filler materials.

M11.21

Templating the Patterning of Gold Nanoparticles using a Stained Triblock Copolymer Film Surface. Ian W Hamley and Imtiyaz A Ansari; Chemistry, University of Leeds, Leeds, W. Yorks., United Kingdom.

We show that the selective staining of the polyisoprene block in a polystyrene-polyisoprene-polystyrene triblock copolymer enables nanoparticles of sputtered gold to be patterned into stripes. Osmication of polydienes offers a new route to nanoparticle patterning, that exploits inexpensive and readily available block copolymers, such as Vector copolymers (Dexco) or Kratons.

M11.22

Coalescence of Nano-Clusters: Direct HRTEM Observation. Wei-Jun Zhang, RD&E, Philip Morris USA, Richmond, Virginia.

Coalescence of nano-clusters is an important step in the synthesis and assembling of nano particles. Understanding the coalescence process will have a great impact on the development of nano materials and nano systems for a wide range of applications such as in catalysis, biology and information technologies. The coalescence of model Au and Pt nanoparticles was studied in 1988. However, no direct observation of the coalescence of oxide nano clusters has been made. In this presentation, we will present the coalescence process of copper oxide clusters of 3 8 nm in size using high-resolution transmission electron microscopy. We found that the coalescence of small clusters which can freely change their orientations is analogous to the coalescence of liquid droplets. The smaller clusters lose their crystalline identity and merge rapidly with the larger clusters, with no interface or defects observed. In contrast, the coalescence of large clusters with misorientation behaves as the sintering of bulk crystalline particles. Formation of interfaces and dislocations were observed during coalescence, with the clusters maintaining their own crystalline orientations. In both cases, surface atom migration is the major mechanism of coalescence. After merging, the newly-formed clusters tend to re-structure their morphologies to a spherical shape to minimize the surface energy. We observed that the crystalline fringes of the clusters disappeared when a spherical cluster formed.

M11.23

Nickel Nanoparticles Produced by an Argon Ion Technique. Alejandro Torres[1], Ubaldo Ortiz[1], Manuel Enrique Lopez[2] and Antonio Aguilar[2]; [1]Doctorado en Ingenieria de Materiales, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza., Nuevo Leon, Mexico; [2]Doctorado en Materiales, Facultad de Ingenieria Mecanica y Electrica, San Nicolas de los Garza, Nuevo Leon, Mexico.

Nickel nanoparticles where been produced using an Argon ion mill. Standard ion polishing system usually used for sample preparation, was utilized to mill a nickel sample. By this way, nickel nanoparticles were deposed on two different surfaces: a double sided carbon tape and a cooper grid covered with a collodion film. Morphology and composition of particle where analyzed using Scanning Electrons Microscopy (SEM) and Transmission Electrons Microscopy (TEM). Energy Dispersive X-ray Spectrometry was used to analyze chemical elemental distrubution. The structure was composed by nickel particles with a size about 20 nm. This method can be utilized to produce metal nanostructures if the deposit surface is controlled using for example a mask.

M11.24

An optimized synthetic route for the preparation of water-soluble nanomagnetic conducting polyaniline with high processability. Sarswati Koul[2] and Arokia Nathan[2]; [1]Department of ECE-waterloo, 200-waterloo university, waterloo, Ontario, Canada; [2]ECE dept, waterloo university, waterloo - ONtario, Ontario, Canada.

The size dependent proeprty of materials at the nanometer scale provides significant insight into the scaling limits of nanomaterials and their use for microelectronics and data storage systems. Synthesis of nanomagnetic conducting polyaniline with controlled kinetic homogenous nucleation was optimized by using a polyelectrolyte based dopant system, folowed by complete elimination of benzidine. High processability of nanomagentic polymer stems from the partial crystalline nature of the matrix. the transition in magnetic behaviour from ferromagnetic to paramagnetic was explored and identified in relation with polyelectrolyte based synthesized dopant system. A linear behaviour up to 6 Tesla magnetic field was observed for synthesized nanomagnetic conducting polyaniline, whereas a clear hystersis loop depicting ferromagnetism was observed for synthesized dopant system, whcih acts both as an oxidant as well as a charge-transfer complex for conducting polyaniline. Morphological and high-resolution TEM studies reveal the presence of an average particle size from 9-12 nm followed by an interparticle average distance of 190-212nm. Diffraction studies indicate the presence of 60% amorphous and 40% crystalline fraction in the matrix structure. An average molecular weight of 5375 Daltons with a polydispersity index of 5.31 was observed. thermal behvaiour of the polymer showed no sharp glass transition except a broad endothermic peak at 137^o, followed by a weight loss of 78.22% while subjecting itf rom 50^{o}C to 1200^{o}C. Elemental analysis reveals the presence of magnetic material in a random order. Structural studies support the presence of aromatic backbone with short-branched dendrameric chains attached randomly to it. An isothermal study carried out under ordinary atmospheric conditions concludes that the polymer is highly resistant to atmospheric conditions both in its neutral as well as in a conduting form without losing its intrinsic proeprties.

M11.25

Template-assisted growth of nanowires using novel nanoporous films fabricated by inorganic nano phase separation. Kazuhiko Fukutani, Taiko Motoi and Toru Den; Canon Inc., Atsugi, Japan.

High densities and small diameters of nanowire arrays are strongly desired for future ultrahigh density data storage and high performance thermoelectric devices. In order to fabricate such nanowire arrays easily, the template-assisted growth of nanowires is an elegant way. We developed new nanoporous films with a narrow pore diameter (<10nm) and high pore density (>5 Tera pores/in2) as a template. Nano phase separation of the eutectic Al-Si system was used for the fabrication of the nanoporous films. Co-sputtered AlSi films prepared by appropriate compositions and deposition conditions form Al nano-cylinder structures perpendicular to the substrate embedded in an amorphous Si matrix during film growth due to nano phase separation. Removal of the Al nano-cylinder structures from the co-sputtered AlSi films by chemical etching gives us novel nanoporous films with a narrow pore diameter (<10nm) and high pore density (>5 Tera pores/in2). The novel nanoporous films consist of mainly oxidized silicon. Depending on film preparation conditions such as the target composition, the pore diameter can be varied systematically from less than 5nm to 15nm with a pore density from 1 to 10 Tera pores/in2. The film thickness can be controlled by the deposition time. The template-assisted growth of Ni nanowires was studied by using the electrochemical deposition. A 7nm Ni nanowire array was fabricated successfully.

M11.26

Temperature dependent energy transfer in CdTe quantum dot solids. Sander Wuister, Rolf Koole, Celso de1 Mello Donega, Andries Meijerink; Chemistry and Physics of Condensed Matter, Utrecht University, Utrecht, , Netherlands.

Efficiently luminescing quantum dots are interesting for both fundamental and applied research. The excitonic emission of semiconductor quantum dots is characterized by a strong dipole moment. In a quantum dot solid the inter-particle distance is very small. Via dipole-dipole interaction energy transfer from smaller to larger quantum dot can occur. The decay kinetics of a quantum dot solid of CdTe (prepared from efficiently luminescing CdTe quantum dots) is studied as function of the temperature. Energy transfer is observed from smaller quantum dots to larger quantum dots. The dipole-dipole transfer rate is small at low temperatures becomes faster when the temperature increases. The measurements are explained by the temperature dependent Singlet-Triplet equilibrium that influences the dipole strength of the CdTe quantum dot and the energy transfer rate. A good agreement between the rate of energy transfer and the radiative decay rate is observed confirming that inter-dot energy transfer is dominated by dipole-dipole interaction.

M11.27

Ion beams meet nanobelts. Carsten Ronning[1], Daniel Schwen[1], Puxian Gao[2], Yong Ding[2] and Zhong Lin Wang[2]; [1]II. Institute of Physics, University of Goettingen, Goettingen, Germany; [2]Dept. of Materials Science & Eng., Georgia Institute of Technology, Atlanta, Georgia.

Zinc oxide (ZnO) and zinc sulfide (ZnS) nanobelts synthesized by thermal evaporation have been ion implanted with a variety of ions. Nitrogen ions were used in order to achieve n-type doping; whereas Mn ions were used in order to obtain a diluted magnetic semiconductor (DMS). Both transmission electron microscopy (TEM) and photoluminescence (PL) investigations show high defective material directly after the implantation process. Upon annealing, the matrix recovers in both in structure and luminescence. In this paper, we will present a detailed analysis of the created defects, the recovery mechanism, as well as some considerations on the doping feasibility of nanowires using ion beams.

M11.28

Effects of Particle Morphology on the Phase Stability Titanium Dioxide at the Nanoscale. Amanda Barnard and Peter Zapol; Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Titanium dioxide nanoparticles are currently receiving a lot of attention due to their inherent suitability for advanced photochemical applications, especially interfacing with organic molecules such as DNA. Size, phase and morphology of the nanoparticles are the critical parameters determining their suitability for particular applications. A new thermodynamic model devised to describe the shape of nanoparticles as a function of size has been used to predict the phase stability of titanium dioxide nanoparticles, with particular attention given to the cross-over of stability between the anatase and rutile phases. Density functional calculations were used to accurately determine surface energies that incorporate the effects of surface stress. The effects of nanocrystal morphology on the phase transition are addressed and comparisons drawn with previously reported studies; and the results used to construct a framework to investigate the extent to which the nanoparticle shape may be manipulated via careful selection of environmental parameters.

M11.29

Confinement of Nanocrystals and Possible Charge Storage Mechanism for MIS Memory Devices with Ge Nanocrystals Embedded in SiO$_2$. Vincent Ho[1], Wee Kiong Choi[1,2], Wai Kin Chim[1,2], Lee Wee Teo[2], An Yan Du[3] and Chih Hang Tung[3]; [1]Electrical and Computing Engineering, National University of Singapore, Singapore, Singapore; [2]Singapore-MIT Alliance, National University of Singapore, Singapore, Singapore; [3]Institute of Microelectronics, Institute of Microelectronics, Singapore, Singapore.

We have observed memory effect in a metal-insulator-silicon (MIS) structure with the insulator layer consisting of a sputtered capping SiO_2 / Ge nanocrystals embedded in SiO_2 / rapid thermal oxide structure. In this paper, we report the influence of Ge concentration on the confinement of Ge nanocrystals in the SiO_2 matrix and speculate on the possible origin for the charge storage phenomenon of our devices. Three types of memory devices with fixed capping oxide and rapid thermal oxide thickness were fabricated to study the effect of Ge concentration. The Ge concentration was varied according to the areal ratio of Ge to SiO_2 of the 4 inch sputtering target. The three types of devices had Ge to SiO_2 areal ratios of 4.44%, 17.78% and 100%. From the high resolution transmission electron microscopy (HRTEM) results, Ge nanocrystals of diameters 3 and 6 nm were found to form in the middle layer when the MIS structures with 4.44% and 17.78% Ge to SiO_2 areal ratios were rapid thermal annealed at 1000øC for 300s in Ar ambient. This means that the RTO and the capping oxide layers were able to confine the nanocrystals within the middle layer to some extent. However, in devices with a Ge to SiO_2 areal ratio of 100%, nanocrystals of sizes varying from 2.5 to 10 nm were obtained with a significant diffusion of Ge through the RTO layer. It was observed that Ge atoms coalesced to form larger nanocrystals that were in contact with the Si substrate. This indicates that the RTO and capping oxide layers were not as effective in confining the Ge nanocrystals as compared to the previous two cases. We have also annealed devices with a Ge to SiO_2 areal ratio of 17.78% in Ar and forming gas to study the effect of annealing ambient on the nanocrystal formation. We have consistently observed memory effect from devices annealed in Ar and the absence of memory effect from devices annealed in forming gas. However, the HRTEM results showed the existence of Ge nanocrystals in devices annealed in both ambient. In addition, we have previously established that no memory effect could be observed if there are no nanocrystals formed. This means that the presence of Ge nanocrystals is a pre-requisite for charge storage to occur, but having nanocrystals does not necessarily imply the presence of charge storage or memory effect. We speculate that the charge storage mechanism is most likely linked to either defects at the surface of the nanocrystals or deep traps in the nanocrystals, i.e. they are not stored in the conduction or valence band of the nanocrystals. We propose that the charges tunnel into the conduction or valence band of the nanocrystal before they thermalize into the surface or deep traps.

M11.30

Nanosprings: Processing, Structure, Property Relationships.

Grant Norton[1], Aaron LaLonde[1], Daqing Zhang[2], Abdullah Alkhateeb[2] and David McIlroy[2]; [1]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [2]Department of Physics, University of Idaho, Moscow, Idaho.

This presentation will describe our work in the formation and characterization of nanosprings of boron carbide and silicon carbide. Spring growth occurs through the vapor-liquid-solid (VLS) growth mode, first described in the 1960s for the growth of silicon whiskers. A key requirement in nanospring formation is that they are amorphous. Our model for spring growth, not accounted for in the original explanation of VLS, is that of contact angle anisotropy at the liquid/solid interface that drives helical growth. Nanosprings are grown in a PECVD chamber by the decomposition of closo-l, 2-dicarbadodecaborane (C2B10H12) onto a silicon substrate. For the formation of SiC nanosprings the catalyst is nickel boride. After growth the resulting structures are characterized by electron microscopy. The results of many observations of nanospring morphology will be presented and the details of the growth mechanism discussed. One of our goals is to be able to selectively produce either nanosprings or nanowires. To do this one must understand the roles of the various deposition parameters on growth morphology. Our efforts in this area will be presented.

M11.31

Effect of Carrier Gas on the Growth Rate, Growth Density, and Structures of Carbon Nanotubes.

Yoke Khin Yap[1], Vijaya Kayastha[1], Steve Hackney[2], Dimovski Svetlana[3] and Yury Gogotsi[3]; [1]Physics, Michigan Technological University, Houghton, Michigan; [2]Materials Science and Engineering, Michigan Technological University, Houghton, Michigan; [3]Materials Science and Engineering, A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania.

One of the challenges of growing carbon nanotubes (CNTs) is to sustain the growth to unlimited tube lengths. The well-accepted growth mechanism of CNTs involves the decomposition of hydrocarbon gases on a catalyst, the diffusion of carbon into the catalyst until saturation, and subsequent segregation of carbon from the catalyst as a tubular structure. Ideally, CNTs will continue to grow if every carbon atom that reached on the catalyst's surfaces can be converted as CNTs. Such an ideal condition has not been achieved due to the lack of control over the decomposition, diffusion, and segregation processes. Here we report our original finding on controlling the decomposition of C_2H_2 on Fe catalysts during the growth of multiwall carbon nanotubes (MWNTs). We found that the use of carrier gases can either suppress or enhance the decomposition rate of C_2H_2 on Fe nanoparticles. Furthermore, the growth density and the structures of these MWNTs vary when different carrier gases are used. These results suggest rational control on the growth rate, the growth density, and the structures of CNTs produced by thermal chemical vapor deposition (CVD). We can grow MWNTs at 800 °C by using pure C_2H_2 gas on SiO_2/Si substrates coated with Fe films. It is notable that ammonia gas is often required for pretreatment and growing of MWNTs by this technique. The typical growth rate of MWNTs from pure C_2H_2 gas is about two microns per hour. However, the growth of MWNTs in this case terminated after half an hour. We found that the addition of Argon allowed continuous growth of MWNTs for at least two hours. In this case, MWNTs grown with the addition of Ar can be as long as ten microns. On the other hand, a different growth morphology was observed when H_2 was used as the carrier gas. The growth of MWNTs with H_2 carrier gas can be extended to at least two hours with a similar growth rate as with Ar. However, the growth density of MWNTs was significantly reduced as compared to that observed for the Ar carrier gas. Further changes on the growth morphology occurred when N_2 was used as the carrier gas. The addition of pure N_2 to C_2H_2 gas has suppressed both the growth density and length of MWNTs. Finally, it is interesting to note that the addition of H_2 and N_2 to C_2H_2 can enhanced the growth rate faster than the mixtures of Ar or H_2. Furthermore, the use of different carrier gases results in MWNTs with either branching, fullerene capped, or bamboo-like structures. These CNTs were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. A growth model and mechanism involved will be discussed.

M11.32

MOCVD Growth of GaN Nanoneedles and Nanowires.

George T. Wang, J. Randall Creighton and Paula P. Provencio; 1126, Sandia National Laboratories, Albuquerque, New Mexico.

GaN nanoneedles and nanowires have been synthesized using a metal organic chemical vapor deposition (MOCVD) process in a rotating disk reactor under typical GaN film growth conditions. The nanoneedles and nanowires were grown on sapphire substrates coated with thin Ni catalyst films using trimethylgallium and ammonia as growth precursors. The majority of nanoneedles grown are several to tens of microns in length and have tip diameters between 60-150 nm and base diameters that can exceed 1 micron. TEM and EDS studies indicate that the nanoneedles are single-crystalline GaN with Ni clusters at the tips, indicating growth via the vapor-liquid-solid (VLS) mechanism. It was found that the presence of catalysts enhanced film nucleation as well, raising the issue of competition between GaN film nucleation and nanowire growth. Different variables and growth conditions have been explored, including temperature, pressure, catalyst, substrate orientation and roughness, and reactant concentrations in order to determine the effect on nanoneedle and nanowire growth morphology, density, and size.

M11.33

Selective Positioning of Ti-Catalyzed Silicon Nanowires.

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

Continuous device miniaturization will soon require the self-assembly of nanometer-scale components via chemical synthesis due to physical and economic limitations of conventional device scaling. Self-assembled semiconductor nanowires are expected to be of interest for a variety of electronic, optical, and optoelectronic device applications. Although significant advances have been made in bulk synthesis of nanowires, in order to integrate semiconductor nanowires into conventional IC technology, the nanowires must be positioned at predetermined locations within a device platform. In this paper, we address some specific issues in the selective nanowire growth using a Ti-silicide catalyzed chemical vapor deposition (CVD) technique. Nanometer scale titanium silicide (Ti-silicide) islands have been previously used to catalyze the growth of silicon in one dimension to form nanowires by CVD. Nanoscale Ti-silicide islands are formed by annealing a thin Ti film (e-beam evaporated or CVD) on a Si substrate at elevated temperatures. In order to grow nanowires at predetermined locations, it is imperative to control the Ti-silicide nucleation. In this paper, we will show the dependence of the Ti-silicide formation on different substrate materials commonly used in Si IC technology and the annealing conditions. We will also demonstrate that surface irregularities, such as facet edges and corners, offer favorable nucleation sites. Lattice mismatch between Ti-silicide and silicon causes an increase in the strain energy. In order to reduce the elastic strain energy, Ti-silicide forms into nanoscale islands. The islands tend to nucleate favorably at the sites with a minimum total energy. The corner and edge sites are the energetically preferred sites as they have a greater tendency for strain relaxation. Thus, the nucleation is easier at the corner and edge sites. These surface irregularities in the form of ridges and mesas can be defined on a wafer using only conventional photolithography, anisotropic etching and deposition processes. The requirement for favorable nucleation, however, is that the lateral dimensions of these features need to be smaller than twice the characteristic Ti diffusion length at the annealing temperatures. We will present our results of selective Ti-silicide nucleation at predetermined locations on an oxide-patterned Si wafer and the subsequent nanowire growth at these locations.

M11.34

simple fabrication of high density quantum dot arrays using anodic aluminium oxide mask. Sung Joon-ho[1], Moon Heesung[1], Bahng Jae ho[2], Koo Ja-Yong[2] and Kim Bongsoo[1]; [1]Chemistry, Korea Advanced Institute of Science and Technology, Daejon, South Korea; [2]Materials Evaluation Center, Korea Research Institute of Standards and Science, Daejon, South Korea.

We fabricated quantum dot arrays using anodic alumina mask. The porous alumina is used as one of the nano-template techniques based on bottom-up type nano structure fabrication. We grew an alumina template on Si wafers by two step anodization. The porous alumina template thus grown is used as a mask for metal deposition. After thermal evaporation and removal of the mask, we fabricated the quantum dot arrarys on a Si substrate. From this template-assisted method we obtained high density array of quantum dots in a large scale. These quantum dots have a narrow size distribution which is easily controlled by a pore widening of templates from 20 to 60 nm. The size controlled quantum dots can be used to control the diameters of a nanowire.

M11.35

Well-Ordered Silicon Nanowire-Bridge Arrays Formed by Metal-Catalyzed Chemical Vapor Deposition. M. Saif Islam, Shashank Sharma, Theodore I. Kamins and R. Stanley Williams; Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

We report simultaneous lateral growth of a high density of highly oriented, metal-catalyzed silicon (Si) nanowires on a patterned (110)-oriented Si substrate with bridging of nanowires between two vertical (111)-Si planes, which can be developed into electrodes of an electronic device. A SiO2 etch mask was defined by optical lithography and aligned along the intersections of vertical (111) planes and the top surface of a (110)-oriented Si wafer so that the subsequently etched trench is bounded by two (111) surfaces. The Si wafer with oxide mask was then etched in 44% KOH-H2O to form vertical (111) surfaces. After angled deposition of catalytic Ti or Au nanoparticles on one of the two opposing vertical Si surfaces, we used a metal-catalyzed chemical vapor deposition (CVD) process to grow nanowires, which can extend across the trench to form mechanically robust "nano-bridges" with either metal catalyst. A disk-shaped deposit forms on the opposite sidewall around the impinging end of the Au-nucleated nanowires. We observed (111)-oriented secondary nanowire growth from the impinging ends of both Au- and Ti-nucleated nanowires. Tertiary nucleation was also occasionally observed for the Au-nucleated nanowires between narrow trenches. The nanowires make mechanically strong and robust connection at both vertical surfaces and resist considerable force. This method of connecting multiple nanowires between two electrodes offers the high surface-to-volume ratio needed for nano-sensor applications. Thus, by employing only optical lithography, a large array of nano-scale sensors can be formed between biasing electrodes. Nano-bridges constructed by this method may provide some of the vital building blocks needed to enable the emerging technology of nano-electronics. This demonstration combines the advantages of "bottom up" fabrication of nanostructures with "top down" formation of the connecting electrodes using only coarse optical lithography.

M11.36

Semiconducting supertetrahedral clusters and their assembly into superlattices. Nanfeng Zheng[1], Pingyun Feng[1] and Xianhui Bu[2]; [1]Department of Chemistry, University of California, Riverside, California; [2]Department of Chemistry and Biochemistry, California State University, Long Beach, California.

Metal chalcogenide supertetrahedral clusters represent a class of important semiconducting nanoclusters. By applying charge matching and thermodynamic rules, we have found that the size and structure could be tuned not only by the compositions but also by the synthetic conditions. So far, the size for the largest supertetrahedral cluster has been pushed to about 2 nm. These nano-sized clusters would likely bridge the gap between well-studied small molecular clusters and nano-crystals. Furthermore, the assembly of these zero-dimensional clusters can be directed either by organic or inorganic templates into superlattices. Based on their diverse building blocks and linkage modes, a large number of superlattices have been synthesized. These superlattices show uniqueness in their well-order structures. Unlike colloidal nanocrystal, the structure of the superlattices including their subunits supertetrahedral clusters could be determined through single crystal analysis. The synthesis, structures, and interesting physical properties will be presented.

M11.37

Transport Properties of Magnetic Nanowires with Multiple Constrictions Formed by FIB. Tie Liu[1,2] and Yihong Wu[1,2]; [1]Data Storage Institute, Singapore, Singapore; [2]Department of Electrical & Computer Engineering, National University of Singapore, Singapore, Singapore.

Ni and Co nanowires were fabricated by electrodeposition in porous membranes. Their diameters range from 30nm to 200nm, depending on the diameters of the membranes used. To study the transport properties of Ni nanowires, an individual nanowire was selected and connected with metal electrodes. The I-V curve was measured to study the transport properties of the nanowires. The magnetization reversal of the nanowires was studied by anisotropic magnetoresistance measurement at room temperature. The switching field was measured on individual nanowires as a function of the angle between the applied magnetic field and the wire axis. The results were quantitatively simulated and analyzed using classical magnetization reversal theories. Single and multiple constrictions were formed on the nanowires by focus ion beam trimming (FIB). The wires were further thinned using oxygen plasma oxidation. The magnetoresistance (MR) was measured with the nanowires parallel and perpendicular to the applied magnetic field. The results were compared before and after FIB trimming and oxidation. It shows that after the FIB trimming the switching field as well as the resistance jump at the switching field increases in the parallel configuration, while the MR ratio increases and the hysteresis decreases in the perpendicular configuration. The above effects were further enhanced by the subsequent oxidization process. The results might be understood by taking into account the domain wall resistance.

M11.38

Fabrication of CdTe Quantum Dot Arrays on GaAs utilizng Nanoporous Alumina Masks. Sun-il Mho[1], Mi Jung[1], Hong Seok Lee[2] and Hong Lee Park[2]; [1]Molecular Science &Technology, Ajou University,Suwon 442-749, Suwon, South Korea; [2]Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, seoul, South Korea.

The fabrication of quantum dot structures (QDs) is attractive because of applications in electronic and optoelectronic devices, such as single electron transistor, laser diode, and infrared photodetector. The CdTe QDs systems have become attractive because of their potential applications in optoelectronics devices of visible range. However, little work has been performed on II-VI/III-V QDs, because of lattice mismatch (14%) between GaAs substrate and CdTe. One of the major challenges in fabricating QDs is the uniformity and reproducibility in size and spatial distribution. The uniformity and reproducibility of QDs can be improved by using the nanoporous alumina template. The geometry of porous alumina may be schematically represented as a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate. The well-ordered nanoporous alumina templates were able to obtain by two-step anodizing processes from aluminum in acid solutions at low temperature. CdTe QDs on GaAs substrate were grown by molecular beam epitaxy method using the porous alumina masks(< 5 μm) with pore diameter (ca.70) nm and the pore density (10^{10}/ cm^2). The temperature of substrate and source (Cd, Te) was an important factor for growth of CdTe QDs on GaAs substrate. The arrays of QDs are examined by atomic force microscopy (AFM), which reveals regular size distribution of alumina mask.

M11.39

Observation of CL peak positions in a single InGaN Nanorod with Indium content. Hwa-Mok Kim[1], Tae Won Kang[1] and Kwan Soo Chung[2]; [1]QSRC, Dongguk University, Seoul, South Korea; [2]School of Electronics and Information, Kyunghee University, Yongin, South Korea.

This work demonstrates the properties of InGaN nanorod arrays with various In mole fractions by modified HVPE using In metal at the low growth temperature. The nanorods grown on (0001) sapphire substrates are preferentially oriented in the c-axis direction. We found that the In mole fractions in the nanorods were linearly increased at $x \leq 0.1$. However, In mole fractions were slightly increased at $x \rangle 0.1$ and then were gradually saturated at $x = 0.2$. CL spectra show strong blue emissions from 428 nm (2.89 eV at $x = 0.1$) to 470 nm (2.64 eV at $x = 0.2$) at room temperature. From this result, we found the fact that increasing In mole fraction in the InGaN nanorod shift CL peak position of InGaN nanorod to the low energy region.

M11.40

Characterization of CdS Quantum Dots and Quantum Wires Generated in Zeolites. Nak Cheon Jeong, Hyun Sung Kim, Yun-Jo Lee, Won Ju Phang and Kyung Byung Yoon; chemistry, sogang univ., Seoul, South Korea.

The CdS quantum dot and quantum wires generated within zeolite nanopores have received great attention due to their potential to be developed into innovative devices. However, there have been controversies over the exact locations of the species in zeolites. This poster will show the precise assignment of the locations of CdS species.

M11.41

Nanowires of β-NaxV2O5 grown by Metalorganic Chemical Vapor Deposition from Vanadyl acetylacetonate. M.B Sahana and S. A. Shivashankar; Materials research centre, Indian Institute of Science, Bangalore, Karnataka, India.

β-NaxV2O5 is a low-dimensional material with interesting electrical and magnetic behavior, which critically depends on the value of x. β-Na0.33V2O5 exhibits three phase transitions as a function of temperature: a sodium-ordering transition at $\geq$240 K accompanied by a doubling of the unit cell along b, a metal-insulator transition at $\geq$136 K involving a tripling of the unit cell, and a paramagnetic$-$canted antiferromagnetic transition at $\geq$22 K. In this work, we report the growth on glass substrates of nanowires of β-NaxV2O5 measuring 20-200 nm in diameter and 10-30 mm in length, by metalorganic chemical vapor deposition using the β-diketonate complex, vanadyl acetylacetonate, as precursor, but without the use of either templates or catalysts. The formation of β-NaxV2O5 on glass is due to the diffusion of sodium from the glass into the growing film. The composition map of the film as analyzed by SIMS will be presented. This is manifested in the absence of a sharp absorption edge in the transmission spectra of the film. Films consisting of nanowires of monophasic β-NaxV2O5 with a preferred orientation along (h0l) are formed only at 550°C, whereas those deposited at 540°C comprise a mixture of nanowires (β-NaxV2O5) and platelets (V2O5). Films deposited at lower temperatures are less crystalline and comprise a mixture of different vanadium oxides. Annealing at 550°C shows β-NaxV2O5 to be volatile. Further, it is observed that nanowires are formed only in the narrow temperature range 540-550°C, and that there is a critical dependence of the formation of nanowires on the balance between the CVD growth rate and the evaporation rate of the film. It is thus inferred that the formation of nanowires of β-NaxV2O5 is due to chemical vapor transport. Also the results of the magnetic measurements of the films comprised of nanowires of β-NaxV2O5 carried out by SQUID magnetometer will be discussed.

M11.42

Improvement of electrical properties of tin oxide nanoparticle by controlling its surface structure. Sung-Jei Hong and Jeong-In Han; Korea Electronics Technology Institute, PyungTaek-Si, KyungGi-Do, South Korea.

In this work, a novel synthetic method of tin oxide nanoparticle is introduced by controlling its surface structure. The control of the surface structure is crucial since the electrical properties are influenced by the structure. One of main factors affecting the properties is the metallic cluster doped on the surface. The cluster plays a key role to suppress grain growth during the synthesis of the nanoparticle. However, current doping onto the tin oxide nanoparticle cannot guarantee the uniformity of distribution. Thus, the electrical properties are unstable with long term aging due to growth of the nanoparticles at the cluster poor region. So, we attempted to disperse the cluster uniformly on the particle and, in result, we developed in-situ synthesis method of the quantum confined tin oxide-cluster nanoparticle. Pd is applied as the surface cluster, and Sn acetate and Pd acetate are used for the in-situ synthesis. These raw materials enable low temperature process of the nanoparticle since the removal of organic components is possible below 300^{o}C. HRTEM observation reveals that the size of the synthesized nanoparticle is ranged in 2 7 nm and the Pd cluster is uniformly distributed on the lattice of tin oxide particle. In fact, XRD analysis certifies the uniform solid solution of the Pd cluster on the tin oxide nanoparticle. Also, the surface-modified tin oxide nanoparticle exhibit a better electrical properties. When the nanoparticle reacts with carbon-hydrogen molecule, the electrical resistance decreases to 95%. In contrary, the nanoparticle without the surface modification shows only a decrease of 68%. The electrical change is very excited when it is applied to a gas sensitive thick film layer. In addition, the electrical properties show very stable phenomena after 400 hours aging at 400^{o}C. So, the quantum confined tin oxide nanoparticle-Pd cluster by using in-situ synthesis method improved the electrical properties.

*M11.43

Effect of small dimensions on Magnetic Metallic and Organic Nanowires Properties. Jean-Luc Duvail[1], Patrice Retho[1], Guy Louarn[1], Olivier Chauvet[1], Sophie Demoustier-Champagne[3] and Luc Piraux[2]; [1]LPC, IMN, Nantes, France; [2]PCPM, UCL, Louvain-la-Neuve, Belgium; [3]POLY, UCL, Louvain-la-Neuve, Belgium.

Among the different strategies developed to elaborate nanomaterials, the chemical or electrochemical synthesis within the nanopores of a template has proven to be reliable for the fabrication of nanowires and nanotubules. Recently, composites nanostructures and multilayered nanowires with unique properties have been obtained. In this work, we report on the synthesis and the physical properties of metallic (magnetic or not) and conducting polymer nanowires or nanotubes prepared using the template method. The resulting cylinders have diameters ranging between 30 nm and 200 nm, a smooth surface, and the controlled length can vary from few nanometers up to 20 micrometers. For the magnetic metallic nanowires, original transport and magnetic properties are due to dimensions comparable to a characteristic physical length (mean free path, spin diffusion length, domain wall thickness). We measured CPP-GMR, that is Giant Magnetoresistance in the Current Perpendicular to the Plane geometry, for different kinds of multilayers like cobalt/copper, permalloy/copper, iron/copper. The spin diffusion lengths for the different metals were deduced from analysis based on the Valet-Fert model. These systems may be used as building-blocks for Spintronics. The CPP-GMR effect has also been proposed to be used for the next generation of Hard-Disk read head. Concerning the conducting polymer nanowires and nanotubes, improved molecular and supermolecular structures induced by the confined synthesis are responsible for physical properties different from the bulk materials. Electrical properties of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires were determined for several nanowire diameters and compared with the case of PEDOT thin films. Different temperature dependences, down to 1.5 K, were evidenced and explained by spectroscopic studies (X.P.S., E.S.R.). In addition, a comparative resonant Raman scattering study was made on film, bundles of wires and individual wires. Vibrational and semi-empirical calculations give interpretation to the changes in the molecular and thus the electronic structure. A comparison with results on polypyrrole and polyaniline nanotubes is proposed. These conjugated polymer nanowires already used as nanoLEDs, are promissing systems for bio- and chemical-sensors. We also succeeded in preparing hybrid conducting polymer-metal nanowires. Such organic-inorganic systems are of interest for functional hybrid materials. In addition, the resulting nano-junctions are key elements for nano-devices.

M11.44

Granular Nanowire Single Electron Transistor for Possible Room Temperature Applications. Lolita Rotkina[1], Jie-Feng Lin[2] and Jonathan Bird[2]; [1]Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Department of Electrical Engineering, Arizona State University, Tempe, Arizona.

We have fabricated Pt-C composite nanowires by electron-beam deposition (EBD) and prototyped the Single Electron Transistor (SET) and studied their electrical characteristics. TEM studies reveal that the nanowires fabricated by the EBD technique have essentially a granular structure, where the grains are Pt crystallites embedded in amorphous carbon matrix. The average size of crystallites is about 2 nm in diameter. Measurements of the low-temperature current-voltage characteristics of the EBD nanowires reveal a clear Coulomb gap at 4.2 K, whose magnitude (0.1 eV) appears consistent with single-electron tunneling between Pt nanocrystals in the wires. The large charging energy associated with the nanocrystals ensures the persistence of the Coulomb-blockade behavior at room temperature. As deposited EBD nanowires are insulating at small applied bias. Rapid Thermal Annealing (RTA) decreases the resistivity of nanowires considerably without evident change the structural properties if the wires deposited as a film. The EBD Pt nanowires may provide a simple and convenient approach to the realization of room-temperature single-electron devices. In our presentation, we will also present the results of studies in which three-terminal device prototypes based on the EBD nanowires have been used to investigate single-electron-transistor action. Of interest here is the potential application of the granular nanowires to single-electron memory structures. Acknowledgements: Work at ASU and UIUC supported by the Office of Naval Research ONR (N00014-98-0594). L.R. acknowledges partial support from DoE (DE-FG02-01ER45932). Fabrication and microscopy were carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by DoE (DEFG02-91-ER45439). Reference: L. Rotkina, J.-F. Lin, J. P. Bird, Appl. Phys. Lett., in press, scheduled for publication in issue 83, 24 November 2003.

M11.45

Synthesis and Growth Kinetics of ZnO Nanoparticles. Yuntao Li and Hung-Jue Sue; Mechanical Engineering, Texas A&M University, College Station, Texas.

A new sol-gel synthesis route has been performed to produce ZnO nanoparticles with particle sizes ranging from 2-4 nm. The new synthesis approach can generate well-controlled, highly concentrated ZnO nanoparticles in solution. Additionally, the new synthesis process is simple and versatile, allowing choices of many different types of solvents as the medium to produce high quality ZnO nanoparticles. In solution, zinc hydroxide species are expected to form in the beginning, followed by dissociation of zinc hydroxide to form ZnO nanoparticles. The size of ZnO nanoparticles can be easily controlled by aging. The particle growth is found to be time and temperature dependent. The particle aging kinetics was determined by monitoring the UV/vis absorption and green luminescence, and found to exhibit exponential relationship. Detailed growth kinentics of ZnO nanoparticle formation in various solvent environments have been investigated, and will be reported. Strategy for producing narrow particle size distribution of ZnO nanoparticles will also be addressed.

M11.46

Fabrication of Conductive Polymer Nanofiber Mats Produced from Multiwall Nanotube Solutions. Max Dudley Alexander and Brandon Black; Polymers, Air Force Research Lab, WPAFB, Ohio.

Electrospinning of polymers offers the ability to reproducibly manufacture sub-micron diameter fibers with desired morphologies. While the process for electrospinning has been available for some time there has been very little work in the area of incorporating useful nanoparticles such as carbon nanotubes into the polymer nanofiber. Methods to produce mats of polyurethanes containing conductive multi-wall nanotubes are illustrated. These mats can serve as the building blocks for collection electrodes in organic-inorganic hybrid photovotaics or can be further functionalized with appropriate receptors for use in detecting (through a change in the electrical conductivity) and filtering out biological contaminates.

M11.47

Synthesis, Characterization, and Modeling of Self-Organized Nanostructure Arrays Generated by Laser Irradiation. Yingfeng Guan and Anthony J Pedraza; Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee.

One- and 2-dimensional arrays of nanoprotrusions can be generated by pulsed laser irradiation. These structures have been produced on the surface of silicon to a height of 80 nm using a Lloyd's mirror configuration. Atomic force and high resolution scanning electron microscopy studies reveal that these structures are preceded by the formation of extended ripples that can reach a height of up to 12 nm. It is shown that one or two identifiable arrays of mutually orthogonal ripples may form. Out of the four differently-spaced ripple arrays that were found, three indicate a very close connection with the production of laser-induced periodic surface structures (LIPSS). Interference of the incoming or refracted laser beam and the laser light scattered by surface undulations has been recognized as the cause of LIPSS formation. The present experiments show that the Lloyd's mirror configuration strongly enhances the formation of ripples and nanoprotrusions that form at the intersection of two mutually orthogonal sets of ripples. Each of the beams, the directly incident and the mirror-reflected beam, independently produce an interference pattern with their corresponding scattered beams. However, these two independently generated patterns coincide because their periodicity is only a function of the angle of incidence. Thus, the two interference patterns reinforce each other's effects on the substrate. On the other hand, when Lloyd's mirror is not added, only ripple formation was observed under direct irradiation of the substrate, with no protrusions. Analyses of the data indicate that the formation of the ripples is due to a hydrodynamic process while a very thin layer of silicon remains melted. AFM shows that first small protrusions appear on top of the ripple hills and as they grow taller and thinner the ripples mostly disappear. A quantitative description of the response of the material to the power modulations is conducted considering that a very thin melted layer during irradiation is required to form the ripple structures. The temperature gradient induced by a modulation of the light intensity in the liquid layer was calculated by means of a 2-D computer model. Next, the effect of this temperature gradient on the melted layer was analyzed using computer and analytical hydrodynamic approximations. It was concluded that the gradient of surface tension is responsible for the formation of the ripple structure and that the break-down of the ripples into aligned protrusions is due to a temperature modulation along the ripple lines. The intersection of two mutually perpendicular ripple structures and the very high reflectivity of the nanoprotrusion tips are two of the causes that promote this secondary modulation of laser light. Possible applications of these nanostructured surfaces are briefly discussed.

M11.48

Metallic and Semiconducting Nanowires from Single Wall Carbon Nanotubes. Kousik Sivakumar, Shaoxin Lu and Balaji Panchapakesan; Electrical and Computer Engineering, University of Delaware, Newark, Delaware.

The focus of todays research has largely shifted from macro scale to micro scale and further to nano scale. The reason being the desire to realize quantum size effects in devices that has long eluded scientists around the world alike. With the discovery of nanoparticles, nanowires, and nanotubes, the ability to realize these effects practically into devices has increased manifold. Particularly, carbon nanotubes are becoming standard materials owing to the big push given to drive research in carbon nanotechnology through out the world. Integration of carbon nanotubes with different types of functional materials may become mandatory in the future for electronics and sensing applications and in this sense, nucleation, growth and evolution of the structure of metallic and semiconducting materials on carbon nanotubes may be necessary. Further, it also provides opportunities to do fundamental research on understanding the structure-property relationships of these nanowires using carbon nanotubes. In this paper, we present a technique to form metallic nanowires using carbon nanotubes themselves as templates. Nanowires of silver and platinum have been fabricated by the electric field assisted deposition of nano particles of these metals on single walled carbon nanotubes. SEM and TEM investigations have shown the dimensions of the nanowires to be dependent only on the size of the nanoparticles, 10 to 100 nm in our case. This technique provides a high degree of selectivity by manipulating the charges on the surface of the nanotubes, which enables the deposition of metals only on the nanotubes and not anywhere else. The versatility of this technique allows for the fabrication of different types of metallic and even semiconducting nanowires at the same dimensions as carbon nanotubes. A few of the many possible applications of these nanowires are integration with nanotubes to fabricate true nanoelectronic devices, nano scale interconnects between devices, extremely sensitive chemical sensors and construction of artificial muscles using reversible electric field induced strain.

M11.49

Ultrasonication: a New Method for Preparing Ceramic and Magnetic Nanoparticles. Muhammed Shafi[1], Abraham Ulman[1], Jr-iuan Lai[1], Claude Estournes[4], Nan-loh Yang[2] and Tom Vogt[3]; [1]Chemical,Biological Science & Engineering, Polytechnic University, Brooklyn, New York; [2]Chemistry, CUNY at Staten Island, Staten Island, New York; [3]Physics, Brookhaven National laboratory, Brookhaven, New York; [4]Materials Group, Institut de Physique et Chimie des Materiaux de Strasbourg, Strasbourg, France.

We present here the preparation of ceramic and magnetic nanoparticles using sonochemical decomposition technique. High Intensity Ultrasonication achieves complete mixing at the molecular level of the precursors and thus the reaction yields amorphous gel nanoparticles which on calcination at relatively low temperatures, temperatures hundreds of degrees lower than the traditional preparative routes using the ceramic method, gives crystalline nanoparticles. The applicability of this method has been exploited in the preparation of Gamma Alumina, Alumina based ceramic (LaAlO3. NdAlO3 BaAl2O4, Y3Al5O12 etc.) and iron based magnetic (YIG, Bi and Al doped YIG and ferroelectric (BaTiO3) nanoparticles. The method can be extended to any other ceramic or magnetic nanoparticles.

M11.50

Annealing Behaviour of Cobalt Nanoparticles on Si (001) Substrates. Chuan-Pu Liu[1], Chih-Chin Wang[1] and Rafal Dunin-Borkowski[2]; [1]Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, Taiwan; [2]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge.

Co nanoparticles are deposited on a Si (001) substrate using ion beam deposition with various ion energy and flux density. The nanoparticles from the as-deposited samples exhibit fcc phase with no specific orientation relationship with the substrate and with each other. However, the size can be controlled to be as small as 10 nm with rather uniform distribution. Subsequently, annealing experiments up to 700?C are performed ex-situ in a Philips CM30 transmission electron microscope on a plan-view foil prepared from the as-deposited samples. The evolution of nanoparticle morphology is subsequently characterized using Si (220) dark field imaging and off V zone bright field imaging. The results show that two different phase transformation mechanisms operate. At thicker regions, incoherent nanoparticles of weak contrast under Si (220) dark field turns into a strong contrast of black and white lobes, typical of coherent precipitates, while the size remains almost the same. This indicates that the incoherent Co nanoparticles become epitaxial with Si upon annealing, possibly by lattice rotation on sinking into the Si substrate. On the other hand, at thinner regions near to the foil edge, cobalt silicide nanowires nucleate at the expanse of the nanoparticles nearby. The nanowires containing various defects grow rapidly in length and slow in width. The detailed structure characterization and mechanisms accounted for the phase transformations are discussed in the paper.

M11.51

Formation of an Ordered Array of nc-Si Dots by Using a Solution Droplet Evaporation Method. Yoshishige Tsuchiya[1], Tatsuya Iwasa[1], Atsushi Tanaka[1], Ko-ichi Usami[1], Hiroshi Mizuta[2] and Shunri Oda[1]; [1]Research Center for Quantum Effect electronics, Tokyo Institute of Technology, Tokyo, Japan; [2]Department of Physical Electronics, Tokyo Institute of Technology, Tokyo, Japan.

Formation of materials with spatially ordered nanometer-scale structures is a key issue for fabricating novel nanodevices. We have succeeded in preparing an assembly of spherical nanocrystalline silicon (nc-Si) dots, with diameter of 8 nm and its dispersion less than 1 nm[1,2]. However, position control of individual nc-Si dots and formation of an ordered array are still challenging. In this paper, we report on formation of nc-Si dots arrays by evaporating a solution droplet. Two kinds of substrate were used in this study: one with a hydrofluoride(HF)-last Si surface and another with a thermally grown 1 nm-thick SiO$_2$ film over the surface. Nc-Si dots were deposited on these substrates by using VHF plasma decomposition of pulsed SiH$_4$ gas supply[2]. Aerial density of nc-Si dots is about 1×10^{11} cm^{-2}, corresponding to less than one monolayer in thickness. Some samples were oxidized after the deposition to form the SiO$_2$ shell around nc-Si dots. The 0.5 % HF was used as a solvent since a chemical reaction between HF and SiO$_2$ might be effective. Experimental procedures of drying a solution droplet are as follows. The droplet of HF solution was put on the substrate with the deposited nc-Si dots. After evaporating the HF solution, the surface was observed by scanning electron microscopy (SEM) and the image was compared with that taken before putting the droplet. Here we describe the result of a sample, where nc-Si dots were deposited on the Si surface and a natural oxide layer was formed around the nc-Si dots. Partially aggregated nc-Si dots were observed clearly in the SEM images after the HF solution evaporation. Many ordered structures such as a linear chain of 5dots and a parallel chain of 10 dots were observed on the Si surface. Possible processes in the HF solution include SiO$_2$ etching by HF, SiO$_2$ formation in water, the interdot attraction, and the attraction between the substrate and the dots, and the final configuration may be determined by the balance of these processes. Although more careful treatments are needed for fabricating larger structures, these results indicate that the solution droplet evaporation method is effective to form an ordered nc-Si dots array. [1]T. Ifuku et al., Jpn. J. Appl. Phys. 36, 4031 (1997). [2] K. Nishiguchi et al., Mat. Res. Soc. Symp. Proc. 571, 43 (2000).

SESSION M12: Poster Session: Nano-bio Materials II

Chair: Gullia Galli
Thursday Evening, April 15, 2004
8:00 PM
Salons 8-9 (Marriott)

M12.1

In Situ Processing of Spinel Ferrite Particle/Organic Hybrid. Toshinobu Yogo, Satoshi Nakamura and Wataru Sakamoto; Center for Integrated Research in Science and Engineering, Nagoya University, Nagoya, Aichi, Japan.

Inorganic/organic hybrid materials have been receiving intensive attention because of their synergic properties dependent upon each phase. Magnetic particle/organic hybrid materials have various applications, such as recording media, printing agent, ferrofluid, magnetic resonance imaging, hyperthermia. The authors reported the synthesis of magnetic iron oxide particle/organic hybrid through hydrolysis of iron-organic compound below 373K [1]. This paper describes in situ processing of spinel ferrite particle/organic hybrid from metal-organic compounds. Spinel particle/organic hybrid was synthesized from iron acetylacetonate derivative and metal acetylacetonate (metal=Ni, Co) below 373K. The formation of crystalline spinel particles in the organic matrix was confirmed by XRD analysis. The crystallinity of spinel particles was dependent upon the processing conditions, such as amount of hydrolysis water and time. TEM and SAD revealed crystalline particles below 10 nm were uniformly dispersed in the organic matrix. IR spectroscopy exhibited the presence of the chelated ligand to nano-sized particles in the hybrid. The BH curves of the nano-sized spinel oxide particle/organic hybrid showed superparamagnetic behavior at room temperature. The relation between processing conditions and magnetic properties was also investigated. 1. T. Yogo, T. Nakamura, W. Sakamoto and S. Hirano, J. Mater. Res. 15, 2114 (2000).

M12.2

Silver Nanosoldering of Gold Nanoparticles Using DNA. Soo Yeon Heo, Dong Hun Lee and Du-Jeon Jang; School of Chemistry(NS60), Seoul National University, Seoul, Sillim-dong, South Korea.

Metal nanoparticles exhibiting remarkable size-dependent properties are regarded as important parts of nano-devices. To construct the devices from the parts, it is necessary to interconnect the parts together to have Ohmic conjunction. Bimetallic nanoparticles exhibit unique electronic, optical properties and also have important biological applications in DNA sequencing. In recent years, it is studied that metal nanoparticles are aligned as two- and three-dimensional crystals by taking advantage of interactions between metal nanoparticles. Specifically, while metallic nanoparticles do not have any Ohmic contact, networks of metallic nanopartices do have Ohmic contact mutually. We will present that in a controlled manner, gold nanoparticles are soldered with silver to have Ohmic contact. A gold nanoparticle was bonded to another via hybridization of DNA strands attached to particles prior to silver nanosoldering.

M12.3

DNA as a template in the integration of top-down and bottom-up nanofabrication. Cecilia Anna Paulette Petit and Jeffrey D Carbeck; Chemical Engineering, Princeton University, Princeton, New Jersey.

This talk describes the integration of top-down and bottom-up fabrication strategies for the construction of hetero-structures composed of proteins, metallic and semi-conducting nanoparticles. Our top-down approach uses photolithography and flow in microfluidic channels to organize single molecules of DNA on a surface. Our bottom-up approach uses these DNA molecules as templates to direct the assembly of proteins and nanoparticles. This approach allows placement of proteins and nanoparticles along the DNA with a theoretical resolution of less than 1 nm. We demonstrate sequence-specific patterning of nanoparticles via the hybridization of functionalized complementary probes to surface-bound single chains of double-stranded DNA. Using this technique, we have assembled heterostructures composed of metals, semiconductors and proteins.

*M12.4

Heterostructures of Nanomaterials and Organic-Inorganic Nanoassemblies. Cengiz Sinan Ozkan, Mechanical Engineering, University of California at Riverside, Riverside, California.

Conventional nanofabrication strategies must be augmented by new techniques including self assembly methods in order to truly take advantage of the quantum nature of novel nanoscale devices and systems and permit the use of these properties for real applications in a larger system ($>$ 10 nm and $<$ 1000 nm). In this talk, I will describe a novel technique for the fabrication of nano-assemblies of quantum dots (QD) and carbon nanotubes (CNT) and -formation of CNT-QD conjugates-. CNTs are primarily functionalized with carboxylic end groups by oxidation in concentrated sulfuric acid. Thiol stabilized QDs in aqueous solution with amino end groups were conjugated to carbon nanotubes using the ethylene carbodiimide coupling reaction. Next, I will discuss the possibilities of using carbon nanotubes for encapsulation and mass transport and present our experimental observations in this area. Fourier transform infrared spectroscopy data for the chemical modification of carbon nanotubes and scanning and high resolution transmission electron microscopy images of the nanobuilding blocks and the nanotube filling process will be presented. Potential applications of our studies include the fabrication of novel electronic and biophotonic devices, crystal displays and biosensors.

M12.5

Photochromic Nanofiber Aggregates of PVA/H3PMo12O40 Hybrid. Jian Gong, Fengmei Gao, Yan Pan, Xiujun Cui, Lunyu Qu and Rongshun Wang; Faculty of Chemistry, Changchun, China.

T. Yamase et al. reported the photochromic behavior of the first hybrid organic-inorganic material contained polyoxometalates in 1973. Recently, photochromic properties of a mass of hybrid organic-inorganic materials contained polyoxometalates were investigated. However, in these studies, photochromic researches about polyoxometalates were mainly focused on powder and solution, which limited their applications, because these materials were difficult to be manipulated into practical devices. Electrospinning is a simple and efficient method for the production of scaffolds composed of nano- to microscale fibers. Fibers prepared from polymer solution can be applied in a wide variety of industrial fields because of the good flexibility and high porosities. In the current work, Poly(vinyl alcohol) (PVA)/H3P—*fadots*—Mo12O40 ultra-fine fiber aggregates contained differential weight percentage of H3PMo12O40 to PVA (20, 50 and 80 wt.%, respectively) have been successfully prepared by electrospinning technique. By means of IR spectrum, wide-angle X-ray diffraction, and scanning electron microscope (SEM) techniques, the fiber aggregates were characterized. The results from scanning electron microscopy (SEM) showed that the average diameter of the fibers was between 240-900 nm. The IR spectra indicated that H3PMo12O40 had been kept the Keggin structure in the PVA/H3PMo12O40 fiber aggregates and combined by intermolecular H-bonding with the residual carbonyl of the PVA. The results from XRD showed that the crystal growth of PVA was extremely inhibited by H3PMo12O40, however, in order with short interlayer distance, and the repeat distance of the polymer decreased with increasing H3PMo12O40 content. The photochromic behavior of the fiber aggregates was investigated by means of IR, UV-Vis spectra and electron spin resonance (ESR). The results showed that the Mo atom of H3PMo12O40 was reduced via one-electron step and the color of the fiber aggregates changed from white to blue under ultraviolet irradiation. IR spectra of the fiber aggregates irradiated by ultraviolet irradiation (365 nm) showed that the intensity of the band at 1705 cm-1, which was the characteric bands of unsaturated ketone, increased. Meanwhile, a set of bands appeared in ca. 1640 cm-1, which were ascribed to C=C (str). These results indicated that PVA was oxidated to unsaturated ketone after the PVA/H3PMo12O40 fiber aggregates was irradiated under UV light. At the same time, alkoxy radicals were found by ESR spectrum of the irradiated PVA/H3PMo12O40 fiber aggregates (g =1.932). The photochromism of the fiber aggregates was reversible in air condition. However, the fadeaway of the color was slow in air condition. The IR and ESR of the irradiated fiber aggregates indicated a conceivable photochromic mechanism as the following equation:. PMo12O403- ↔ PMo11MoVO404- -CH2-CHOH ↔ -CH2-CHO•- → -CH2-CO-CH=CH-

M12.6

Site selective electrodeposition of metallic, semi-conductive and conductive polymer nano-structures on isolated carbon nanotubes using electric fields. Nadarajan Sundar Babu, Jean-Claude Bradley and Patrick Ndungu; Chemistry, Drexel University, Philadelphia, Pennsylvania.

We report the successful application of bipolar electrochemistry for depositing metals, semi-conductive and conductive polymer nano-structures on isolated template-grown carbon nanotubes. Metals such as tin, palladium, cobalt and nickel were reduced electrochemically at the tips of isolated nanotubes from their chloride or nitrate salts. Semi-conductive deposits such as CdS were deposited by a similar electrochemical strategy. Polypyrrole dendrites could also be grown on both ends of selected nanotubes. The potential applications of thus encapsulated nanotubes in nano-fluidics and other areas will be discussed.

M12.7

Chemical Gating of In2O3 Nanowires by Organic and Bio molecules. Chao Li[1], Bo Lei[1] and Chongwu Zhou[1]; [1]USC, LA, California; [2]EE-physics, USC, LA, California.

Chemical Gating of In2O3 Nanowires by Organic and Bio molecules Chao Li, Bo Lei, Tao Tang, Daihua Zhang, and Chongwu. Zhou* Dept. of E.E.-Electrophysics, University of Southern California, Los Angeles, CA 90089 In2O3 nanowire transistors were used to investigate the chemical gating effect of organic molecules and biomolecules with amino or nitro groups. The nanowire conductance changed dramatically after adsorption of these molecules. Specifically amino groups in organic molecules such as butylamine donated electrons to In2O3 nanowires and thus led to enhanced carrier concentrations and conductance, whereas molecules with nitro groups such as butyl nitrite made In2O3 nanowires less conductive by withdrawing electrons. In addition, intra-nanowire junctions created by partial exposure of the nanowire device to butyl nitrite were investigated, and pronounced rectifying current-voltage characteristics were obtained. Furthermore, chemical gating by low-density lipoprotein cholesterol, the offending agent in coronary heart diseases, was also observed and attributed to the amino groups carried by the bio species. * Corresponding author. Email: chongwuz@usc.edu.

M12.8

Synthesis of Calcium Carbonate Nanoparticles for Drug Detoxification. Debra Holly Lush, Vishal Patel, Allison Kurz, Piyush Sheth, Javier Gutierrez and Laurie Gower; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Nanoparticulate systems are being developed for use in pharmaceutical and industrial controlled release applications. In the Unites States alone, over 300,000 patients enter the emergency room each year due to complications from overdose of prescription drugs. In fact, the leading method of suicide is via overdose of amitriptyline, a popular anti-depressant. There currently exists no quick and effective method to detoxify these patients. The goal here is to synthesize "soft" emulsion particles coated with an inorganic shell with tailorable porosity and degradation properties, which when introduced to the blood intravenously, act as drug "sponges" for patients overdosed on these lipophilic drugs. This is done via a biologically inspired mineralization process of surface-induced deposition of calcium carbonate coatings templated onto charged emulsion particles. The experimental technique includes the addition of ammonium carbonate into a combination of oil-in-water microemulsion, calcium chloride, magnesium chloride, and a highly acidic polymer. Nanoparticles with diameters of about 200nm have successfully been synthesized. Current experiments on these particles are directed towards in vitro testing of drug uptake capabilities and templating porosity of the inorganic shell using binary surfactant systems in order to achieve molecular filtration.

M12.9

Functionalized Polymeric Nanoparticles. Eric Sussman[2] and V. Prasad Shastri[1]; [1]Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Surface-functionalized polymeric nanoparticles (NP) are a versatile medium for drug delivery and imaging. The surface functionality is exploited to introduce molecules such as polymers, biomolecules, and DNA, to improve cellular localization and circulation. Typically, surface functionalized nanoparticles are derived from polymers possessing functionalizable backbones or by layer-by-layer assembly of polyelectrolytes on to particles. We have developed a novel approach to produce functionalized polymeric nanoparticles (NP) in a single step using non-functionalized polymers and in the absence of mechanical dispersion and emulsifying agents by tailoring the solvation core of a polymer such that upon addition of water a thermodynamically stable suspension of NP is formed due to rapid mixing of phases. We hypothesized that since the NP formation is driven by the addition of the water phase, water-soluble polymeric species can be entrapped during NP formation. Furthermore, by employing a water phase rich in polyelectrolytes, the functionality of the polyelectrolyte can be introduced on the surface of the NP. Using this approach poly(lactic acid) (PLA) and poly(lactic-co-glycolic acid) (PLGA) NP ranging in size from 70−400 nm bearing amine, sulfonic acid, and carboxylic acid groups, with narrow polydispersity (0.1) have been prepared. The NP were characterized using light scattering, scanning electron microscopy, zeta potential (ζ) measurement and X-ray photoelectron spectroscopy. The presence of a polyelectrolyte rich surface was verified by following z as a function of pH. In all cases an inversion in the ζ of the particle was observed at a pH corresponding to the pKa of the functional group. The importance of the water phase in NP formation was confirmed by following particle size as a function of viscosity, which was modulated by the addition of glycerol. Increasing glycerol (increased viscosity) resulted in an increase in NP particle size. Since the polymer solvation shell is tuned using a binary solvent system, the affinity of water to the polymer solvation core can be altered. Increasing the rate of diffusion of water into the solvation core should result in a decrease in NP size due to faster polymer precipitation. For example, in a tetrahydrofuran (THF) and acetone (Ac) system, where THF is less polar than Ac, increasing the Ac volume fraction (u) should increase the affinity of water and diminish NP size. We observe that indeed there is a linear relationship (R2=0.99) between PLGA particle size (450−250 nm) and acetone u (0.25−0.75). NP with surface charge ranging from −30 to +16 mV can be achieved at physiological pH of 7.4. NP bearing biologically relevant molecules such as heparin and poly(ethylene glycol) (MW 10k) have also been prepared. We foresee a number of uses for these functionalized nanoparticles, including drug delivery and modification of hard and soft material surfaces (both synthetic and biological) for tissue engineering.

M12.10

Monolayer Nanocrystal Self-Assembling Process in Liquid Film Studied by in situ Small-Angle X-ray Scattering. Xiao-Min Lin[1], Suresh Narayanan[2] and Jin Wang[2]; [1]Materials Science Division, Chemistry Division and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; [2]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

Self-assembly is an important process nature adopts to form much of the physical world around us. Many supermolecular systems use nanoscale building blocks, such as proteins, to form complex macroscopic structures. Self-assembly of chemically synthesized monodispersed colloidal nanocrystals can provide a simple model system to mimic this process. Understanding the nanoscale self-asembly dynamics requires in situ measurements with high spatial and temporal resolution. We describe here the first in situ small-angle x-ray scattering measurement of the formation of a highly ordered nanocrystal superlattice monolayer during colloid droplet evaporation. We show that the kinetics of the droplet evaporation determines the dimensionality of the superlattices. Above a critical evaporation rate, a two-dimensional nanocrystal superlattice monolayer can preferentially form at the liquid-air interface, whereas slow evaporation leads to three dimensional nanocrystal superlattice formation inside the colloidal droplet.

M12.11

Nanogold Synthesis by Inert Gas Condensation for Immuno-Chemistry Probes. Kwang-Min Lee, Dept. of Materials Science and Engineering, Chonnam National University, Gwangju, South Korea.

Nanogold clusters synthesized through a chemical process involving 11 or 55 atoms of gold have been widely used for immuno chemistry probes, in the form of nanoclusters conjugated with biomolecules. The creation of 1 nm size nanogold particles by a materials engineering process has been largely undeveloped. Therefore, the objective of this study is to minimize the size of gold nanoparticle by means of controlling the operating temperature and the chamber pressure during inert gas condensation processing. The evaporation temperature was controlled by inputting a current ranging from 50 A to 65 A. The chamber pressure was controlled using argon gas with a range of 7 to 266 Pa. The gold nanoparticles were evaluated using field-emission transmission electron microscopy. Atomic force microscopy was used to observe the MUA coated gold nanoparticles on glass slides. The size of the gold nanoparticles was resultant of the processing conditions such as the evaporation temperatures and chamber pressures. At a temperature of 1124 C and pressure of 133 Pa, we were able to obtain approximately 1 nm size nanogold particles.

M12.12

Portable and Organized Semiconductor Nanowire Arrays by Hybrid Electrochemical/Chemical Method. qiguang li and Reginald M Penner; Chemistry, UC Irvine, Irvine, California.

We propose a hybrid electrochemical/chemical method for the synthesis of portable semiconductor nanowires of millimeter length that are organized into arrays. Our method involves two steps: First, electrochemical step edge decoration was adopted to obtain the precursor nanowires (metal or metal oxide nanowire) on highly oriented pyrolytic graphite (HOPG). Second, the as-deposited nanowires were chemically converted to semiconductor nanowires. MoS_2 has a band-gap of 1.2 eV (indirect) that is well suited to solar cell applications. Here MoS_2 nanowires were synthesized by heating electrodeposited MoO_2 nanowire in H_2S at elevated temperatures. Two discrete morphologies were observed depending on whether the conversion temperature was below 700^oC or above 800^oC. For nanowires annealed at or below 700^oC, the MoS_2 nanowires were composed of randomly distributed MoS_2 ribbons with 5-10 atomic layers in each ribbon. The morphology of these nanowires were identical to that of the MoO_2 precursor wires and, consequently, the diameter of these MoS_2 wires (20 - 300nm) could be precisely controlled using the deposition time of their MoO_2 precursor wires. For nanowires annealed at 800^oC, rapid growth of MoS_2 grains was observed and MoS_2 atomic layers oriented parallel to the HOPG basal plane emerged. These layers exhibited a hexagonal shape, consistent with the MoS_2 crystal symmetry. Arrays of MoS_2 nanowires were transferred to insulator surfaces for electrical characterization. Conductivity in both types of wires was thermally activated, but MoS_2 nanowires annealed at 800^oC exhibited a lower activation energy (25 meV vs. 125 meV) than those annealed at 700^oC. This disparity can be understood in term of the MoS_2 anisotropic crystal structure. The described hybrid E/C method is a general method capable of synthesizing various semiconductor nanowire arrays. Such organized and portable nanowire arrays are likely to find applications in nanoelectronics and optoelectronics.

M12.13

Unexpected Resistance Increases in Silver Nanowires Exposed to Adsorbate. Benjamin J Murray, Erich C Walter and Reginald M Penner; Chemistry, UC - Irvine, Irvine, California.

Understanding the interactions of metals with their surroundings has become increasingly important as the semiconductor industry pushes the critical dimensions of integrated circuits to the nanoscale. Numerous studies have shown that gas adsorption causes a resistance increase of 1-4% in thin metal films. Surprisingly, there has been limited work concerning metal nanowire; one would expect resistance changes on the same order of magnitude as thin films. In this work, silver wires with diameters ranging from 150 nm to 500 nm and lengths of 100 um or more were prepared by electrochemically fusing a 1-D ensemble of silver nanoparticles. A minority of these "fused particles" were narrowly connected with 10-30 nm of silver. These short nanoscale components were connected with slightly larger 100-300 nm wires extending the length of a device. Upon exposure to ammonia (NH3), arrays of these "fused particle" (FP) wires showed a resistance increase, R/Ro, that was large (in some cases up to 10,000%) and reversible. Platinum and copper FP wires showed a similar effect. A fast, irreversible resistance increase was also observed on exposure of silver wires to H2S. However, gases that do not chemisorb on silver, such as carbon monoxide, hydrocarbons, argon, and water, caused no change in resistance. Approximately half of the silver wire arrays examined showed a relative resistance change (R/Ro) larger than previously reported for thin films. The other half showed a response of less than 5%. The response of these "dead" arrays could be increased by removal of silver from these wires through anodic etching. These data, coupled with atomic force microscopy analysis of individual silver FP wires, lead to the conclusion that the increased resistance of silver FP wires in NH3 was concentrated at a minority of the interparticle boundaries present along the axis of these wires. These ammonia sensors showed that metal nanowires can be extremely sensitive to adsorbate and somewhat selective.

M12.14

Optimization of DNA Colloid Immobilization in Self-Assembled DNA Nanoarrays. Krisanu Bandyopadhyay[1], Doris Nguyen[1], Yolanda Zhang[3], Sarah Bundick[2], Shenda M Baker[2] and Angelika B Niemz[1]; [1]Keck Graduate Institute, Claremont, California; [2]Chemistry, Harvey Mudd College, Claremont, California; [3]Bioengineering, University of California at Berkeley, Berkeley, California.

We report immobilization of DNA-conjugated gold colloids (of size 35 to 42 nm) on amine functionalized silicon surfaces through electrostatic interaction. The ultimate goal is to optimize the organization of these colloids within ordered arrays of surface nanopores. Colloids are synthesized using thiol-Au chemistry, either with or without short spacer oligonucleotides. Using three different silane monomers with an increasing number of amines in their backbone, surface charge has been systematically increased to effect an increase in the surface coverage of negatively charged DNA colloids. Atomic force microscopy (AFM) is used to follow the adsorption behavior of these DNA modified Au colloids. Our results show that surface coverage strongly depends on the surface charge and the time of exposure. It is evident from the AFM studies that surface coverage peaks after an optimal exposure time. Additionally, these surface-immobilized colloids are extremely stable at high salt concentration (as high as 300 mM). In order to organize the DNA modified colloids in surface nanopores, size matching between the two components is an important prerequisite. The nanopores are prepared through the selective removal of polymethyl methacrylate (PMMA) cylinders from hexagonally ordered thin films of poly (styrene)-b-polymethyl methacrylate (PS-PMMA) diblock copolymer on silicon. The exposed SiO2 surface at the bottom of the nanopores is modified to introduce positive charge, which facilitates electrostatic interaction with the negatively charged DNA colloids. Using two different sizes of DNA colloids we can produced self-assembled DNA nanoarrays with high inclusion efficiency.

M12.15

Synthesis and Characterization of Gold Nanoparticles by Water-in-Oil Microemulsion. Yong-Jin Kim[1], Ji-Hun Yu[1], Byung-Kee Kim[1] and Jung-Ho Ahn[2]; [1]Materials Technology Department, Korea Institute of Machinery and Materials, Kyungnam, South Korea; [2]School of advanced materials engineering, Andong National University, Kyungbuk.

Nanosized gold particles with spherical and uniform size distribution is og great interest to their potential application in the fields of electrical and biomedical industries. Gold nanoparticles can be utilized as probe materials for DNA, bio-sensors for detecting cncerous cells and nanoscale drug delivery system(DDS). Synthesis of nano and micron size powder using microemulsion was first reported by Boutonnet et al. when they obtained the nanosized metal particles such as Pt, Pd and Rh. Water-in-oil microemulsion can make the fine ans monodispersed nanoparticles because the process can effectively control the particle size, shape and its distribution by controlling water droplets in oil phase. In this study, we develop a microemulsion process for fabrication various size of gold nanoparticles having spherical and unform size distribution. The two microemulsion systems used in this study were consisted of CTAB and 1-butanol/octane/aqueous solution. CTAB(centyltrimethylammonium bromide, C19H42BrN) was used as the surfactant, 1-butano as the cosurfactant, octan as the oil phase, aqueous solution as the water droplets. Gold nitrate(HAuCl4) solution of below 0.5 mole was used as aqueous solution for source of gold ion. NaBH4 solution was used for reducing agent. Gold nanoparticles were fabricated by mixing two microemulsions containing the HAuCl4 solution and the NaBH4 reducing agent solution. After mixing for 2-4hr in magnetic stirrer, the solution was centrifused at 3000rpm for 1hr to separate the reactant and then washed several times with a mixture of chloroform and methanol. The washed particles then dried in vacuum at 70C for 2hr. The particle morphology, size and phase were analyzed bu using TEM, EDS and XRD. The gold nanoparticles fabricated by this study were very spherical shape and had very uniform size distribution. The mean particle size was controllrd from 5 to 50nm by optimization the process parameter. The particle size, shape and distribution the gold nanopowder were very closely related to water/surfactant ratio and the molar ratio of reducing agent. The mena particle size of gold increased with increasing water/surfactant ratio. The spherical and monodispersed gold nanoparticles did not fabricate when water/surfactant ratio was over a certain value. Increasing the molar ratio of reducing agent resulted in large gold particles with nonuniform particle distribution.

M12.16

Emerging Applications of Nanocrystalline Cerium Oxide. Swanand Dilip Patil, Suresh C Kuiry, Sudipta Seal and B. Rzigalinski; Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida.

Over the past two decades, cerium oxide based materials have been extensively studied for their use in various applications such as glass polishing, ultra violet (UV) ray blocking, oxygen sensing, catalysis etc. Nanocrystalline ceria possesses unique properties such as increase in lattice parameter, shifting and broadening of Raman allowed peaks, and blue shift in UV absorption spectra, that makes it more technologically important material than its bulk counterpart. But nanocrystalline materials have a very high tendency to agglomerate due to high surface energy, which is likely to downgrade such wonderful properties of ceria nanoparticles. Therefore, it is very important to synthesize nanocrystalline material with controlled particle size without agglomeration. The present study shows the usefulness of microemulsion method to obtain nonagglomerated nanocrystalline cerium oxide particles with particle size below 5 nm which were applied for various applications. It was found that the synthesized ceria nanoparticles increase th e neuronal lifespan in culture [1] and protect against neuronal damage associated with in vitro trauma [2]. The possible mechanisms to explain the beneficial effects of cerium oxide nanoparticles are presented.

M12.17

Line pattern in plasma polymer films with embedded gold and silver nanoparticles induced by ultrashort, linearly polarized laser pulses. Andreas Heilmann[1], Andreas Kiesow[1], Sven Strohkark[1], Dieter Katzer[1], Seifert Gerhard[2], Alexander Podlipensky[2] and Heinrich Graener[2]; [1]Fraunhofer Institute for Mechanics of Materials, Halle (Saale), Germany; [2]Department of Physics, Martin Luther University, Halle (Saale), Germany.

We report on a new and simple method to generate parallel grid-likely arranged line structures in thin organic films with embedded gold or silver nanoparticles. The films with a thickness of about 100 nm were deposited by alternating plasma polymerization of hexamethyldisilazane and metal evaporation. to observe a multilayer structure, i.e., all particles are arranged in one plane within the plasma polymer matrix. Irradiating these samples with linearly polarized, ultrashort (130 fs) laser pulses in far field arrangement, clearly visible colour changes occur in the film. The change in the optical properties is the result of nanostructural changes. As we find out from transmission and scanning electron microscopic (TEM, SEM) investigations, periodically arranged line-like structures are formed after the irradiation. Three different laser wavelength (800 nm, 400 nm, 266 nm) we have used so far, and it seems that the period length of the line structures is a linear function of the wavelength of the incident laser light. As typical periodic length, values in the range of 170 nm to 600 nm could be determined, respectively. This means that the generated structure widths are smaller than the laser wavelength used. The direction of the particle lines correlates to the linear polarization of the laser pulses. This structural dependence on the laser polarization is mirrored in corresponding anisotropic optical and electrical film properties. Line arrays with areas up to hundred of microns could be generated. Further factors, which influence the periodic changes in the nanostructure, are both the proportion of embedded metal and the intensity distribution of the laser.

M12.18

Electron Magnetic Resonance (EMR) of Iron Oxide Particles Mineralized in Protein Cages. Robert John Usselman[1,4], Michael T Klem[1,4], Mark Young[3,4], Yves Idzerda[2,4], Trevor Douglas[1,4] and David J Singel[1,4]; [1]Chemistry and Biochemistry, Montana State University, Bozeman, Montana; [2]Physics, Montana State University, Bozeman, Montana; [3]Plant Science, Montana State University, Bozeman, Montana; [4]Center for Bioinspired Nanomaterials, Montana State University, Bozeman, Montana.

Magnetic and structural properties of monodisperse (Fe3O4 & ?-Fe2O3) nanoparticles formed by template-constrained mineralization within spherical protein cages determined by Electron Magnetic Resonance (EMR) spectroscopy are reported. Bio-mimetic mineralization within spherical protein cages provides a novel approach to the systematic control of composition, size and size distributions of nanoscale mineral particles. Template-constrained monodisperse particles of magnetic iron oxides (Fe3O4/?-Fe2O3) , in particular, have been stoichiometrically produced within spherical protein cages of horse spleen apoferritin, and a ferritin-like protein isolated from Listeria Innocua; these protein cages have inner diameters of 12 nm and 8 nm respectively. Iron oxide mineralization was also recently performed in a genetically and chemically modified plant virus, CCMV (Cowpea chlorotic mottle virus (SubE)) with an inner diameter of 25 nm. EMR spectra of the iron oxide containing protein cages were obtained at 9.2 GHz over a range temperatures spanning 4-300 K. The spectra show dramatic temperature dependent trends in line-shape, line-width, resonance-field shifts, and integrated intensities that are markedly different for different cage sizes and different iron loadings. Detailed simulations of the EMR spectra that include effects arising from magnetic anisotropy, mean particle size, and size distributions provide a quantitative accounting for the observed behavior. Results obtained with these novel materials are compared to prior EMR studies of iron oxide particles formed without template-constraint.

M12.19

Separation of Nanoparticles with Sub-1% Resolution. Lotien Huang, Electrical Engineering, Princeton University, Princeton, New Jersey.

Sorting of nanoparticles on size is a fundamental technique for their characterization. Here we report a new method for continuous-flow separation of nanoparticles according to size, using an array of obstacles aligned at an angle with respect to a driving flow. Because of the asymmetry of the array about the flow, fluid streams are sequentially bifurcated around the obstacles. Particles in such an array are driven in different directions, depending on their sizes. Small particles migrate in the same direction as the flow, whereas large particles deviate from the flow direction due to a series of collision with the obstacles. Polystyrene microspheres of 0.2 to 1.0 micrometer diameter are sorted using this method in 40 s with a resolution of < 10 nm, corresponding to resolutions better than 1%. We have also applied the method to separate biological molecules. Deoxyribonucleic acids (DNA)of 48.5 and 167 kilo-base-pairs are sorted in 10 min, with a resolution of 40%. A DNA molecule migrates in molecular-weight-dependent direction as if it were a nanoparticle with a radius equal to about half the radius-of-gyration of the molecule. The resolution is significantly less than that observed with nanoparticles, perhaps due to deformation of DNA. The technique does not rely on the stochastic behavior of particles being separated, and thus increasing flow speeds results in higher resolutions.

SESSION M13: Group IV Nanoparticles I

Chairs: Jerry Bernholc and Julie Biteen
Friday Morning, April 16, 2004
Room 2002 (Moscone West)

8:30 AM *M13.1

Ab initio simulations of organic and inorganic nanoscale systems and interfaces. Jeff Grossman, LLNL, Livermore, California.

We employ a combination of forefront quantum simulation tools, including ab initio molecular dynamics and quantum Monte Carlo methods, to investigate the electronic, structural, and optical properties of a variety of nanoscale systems. Our aim is to use these simulations to make predictions that contribute to the development of real devices that take advantage of the unique effects manifest at the nanoscale. In particular, we will discuss our results for the impact of surface chemistry and synthesis process on optical properties of quantum dots, the formation of new molecular solids made of the recently discovered buckdiamond, and the reaction chemistry of DNA alkylating agents in solution. Further, we address the vital question of the behavior and interaction of water with nanoscale devices through a study of the electronic and structural properties of water at both hydrophilic and hydrophobic interfaces.

9:00 AM *M13.2

The role of silicon nanocrystal functionalization and passivation in photoluminescence. Julie Suzanne Biteen[1], Nathan S. Lewis[1], Albert Polman[2,1] and Harry A. Atwater[1]; [1]California Institute of Technology, Pasadena, California; [2]FOM Institute for Atomic and Molecular Physics, Amsterdam, Netherlands.

We have examined silicon nanocrystals with different terminations to probe the role of the surface in quantum-confined excitonic emission from Si nanocrystal arrays. Recent theoretical studies of Si nanocrystals[1] propose that double-bonded surface groups (such as Si=O) should produce deep-lying states within the Si band gap, while single-bonded surface groups (like Si-H and Si-CH_3) should leave the band gap nearly unaltered. A study of the effect of surface functionalization on photoluminescence behavior therefore will further our understanding of the energetics of Si nanocrystals and allow engineering of the emission energy in optical three- and four-level systems, to better assess the arguments and prospects for population inversion and lasing in Si nanocrystals.[2] Experiments on oxide-terminated nanocrystalline Si support theoretical predictions of the existence of a deep-lying donor state which decreases the emission energy with respect to the excitonic band gap.[3] We will present the first *insitu* experimental evidence for the formation of a donor state on an initially oxide-free surface. Our system of Si nanocrystals, which have narrow size distributions and diameters that can be varied in the range of 2 to 5 nm, are synthesized by ion implantation and deposited as a submonolayer ensemble of isolated nanocrystals on Si or sapphire substrates by HF etching, leaving unembedded, hydrogen-terminated samples. We will discuss the time evolution of the photoluminescence of these samples subject to ambient oxidation, using an argon flow chamber to avoid beam-induced photo-oxidation during the measurements. Very small (sub-3.0 nm diameter) nanocrystals show anomalous oxidation behavior over the course of ambient exposure: we observe a 0.1-0.2 eV emission energy blue-shift from the initial energy of 2.0 eV or more that is followed by a pronounced (0.1 eV) red-shift. A five-fold decrease in PL intensity over the course of oxidation in the dark is also consistent with the formation of a deep donor state that acts as an electron trap, and the dynamics of this state are explored with photoluminescence decay measurements. A second set of samples is methyl-passivated with a two-step halogenation/alkylation reaction. X-ray photoelectron spectroscopy verifies the identities of the surface groups and indicates that the methyl-terminated nanocrystals have enhanced resistance to oxidation with respect to their hydrogen- and chlorine-terminated counterparts. We will present photoluminescence spectra and excitonic decay lifetime measurements of methyl- and chlorine-passivated Si nanocrystals, and compare them to those of their hydrogen-terminated precursors. [1] A. Puzder et al., J. Am. Chem. Soc., **125**, 2786 (2003). [2] L. Pavesi et al., Nature, **408**, 440 (2000). [3] M.V. Wolkin et al., Phys. Rev. Lett., **82**, 197 (1997).

9:30 AM M13.3
Characterization and Manipulation of Exposed Ge Nanocrystals. Ian D. Sharp[1,2], Qing Xu[1,2], Christopher Y. Liao[1,2], Diana O. Yi[1,3], Joel W. Ager[1], Jeffrey W. Beeman[1], Kin Man Yu[1], Dmitri N. Zakharov[1], Zuzanna Liliental-Weber[1], Daryl C. Chrzan[1,2] and Eugene E. Haller[1,2]; [1]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California; [3]Applied Science and Technology Graduate Group, University of California, Berkeley, Berkeley, California.

We have fabricated isotopically pure ^{70}Ge and ^{74}Ge nanocrystals embedded in SiO_2 thin films on Si substrates through ion implantation and thermal annealing. Nanocrystals were subsequently exposed using a hydrofluoric acid etching procedure to selectively remove the oxide matrix while retaining up to 75% of the implanted Ge. We show that nanocrystals may be transferred to a variety of substrates, such as conducting metal films and optically transparent insulators. Comparison of transmission electron micrographs of as-grown crystals to atomic force microscope (AFM) data of exposed and transferred crystals, reveals that the nanocrystal size distribution is very nearly preserved through the transfer process. Therefore, this process provides a new means to use AFM for rapid and straightforward determination of size distributions of nanocrystals formed in a silica matrix. Furthermore, extended exposure of nanocrystals to ambient atmospheric conditions followed by additional etching allows for direct measurement of the kinetics of self-limiting native oxide formation on nanocrystal surfaces. Direct contact manipulation of individual nanocrystals is achieved using AFM. Preliminary scanning tunneling microscopy (STM) measurements of the electrical properties of individual isolated nanocrystals on gold films are also presented. This work was supported in part by U.S. NSF Grant No. DMR-0109844 and by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

9:45 AM M13.4
Laser-grown silicon nanoparticles and photoluminescence properties. Nathalie C Herlin-Boime[1], Kristyna Jursikova[1], Enrico Trave[2], Elisabetta Borsella[3], Olivier Guillois[1], Jean Vicens[4] and Cecile Reynaud[1]; [1]SPAM/LFP, CEA, Gif sur Yvette Cedex, France; [2]INFM, Padova, Italy; [3]ENEA, Roma, Italy; [4]LERMAT - ENSICAEN, CNRS, Caen, France.

Light-emitting silicon nanocrystals (Si nc) have attracted much interest due to their possible application optoelectronic devices. The interest for Si nanopowders is reinforced by their photoluminescence (PL) emission intensity that can be very strong at room temperature. Due to the intrinsic biocompatibility of Si nanoparticles, this strong optical emission intensity together with the long decay time (mean life time around hundred microseconds) make also these powders potential candidates as tracers for in-vivo applications. Si nanopowders were obtained in gram quantities by CO2 laser pyrolysis of silane. The produced powders are in the size range 10-15 nm. These nanoparticles exhibit strong red photoluminescence after heat treatment. The appearance of intense PL emission is clearly related to the surface oxidation of the powders which must be carefully controlled. Several steps have been identified in the oxidation process. This paper presents a detailed study of the evolution of both the photoluminescence intensity and spectral dependance and of the cristalline structure as a function of the heat treatment. We also show that the nanopowders can be dispersed in liquids and incorporated in gel samples while keeping their intense photoluminescence. This result opens a route towards the fabrication of novel devices.

10:30 AM M13.5
Template-directed nanotube network using self-organized Si nanocrystals formed via the decomposition of thin Silicon-on-Insulator. Bin Yang, Mathew S Marcus, Pengpeng Zhang, Zhiwei Li, Mark A Eriksson and Max G Lagally; University of Wisconsin-Madison, Madison, Wisconsin.

Assemblies of nanostructures, such as quantum dots, carbon nanotubes (CNTs), and nanowires (NWs), promise a variety of applications in nanoelectronics, nano-electromechanical systems (NEMS), artificial neural networks, and sensor networks. Their fabrication remains a challenge, however. Many studies have focused on directed self-assembly using templates. To achieve high integration density of the nanostructures, templates on the nanometer scale are desirable. These nanometer features have been achieved only via advanced lithography (see, e.g.[1]), such as e-beam lithography, which is time consuming and costly. We present a novel way to grow CNT networks using a self-organized template, without any lithography process. The template is formed via thermal agglomeration of Si that becomes available during the thermal decomposition of the Si template of thin silicon-on-insulator (SOI) substrates [2-4], in which Si nanocrystals are self-organized on 100nm scale. The Si crystals are about 90nm wide and 100-150nm tall, with 200nm spacing. We use this array of Si nanocrystals as a template for directed growth of CNT by chemical vapor deposition, using a Fe-Pt salt solution or evaporated Fe thin films as the catalyst. CNTs connect the silicon nanocrystals to form a network. More interestingly, the nanotubes form on top of the Si nanocrystals. We explain this preferential growth by the gas flow pattern in CVD on this template. This simple template-directed network growth could be easily generalized to other NW systems. Research supported by DOE [1] Y. Homma, Y. Kobayashi, T. Ogino, T. Yamashita, Appl. Phys. Lett. 81, 2261 (2002); [2] B. Legrand, V. Agache, J. P. Nys, V. Senez, and D. Stievenard, Appl. Phys. Lett. 76, 3271 (2000); [3] R. Nuryadi, Y. Ishikawa, and M. Tabe, Appl. Surf. Sci. 159, 121 (2000); [4] B.Yang, P.P. Zhang, F. Liu, M. G. Lagally, to be published.

10:45 AM M13.6
Sn in Ge and Si: Thin films and Quantum Dots. Jordana Bandaru, L Douglas Bell and Shouleh Nikzad; Jet Propulsion Laboratory, Pasadena, California.

Sn_xGe_{1-x}, Sn quantum dots, and related materials offer the potential for developing completely group IV-based optoelectronic devices with tunable direct bandgaps. These materials could be used in a wide range of applications such as thermophotovoltaics (TPV) and infrared detectors. Using low temperature Molecular Beam Epitaxy (MBE) we have grown Sn_xGe_{1-x} and Sn_xSi_{1-x} thin films. Extremely low growth temperatures (<200 °C) make it possible to grow fully strained epitaxial films with Sn concentrations well above the equilibrium solid solubility. Post-growth annealing treatments of these films were explored in order to form quantum dots which were observed by Transmission Electron Microscopy (TEM). Strain relief is an important factor determining the location, ordering, and alloy composition of Sn in the thin film structure. For example, segregation into Sn-rich quantum wires was observed in Sn_xGe_{1-x} thin films. X-Ray Diffraction, TEM, and Rutherford Backscattering Spectrometry (RBS) data indicate high quality epitaxial films with incorporation of 10% Sn. The effects of varying substrate temperature, Sn concentration, film thickness, and annealing temperature on morphology will be discussed. Optical properties studied by Fourier Transform Infrared (FTIR) spectroscopy will be presented.

11:00 AM M13.7
Composition and stability of Ge/Si(111) nanocrystals. fulvio ratto and federico rosei; EMT, INRS, Varennes, Quebec,

Canada.

The epitaxial growth of Ge on Si surfaces proceeds in the Stranski Krastanov mode: after the formation of a 2D wetting layer (WL), the strain energy due to the 4.2% mismatch of the Ge and Si lattice parameters leads to the nucleation of 3D islands [1]. These may act as quantum dots (QDs), whose properties may be exploited to fabricate novel devices, compatible with the existing Si technology. Still, there are at least two critical issues to be fully understood, on which this possibility depends: alloying and stability. Alloying strongly influences the structural and electronic properties of the 3D islands. It has been shown that a considerable amount of intermixing is present in the WL and in the QDs, but a clear picture of the temperature dependent dynamics of the process is presently not available [2]. At the same time, nanocrystal stability is essential for device fabrication. Again a comprehensive study of QDs evolution is presently lacking [3]. To address the first issue, we report the first measurements of Ge/Si intermixing from individual 3D islands, by means of X ray photoemission electron microscopy (XPEEM). Germanium was deposited by physical vapor deposition on Si(111) at different temperatures. The novel analysis techniques we have developed have enabled us to produce a quantitative estimate of the QDs composition, by comparing Si2p and Ge3d core levels spectra. This represents a fundamental improvement in relation to previous results obtained using other experimental techniques, which could not provide the necessary spatial resolution. Further, we discuss the behavior of the QDs during the annealing of the substrate, recorded by an energy electron microscopy (LEEM) movie. The observation of the evolution of individual islands yields unique information on QDs stability. [1] F. Boscherini, G. Capellini, L. Di Gaspare, F. Rosei, N. Motta, S. Mobilio, Appl. Phys. Lett. 76, 682 (200); [2] F. Rosei, R. Rosei, Surf. Sci. 500, 395 (2002); [3] R. Magalhaes-Paniago, G. Medeiros-Ribeiro, A. Malachias, S. Kycia, T. I. Kamins, R. Stan Williams, Phys. Rev. B 66, 245312 (2002).

11:15 AM *M13.8

Theory and simulations of nanotubes, nanowires and ferroelectric polymers. Jerry Bernholc[1,2], M. Buongiorno Nardelli[1,2], W. Lu[1], V. Meunier[2], S. Nakhmanson[1], W. G. Schmidt[1], S. Wang[1] and Q. Zhao[1]; [1]NC State University, Raleigh, North Carolina; [2]Oak Ridge National Laboratories, Oak Ridge, Tennessee.

We describe simulations of mechanical, electrical and polarization properties of nanotubes, nanotube-cluster systems, novel ferroelectric polymers and atomic nanowires on semiconductor surfaces. Our calculations show that carbon nanotubes are the strongest materials known. These predictions have already been confirmed experimentally. However, our most recent results reveal that the ultimate strength of nanotubes is far greater than currently observed. Turning to nanotube-cluster systems, we have shown that they behave effective chemical sensors, whose electrical response changes dramatically upon adsorption of small molecules onto the metal clusters. BN nanotubes have polar bonds but no spontaneous polarization, due to exact cancellation between the electronic and ionic terms, but are excellent piezoelectrics that could form the core of high-performance actuators and sensors. We also discuss polarization in ferroelectric polymers and suggest, on the basis of highly precise ab initio calculations, new polymers with 100% improved polar properties. As the last example, we demonstrate that optical response of nanowires on a semiconductor surface provides a unique signature of their atomic structure, which can be unambiguously uncovered and confirmed by comparison between experimental data and ab initio calculations.

SESSION M14: Group IV Nanoparticles II

Chairs: Daniele Gerion and Anthony van Buuren
Friday Afternoon, April 16, 2004
Room 2002 (Moscone West)

1:30 PM *M14.1

Ge nanocrystals by high temperature solution routes : success and open challenges. Daniele Gerion, Lawrence Livermore National Laboratory, Livermore, California.

We present a synthesis methodology that yields near gram quantity of nanometer size crystalline germanium in the form of a black powder. It relies on high temperature decomposition of an organogermane precursor in organic solvents. The presence of pure germanium is unambiguously attested by powder XRD measurements, and low resolution TEM. Ge nanocrystals are between 5 to 30 nm in size. The as-synthesized Ge powders are sparingly soluble in conventional solvents because Ge nanocrystals seem embedded in an organic matrix. Post-dissolution of this matrix is achieved in a random manner so far. The difficulty to consistently control the properties of the as-synthesized powders seems to be a hallmark of high temperature solution syntheses. For instance XRD analysis of powders can produce surprisingly complex patterns that do not correspond to Ge, although such powders suspended in toluene fluoresce bright blue. Such observation clearly indicates that high temperature solution syntheses present open challenges that need to be solved prior to any optical characterization of the Ge dots.

2:00 PM M14.2

Characterization of Charging Phenomena of Silicon Nanocrystals –Connecting Device Measurements to Scanning Probe Microscopy. Tao Feng and Harry A Atwater; Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California.

Understanding the mechanisms of charge injection into arrays of Si nanocrystals embedded in silicon dioxide is the central issue governing device performance in silicon nanocrystal nonvolatile memories. In the past, charge injection has been investigated either by examining performance of MOS devices [Tiwari et al, Appl. Phys. Lett. 68, 1377 (1996)] [Ostraat et al, Appl. Phys. Lett. 79, 433 (2001)] or by electrostatic force microscopy charging of silicon nanocrystals [Boer et al, Appl. Phys. Lett. 78, 3133 (2001)]. To date, however, results from these two kinds of studies have not been meaningfully linked. While MOS device measurements provide information about device operation, they provide only ensemble average information about the nanocrystal array with no spatial resolution. Electrostatic force microscopy enables spatially-resolved characterization of nanocrystal charging and discharging, but since a top gate is absent, these studies have provided limited connection to actual device performance. We present recent studies on charging phenomena for silicon nanocrystals that connect these two regimes of characterization. Nanocrystals were fabricated by Si ion-implantation into a 15nm SiO_2 layer on Si (001) substrates with the implanted Si peak position of 10nm below the sample surface. The crystalline structure and morphology of the 2-4 nm size nanocrystals was verified by atomic force microscopy (AFM) and reflection high energy electron diffraction (RHEED). Capacitance-voltage characteristics of large-area (few mm^2) MOS capacitors including Si nanocrystals showed both electron charging and hole charging. It was noticed that obvious hole charging begins around 3V, while obvious electron charging begins around 4.5V. Capacitance decay measurements were done to find the charge retention time at room temperature, which indicate a discharging time constant of 1 hour for electrons, while the hole discharging time constant was found to be 10^4 hours. Fabrication of tiny (device area 900 nm^2) MOS capacitors with Si nanocrystal floating gates by electron beam lithography and wet chemical etching enables us to connect MOS capacitance-voltage characteristics to electrostatic force microscopy results. The dimensions of the top gates allow them to be charged conveniently at different biases using a conducting AFM tip, and after that the discharging kinetics can also be directly monitored by electrostatic force microscopy at different temperatures. The electrostatic force microscopy results of temperature-dependent charging/discharging dynamics and their relation to conventional capacitance-voltage characteristics will be presented.

2:15 PM M14.3

Excitons in size-controlled Si nanocrystals: confinement and migration effects. Johannes Heitmann[1], Frank Mueller[1], Margit Zacharias[1] and Dmitri Kovalev[2]; [1]Exp. Dep. II, MPI fuer Mikrostrukturphysik, Halle (Saale), Saxony Anhalt, Germany; [2]Physik-Department E16, Technische Universitaet Muenchen, Garching, Bavaria, Germany.

Size controlled Si nanocrystals synthesized by the thermal induced phase separation of SiO/SiO2 superlattices [1] are used for a detailed analysis of the very efficient room-temperature photoluminescence. By this method an investigation of confinement and migration effects on the excitons within the Si nanocrystals were possible. Both effects are already observed in similar systems, but normally a separation of both processes is very difficult due to the broad size distribution of the synthesized nanocrystals. In our system the very good size control allows to investigate both effects and their correlation. Quantum confinement effects like the blue shift of the luminescence signal, an increasing no-phonon to phonon assisted transition probability ratio and a decreasing singlet lifetime with decreasing crystal size were observed and quantitatively analyzed. We demonstrate the importance of migration effects of the excitons, for instance their thermalization behaviour which affect the temperature dependence of the time decay, the bandwidth and the spectral position of the emission band. All experimental data can be described in the framework of the generation, migration and spatial confinement of excitons in the Si nanocrystal core. A simulation of the temperature and time behaviour of the luminescence peak position and its linewidth by the described processes will be demonstrated. [1] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, J. Bläsing, Appl. Phys. Lett 80 (2002) 661.

2:30 PM M14.4

Silicon Nanoparticle Synthesis Using Constricted Mode

Capacitive Silane Plasma. Ameya Bapat[1], Christopher Perrey[2], Uwe Kortshagen[1], C.Barry Carter[2] and Stephen Campbell[3]; [1]Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [3]Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Crystalline semiconductor nanoparticles are of interest due to variety of electronic and opto-electronic applications. We report experimental studies for synthesis and characterization of crystalline silicon nanoparticles using an RF constricted-mode capacitive plasma. The plasma is operated using a dilute mixture of 5% silane in helium and argon at 500-800 mTorr. The plasma is run for 90 seconds with a 200W RF power input. The RF electrode is in form of a ring and a metal plate is used as the ground electrode. The constricted-mode discharge is a high density plasma instability which rotates at a high frequency. Silane is dissociated, leading to particle nucleation and growth. Particles are extracted by passing the particle-laden gas through a 1mm orifice to form a beam. Particles are collected by inertial impaction. We are able to reproducibly synthesize highly oriented freestanding single crystal silicon nanoparticles. Monodisperse particle size distributions centered at 35nm with a geometric standard deviation of 1.5 are obtained. Transmission electron microscope (TEM) studies show uniform cube shaped particles. Selected area electron diffraction indicates diamond cubic structure of the silicon lattice. High-resolution TEM studies indicate high quality material with very low defect density. Analysis of the constricted-mode plasma and the effect of parameters like silane concentration, plasma on time are described.

2:45 PM M14.5
Assembled nanoparticle thin films: controlling the particle-particle interaction. Anthony van Buuren, LLNL, Livermore, California.

We investigate the change in the electronic structure of nanoparticle assemblies as the density of particles is increased from non-interacting individual particles to concentrated arrays of nanoparticles. The production of these nanostructures in the gas phase gives control over not only the size of the nanoparticles, but also over surface passivation, which is typically not possible in other growth modes. Silicon (Si) and Germanium (Ge) clusters are condensed out of supersaturated vapor, which is cooled down in a He-atmosphere and are subsequently deposited on a variety of substrates. Their surfaces can be passivated with different materials evaporated into the vacuum chamber. This approach allows us to probe in a controlled and dynamic fashion the effect of surface passivation on nanocluster properties. X-ray absorption spectroscopy (XAS) and photoemission (PES) were performed to investigate the electronic structure of the nanocrystal films. Clear effects of quantum confinement are measured in the electronic structure of the isolated nanoparticles however this is lost in the concentrated assemblies. When the nanoparticle-surface is passivated the clusters keep their original properties even in multilayer depositions and it is possible to generate nanocluster-assembled materials with unique electronic properties. This effect is interpreted in terms of a particle-particle interaction model. Results are compared to the measured electronic of Si and Ge quantum dots prepared my other methods such as ion implantation. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W−7405−Eng−48.

3:00 PM M14.6
Analysis of the 3D Relationship of Ge Quantum Dots in a Si Matrix Using Focused Ion Beam Tomography. Alan J. Kubis[1], Robert Hull[1], Tom Vandervelde[3], John Bean[2] and Derren Dunn[4,1]; [1]Department of Materials Science and Engineering, Univ. of Virginia, Charlottesville, Virginia; [2]Department of Electrical and Computer Engineering, Univ. of Virginia, Charlottesville, Virginia; [3]Department of Physics, Univ. of Virginia, Charlottesville, Virginia; [4]IBM Microelectronics, Hopewell Junction, New York.

It is well documented that in the growth of three-dimensional epitaxial semiconductor quantum dot (QD) arrays, QDs have the potential to self-organize through strain field interactions. Using the Focused Ion Beam (FIB) tomographic technique we have reconstructed the 3D relationship of successive layers of coherent Ge QDs separated by epitaxial Si layers- a "QD super lattice". Techniques such as Atomic Force Microscopy and Scanning Tunneling Microscopy can only look at a single layer od QDs or, in the case of Transmission Electron Microscopy, look at a two-dimensional projection of a three-dimensional volume so that 3D interactions need to be extrapolated. Since the strain interactions are complex an enhanced fundamental understanding of these self-organization mechanisms can more directly be obtained from full 3D reconstructions of these structures. We have optimized the QD super lattice structures for 3D reconstruction given the spatial resolution of our technique (c. 20 nm using the primary ion beam for both material removal and imaging). When capped by Si at temperatures above 400°C Ge QDs decrease in height to only several nanometers making them difficult to reconstruct using the FIB tomographic technique. By capping at 300°C we were able to grow QD super lattices with QDs tens of nanometers in height. This places them within the ability of the FIB tomographic technique to reconstruct. Using the FIB we performed in-situ serial sectioning of the QD super lattice at 20 nm intervals and then reconstructed the QD super lattice. The reconstruction was then analyzed to investigate the ordering of the QDs. Results from a reconstruction of a super lattice matrix will be presented with analysis of the self-ordering of the QDs. Observations of novel self-limiting (in height) morphologies, the quantum mesa, associated with the capping technique used will also be discussed. This work was funded by the National Science Foundation Materials Research Science and Engineering Center on "Nanoscopic Materials Design" at the University of Virginia.