

SYMPOSIUM C

Anisotropic Nanoparticles—Synthesis, Characterization, and Applications

November 27 – 29, 2000

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* Invited paper

SESSION C1: METALLIC NANOPARTICLES AND CLUSTERS I

Chair: L. Andrew Lyon
Monday Morning, November 27, 2000
Liberty (Sheraton)

9:00 AM *C1.1

ORDERED 3D, 2D, AND 1D ARRANGEMENTS OF Au55 CLUSTERS. Günter Schmid, Monika Bäuml, Norbert Beyer Institute for Inorganic Chemistry, University of Essen, GERMANY.

Ligand protected Au55 clusters with a diameter of 1.4 nm have turned out to work as single electron transistors even at room temperature. Consequently they are promising candidates for building blocks in future nanoelectronics. To reach that goal the clusters have to be organized in well defined structures. 3D cluster assemblies become available in microcrystals with hexagonally packed Au55(PPh3)12Cl6 clusters. 3D Assemblies of naked Au55 clusters are prepared by careful elimination of the ligands of Au55(PPh3)12Cl6 by thiol-functionalized fourth generation dendrimers. Ordered 2D layers of the same clusters can be generated by a self-assembly process at the phase boundary between water and dichloromethane using amphiphilic polymers as structural directors. Hexagonal and square orders are observed. Defect free areas of some μm^2 can be generated. The cluster monolayers can be transferred to solid substrates. Among various matrices to generate 1 D cluster wires, rigid polymer molecules turned out to work best.

9:30 AM C1.2

STRUCTURE AND ELECTRICAL PROPERTIES OF AN ASSEMBLY OF GOLD NANOCLUSTERS. G. Muralidharan, L. Maya and T. Thundat, Oak Ridge National Laboratory, Oak Ridge, TN.

The phenomenon of Coulomb-blockade has been observed in charge transport through metal or semiconductor islands separated by a tunneling barrier. While Coulomb-blockade has been studied extensively at low temperatures, there is increasing interest in conducting such studies at room temperatures. In the past, various fabrication methodologies have been adopted to prepare an assembly of metal clusters coupled by an insulating barrier. In the present study, we focus our effort on studying the electrical properties of metallic clusters assembled through chemical interactions. It has been shown recently that free-standing, space-filling films, essentially one monolayer thick, can be assembled using gold clusters functionalized with carboxylic acid moieties. Such assembly is mediated by the presence of low molecular weight polymers containing amine functionalities. Assembly is generally promoted through the formation of peptide bonds in the presence of a carbodiimide while in the absence of the carbodiimide, assembly occurs through ion pairing. It has also been found that the spatial distribution of the gold clusters within the films is sensitive to the nature of the acid coating on the clusters. A systematic study of the structure of these films has been carried out using transmission electron microscopy and scanning probe microscopy. Since such films provide an excellent experimental framework for understanding coulomb blockade effects, electrical properties of the films have been measured at room temperature. This work will present some of the observed characteristics in the structure of the films. In addition, the electrical properties of the films will be presented with special reference to coulomb blockade effects in nanoscale metallic clusters.

9:45 AM C1.3

'BRICKS AND MORTAR' SELF-ASSEMBLY OF NANOPARTICLE AGGREGATES. Andrew Boal, Faysal Ilhan, Vincent Rotello, Dept. of Chemistry, University of Massachusetts, Amherst, MA; Thomas Russell, Dept. of Polymer Science and Engineering, University of Massachusetts, Amherst, MA.

Multi-scale ordering of materials is central for the application of molecular systems to macroscopic devices. Self-assembly based on selective control of non-covalent interactions provides a powerful tool for the creation of structured molecular-level systems; application of this methodology to macromolecular systems supplies a potential means for the extension of this structure to the macroscopic level. Polymers provide a means for assembly of colloidal nanoparticles. Using a "bricks and mortar" strategy, colloidal gold particles functionalized with recognition elements serve as the bricks, while polymers bearing complementary functionality serve as mortar, holding together the colloidal particles. With this strategy, the conformational flexibility of the polymer compensates for irregularities in the size and shape of the aggregate structure. We have used this method to efficiently propagate structure during the self-assembly process, creating discrete micrometer-scale spherical assemblies based on 2 nm gold nanoparticles. (1) Both the size and morphology of these assemblies can be controlled, allowing access to spherical assemblies ranging from 50 nm to 1500 nm, as well as extended network structures. (1) "Self-Assembly of Nanoparticles into Giant Spherical Arrays" A. Boal, F. Ilhan, J. DeRouchey, T. Thurn-Albrecht, T. Russell, V. Rotello, *Nature*, 2000, 404, 746-749.

10:30 AM *C1.4

ELECTRONIC AND OPTICAL PROPERTIES OF MOLECULARLY-BRIDGED METAL NANOPARTICLE ARRAYS. James P. Novak, Louis C. Brousseau, Dan L. Feldheim, North Carolina State University, Department of Chemistry, Raleigh, NC.

Nanometer-sized metal and semiconductor particles (e.g., gold and CdSe) are certain to be important fundamental building blocks of future electronic and optical devices. This presentation will describe the assembly of nanoparticles into dimer, trimer, etc. arrays in which array symmetry and interparticle distance is well-defined. Electronic communication between particles in an array has been characterized by cyclic voltammetry, visible spectroscopy, and hyper-Rayleigh scattering spectroscopy. Prospects for wiring-up individual nanoscopic metal/semiconductor junctions will also be discussed.

11:00 AM C1.5

STRUCTURAL AND OPTICAL PROPERTIES OF GOLD IN MgO: EFFECTS OF SHAPE AND THE INTERFACE. Don O. Henderson, A. Ueda, M.H. Wu, A. Zavalin, R. Mu, Fisk University, Chem. Phys. Lab, Dept of Phys., Nashville, TN.

Over the years, much has been learned about the fundamental physics and chemistry of metal nanoparticles embedded in various host materials due to the reduction of their size. Both experimental results and theories have shown qualitative and sometimes semi-quantitative agreements. The challenges remain to precisely control physical parameters such as size, shape (isotropy vs anisotropy), particle number density and coordination of the nanoparticles as well as the effects from the confining host and structure and chemistry at the host-guest interface. In this report, we have chosen an intriguing system - gold nanoparticles confined in crystalline MgO to demonstrate how each individual parameter affecting the overall properties of Au nanoparticles by proper sample fabrication, shape and interface tailoring and comprehensive optical and structural characterizations. The techniques include pulsed laser deposition, e-beam evaporation and ion implantation for sample fabrication, thermal and laser treatments for size and shape control, and optical and laser spectroscopy, TEM and RBS for property analysis. Depending on the fabrication sample treatment used, a single surface plasmon absorption peak of Au in MgO can be tuned from 560 to 660 nm, and/or more than one peaks observed. Thermal and laser treatments can lead to gold nano-cube and nano-sphere formation. In addition, it is also shown that the creation of the defects on MgO host matrix can also alter the optical properties of the nano-composite materials. Theoretical modeling will also be used to evaluate the underlying mechanisms of each individual parameters which often are reported as an ensemble of all the parameters together.

11:15 AM C1.6

OPTICAL CHARACTERIZATION AND MANIPULATION OF SILVER AND IRON OXIDE NANOCRYSTALS. Stanislaus S. Wong, Columbia Univ, Dept of Chemistry, New York, NY, present affiliation: State University of New York at Stony Brook, Dept of Chemistry, Stony Brook, NY, and Brookhaven National Laboratory, Dept of Applied Sciences, Upton, NY; Louis E. Brus, Columbia Univ, Dept of Chemistry, New York, NY.

Because of their 2-50 nm size range, nanocrystals are unique in that the number of surface atoms is a large fraction of the total. Hence, their intrinsic properties are transformed by quantum size effects due to the spatial confinement of excitations. Nanomanipulation of nanoparticles (both silver and iron oxide) has been accomplished using the atomic force microscopy (AFM). Using a silicon AFM tip in conjunction with nanolithographic algorithms which are part of the microscope software, we have successfully been able to move and push particles (50-150 nm in size) together in a controllable, reproducible, and nondestructive fashion. The goal initially then has been to obtain Mie scattering on two nanoparticles, as a function of their interparticle distance. It is predicted and has been found that the electromagnetic interaction between the irradiated particles strengthens as the particles are brought together from a distance of microns to a point of contact, with noticeable effects on the optical spectra. The second aim of our studies has been to study in great detail the optical spectra of individual iron oxide (hematite) nanocrystals, which are important for understanding the radiative behavior of hematite particles present in atmospheric aerosols as well as phenomena involving the formation of metal oxides such as metal corrosion. Correlations between the peak position and shape of the absorption curves with the morphology of these nanoparticles have been obtained. As expected, the wavelength of the individual particle Mie resonance shifts red as the particle size increases. The single nanocrystal spectra are far sharper than the extinction spectra of the parent colloid which contains a range of sizes and shapes.

11:30 AM C1.7

ANISOTROPIC FCT-STRUCTURED FEPT NANOPARTICLE ASSEMBLY. Shouheng Sun, C.B. Murray, D. Weller, L. Folks, A. Moser.

We present our chemical approaches to anisotropic fct-FePt hard magnetic nanoparticle assemblies and their potential applications in ultrahigh density magnetic recording. The monodisperse FePt nanoparticles are synthesized by reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl in the presence of oleic acid and oleyl amine stabilizers. The FePt particle composition is readily controlled and the size is tunable from 3 to 10 nm diameter with a standard deviation less than 5%. These nanoparticles self-assemble into 3D superlattices. The as-synthesized FePt nanoparticles have magnetically soft fcc structure and are superparamagnetic at room temperature. Thermal annealing converts the internal particle structure from a chemically disordered fcc phase to the chemically ordered high-anisotropy fct phase and transforms them into room temperature nanoscale ferromagnets. The assemblies of these nanoferrromagnets are chemically and mechanically robust and can support high-density magnetization reversal transitions.

11:45 AM C1.8

SYNTHESIS AND MAGNETIC STUDIES OF UNIFORM IRON NANORODS. Taeghwan Hyeon, Sang-Jae Park, Seungsoo Kim, Suyoun Lee, Zheong G. Khim, Kookrin Char.

The manuscript describes the fabrication of novel iron nanorods with dimensions of 2 nm x 12 nm, 2 nm x 20 nm, 2 nm x 30 nm, from the controlled growth of uniform 2 nm sized spherical nanoparticles. This is the first report on the synthesis of rod-shaped magnetic nanoparticles in this size regime. These iron nanorods exhibited high shape anisotropy. The blocking temperature of these nanorods was found out to be much higher (110 K) for 2 nm x 12 nm than that of the 2 nm spherical nanoparticles (12 K). Synthesis, characterization and magnetic studies of these iron nanorods will be discussed in the presentation.

SESSION C2: METALLIC NANOPARTICLES AND CLUSTERS II

Chair: Christine D. Keating
Monday Afternoon, November 27, 2000
Liberty (Sheraton)

1:30 PM *C2.1

OPTICAL PROPERTIES OF NANOPARTICLE PAIR STRUCTURES. Marie Sandrock, Mahnaz El-Kouedi, Maryann Gludenis, and Colby A. Foss, Jr., Department of Chemistry, Georgetown University, Washington, DC.

The synthesis of nanoparticle pair structures via porous host electrochemical template synthesis and bulk solution chemical methods is reviewed. Electrochemical template synthesis offers two advantages over solution methods, namely: 1) control over particle pair structure orientation; and 2) control over the geometry, size and composition of each member of the pair. These features of electrochemical template synthesis allow for straightforward comparison of experimental and theoretical spectra. Orientation control also allows for the evaluation of second order nonlinear optical properties of centrosymmetric and non-centrosymmetric nanoparticle pair systems. The dependence of Second Harmonic Generation intensity on particle pair shape, size, and orientation is discussed. The linear spectra of non-centrosymmetric structures composed of metal spheres and rods in solution are also discussed.

2:00 PM C2.2

INTERFACIAL REACTIVITIES OF NANOPARTICLES AND THEIR ASSEMBLIES. Chuan-Jian Zhong, Li Han, Yongbin Luo, Mathew M. Maye, David R. Daniel, Lisa B. Israel, Jason G. Daras, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Nanometer-sized metal or alloy particles serve as fine-tunable building blocks for constructing functional nanomaterials partly because of the interface-dominated electronics, structures and reactivities. Crucial to the utilization of such building blocks is the development of capabilities to control the interfacial reactivities. This presentation deals with two types of core-shell nanoparticle-based reactivities where both isotropic and anisotropic structural properties are operative. One type involves thermally-activated shell desorption and re-encapsulation by which the nanocrystal cores evolve in size and shape. The driving force is the minimization of chemical potentials of the core-shell nanocrystals. The other involves exchange-crosslinking reaction by which nanoparticles are linked into 2D/3D assemblies. The driving force is the chemical binding through core-shell, shell-shell and

intermolecular van der Waals interactions. Infrared reflection spectroscopy, scanning probe microscopy, spectrophotometry and electrochemical techniques are used to characterize these interfacial reactivities. While gold and alloy nanoparticles and functionalized thiols were studied as a model system, the insights are potentially applicable to many emerging nanoparticle systems. The results will be discussed in terms of the manipulation of interfacial structures and reactivities for tailoring nanostructured architectures for molecular recognition, bioanalytical and catalytic applications.

2:15 PM C2.3

SHAPE CONTROLLED COBALT MAGNETIC NANOCRYSTALS AND THEIR ASSEMBLY. Z.L. Wang, Z.R. Dai, School of Materials Science and Engineering Georgia Institute of Technology, Atlanta, GA; S. Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Controlled assembly of monodisperse nanocrystals (NCs) has been a key issue in fabricating functional nanodevices. A relatively simple and new approach for constructing NC assembly is to use structurally stabilized monodisperse NCs as building blocks, which can self-assemble into 2D and 3D structures. Extensive investigations in NC assemblies have revealed that the symmetry of the observed superlattices is influenced by the size, shape and relative dimensions of the NC core and the organic capping. The key challenges in self-assembly method of magnetic NCs are to control the defects of the self-assembly to ensure an ordered structure for data storage and read-out, and to prepare an assembly with uniform thickness and large lateral dimension. These two technical concerns are closely related to the shapes of the NCs. In this study, cubic β -Mn structured ϵ -Co NCs with a size of 11nm were prepared from solution phase reduction of cobalt chloride in the presence of stabilizing agents at high temperature. A long-range translation ordered but short-range orientation ordered self-assembly of the Co NCs was achieved, which exhibits a packing form being rather different from the sphere-shaped ones. These Co NCs have an anisotropy polyhedral shape enclosed by {221} and {310} facets. The self-assembly of the NCs and the defect structures in the NC arrays are governed by their shapes. The NC assembly follows a principle of face-to-face stacking. Twins and stacking faults are created in the assemblies due to the mismatched faces of the adjacent NCs.

2:30 PM C2.4

STRAIN ANISOTROPIES IN CORE/SHELL MAGNETIC NANOSTRUCTURES. Georgia C. Papaefthymiou, Department of Physics, Villanova University, Villanova, PA.

The magnetic properties of nanosize iron-oxo molecular clusters have been investigated via Mössbauer spectroscopy and compared to those of silica coated iron-oxide nanoparticles. The clusters, prepared by controlled hydrolytic iron polymerization reactions¹, contain a \sim 1.2 nm diameter magnetic core of spin-coupled iron ions surrounded by a shell of benzoate ligands. The nanoparticles, prepared via sol-gel synthesis², contain a \sim 4.0 nm average diameter γ -Fe₂O₃ core coated by a shell of SiO₂. Both systems exhibit magnetic bistability at low temperatures with estimated magnetic anisotropy constants of $K=0.63 \times 10^5$ J/m³ for the clusters and $K=0.55 \times 10^5$ J/m³ for the particles. The similar values of K indicate that these two systems experience similar degrees of strain at the core/shell interface. This is further supported by the values of the quadrupole splitting, $\Delta E_Q=0.77$ mm/s for the clusters and $\Delta E_Q=0.75$ mm/s for the particles, pointing to same degree of distortion from pure octahedral or tetrahedral symmetry at the iron coordination sites for either system. Implications of these observations for the surface atomic structure of γ -Fe₂O₃ nanoparticles are discussed.

¹W. Micklitz, V. Mckee, R. Lyn Rardin, L.E. Pence, G.C. Papaefthymiou, S.G. Bott and S.J. Lippard, *J. Am. Chem. Soc.*, **116**, 8061 (1994).

²L. Zhang, G.C. Papaefthymiou and J.Y. Ying, *J. Appl. Phys.* **81**, 6892 (1997)

2:45 PM C2.5

PREPARATION OF Ni AND Fe NANOPARTICLES WITH TAILOR-MADE MORPHOLOGY USING INTERCALATED LAYERED DOUBLE HYDROXIDES. Alexey A. Vertegel, Univ Missouri-Rolla, Materials Research Center, Rolla, MO; Alexey V. Lukashin, Andrey A. Eliseev, Yuri D. Tretyakov, Depart. of Materials Science, Moscow State University, Moscow, RUSSIA.

In the present work, a novel method for the preparation of magnetic nanostructured materials is discussed. The method is based on chemical modification of anion-substituted layered double hydroxides (LDH). It combines the simplicity of chemical methods and the possibility to prepare two-, one-, or zero-dimensional nanoparticles in oxide/hydroxide matrices. LDHs have a general formula $M'_{1-x}M''_x(OH)_2[(anion)^{n-}_{x/n} \cdot mH_2O]$, where M' and M'' are metals in the oxidation state 2 and 3, respectively, and $anion^{n-}$ is virtually any anion, which does not form a stable complex with M' or

M^{II}. A structure of an LDH consists of positively charged hydroxide layers [M^I_{1-x}M^{II}_x(OH)₂]^{+x} bonded with negatively charged anions, which occupy the interlayer space. During chemical reactions of anions in the interlayer space, reaction zone is spatially constrained by the rigid hydroxide layers, giving rise to the conditions similar to those in 2D nanoreactors, such as Langmuir-Blodgett films or self-assembling monolayers. Here we used LDH precursors for the preparation of the Fe- and Ni-based nanocomposites. The precursors were obtained by intercalation of anionic complexes of Fe(III) or Ni(II) into the interlayer space of Mg-Al LDH. The amount of the corresponding complex intercalated into the interlayer space can be easily controlled by varying the Mg:Al ratio in the initial LDH. Substituted LDHs were reduced by H₂ to give metal nanoparticles entrapped into the inert Mg-Al-O matrix. It was found that reduction of anion-substituted LDHs results in the formation of metal nanoparticles with different morphology (platelets, rods or dots), depending on the initial content of anionic complexes in the LDH precursor. The formation of anisotropic metal nanoparticles is believed to be due to the spatial constraints of the reaction zone. The formation of nanoparticles incorporated into LDH matrix was investigated by TEM, SQUID magnetometry, and XRD. This work is supported by RFBR (grant 00-03-32579).

SESSION C3: METALLIC NANOWIRES

Chair: Brian D. Reiss

Monday Afternoon, November 27, 2000

Liberty (Sheraton)

3:30 PM C3.1

MAGNETOTRANSPORT PROPERTIES OF ELECTRO-CHEMICALLY DEPOSITED METALLIC NANOWIRES.

Peter C. Searson, Li Sun, Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD; Chia-Ling Chien, Daniel H. Reich, Johns Hopkins University, Department of Physics, Baltimore, MD; G.J. Meyer, Johns Hopkins University, Department of Chemistry, Baltimore, MD.

Long, ultrathin materials may be considered quasi one dimensional and are often referred to as nanowires. Such artificially structured materials may exhibit highly anisotropic properties in comparison to a bulk film due to the extra degrees of freedom associated with the length scales and the composition of the film. Further degrees of freedom can be achieved by fabrication of layered nanowires. If the dimensions of the wire diameter or layer thickness become smaller than a characteristic length scale of interest, then significant enhancements in the properties may be observed. The fabrication of nanowire arrays by electrochemical deposition into nanoporous templates formed by nuclear track etching of single crystal mica films will be described. Measurements on single nanowires are carried out using self-assembly techniques from suspensions prepared by stripping the nanowires from the template and dissolving in a suitable solvent. Examples of property enhancements in Ni, Bi, and Cu/Co nanowires will be discussed.

3:45 PM C3.2

PREPARATION OF NOBLE METAL NANOWIRES USING HEXAGONAL MESOPOROUS SILICA SBA-15. Yong-Jin Han, Ji Man Kim, Nathan Mitchell, Galen D. Stucky, University of California at Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

With increasing miniaturization of electronic and mechanical materials, the field of nanostructured materials has received much attention. Due to their size, nanomaterials exhibit optical, electrical and mechanical properties which differ from the properties of the bulk materials. Various nanostructured materials have been synthesized using conductive polymers, metals and semiconductors. Metal nanowires in particular have been the focus of many researchers due to their potential applications in fields such as nanoelectronic circuits and nanorobotics. We demonstrate a novel preparation method for the formation of metallic nanowires from gold, platinum and silver using mesoporous silica SBA-15 as a template. SBA-15 controls the size and the growth direction of the nanowires and also prevents bulk aggregation of the metal. Nanowires can be isolated from the silica framework by treatment with HF. Nanowires obtained by this method are homogeneous in diameter and can be synthesized in the ranges of 6 to 30 nm in diameters and have an average length of 0.5 μ m.

4:00 PM C3.3

MATRIX ASSISTED SYNTHESIS OF PALLADIUM NANOCAGE AND NANOWIRES. J. Cheon, H. Kang, R. Ryoo, Department of Chemistry and School of Molecular Science-BK21, Korea Advanced Institute of Science and Technology (KAIST); S.J. Oh, H.-C. Ri, Korea Basic Science Institute Taejon, KOREA.

Our study describes the synthesis of novel nanoscale Pd cage and wires whose sizes and shapes are templated by mesoporous matrices. The templates used are cubic phase MCM-48 and hexagonal phase SBA-15, which have pore diameters of \sim 3 nm and \sim 9 nm, respectively. For Pd@MCM-48, the Pd metal forms spherical domains (\sim 35-40 nm) consisting of three dimensionally interconnected into Pd arrays; for Pd@SBA-15, the Pd metal forms larger ellipsoidal domains (\sim 150 nm) consisting of one-dimensional wires. Etching out the matrix produces porous Pd cages (pore sizes of \sim 1.5-2.0 nm) with domain sizes of \sim 35-40 nm; similarly Pd@SBA-15 affords Pd nanowires (lengths of \sim 100 nm and thickness of \sim 9 nm). All the materials are examined by HRTEM, XRD, BET, EDX analyses. This study constitutes the novel synthesis of shape- and size-controlled pure free standing Pd nanomaterials and this method can be extended to the synthesis of other kinds of shaped nanomaterials.

4:15 PM C3.4

UNIDIRECTIONAL PLASMON PROPAGATION IN METALLIC NANOWIRES. Robert M. Dickson and L. Andrew Lyon, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

We report the observation of unidirectional plasmon propagation in metallic nanowires over distances $>$ 10 μ m. Through control of the incident excitation wavelength and rod composition, we demonstrate the selective coupling of photons into the plasmon mode of a 20 nm diameter nanowire. This mode then propagates in a nonemissive fashion down the wire length before being emitted as an elastically scattered photon at the distal end. As expected from previous studies of plasmon excitation in nanoparticles and thin films, we observe a strong wavelength and material dependence of this phenomenon. This metal-dependent plasmon propagation is exploited to produce a wire through which plasmons propagate unidirectionally. A bimetallic wire with a sharp Au/Ag heterojunction is shown to display both wavelength dependence and unidirectionality with respect to plasmon propagation across the heterojunction. It is expected that these results will contribute to the growing interest in optical energy transport in molecular-level and nanoscale devices.

4:30 PM C3.5

BAR-CODED METAL NANORODS AS PLATFORMS FOR BIOANALYSIS. Sheila R. Nicewarner, David J. Peña, Christine D. Keating, The Pennsylvania State University, Department of Chemistry, University Park, PA; Michael J. Natan, Surromed Inc., Palo Alto, CA.

A novel bar-coding technology is described that could enormously impact the life sciences or any area in which a need exists to identify and track a large number of samples. We have adapted technology from the macroscopic world to the biologically relevant microscopic level. The use of barcodes in bioanalysis has many advantages over current technology: (i) the theoretical number of possible combinations is greater than a million, which stems from the composition and length of metal segments in the barcode pattern. (ii) Stability for long periods of time has been observed. (iii) "Solution based" analysis yields increased analyte binding efficiency as compared to planar surfaces. (iv) Different metals can be differentially derivatized for multiplexed assays or an internal control. (v) Analyte identity can be directly determined by optical interrogation in real-time. And (vi) quantitation of analyte is possible. This technology exploits the inherent differences in reflectivity of metals, which can be visualized easily using conventional optical microscopy. The composition and sequence of metal striping pattern can be controlled during synthesis and provides a unique tag for molecule identity (e.g. Au-Pt-Au or Au-Ag-Au-Au). Based on recent chemistry developed through collaborative work, we have shown the ability to produce free-standing nanorods in solution (Martin, B. R. et al. Adv. Mater. 1999, 11, 1021-1025), which renders them useful for bioanalysis. In short, a bioassay can be performed directly on the rod, with analyte identity provided via the barcode pattern. Barcode rods have been fabricated ranging in sizes from 30 - 200 nm diameters and 0.4 - 8 μ m lengths employing various metal compositions, including Au, Ag, Pt, Pd, Ni, Cu, and Co. The data to be presented will focus on concept demonstration employing fluorescent tags for detection of analyte binding to the nanorod, with analyte identity determined via optical readout of the barcode pattern.

4:45 PM C3.6

AUTOMATED SYNTHESIS AND APPLICATIONS OF NANOSCALE BARCODES. Lou Dietz, SurroMed, Inc, Palo Alto, CA.

Many bioanalytical applications exist for nanoparticles that can be utilized as nanoscale barcodes (nanobarcode). Free-standing, cylindrically-shaped colloidal metal nanoparticles have been previously described, in which the metal composition can be alternated (e.g. Ag-Au-Ag-Au-Ag) along the length, and in which the metal segments can be both length-tuned and selectively chemically

functionalized with a variety of biomolecules. Differences in metal reflectivity, which can be observed using conventional optical microscopy, give rise to a series of stripes that resemble a macroscopic barcode. We will describe the development of an automated template-directed synthesis system that has been used to simultaneously synthesize 25 different types of nanobarcode in 25 different templates. Additionally, image analysis software has been developed to uniquely identify each type of nanobarcode from microscope images and to quantitate fluorescence signal from each particle. Data from multiplexed immunoassays will be presented to demonstrate the utility of nanobarcode in bioanalytical measurements.

SESSION C4: POSTER SESSION

Chairs: L. Andrew Lyon and Stephan J. Stranick
Monday Evening, November 27, 2000
8:00 PM
Exhibition Hall D (Hynes)

C4.1

AN INVESTIGATION OF MIXING IN Au/AgX HETERO-JUNCTION NANORODS. Mahnaz El-Kouedi, and Colby A. Foss Jr. Department of Chemistry, Georgetown University, Washington, DC.

We have electrochemically synthesized nanorods composed of gold and silver halides using a template synthesis technique in a porous aluminum oxide matrix. In this set of experiments we have looked at the optical spectra of composites in which the Au and AgX phases are either in intimate contact or separated. We have been able to separate the Au and AgX nanoparticles by creating a gap between the two particles that can be varied in size, or by addition of a third material (Au₂S) to form Au/Au₂S/AgX nanoparticles. In the case of the Au/AgI rods we observe a broadening of the plasmon resonance and a disappearance of the exciton peak associated with the band edge of the semiconductor when the two particles are brought close together. P-polarization tilt studies also indicate that there is some interaction between the metal and semiconductor particles that lead to the observed changes in the spectra. Our data suggests that we have possible mixing between the two phases. Computer simulations performed including Maxwell-Garnett and Bruggeman theories suggest that the mixing is on the atomic level and may lower the mean free lifetime of the metal particle. Mixing does not seem to be a problem with the Au/AgBr systems or when Au₂S is introduced between the Au and AgI. We attempt to interpret all these results with respect to the intermixing model we have proposed.

C4.2

SITE-SPECIFIC ATTACHMENT OF GOLD NANOPARTICLES TO DNA TEMPLATES. Karen Stevenson, Govindarajan Muralidharan, Thomas Thundat, Oak Ridge National Laboratory, Life Sciences Division; Leon Maya, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division; Jacob Barhen, Oak Ridge National Laboratory, Computer Science and Mathematics Division, Oak Ridge, TN.

The need to produce regular arrangements of nanoparticles led to the idea of using DNA as a scaffold or template for assembly of nanoscale arrays. Beginning in the 1980s Seeman et al. experimented with combining DNA fragments to produce geometrical shapes, including cubes, triangles, two-dimensional arrays and various forms of DNA knots. Using DNA as a structural molecule has many advantages. It can be easily synthesized in lengths from 5 to over 100 nucleotides. It can be joined end to end to produce longer linear molecules or more complex shapes, and it can be modified at predetermined sites to allow for the attachment of other molecules in a specific manner. We are creating linear arrays of DNA with gold binding sites located at periodic intervals. As a first step, we designed a DNA template with amino modified thymines located every 3.7 nm, which would allow the attachment of carboxylic acid functionalized gold nanoparticles. The gold particles were covalently bound to the amino groups on the DNA using standard EDAC chemistry in the presence of a competitor to block excess gold binding sites. The products were analyzed by gel electrophoresis, transmission electron microscopy and atomic force microscopy. Using this method DNA up to 55 nm long containing about 15 gold particles was produced.

C4.3

MAGNETIC PROPERTIES AND FREQUENCY BEHAVIOR OF SUPER-FINE Ni_{0.6-x}Co_xZn_{0.4}Fe₂O₄ FERRITE POWDERS. Mao Changhui, Su Lanying, Du Jun, Yang Zhimin, General Research Institute for Nonferrous Metals, Beijing, CHINA.

Super-fine S-type Ni_{0.6-x}Co_xZn_{0.4}Fe₂O₄ ferrite powders have been synthesized by chemical co-precipitation method. X-ray diffraction and Rietveld fitting were carried out to study the particle structure. The results show that the grain size of the powders can be controlled

by different co-precipitation and subsequent sintering conditions. Magnetic properties have been measured using a vibrating sample magnetometer (VSM) with an applied field up to 80kOe. It was found that the coercivity H_c decreased rapidly with the decrease of Co content and the variation of X did not significantly decrease the saturation magnetization. Magnetic permeability of the powders were investigated by HP8510B net analyzer in the 2~18GHz frequency range. The results reveal that the magnetic loss resonance frequency of Ni_{0.6-x}Co_xZn_{0.4}Fe₂O₄ ferrite powders shifts to lower frequency with the decrease of Co content and the increase of powder weight fraction (wt%) in a ferrite powder and proxy resin mixture.

C4.4

TETRADECANETHIOL DERIVATISED GOLD NANOPARTICLE FILMS AT THE AIR/ WATER INTERFACE. H.J. White, K. Shin, M.H. Rafailovich, J. Sokolov, G. Halada, State University of New York at Stony Brook; R.B. Lennox, A. Badia, C.J. Clarke, McGill University; A.H. King, Purdue University, D. Nguyen, B.M. Ocko, Brookhaven National Laboratory.

The gold particles (AuC14) were shown to form a uniform film, ~1.3nm thick when spread at the air/water interface. Grazing incidence diffraction (GID) indicated a mean interparticle spacing of 3.2nm, which was in good agreement with TEM on LB films. The surface pressure- area isotherms were measured as a function of subphase temperature. Features in these isotherms have been interpreted in terms of structural changes in the film, deduced from the scattering data. Very different behavior of the films was observed above and below the melting temperature of the chains. At room temperature, the films were stiff and become very rough on compression. Above the melting point one observes a single layer which continuously thickens.

C4.5

NANOPARTICLE-DERIVED ASSEMBLIES: A COMPARATIVE SPM AND TEM CHARACTERIZATION. Li Han, Mathew M. Maye, Chuan-Jian Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

The ultimate utilization of nanometer-sized particles in micro-electronics, molecular recognition and chemical/biological sensing relies on the preparation of macroscopic materials with isolated or organized nanoscale structures and properties. This work employs scanning probe microscopy (SPM) and transmission electron microscopy (TEM) to study the formation of nanoparticle assemblies and organizations on different substrates. The basic strategy explores spontaneous core-shell and shell-shell reactivities at thiolate-capped metal nanoparticles. Gold nanoparticles of different sizes and shape properties are used as the nanocrystal cores, and thiols of different functionalities, e.g., thiol, carboxylic acid, and amino acid, are exploited as molecular linkers. The inter-core or inter-shell reactivities involve covalent Au-thiolate bonding or non-covalent hydrogen-bonding or electrostatic interactions. While spectrophotometric and mass microbalance measurements provided kinetic assessments of the reactivities, SPM and TEM microscopic imaging measurements of the nanostructures are demonstrated to probe the morphologies with different nanoscale capabilities. Interesting 2D/3D nanostructures are analyzed by a comparative SPM and TEM assessment. The correlation of the nanostructural morphologies of the assemblies with the core size and shape properties will be discussed.

C4.6

TRANSVERSE SUSCEPTIBILITY AND MAGNETIC ANISOTROPY IN NANOPARTICLE SYSTEMS. L. Spinu, H. Srikanth, J. Fang, W.L. Zhou, C.J. O'Connor, Univ of New Orleans, AMRI, New Orleans, LA; S. Li, Tulane Univ, Dept of Chemical Engineering, New Orleans, LA; E.E. Carpenter, Naval Research Laboratory, Complex Materials Section, Washington DC; M. Farhoud, C.A. Ross, Massachusetts Institute of Technology, Dept of Materials Science, Cambridge, MA.

A radio-frequency (RF) resonant method based on a tunnel-diode oscillator (TDO) has been used to investigate the dynamic transverse susceptibility in a number of magnetic nanoparticle systems like γ -Fe₂O₃, Fe and Ni. The systems ranged from simple spherical particles to nanoparticles with varying degrees of anisotropy having acicular and core-shell structures. The nanoparticles were synthesized primarily using reversed-micelle techniques while some structures were patterned with interferometric lithography. Our unique RF method affords precise tracking of switching and anisotropy fields over a wide range in magnetic fields (0 to 9 Tesla) and temperature (5 to 300K) as the nanoparticle systems evolve from superparamagnetic to blocked regimes. In this systematic study, we present our results and discuss the influence of structural anisotropy on the magnetic anisotropy and switching field distributions. Theoretical modeling based on Stoner-Wohlfarth coherent rotation mechanism will also be presented. Work at AMRI supported by DARPA Grant No. MDA-972-97-1-0003

C4.7

THE MAGNETIC PROPERTIES OF Nd-Fe-Mo-B NANO-STRUCTURED MAGNETS WITH DIFFERENT α -Fe CONTENT. B.Z. Cui^{a,b}, Y.C. Sui^a, X.K. Sun^b, L.Y. Xiong^b, Z.D. Zhang^b, J. Feuchtwanger^a, J.M. Saniger^a. ^aCentro de Instrumentos UNAM, Mexico DF, MEXICO; ^bInstitute of Metal Research, Academia Sinica, Shenyang, PR CHINA.

The structure, magnetic properties and coercivity mechanism of (1 - x wt.%) Nd₁₅Fe₇₅Mo₂B₈ x wt.% α -Fe (x = 0 - 50) nano-structured magnets prepared by mechanical milling (MM), have been studied. With increasing α -Fe content, the intrinsic coercivity $\mu_0 H_c$ decreases monotonously, whereas the reduced remanence J_r/J_s , the remanence J_r and maximum magnetic energy product $(BH)_{max}$ for the nanocomposite magnets basically increase monotonously due to the exchange coupling between α -Fe nano-grain and its nearest Nd₂(Fe, Mo)₁₄B nano-grains. On the other hand, with increasing α -Fe content, the crystallization temperatures of the amorphous phases prepared by high-energy ball milling and the mean grain sizes of α -Fe increase monotonously, whereas the mean grain sizes of Nd₂(Fe, Mo)₁₄B decrease monotonously. The positron annihilation studies have shown that the positron lifetime of τ_1 and τ_2 of the samples with x is 30 ~ 50 are a little smaller than those of the samples with x are 0 or 17. The value of I_1/I_2 increases monotonously with increasing α -Fe content. The smaller values of τ_1 , τ_2 and larger value of I_1/I_2 imply a smaller volume of single vacancy, vacancy-clusters and a more compact structure in Nd₂(Fe, Mo)₁₄B/ α -Fe-type nanocomposite magnets with x is 30 ~ 50 than in the nominal single phase of Nd₂(Fe, Mo)₁₄B nano-structured magnets with x is 0 or 17. The smaller value of τ_2 and larger value of I_1/I_2 would be favorable for improving $\mu_0 H_c$ of the typical Nd₂(Fe, Mo)₁₄B/ α -Fe-type nanocomposite magnets with x is 40. The reversal magnetization nucleation mechanism in the nanocomposite magnets with x is 30 ~ 50 prepared by MM may control the coercivity. The magnetic domain pinning mechanism in the nominal single phase of Nd₂(Fe, Mo)₁₄B nano-structured magnets with x is 0 or 17 prepared by MM may control the coercivity.

C4.8

SIZE CONTROLLED SYNTHESIS OF MAGNETIC NANO-CRYSTALS AND MULTI DIMENSIONAL ARRAYS. J. Cheon, J. Park, K.B. Lee, Department of Chemistry and School of Molecular Science-BK21, Korea Advanced Institute of Science and Technology (KAIST); S.J. Oh, H.-C. Ri, Korea Basic Science Institute, Taejeon, KOREA.

The chemical and physical properties of metals in highly divided forms such as nanoparticles are presently the subject of intensive fundamental research with many potential applications. In particular, these studies concern catalytic, optical, or magnetic properties. Here, we focus on the magnetic properties of Co nanoparticles synthesized by thermal decomposition of organometallic precursors in the presence of surface capping stabilizers. We control the size of Co metal nanoparticles from 4 to 8 nm by varying the concentration of stabilizers. Obtained Co nanoparticles are highly monodispersed and have a narrow size distribution. The blocking temperature (T_B) is changed from 280K to 40K with decreasing Co nanoparticle size. Co nanoparticles is ferromagnetic below blocking temperature. The Co particles condense into hexagonal close packed array to form 1, 2-D structures. We elucidate the relationship between the size and magnetism in Co nanoparticles in this study.

C4.9

MAGNETIC PROPERTIES OF A THIN LAYER OF ORIENTED SINGLE DOMAIN MAGNETIC NANOPARTICLES. Korey D. Sorge, James R. Thompson, Frank A. Modine, Tony E. Haynes, Thomas C. Schulthess, Shin-ichi Honda, Alkiviathes Meldrum, John D. Budai, C.W. White and Lynn A. Boatner, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Magnetic ions—Fe, Co, and Ni—have been implanted into the near-surface region of single crystals of Al₂O₃ and yttria stabilized zirconia (YSZ). With thermal processing, the implanted species precipitate to form predominantly single-domain, single-crystal ferromagnetic nanoparticles that crystallographically align with the host substrate, thereby forming a magnetically anisotropic nanocomposite surface. In the case of Fe, precipitates were formed in YSZ by implantation of Fe⁺ at an energy of 140 keV and a dose of 8×10^{16} ions/cm², followed by annealing in a reducing atmosphere. Similarly for Co, precipitates were formed in Al₂O₃ by implantation of Co⁺ at an energy of 140 keV and a dose of 8×10^{16} ions/cm², followed by annealing in a reducing atmosphere. To form Ni precipitates, Ni⁺ was implanted in Al₂O₃ at an energy of 750 keV and doses of 5×10^{16} , 1×10^{17} , and 2×10^{17} ions/cm², followed by annealing in a reducing atmosphere. Typical dimensions for the particle size and layer thickness are 10 nm and 80 nm, respectively, allowing for nearly 10% volume filling in the layer, as measured by RBS/channeling,

transmission electron microscopy, and x-ray diffraction. Studies on these ferromagnetic particle layers were conducted in the temperature range of 5 to 300 K and applied fields of 10 kG using a superconducting quantum interference device (SQUID)-based magnetometer. An analysis of the magnetic properties including retentivity, coercivity, and saturation moment will be presented as well as the effects of magnetocrystalline and shape anisotropy. Additionally, the particle/host orientation dependence will be treated by comparisons with Ni precipitates in an amorphous substrate of SiO₂.

C4.10

Abstract Withdrawn.

C4.11

HIGH RESOLUTION TEM STUDIES OF GOLD NANORODS. Miguel José Yacamán, Instituto de Física, UNAM and Instituto Nacional de Investigaciones Nucleares; J.A. Ascencio, P. Santiago and G. Canizal, Instituto Nacional de Investigaciones Nucleares, MEXICO.

Gold nanorods were studied high resolution TEM, image simulation and electron diffraction. It is found some FCC nanorods present a complex structure of planar defect running parallel to the nanorod axis. The detailed atomistic structure of defects is discussed. In addition it is found a new kind of nanorod based on a pentagonal multiple twinned structure. It is shown that pentagonal nanorods are the direct result of coalescence of a pentagonal and FCC particle.

C4.12

NANOPARTICLES AND NANOCOMPOSITES IN RF PLASMAS. Jin Cao, Themis Matsoukas, Penn State Univ, Dept of Chemical Engineering, University Park, PA.

Via reactions not observed in thermally activated reactors, organic molecules in plasma form solid materials of varying degrees of cross-linking, referred to as "plasma polymers." They may nucleate to form particles in the low nanometer range, or deposit onto substrates as film. In this work, we report our efforts on the use of low pressure plasma for particle formation and thin film deposition on suspended particles. Plasma polymer particles are synthesized in a capacitively-coupled radio-frequency (RF) Ar/monomer discharge at low system pressure, RF power, and monomer flow rate. A variety of particle structures are observed, including monodispersed nanospheres and liquid-like viscous nano-droplets. Styrene in particular is observed to produce hollow nanospheres. By manipulating the process parameters, films of plasma polymers can be deposited onto suspended submicron particles. We take advantage of electrostatic trapping to suspend small particles in plasma for extended periods of time until the desired coatings thickness is achieved. Sub-micron silica particles introduced into a low pressure RF Ar/isopropanol plasma are coated with film whose thickness ranges from 3 to 50 nm. The thickness of the coating is controlled through the reaction time, whereas the properties of the coating are varied via the discharge conditions. We discuss the characterization of the structures, operating conditions, and proposed formation mechanisms.

C4.13

HIGH SPIN Mn MOLECULAR CLUSTERS: SPIN STATE EFFECTS ON THE OUTER CORE-LEVEL MULTIPLET STRUCTURES. Art J. Nelson, J.G. Reynolds, University of California, Lawrence Livermore National Lab, Livermore, CA; George Christou, Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN.

Oxo-bridged manganese polynuclear complexes have applications in a variety of technologies, such as molecular-based magnetic materials, nanoscale magnets, catalysis and photosynthetic redox chemistry. The reason that these types of compounds are capable of such important and varied technologies is thought to be because they possess ground states with large spin values. However, the electronic, structural and magnetochemical relationships are not well understood and need to be thoroughly investigated to adequately explain why Mn is such an integral part of so many useful processes. X-ray photoemission spectroscopy was used to study the Mn 3p, 3s and valence band electronic behavior as a function of Mn cluster structural properties, where the cluster size and nuclearity are systematically varied. Results show a chemical shift of the Mn 3p_{3/2-1/2} spin-orbit pair related to the cluster size and nuclearity. Also, the Mn 3s ⁷S and ⁵S final state multiplet components shift considerably since it involves the binding energy of a ligand valence electron. In addition, the branching ratio of the ⁷S;⁵S states is related to the 3s-3d electron correlation. Specifically, in the ⁷S state, the remaining 3s electron is well correlated with 3d electrons of parallel spin, while in the ⁵S state the two spins are antiparallel. Changes in this electron correlation are clearly observed in the ⁷S;⁵S branching ratio as a function of cluster size.

C4.14
ANISOTROPY AND NANODIMENSIONALITY IN
TIN(II)-STRONTIUM FLUORIDES AND FLUORIDE NITRATES.
Georges Dénès and Alena Peroutka, Concordia University, Dept. of
Chemistry and Biochemistry, Laboratory of Solid State Chemistry
and Mössbauer Spectroscopy, and Laboratories for Inorganic
Materials, Montréal, Québec, CANADA.

PbSnF₄ is the highest performance fluoride-ion conductor and it has found applications in chemical sensors. The highest fluoride ion conductivity is found in tin(II)-metal(II) fluorides, where the metal(II) is a large alkaline earth (Sr, Ba) or lead. In addition, their conductivity is purely ionic, i.e. the transport number for electron is very small ($\tau_e < 0.01$). However, the combination of tin(II) and lead(II), two weak metals in suboxidation states, in the same material, results in instability under oxidizing conditions. Tin(II) cannot be eliminated, since we established earlier that it is necessary for enhancing the fluoride ion conduction. It is therefore tempting, in order to minimize the chance of sample oxidation, to replace lead(II) by strontium or barium, both of which are very stable in the divalent state, and have no suboxidation state. We studied the properties of SrSnF₄ in an earlier work. In this work, we have concentrated our effort on the preparation and properties of SrSn₂F₆ and Sr₂Sn₂NO₃F₇·2H₂O, the latter being obtained in some preparations and in some attempts to recrystallize the former. Both materials can be obtained in the form of very highly anisotropic samples. Both give rapidly nanocrystals on ball-milling. Their preparation, characterization, and properties will be described, with emphasis on the anisotropy and the formation of nanoparticles.

C4.15
NOVEL MORPHOLOGIES IN NANO-FILLED POLYMER FILMS.
Vincent Ferreiro, Jack F. Douglas, Archie P. Smith, Alamgir Karim,
Polymers Division, NIST, Gaithersburg, MD.

We investigate the influence of montmorillonite-clay filler on the morphology of poly(ethylene oxide), PEO / poly(methyl methacrylate), PMMA blends films formed by spin casting from chloroform solution onto a silicon substrate. In the absence of any clay filler, we observe a spherulitic morphology when the composition is relatively rich in PEO, relative to the critical composition phase separated morphology observed for PMMA rich films. Addition of the clay filler has a dramatic effect on the blend film morphology. A transition from spherulitic to a "dendritic structure maltese-cross" like to an axially symmetric dendritic structure is observed with increasing PMMA concentration of the blend. We are investigating the effect of other fillers (nanotube, dendrimer) on the morphology and the properties of the films. The nano-mechanical properties of coated films have been obtained using atomic force microscopy by analyzing force curves.

C4.16
STABILIZATION AND SEGREGATION OF GOLD NANO-
PARTICLES USING POLY(METHYLPHENYL-PHOSPHAZENE)
DERIVATIVES AND GRAFTS. John V. St. John, Patty
Wisian-Neilson, Caroline Walker, Southern Methodist University,
Dallas, TX.

Poly(methyl/phenylphosphazene), PMPP, is one example of a unique class of inorganic polymers with alternating -(P=N)- backbones. The reduction of gold salts in the presence of PMPP in solution forms stabilized gold nanoparticles. The ratio of gold salt to PMPP allows some control over the size of the synthesized nanoparticles. Termination of a percentage of methyl groups of PMPP with thiols allows further stabilization and passivation of gold nanoparticles. The introduction of carboxylic acid side groups provides regions of hydrophilic character on the polymer, giving rise to hydrophobic/hydrophilic interactions to order the nanoparticles into specific domains. Grafts and block copolymers of PMPP with conventional organic polymer systems are used to stabilize gold nanoparticles at localized domains of PMPP. Solutions of PMPP / gold nanoparticles, and PMPP derivatives with gold nanoparticles are studied with optical spectroscopy, and microscopy. Films of the PMPP / nanoparticle composites are studied with optical spectroscopy and microscopy to determine conditions which promote growth of the nanoparticles and stabilization to form short wires and non-spherical aggregates within the localized domains.

C4.17
CHARACTERIZATION OF ANISOTROPIC NANOPARTICLE
MATERIALS USING SMALL-ANGLE SCATTERING.
John D. Barnes, NIST Polymer Characterization Group,
Gaithersburg, MD.

Small-Angle Scattering methods using both x-rays and neutrons are well established as tools for characterizing the morphology of materials on nanometer distance scales. This presentation provides a

general overview of these methods as they have been traditionally used to characterize materials ranging from virus particles to microphotonic structures. More recent research studies on materials whose anisotropy is due to anisometric particles in assemblies with preferred orientation will be described to illustrate the general principles used to elucidate such morphologies.

C4.18
FABRICATION OF AMPHILIC GOLD NANOPARTICLES.
Joseph M. Simard, Cheryl L. Briggs, Andrew K. Boal, Vincent
Rotello, University of Massachusetts at Amherst, Dept of Chemistry,
Amherst, MA.

Mixed monolayer-protected gold clusters (MMPCs) provide versatile precursors for the fabrication of nanoscale systems. One potentially powerful application of MMPCs is biomolecular recognition: in recent investigations we have demonstrated that the mobility of thiolate ligands on nanoparticles can be exploited to create templated multivalent receptors. The extension of this methodology to the recognition of protein surfaces, however, has been limited by the inaccessibility of water-soluble amphiphilic MMPC's. To provide these essential systems, we have explored the exchange of polar functionality into gold nanoparticles featuring nonpolar monolayer coverage. We report here the direct formation of water-soluble amphiphilic colloids through place exchange of solubilizing groups including alkanethiolates with w-thiol carboxylic acids. The fabrication and properties of these systems will be discussed.

C4.19
EFFECT OF CHAIN LENGTH ON INTRA-MONOLAYER
NONCOVALENT INTERACTIONS IN SAMS ON GOLD
NANOPARTICLES. Andrew K. Boal, Vincent Rotello, University of
Massachusetts at Amherst, Amherst, MA.

Unlike the highly ordered Self-Assembled Monolayers (SAMs) formed on flat gold surfaces, those on gold nanoparticles radiate form a roughly spherical center and are amorphous in structure. One result of this structural motif is that the strength of intra-monolayer non-covalent interactions, such as p-stacking and hydrogen bonding, are a function of the distance of the recognition element from the colloidal core. We present here an exploration of these phenomena in a number of systems, and present some fundamental rules for incorporating intra-monolayer noncovalent interactions in the design of new SAM-nanoparticle systems.

C4.20
PLANAR SYNTHESIS OF OBLATE NANOPARTICLES.
Gennady B. Khomutov, Yury A. Koksharov, Alexander Yu. Obidenov,
Eugeny S. Soldatov, Artem S. Trifonov, Faculty of Physics, M.V.
Lomonosov Moscow State Univ, Moscow, RUSSIA; Sergey P. Gubin,
Institute of General and Inorganic Chemistry RAS, RUSSIA.

The control of matter on the nanometer-length scale and nanoparticles research are the key components of nanoscience, nanoengineering and nanotechnology. Shape and size control of nanoparticles is important for practical applications. The method of nanoparticles synthesis often influences the properties of the product, particularly the shape, size, crystal morphology and degree of crystallinity. A novel method of two-dimensional synthesis of anisotropic nanoparticles was introduced recently [1]. In this method oblate nanoparticles are fabricated via decomposition of a volatile insoluble organometallic precursor compound in a mixed surfactant monolayer at the gas/liquid interface, and nanoparticles growth is an example of two-dimensional process where surfactants, precursors, intermediates, nucleus and nanoparticles form a monolayer at the interface. In our experiments nanoparticles were generated by ultraviolet decomposition of iron pentacarbonyl, dicobalt octacarbonyl and by chemical reduction of metalorganic cluster molecules in a mixed monolayer with stearic acid on the water surface. The properties of fatty acids to form Langmuir monolayer and to prevent aggregation of nanoparticles were here combined successfully. Synthesis was carried out in a gaseous phase of monolayer and the shape and size of resulting nanoparticles was dependent on the monolayer compression extent. AFM and STM study of mixed monolayers deposited onto mica and graphite substrates revealed circular ultraflat nano-disks (diameter can be widely varied from tens nanometers to hundreds of nanometers with thickness about 1-8 nm). X-rays scattering in the low angle range revealed several Bragg reflections indicating layered structure of ultraflat nanoparticles in multilayer particulate Langmuir-Blodgett films formed in agreement with scanning probe microscopy measurements. TEM data point out to the amorphous structure of iron-containing nanoparticles formed. Two-dimensional monolayer synthesis produces ultraflat nanoparticles with very high surface to volume ratio, what is perspective for catalysis, optical and other applications. [1]. G.B. Khomutov et.al. Mat. Sci. Eng.: C, 8-9 (1999) 309-318.

C4.21

SYNTHESIS AND CHARACTERIZATION OF POLY-(N-ISOPROPYLACRYLAMIDE)/ACRYLIC ACID COPOLYMER FILAMENTS. William D. Holliday, L. Andrew Lyon, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

We report the preparation of environmentally responsive, rod shaped hydrogel nanoparticles via template-directed synthesis. Poly-(N-isopropylacrylamide)/acrylic acid copolymer matrices (both monoliths and spheroidal particles) have been shown to reversibly swell in response to a temperature change in the surrounding environment. Temperature phase transitions were studied on this system and compared to literature values of monolith systems and sub-micron spherical particles of similarly composed hydrogels. Characterization of particle size, shape, and responsivity was carried out using optical and confocal microscopies.

C4.22

PHOTOMECHANICAL RESPONSE OF AZOBENZENE / FLUOR-MICA COMPLEXES: I. ORGANOPHILIC MICA AS HOST. Taketoshi Fujita, N. Iyi, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN; Zenon Klapayta, Faculty of Geology, Geophysics and Environmental Protection, University of Mining and Metallurgy, Krakow, POLAND.

The photomechanical properties of organophilic fluor-tetrasilic mica (α -TSM) / azobenzene complexes was investigated to reveal optimum conditions for large photomechanical response. The alkyl chain length and the concentration of trimethyl-alkylammonium (TMAA) were varied to prepare 16 α -TSM hosts. These were classified as having either bimolecular, pseudo-trimolecular or paraffin type structure based on judgments of basal spacings. Azobenzene/ α -TSM complexes were prepared by vapor-phase intercalation of azobenzene (AzBz) into α -TSM, and were characterized by CHN analyses and XRD measurements. Photomechanical responses for the complexes were monitored by changes in $d(001)$ under UV irradiation ($\lambda = 365$ nm). A large photoresponse, indicated by a 0.25 - 0.5 nm decrease in $d(001)$, was observed for the complexes with α -TSM hosts classified as having a pseudo-trimolecular structure with basal spacing of 2.2 - 2.5 nm. The increase in the basal spacing of these hosts due to AzBz incorporation was 1.2 - 1.4 nm, which, being almost equal to the long-axis length of AzBz, suggests a vertical arrangement of AzBz within the layer. For the complexes which little or no photo-responsiveness, the basal spacing of the α -TSM hosts were either less than 2.0 nm or about 3.9 nm, which were classified as having bimolecular and paraffin-type structures respectively. These results indicate that photoresponsiveness is closely related to the structure of the α -TSM hosts for these complexes, and that pseudo-trimolecular structure α -TSM hosts can provide complexes with good photoresponsive properties. The photo-mechanical properties of the another azobenzene complexes with organophilic taeniolite (α -TN) would be presented.

C4.23

Abstract Withdrawn.

C4.24

POLYMERIC SURFACTANTS BASED ON OLEIC ACID. Qinghong Fu, Institute of Materials Science, University of Connecticut, Storrs, CT.

The lamellar liquid crystalline (LLC) region in the system consisting of sodium oleate (NaOL), oleic acid (OLA), and water was determined. The interlayer spacings (d) of the lamellar liquid crystals were measured and extrapolated to zero water content to obtain d_0 values. The d_0 values showed the oleic acid to be solubilized between the methyl group layers at low concentrations and interdigitating between the hydrocarbon chains for greater contents. Cross-linking agents were added to the system. They were found located partly between the end methyl group layers and partly interdigitated between the hydrocarbon chains. The LLC phase of NaOL/OLA/H₂O system with the cross-linking agent was polymerized. The system after polymerization was a mixture of LLC phase and solids. It was shown that d values decreased by about 10 Å, indicating a disruption of the ordered structure by the polymerization. The polymerization took place not only in the middle of the hydrocarbon chains, affecting the order of the arrangement in LLC phase, but also in the hydrophobic layer between the methyl groups. The polymer lowered the surface tension of water to below 30mN/m with a CMC of 0.25g/L.

C4.25

FABRICATION AND CHARACTERIZATION OF CHROMIUM OXIDE NANOPARTICLES. Zhenchen Zhong, Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA; Department of Physics, Grambling State University, Grambling, LA.

Well-dispersed nanoscale textured chromium oxide particles can be fabricated under certain conditions by laser-induced solution deposition (LISD) from organic solutions. The fabricated nanoparticles are characterized by scanning electron microscope with EDX, transmission electron microscope, X-ray diffraction and magnetic measurements. We have successfully demonstrated that the LISD is a unique technique for fabricating uniformly-distributed but anisotropic chromium oxide particles, which can be used in electronic/magnetic devices.

C4.26

HIGH COERCIVITY IN NANOCRYSTALLINE FERRITE MATERIALS. Yu Shi, Jun Ding, National University of Singapore, Department of Materials Science, SINGAPORE.

In this work, nanocrystalline barium and cobalt ferrites were prepared by mechanical milling and sputtering. It has been found that the coercivity of these compounds could be dramatically enhanced by adding nonmagnetic elements. The magnetic properties were strongly dependent on the concentration of nonmagnetic elements (alumina and silica, respectively) and heat treatment condition (annealing temperature and duration). A coercivity as high as 9.3 kOe was obtained in Al substituted Ba-ferrite, while the coercivity values of the Ba-ferrite samples without doped Al with a similar particle size were in the range of 5~6 kOe. Cobalt ferrite/silica nanocomposite with a coercivity of 3.3 kOe and a magnetization of 77 emu/g was obtained. The sputtered Co ferrite/silica nanocomposite possessed a coercivity as high as 7.5 kOe, which is the highest value for Co ferrite according to our knowledge. The structure and magnetic behavior of these nanocrystalline specimens were investigated by X-ray diffraction, Mossbauer spectroscopy, Transmission electron microscope, Scanning electron microscope and Vibrating sample magnetometry.

C4.27

VOLUME CONFINED STATES IN ELLIPSOIDAL QUANTUM DOTS. Giovanni Cantele, Domenico Ninno and Giuseppe Iadonisi, Istituto Nazionale di Fisica della Materia (UdR Napoli) and Univ. di Napoli Federico II, Dipartimento di Scienze Fisiche.

The Schrödinger equation has been solved, within the effective mass approximation and using hard walls boundary conditions, in an ellipsoidal quantum dot (QD) with azimuthal symmetry for studying the role of the QD shape on the system physical properties. An exact numerical solution allowing the calculation of all the spectrum has been obtained using a suitable coordinates system in which the wave function is separable. The variable separation leads to a one-dimensional Schrödinger equation which has been solved numerically with a mid-point shooting algorithm. Our main result is that it is not enough to specify the system mean dimensions and volume in order to determine the energy spectrum. We have, indeed, shown that if one consider a family of ellipsoidal QDs with constant volume, the ground state energy depends on the anisotropy degree (the ratio c/a between the major and minor semi-axes) of the structure. Looking at the ground state energies as a function of c/a (keeping the volume constant) it is found that minimum is reached for the spherical QD. We have also considered excited states and found that the ellipsoidal deformation determines both a splitting of the states with different z -component of the angular momentum, and a volume effect similar to that found for the ground state. The system geometry plays a very important role also in determining the wave function angular dependence. We have found, in particular, that while in the spherical QD the ground state wave function does not depend on the angular coordinates (reflecting the full rotational symmetry of the system), for ellipsoidal QDs it presents a localization in the points corresponding to the ellipsoid section passing for its centre and orthogonal to the major axis. Finally, surface dielectric effects due to the dielectric constant difference between the dot and the surrounding medium are discussed.

C4.28

DEPOSITION OF AN EXTREMELY THIN POLYMER FILM ON CERAMIC NANOPARTICLES. Donglu Shi, Wim van Ooij, Jiangang Zhao, and Zhou Yu, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH; Shixin Wang and Lumin Wang, Dept. of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI.

To achieve unique properties in fundamental research and cutting edge technology there is a critical need to develop structures on nanoparticle surfaces. Such a structure has to be at nano-scale so that it can be a sub-structure of the nanoparticle. This implies that the surface of a nanoparticle is tailored only at a few nanometers in terms of structure, composition, and uniformity. The great challenge therefore lies critically on the deposition of a film on the order of a few nanometers on the surfaces of the nanoparticles. Here we demonstrate, for the first time, the uniform deposition of ultrathin polymer films of 2 nm on the surfaces of alumina nanoparticles using a plasma

polymerization treatment. High resolution transmission electron microscopy (HRTEM) experiments showed that an extremely thin film of the pyrrole layer (2 nm) was uniformly deposited on the surfaces of the nanoparticles. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) experiments confirmed the nanosurface deposition of the pyrrole films on the nanoparticles. The deposition mechanism of ultrathin polymer film on nanoparticle surfaces is discussed.

C4.29

SYNTHESIS AND CHARACTERIZATION OF NONSPHERICAL COLLOIDAL PARTICLES WITH UNIFORM AND WELL-CONTROLLED SIZES AND SHAPES. Yu Lu, Yadong Yin, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated several effective methods for generating monodispersed, nonspherical colloidal particles with well-defined dimensions and shapes. Typical examples include ellipsoidal polymer beads, peanut-shaped polymer beads, and dumbbell-shaped oxides. In this presentation, we will outline the detailed procedures, as well as the unique features and applications of these nonspherical colloidal particles.

C4.30

TRANSPORT PROPERTIES OF BI-RELATED NANOWIRE ARRAYS. Yu-Ming Lin^a, S.B. Cronin^b, O. Rabin^c, J. Heremans^e, M.S. Dresselhaus^{a,b}, J.Y. Ying^d. ^aDepartment of Electrical Engineering and Computer Science, ^bDepartment of Physics, ^cDepartment of Chemistry, and ^dDepartment of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA; ^eDelphi Automotive Systems, Warren, MI.

Due to their reduced dimensionality and enhanced surface/volume ratio, one-dimensional nanowires exhibit unusual physical properties and have great potential for application in novel optical, electrical, magnetic and thermoelectric devices. Recently, anodic alumina templates have been exploited extensively for the synthesis of large-scale self-assembled nanowire arrays for a variety of materials using pressure injection, electrochemical deposition or vapor deposition techniques, resulting in hexagonally-packed nanowire arrays. In this paper, bismuth (Bi), antimony (Sb) and Bi-Sb alloyed nanowire arrays with wire diameters ranging from 200 nm down to 10 nm are fabricated in porous alumina templates by pressure injection or vapor deposition techniques. These nanowire arrays are characterized by SEM and X-ray diffraction to determine the crystal structure, and transport measurements of these nanowire arrays are performed. Bi, as a semimetallic Group V element, is a promising candidate for the study of quantum confinement effects at larger, easily accessible sizes because of the very small electron effective masses in Bi. In addition, it is expected that the band structure of Bi nanowires can be controllably engineered by alloying Bi with antimony (Sb) to produce an enhanced thermoelectric efficiency. A theoretical calculation for the band structures of these nanowires is developed, which predicts a semimetal-semiconductor transition for Bi and Sb nanowires at wire diameters around 50 and 9 nm, respectively. Based on their respective band structures, a semi-classical transport model for nanowires has been developed and compared with experimental results.

[†]We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grant DMR-98-04734, and the US Navy contract N00167-98-K0024.

C4.31

TAILORING GRAPHITE SHEETS TOWARD MESOSCOPIC DEVICES. Erik Dujardin, Tineke Thio, NEC Research Institute, Princeton, NJ; Henri Lezec, Thomas W. Ebbesen, ISIS, Louis Pasteur University, Strasbourg, FRANCE.

For a number of reasons, graphite can be considered as a frontier material between the solid state and the molecular worlds. Hence, in the recent years, both condensed matter physicist and chemists have united their efforts to shape and study the properties of graphite in a variety of its morphologies: fullerenes, nanotubes, cones, etc For theorists, the ideal graphitic object is the graphene sheet, which is a single layer of planar graphite. The very unusual transport properties of graphene, when constrained in its lateral dimensions, have been widely studied theoretically [1]. For instance, it has been shown that the dangling bonds (unpaired electrons) of one edge of a narrow band of graphene would be ferromagnetically coupled [1]. To the best of our knowledge, although nanometric ribbons of graphene have been observed [2], no experimental data on properties of small constrictions of graphene have been made available. We will present our experimental results on 70 nm wide constrictions in graphite nanofabricated by Focused Ion Beam lithography (FIB). In our samples, both the mesoscopic constriction and the terminal electrodes are cut in isolated graphitic discs having a diameter of 1 to 2 microns and a thickness of about 100 basal planes. The preparation of the samples along with the advantages of our approach will be discussed.

The magneto-transport properties of the constrictions have been characterized and evidences of size effect on the electronic properties of graphite have been observed [3]. Perspectives of our promising results toward the experimental study of mesoscopic graphene and standing challenges will conclude the presentation. [1] K. Wakabayashi, M. Fujita, H. Ajiki, M. Sigrist, Phys. Rev. B, 1999, 59, 8271-82 and ref. therein. [2] T.W. Ebbesen, H. Hiura, Adv. Mater., 1995, 7, 582-6. [3] E. Dujardin, T. Thio, H. Lezec, T.W. Ebbesen, in prep.

C4.32

STUDIES OF THE DIELECTRIC CONSTANT OF THIN FILM BISMUTH NANOWIRE SAMPLES USING OPTICAL REFLECTOMETRY. Marcie R. Black^a, Megha Padi^b, M.S. Dresselhaus^{a,b}. ^aMIT, Department of Electrical Engineering and Computer Science, Cambridge, MA; ^bMIT, Department of Physics, Cambridge, MA.

Arrays of 10 to 120 nm diameter single crystalline bismuth nanowires have been formed inside amorphous alumina templates. Since bismuth has a small effective mass compared to other materials, significant quantum mechanical confinement is expected to occur in wires with diameter less than 50nm. The subbands formed by quantum confinement cause interesting modifications to dielectric function of bismuth. This study measures the dielectric function of bismuth nanowires in an energy range where the effects of quantum confinement are predicted (0.08 to 0.5 eV). Using Fourier transform infrared reflectometry, the dielectric constant as a function of energy is obtained for the alumina/bismuth composite system. Effective medium theory is used to subtract the effect of the alumina template from the measurement of the composite material, thus yielding the dielectric function of bismuth nanowires. Several oscillators are observed in the frequency dependent dielectric function in the photon energy range measured. The dependence of the frequency and intensity of these oscillators on doping, polarization, and diameter of the nanowires will be reported. We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grant DMR-98-04734, and the US Navy contract N00167-98-K0024.

C4.33

SURFACE ELECTRICAL TRANSPORT AND LONG - RANGE ELECTROSTATIC TRAPPING OF DNA MOLECULES.

V. Samuilov, Y.S. Seo, D. Gersappe, J. Sokolov, M. Rafailovich, Dept of Materials Science, SUNY at Stony Brook, NY; N. Pernodet, Dept of Biology, SUNY at Stony Brook, NY; B. Chu, Dept of Chemistry, SUNY at Stony Brook, NY.

The electrical transport properties of long DNA molecules were studied based upon a newly developed method of electrophoresis on flat surfaces [1]. The electrophoretic mobilities of DNA in the presence of Si surface were found to be approximately one order less than in free solution. The electropherogram peaks of 1 kb- and Hind III DNA ladders have been clearly identified. The experimental dependencies of the mobilities on molecular weight were found to be scaled by power law with the exponents of an opposite sign at 2 different buffer concentrations: negative for surface transport at 10^{-2} M concentration of TBE buffer and positive at 10^{-3} M. A novel mechanism responsible for DNA molecules separation in the presence of the surface at low buffer concentrations has been developed. The long-range electrostatic trapping [2,3] creates molecular weight distribution of DNA within the electric double layer in normal to the surface direction. The electric double layer is responsible for a velocity profile of the electroosmotic flow. The net electrophoretic mobility of longer DNA, being trapped closer to the surface, is higher than of the shorter ones in the electric field, oriented along the surface. The main features of the electro-hydrodynamic instability [4] related to λ and T2 DNA molecules aggregation, observed in our system, are consistent with the concept of long-range electrostatic trapping. This work was supported by NSF-MRSEC Program. 1. N. Pernodet et al., submitted to Phys. Rev. Lett. 2. X.-H.N. Xu et al., Science, 281, 1650 (1998) 3. A. Larsen et al., Nature, 385, 230 (1997) 4. L. Mitnik et al., Science, 267, 220 (1995)

C4.34

CONTROL SYNTHESIS OF HIGHLY LUMINESCENT CdSe AND (CdSe)ZnS QUANTUM DOTS. Wing Woo, Mounji Bawendi, MIT, Dept of Chemistry, Cambridge, MA.

Physical properties and potential applications of CdSe quantum dots (QDs) have been extensively explored in the last decade. CdSe QDs with high photoluminescence (PL) quantum efficiency (QE) not only increase the sensitivity of experiments, but also make their potential applications more promising. We report here a simple but powerful recipe to improve the QE of CdSe QDs and core-shell (CdSe)ZnS QDs. The QE of these treated QDs is increased by upto an order of magnitude from untreated values. Subsequent overcoating of these QDs with ZnS reproducibly yields composites with QE as high as

50%. Additional advantages of this route include greater control over growth dynamics as well as enhanced reaction yields. All of these attributes should significantly improve the properties of QDs as novel fluorophores in tagging and display applications.

C4.35

PHOTOPHYSICS OF CHARGED CdSe QUANTUM DOTS.

Wing Woo, Ken Shimizu, Robert G. Neuhauser, Catherine A. Leatherdale, Mouni G. Bawendi, MIT, Dept of Chemistry, Cambridge, MA; Michael F. Rubner, MIT, Dept of Materials Science and Engineering, Cambridge, MA.

A charged quantum dot (QD) is believed to be 'dark' as the free charge quenches the photoluminescence (PL) through non-radiative Auger processes. This model has been applied to explain both photodarkening effects observed in QD glasses and PL intermittency observed in single QDs. However, direct experimental proofs have been lacking. We discuss here results that show electrical injection of carriers into CdSe QDs causes a reversible reduction of the PL efficiency consistent with the model.

C4.36

STRUCTURE, COMPOSITION, AND ELECTRONIC PROPERTIES OF NANOWIRE ARRAYS. M.S. Sander, A.L. Prieto, UC Berkeley, Dept of Chemistry, Berkeley, CA; Y.M. Lin, M.S. Dresselhaus, MIT, Depts of Electrical Engineering & Computer Science and Physics, Cambridge, MA; R. Gronsky, T.D. Sands, UC Berkeley, Dept of Materials Science & Engineering, Berkeley, CA; A. Stacy, UC Berkeley, Dept of Chemistry, Berkeley, CA.

Because transport in nanowires is confined to one dimension, nanowire properties are particularly sensitive to even slight variations in structure and composition, as well as wire diameter. The properties of nanowire arrays, composite materials that are of interest in thermoelectrics, photonics, and information storage, for example, are strongly dependent on the structure and composition of not only the nanowires but also the wire-matrix interfaces. In this work, we have employed transmission electron microscopy (TEM) and analytical electron microscopy to assess the structure, composition, and electronic properties of arrays of bismuth and bismuth telluride nanowires at high spatial resolution. The arrays were fabricated by pressure injection (Bi) or electrodeposition (Bi_2Te_3) into porous anodic alumina templates. Using imaging and diffraction in the TEM, we have found that the wires are polycrystalline with varying grain sizes depending on the processing conditions. Energy dispersive x-ray spectroscopy has been employed to assess the local composition of the wires. The bismuth telluride wires are constant in composition except in a localized region at the wire base, which is Te-rich due to the deposition mechanism. Finally, the local electronic properties of the bismuth nanowire arrays have been assessed using electron energy loss spectroscopy in conjunction with energy-filtered imaging. We have found that the bismuth volume plasmon peak varies in energy and width as a function of wire diameter, due to quantum confinement and surface effects, and a localized plasmon is present at the bismuth-alumina interface.

C4.37

CRYSTALLOGRAPHIC DESCRIPTIONS FOR NANOPARTICLE ASSEMBLIES - APPLICATION TO SELF-ASSEMBLED SIZE-SELECTED CADMIUM SELENIDE CLUSTERS. Alexandre V. Vassiliev, Mark Aindow, Dept of Metallurgy and Materials Engineering, Univ of Connecticut, Storrs, CT; Jeunghoon Lee, Fotios Papadimitrakopoulos, Dept of Chemistry, University of Connecticut, Storrs, CT; Faquir Jain, Dept of Electrical and Computer Engineering, University of Connecticut, Storrs, CT.

Self-assembled mono-modal size-selected nanoparticles frequently adopt close-packed three-dimensional arrangements. The resemblance of these arrangements to the face-centered cubic or hexagonal close-packed crystal structures exhibited by many elements has led to the widespread adoption of these crystallographic terms to describe the assemblies. More recently, however, it has been shown that well-ordered non-close-packed assemblies of both mono-modal and bimodal size-selected clusters can be produced. Such arrangements can also be described crystallographically as the analogues of structures exhibited by binary alloys and compounds. In this paper, a brief review will be presented of the different structure types which can be exhibited. These types will be illustrated using transmission electron microscopy data obtained from assemblies of CdSe nanoparticles produced by solution pyrolysis of organometallic precursors in trioctylphosphine oxide. The effects of surface states and the ratio of particle diameter (for bimodal size distributions) on the structure adopted will be discussed. It is shown that such descriptions provide not only a convenient notation for the arrangement exhibited in a particular assembly, but also a framework for describing imperfections in the assembly (which could influence collective properties) as crystal defects.

C4.38

GROWTH OF HIGHLY TEXTURED DIAMOND FILMS ON Si (100) SUBSTRATES BY NANO-PARTICLE SEEDING TECHNIQUE. Ashok Kumar, Department Electrical and Computer Engineering, University of South Alabama, Mobile, AL.

Nanostructures powders, with particle size in the 1-10 nm range, have shown great promise in the forming of advanced structural and functional materials for applications as tribological coatings, high surface area catalyst support for cutting tools, thermal barrier coatings, capacitor and battery materials, dielectric and optoelectronic materials. CO₂ laser synthesis of ceramic powders from gas-phase precursors is an ideal method for growing nanosized, pure and nearly mono-dispersed particles. The silicon nano-particles have been grown by CO₂ laser induced pyrolysis of silane in gas flow reactor. The Si nano-particles have been characterized using SEM, TEM, XRD and XPS techniques. We report a novel approach of seeding Si nano-particles on Si(100) substrates, which has resulted high quality smooth diamond films deposited by HFCVD method. The seeding technique has increased the adhesion of diamond films and helps to grow high quality textured diamond films. The detailed investigations to grow high quality diamond films will be discussed in this paper. This research was supported by Alabama NASA-EPSCoR program.

C4.39

SHEAR ORIENTATION OF VISCOELASTIC POLYMER-CLAY SOLUTIONS. Gudrun Schmidt, Alan I. Nakatani, Paul D. Butler, Alamgir Karim, Charles C. Han, NIST.

The influence of shear on viscoelastic clay-polymer solutions was investigated by means of rheology, flow birefringence and small-angle neutron scattering (SANS). Oscillatory shear showed a broad linear viscoelastic region and flow occurred when a critical strain was reached. With increasing steady shear rate a pronounced minimum in birefringence was observed at a critical shear rate corresponding to the orientation of the polymer-clay system. The polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. The same degree of orientation could be achieved by either constant shear rate or constant stress experiments. SANS measured the shear-induced orientation of polymer and platelets as a function of shear rate. At rest and at low shear rates a diffuse isotropic ring of scattering intensity was observed. With increasing shear rate an anisotropic scattering pattern developed. At higher shear rates, the scattering anisotropy increases due to the increased orientation of the clay platelets in the shear field. Cessation of shear leads to fast recovery demonstrating the system to be highly elastic.

C4.40

OPTICAL RESPONSE OF GOLD NANOCRYSTALS IN DIELECTRIC MATERIALS. Akira Ueda, Elana M. Bryant, Carlton B. Maxwell, Charlene M. Blake, Richard R. Mu, Marvin H. Wu, Andrey I. Zavalin, and Don O. Henderson, Chemical Physics Laboratory, Department of Physics, Fisk University, Nashville, TN.

Surface plasmon resonance (SPR) of mesoscopic metal particles has been paid attention for many years. Beside the potential applications, there still have been fundamental interests and questions of such small metallic particles. We have fabricated nano-sized metallic particles in/on some transparent substrates by using several methods such as ion implantation, pulsed laser deposition, and electron beam evaporation. Previously we have reported that the annealing atmosphere affects the position of SPR in the system of MgO implanted with Au [1]. In addition to this study, recently, by using the pulsed laser deposition method, gold nanocrystals were formed on several substrates, and the gold deposited samples were coated with some insulating materials by the e-beam evaporation method to investigate the surrounding material dependence of SPR band of gold particles. [1] A. Ueda et. al, Nucl. Instr. and Methods in Phys. Res. B. 141 (1998) 261-267.

C4.41

AMINE BASED LAYER BY LAYER GROWTH OF SEMICONDUCTOR NANOCRYSTAL FILMS FOR EL APPLICATIONS. Jeunghoon Lee and Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory (NOEL), Polymer Program, Department of Chemistry, University of Connecticut, Storrs, CT; Faquir Jain, Nanomaterials Optoelectronics Laboratory (NOEL), Department of Electrical and Systems Engineering, University of Connecticut, Storrs, CT.

Building a precisely controlled assembly is essential for application of semiconductor nanocrystals in optoelectronic devices such as light emitting diodes (LEDs). CdSe nanocrystals were synthesized by pyrolysis of organometallic precursors. Dimethyl cadmium and selenium were used for the synthesis of CdSe core in coordinating solvent trioctylphosphine (TOPO). Diethyl zinc and hexamethyl-

disilthiane were used to grow ZnS cladding layer on the surface of CdSe core. Nanocrystals were self-assembled with α,ω -diamines on substrates pretreated with diethyl zinc. A dipping cycle consisted of alternating immersion of the substrate in each solution for 2 mins with a 2-3 mins rinse step in between. The thickness of the film showed a monotonous growth which was proportional to the number of dip cycles. The growth in these layer-by-layer assemblies were characterized via spectroscopic ellipsometry and UV-Vis/photoluminescence (PL) spectroscopy. Single and multi layer electro-luminescence (EL) devices of these assemblies were also fabricated and will be discussed in this paper.

C4.42

GENERALIZED ELLIPSOMETRY USING A ROTATING SAMPLE. W. Xu, L.T. Wood, and T.D. Golding, University of Houston, Department of Physics, Houston, TX.

We propose a generalized ellipsometric technique using a rotating sample. The ellipsometer consists of a polarizer, a rotatable sample holder, an analyzer, and a detector. Fourier coefficients are measured and used to extract the system's dielectric tensors and film thicknesses. The main advantage of the technique is that all parts of the ellipsometer are fixed except the sample, whose azimuth angle can be modulated. We show calculated responses to isotropic and anisotropic materials as well as to anisotropic superlattices. Potential applications for characterization of anisotropic nanostructures are discussed.

C4.43

Abstract Withdrawn.

C4.44

SYNTHESES AND PROPERTIES OF Ge AND ZnO NANOWIRES. Yiyang Wu, Michael Huang, Peidong Yang, Department of Chemistry, University of California, Berkeley, CA.

Chemical vapor transport and deposition in both open-tube and sealed-tube system was used to synthesize single crystalline semiconductor (Ge, Si) and ZnO nanowires. These nanowires were grown through the vapor-liquid-solid process. Their diameters are in the range of 5 - 100 nm depending on different sizes of metal cluster catalysts (Au) we use and can be hundreds micrometer long. In addition, the photoluminescence (PL) of these wires were studied using HeCd laser and 3rd harmonic of Nd:YAG laser as the excitation sources. For Ge nanowires, blue and IR emission were observed while UV and green emission were recorded for ZnO nanowires. The size-dependent and excitation power-dependent of the PL for the nanowires were investigated. Possible amplified spontaneous emission from ZnO nanowires will be presented.

C4.45

MELTING, RECRYSTALLIZATION AND SOLID STATE REACTION OF SEMICONDUCTING NANOWIRES. Yiyang Wu, Peidong Yang, Department of Chemistry University of California, Berkeley, CA.

The melting and recrystallization behavior of the Ge and Si nanowires was examined using an in-situ transmission electron microscope. During the thermal treatment, nanostructures such as Ge/C core-sheath and junction can be readily synthesized. We observed significant decrease of melting point for the Ge nanowires with diameter of 5 - 100 nm. For example, a Ge nanowire with diameter of 20 nm starts melting at around 630°C. Melting of these nanowires generally initiates at the two ends of the wire and the molten liquid front moves towards the middle of the wires. In addition, we also observed significant supercooling during the solidification process, the recrystallization of these liquid Ge nanowires occurs at much lower temperature than the initial melting temperature (for example, 450°C for a 20-nm wire). The thermal behavior of the nanowire can be explained using a confined one-dimensional liquid model. Based on this study, solid state reaction between the nanowires is investigated as a possible route for direct synthesizing semiconductor nanoscale junctions.

C4.46

A 'BUILDING BLOCK' APPROACH TO MIXED-COLLOID ENSEMBLES THROUGH ELECTROSTATIC SELF-ORGANIZATION. Trent H. Galow, Andy K. Boal, Vincent M. Rotello, Department of Chemistry, University of Massachusetts, Amherst, MA.

Molecular self-assembly is the association of molecules into structurally well-defined, stable aggregates via thermodynamically-controlled non-covalent interactions. Application of self-organization to multi-scale ordering of colloidal nanoparticles provides a platform for the creation of macroscopic devices. The ability to finely control the spatial arrangement of nanoscopic entities in self-assembled

composites allows the creation of structured materials, with interesting electronic, optical, optoelectronic, and magnetic properties. In recent research, we have developed a "building block" approach to electrostatically-mediated construction of modular self-assembled colloid-colloid ensembles. Our strategy involves functionalization of one type of colloidal building block with a primary amine, and a counterpart building block with a carboxylic acid derivative. By combining the two systems, acid-base chemistry followed by immediate charge-pairing resulted in the spontaneous formation of electrostatically-bound mixed-colloid constructs. The shape and size of these ensembles was controlled via variation of particle size for the two components and their stoichiometries.

C4.47

CONVENIENT MOLECULAR APPROACH OF SIZE AND SHAPE CONTROLLED ZnSe AND ZnTe NANOCRYSTALS. Y. Jun, J. Park, J. Cheon, Department of Chemistry and School of Molecular Science-BK21, Korea Advanced Institute of Science and Technology (KAIST), Taejon, KOREA.

Our study describes a convenient one-step synthesis of ZnSe and ZnTe nanocrystals (NC) whose sizes and shapes are precisely tuned by the growth temperature or growth time. We utilized molecular precursors; bis(phenylselenolato or tellurolato)zinc-N,N,N',N'-tetramethylethylenediamine (TMEDA), which effectively produce 0-dimensional spheres or 1-dimensional nanorods of ZnSe and ZnTe. Nanocrystals are highly monodispersed and luminescent; the emission wavelength varies over a wide range depending on the particle size. This study constitutes a nice demonstration of direct size and shape controlled synthesis of semiconductor NCs and this method can be extended to the synthesis of nanocrystals of other materials.

SESSION C5: NANOWIRES AND NANOTUBES

Chair: Peter C. Searson

Tuesday Morning, November 28, 2000

Liberty (Sheraton)

8:30 AM *C5.1

SEMICONDUCTOR NANOWIRES: SYNTHESIS, ELECTRICAL TRANSPORT AND ASSEMBLY OF FUNCTIONAL NANODEVICES. Charles M. Lieber, Harvard University, Department of Chemistry and Chemical Biology, Division of Engineering and Applied Sciences, Cambridge, MA.

One dimensional structures, such as semiconductor nanowires, represent the smallest dimension for efficient transport of electrons, holes and excitons, and thus represent potentially critical building blocks for the two and three-dimensional assembly of nanoelectronic and nano-optoelectronic devices. To achieve the potential of such structures will, however, require readily available materials in which the size, composition, electronic and optical properties are controlled. To this end, we describe a general synthetic approach— laser-assisted catalytic growth— to a wide range of semiconductor nanowires with controlled diameter, chemical composition and doping. Single crystal n-type and p-type Si, GaAs and InP nanowires have been prepared by our approach and characterized using two terminal gate-dependent transport measurements. These measurements demonstrate the ability to control carrier type and to vary the carrier concentration over a wide range. A rational approach for orthogonal assembly of nanowires into integrated multi-terminal devices, such as bipolar transistors and light emitting diodes, will be presented. The implication of nanowire assembly for high density integrated nanoscale electronics and optoelectronics will be discussed

9:00 AM C5.2

APPLICATION OF POLYIMIDE CONTAINING AN AZOBENZENE PENDANT GROUP FOR THE ALIGNMENT OF SINGLE WALL CARBON NANOTUBES. Sung-Goo Lee, Hyung-Suk Woo, Richard Czerw, Scott M. Webster, David L. Carroll, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC.

We have synthesized polyimide with a p-nitroazobenzene (PI-Azo) as a pendant group. The chemical structure of PI-Azo obtained was characterized by ¹H-NMR, IR, UV and elemental analysis. PI-Azo absorbed polarized UV at 480nm and self-aligned by photo-isomerization. The PI-Azo was used for the alignment of single wall carbon nanotubes (SWNTs) after preparing a polymer composite. The PI-Azo/SWNT composite was formed by a solution blending method with blending ratios of 1/10, 1/2 and 1/1 by weight, respectively. The alignment of SWNTs in PI-Azo was observed by polarized UV-VIS absorbance and scanning tunneling microscopy (STM). As the function of PI-Azo concentration, the alignment of SWNTs in terms of optical anisotropy of absorbance and microscopic morphology will be discussed.

9:15 AM C5.3

NANOCOMPOSITE ELECTRODES FOR HIGH-POWER, RECHARGEABLE LITHIUM BATTERIES. Simon C. Mui, Patrick E. Trapa, Biying Huang, You-Yeon Won, Anne M. Mayes, Donald R. Sadoway, Dept of Materials Science and Engineering, MIT, Cambridge, MA; Azzam Mansour, Naval Surface Warfare Center, Carderock, MD.

To confer upon rechargeable lithium batteries the capability of delivering very high currents, nanocomposite electrodes have been designed, synthesized, and tested. Anodes comprising carbon nanotubes connected to a dispersion of metal nanoparticles, all self-assembled within a block copolymer acting as template, have been characterized in coin-cell battery test configurations. The same is true for cathodes comprising carbon nanotubes coated with vanadium oxide self-organized with a block copolymer. In charge/discharge tests over hundreds of cycles at rates as high as 4 C these electrodes exhibited high resistance to capacity fade.

9:30 AM C5.4

Abstract Withdrawn.

10:15 AM *C5.5

ELECTROCHEMICAL PATHWAYS TO NANOWIRES AND NANOTUBULES. Martin Moskovits, Konstantin Shelimov, Anita Osika, Diyaa Almalawi, Dmitri Davydov, Jody Yang, University of Toronto, Chemistry Department, Toronto, CANADA.

Highly regular periodic arrays of pores can be fabricated electrochemically in anodic oxide films. The dimensions of the pores can be controlled almost continuously with pore diameters ranging from 10-400 nm, pore lengths from 0.5 to over 100 μm and pore densities from $10^9 - 10^{12} \text{ cm}^{-2}$. These porous films can then be used either as templates in which to cast metal or semiconductor nanowires or nanotubules by judicious use of electrodeposition or chemical vapor deposition or as contact masks for nanoscale lithography or etching. In this manner we have successfully generated carbon and boron nitride nanotubules, layered nanotubules that act as arrays of nanocapacitors, nano-scale tunnel junction devices that display room-temperature Coulomb blockade effects and field-emission cathodes. Electrical measurements on single nanowires as well as on nanowire arrays have been carried out using STM as a single wire probe.

10:45 AM C5.6

ANISOTROPIC NANOMECHANICS OF BORON NITRIDE NANOTUBES. Madhu Menon, University of Kentucky, Department of Physics, Lexington, KY; Deepak Srivastava, NASA Ames Research Center, Moffett Field, CA.

Investigation of mechanical properties of boron nitride nanotubes using a generalized tight-binding molecular dynamics, and ab-initio total energy methods reveal many interesting anisotropic characteristics that can be directly attributed to bond buckling effects. In particular, zigzag BN nanotubes are observed to undergo a novel anisotropic strain release plastic buckling in which tubes plastically buckle only on one end when axially compressed from both ends. Based on this a model of nanostructured skin effect in zig-zag BN nanotube reinforced composites is proposed which will have distinct anisotropic characteristics against external compression and tensile deformations.

11:00 AM C5.7

4-POINT RESISTANCE MEASUREMENTS OF INDIVIDUAL Bi NANOWIRES. S.B. Cronin^a, Yu-Ming Lin^b, J. Heremans^c M.S. Dresselhaus^{a,b}, ^aDepartment of Physics and ^bDepartment of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA; ^cDelphi Automotive Systems, Warren, MI.

4-point resistance measurements are made on individual Bi nanowires with diameters ≤ 200 nm. The nanowires are fabricated using a self-assembly non-lithographic technique by filling anodized alumina templates with molten Bi. (Wires of PbTe and Bi₂Te₃ prepared in the alumina templates will also be discussed.) The 4-point contacts are affixed to the nanowires using an electron beam lithography technique. Measurements are made as a function of temperature and magnetic field for a variety of wire diameters in the range from 40nm to 200nm. The theoretically predicted semimetal-to-semiconductor transition due to the shifting of band edges arising from the quantum confinement of electrons is reported. The resistance versus temperature $R(T)$ results are explained by considering the predicted band shifts due to quantum confinement effects and various scattering mechanisms. The role of wire boundary scattering, which is found to be particularly important in the Bi nanowires relative to bulk Bi, is discussed. We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grant DMR-98-04734, and the US Navy contract N00167-98-K0024.

11:15 AM C5.8

HYDROPHOBIC INORGANIC MOLECULAR CHAINS [Mo3Se3-n] AND THEIR MESOSCOPIC ASSEMBLIES. Benjamin Messer, Jae Hee Song, Franklin Kim, Peidong Yang, Department of Chemistry, University of California, Berkeley, CA.

Negatively charged individual infinite [Mo3Se3-n] chains are obtained by dissolving quasi-one-dimensional LiMo3Se3 crystals in the polar solvent. These infinite chains undergo mesoscopic organization when exposed to opposite-charged surfactants. Low angle X-ray diffraction and transmission electron microscopy studies indicate that the inter-chain spacing can be varied from 20 to 40 depending on the alkane length of the surfactants while the crystallinity along the chains is maintained. We observed several mesostructures based on these molecular chains, including hexagonal, lamellar. Preliminary measurement indicates these infinite [Mo3Se3-n] chains can be used as one-dimensional molecular conductors. In addition, these molecular wires can be readily patterned on the substrate into multiterminal devices and complex circuits. The process reported here could be a viable chemical approach for their potential integration into functional molecular devices.

11:30 AM C5.9

SILICON/SILICA BASED NANOWIRES, NANOSTRUCTURES, NANOAGGLOMERATES, NANOTUBES AND NANOFIBER ARRAYS FOR OPTOELECTRONICS AND CATALYSIS. J.L. Gole¹, J. Stout¹, Z.R. Dai², Z.G. Bai², R.P. Gao², Z.L. Wang², and Mark White³; ¹Schools of Physics, ²Material Science, and ³Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

Semiconductor nanostructures, nanoagglomerates, and nanowires have attracted considerable attention because of their potential applications in mesoscopic research, the development of nanodevices, and the potential use of large surface area structures for catalysis. In order to contribute to evaluation, correlation, and applications in this unique structural regime, we have been concerned with the formation, derivatization and characterization of silicon based nanowires, silica based nanostructures and their agglomerates, and silica nanotubes and nanofiber arrays focusing on their synthesis and optical and mechanical properties.

A series of experiments¹⁻⁴ has been undertaken to generate and characterize silicon nanowires,¹ silicon based - silicon/oxygen nanostructures¹, silica nanotubes and silica nanofiber arrays,² and bi- and coaxial SiC/SiO₂ nanowires.³ SiO₂ passivated (sheathed) crystalline silicon nanowires have been generated from a heated Si-SiO₂ mix in a manner similar to that reported by Lee et al.⁵ Lee et al. produce a jumble of uniform SiO₂ coated crystalline silicon nanowires of various sizes which, when straight, have their axes parallel to the 112 directions and display twinning, high order grain boundaries, and defect sites (stacking faults). In contrast, the modified approach produces SiO₂ cladded crystalline silicon core wires whose axes are parallel to the 111 direction which are, amazingly, virtually defect free and demonstrate no twinning. They appear ideally suited for photonic waveguide applications. Newly developed techniques, which have successfully been applied to the electrodeless metallization of porous silicon, are being used to fabricate gate all around (GAAT) nanotransistors constructed from silicon nanowires. Here the SiO₂ sheathed crystalline silicon wire will be further sheathed by a copper or silver layer whose deposition is controlled through excitation of a surface-based photoluminescent excimer. Additional unique results obtained, with varying experimental conditions, demonstrate the possibility (with metallization) of forming novel extremely high surface area catalysts. Silicon nanocrystal embedded SiO₂ nanowires and nearly monodisperse SiO₂ nanospheres of diameter ~ 30 nm have been generated as macroscopic gram quantity powders. These powders have been used as a means of developing large surface area selective Cu/SiO₂ catalysts.⁴ These nanospheres, first agglomerated to wire-like configurations,¹ have now been used to grow the first silica nanotubes and to produce unique silica nanofiber arrays.² The silica nanotubes may fill an existing need for the catalytic conversion of high molecular weight substrates (MW ~ 1000).

References:

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4. "Nanocatalysis: Selective Conversion of Ethanol to Acetaldehyde Using Mono-Atomically Dispersed Copper on Silica Nanospheres", J.L. Gole and M.G. White, Chemistry of Materials, submitted.
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SESSION C6: NANOPARTICLES IN BIOLOGY

Chair: Stephan J. Stranick

Tuesday Afternoon, November 28, 2000

Liberty (Sheraton)

1:30 PM *C6.1

NANOPARTICLE-BASED DETECTION METHODS FOR DNA.

Chad A. Mirkin, T. Andrew Taton, Northwestern University, Chemistry Department, Evanston, IL; Robert Letsinger, Nanosphere, Inc, Willmette, IL.

Nanoparticle-based methods for detecting DNA will be described. These methods, which are based upon metallic and semiconductor quantum dot materials, offer significant advantages over conventional methods with regard to speed, selectivity, sensitivity, and ease of use. The origins of these advantages and their technological implications will be discussed.

2:00 PM C6.2

DNA-DIRECTED ASSEMBLY OF ANISOTROPIC NOBLE METAL NANOPARTICLES ON LITHOGRAPHICALLY DEFINED Au PADS. Brian Reiss, Jeremiah K. N. Mbindyo, Sheila R. Nicewarner, Thomas E. Mallouk, Michael J. Natan, Christine D. Keating, Department of Chemistry, The Pennsylvania State University, University Park, PA.

Recently there has been a great deal of interest in DNA as "smart glue" for assembling nanostructures of inorganic building blocks. To date, most of this work has focused on isotropic nanostructures, but anisotropic nanostructures possess the ability to assemble more complex nanostructures. In this work, anisotropic, noble metal nanoparticles have been synthesized using a template synthesis strategy. The particles have been released from the template to form colloidal sols of anisotropic nanoparticles. These nanoparticles have been modified with DNA oligomers of varying length using several different attachment chemistries. The thermodynamics and kinetics of modifying these particles with DNA has been explored, and the DNA has been used to assemble the particles on planar Au surfaces as well as lithographically defined Au pads on Si wafers.

2:15 PM C6.3

NANOSPHERE LITHOGRAPHY: SYNTHESIS OF NANOPARTICLES WITH INHERENTLY ANISOTROPIC STRUCTURES AND SURFACE CHEMISTRY. Christy L. Haynes, Amanda J. Haes, Michelle Duval Malinsky, Richard P. Van Duyne, Northwestern University, Dept of Chemistry, Evanston, IL.

Early work with size-tunable periodic particle arrays (PPAs) fabricated by nanosphere lithography (NSL) demonstrated that the localized surface plasmon resonance (LSPR) could be tuned throughout the visible region of the spectrum. The LSPR is sensitive to changes in nanoparticle aspect ratio and local dielectric environment. Single layer PPAs consist of size-tunable anisotropic nanoparticles that can be modified to exhibit anisotropic surface chemistry. This work demonstrates multiple schemes for PPA modification using self-assembled monolayers and colloid decoration. Nanoparticle anisotropy can be further exploited with the recent combination of NSL and reactive ion etching (RIE); this extends the two-dimensional PPA structure into the third dimension. The LSPR of nanoparticles in nanowells can be measured and tuned in the same fashion as the two-dimensional arrays. This, as well as the added control of the nanoparticle dielectric environment, generates a new class of PPA-based nanostructures. Potentially useful new nanostructures include encapsulated PPAs, high aspect ratio nanorods, and electromagnetically-coupled stacked nanoparticles.

2:30 PM C6.4

OPTICAL CHARACTERISTICS OF CdSe QUANTUM DOTS IN BIOLOGICAL APPLICATIONS. William Molenkamp, Stephen Empedocles, Jian Jin, Joseph Treadway, Marcel Bruchez, Thearith Ung, Edward Adams, Quantum Dot Corporation, Palo Alto, CA.

Semiconductor nanocrystals have generated considerable interest as biological labels. Their unique combination of properties, such as high luminescence, photostability, broad excitation spectra, narrow emission spectra and long fluorescence lifetimes, provide for an extremely versatile fluorophore with the potential to outperform existing biological markers. Characterization of quantum dots within biological assays is essential so that the preparation and detection of these materials is optimized for performance as biological markers. Thus, how quantum dot properties evolve due to environmental changes inherent in biological applications, such as surface modification, solvation by water, bioconjugation and binding to an assay surface, must be understood and controlled. This presentation will describe several unique characteristics of CdSe/ZnS core/shell quantum dots, methods of measurement and how they can be exploited in biological detection systems.

3:15 PM *C6.5

THEORETICAL MODELING OF THE OPTICAL PROPERTIES OF ANISOTROPIC METAL NANOPARTICLES AND AGGREGATES. George C. Schatz, Anne A. Lazarides and K. Lance Kelly, Department of Chemistry, Northwestern University, Evanston, IL.

This paper will describe our recent theoretical work on modeling the optical properties of silver and gold nanoparticles and their aggregates. The nanoparticles are fabricated using lithography methods, and they typically have truncated tetrahedral shapes, and are located in a complex dielectric environment with multiple adsorbed layers and an underlying substrate. Our primary tool for this work has been a finite element approach known as the discrete dipole approximation, and in this talk we show how this approach can be used to describe plasmon resonance shifts associated with small changes in adsorbate dielectric constants. We are also interested in aggregates of colloidal nanoparticles, particularly in DNA-linked gold aggregates. Here we have developed several theoretical tools, ranging from coupled multipoles for small aggregates to a new dynamical effective medium approximation for large aggregates. These theories indicate that plasmon resonance shifts observed in DNA-linked aggregates arise from many thousands of weakly coupled particles. Applications to chemical and biological sensors is described.

3:45 PM C6.6

UNIAXIAL ORGANIZATION OF METALLIC NANOPARTICLES AND ARRAYS OF NANOWIRES BY BIO-TEMPLATING. Erik Dujardin, Wayne Shenton, Steve Mann, School of Chemistry, University of Bristol, Bristol, UNITED KINGDOM.

The now better known optical, electrical, magnetic and chemical properties of metallic and semiconductor nanoparticles have raised numerous hopes as to their incorporation into macroscopic quantum devices. However, in such devices, the spatial distribution of the particles is essential. For spherical nanoparticles, self-assembly leads to isotropic close packed macroscopic architectures. Various approaches have already been developed to better control the organization of the quantum dots. Templating by DNA or biological amphiphiles, incorporation in block copolymer or metal oxide matrices, derivatization of particles surface with recognition moieties are some of those strategies. We will show how the tobacco mosaic virus (TMV) has been used as a template to get arrays of 2-3 nm metallic nanoparticle chains and arrays of continuous nanowires. In our case, anisotropy is induced in the macroscopic system by the template: TMV is a 300 nm long hollow tubule with a 18 nm outer diameter and a 4 nm inner cavity. It spontaneously forms a nematic mesophase at high concentration and can sustain extreme environment conditions. By making the proper choice of the nanoparticles surface groups as well as the controlling the virus aggregation stage and surface charge, it is possible to obtain a 2D or 3D uniaxial arrangement of the particles. We will also discuss how the powerful tools of genetic engineering can be used to modify the biological substrate to improve the templating effect. Perspectives of our work toward the synthesis of macroscopic samples, the properties of which are controlled by their mesoscopic sub-units, will conclude the presentation.

4:00 PM C6.7

SELF-ASSEMBLY OF COLLOIDAL SPHERES INTO WELL-DEFINED STRUCTURES. Yadong Yin, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated a convenient method for self-organizing monodispersed colloidal spheres (> 50 nm in diameter) into discrete units with well-defined structures – for example, linear chains and polygons. In this talk, we will discuss the self-assembly mechanism for the formation of these anisotropic structures. The unique optical properties of these mesostructures will also be presented.

4:15 PM C6.8

MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF CORE-SHELL Ni-Ce NANOCOMPOSITE PARTICLES ASSEMBLIES. Xiangcheng Sun and M. Jose Yacaman, ININ, México, MÉXICO.

A new type of magnetic core-shell Ni-Ce nanocomposite particles, with an average grain size about 15-50nm, have been presented. SEM observations and EDX analysis indicate, this particle showing a strongly ferromagnetic interacting order with chain-like features of view. HREM, NANO-EDS studies demonstrate that many planar defects (i.e. nanotwins and stacking faults) exist in large Ni core zone (10-45nm); the shell layers (3-5nm) consisted of innermost NiCe alloy as well as outermost NiO oxide. SAED patterns show an indication of well-defined rings and spots characteristic of nanocomposite materials,

which the certain crystal relation between orthorhombic [110] of NiCe and cubic [311] of Ni₂Ce, face-center crystal [222] of NiO, cubic [111] of nickel have been identified and confirm the nature of this core-shell nanocomposite particles. It is evidence that this is an interesting magnetic nanoparticle stemmed from the nature of core-shell of microstructure.

Magnetization measurements of these particles assemblies have been performed using a SQUID magnetometer at different applied fields and low temperature. It is suggested, this nanocomposite particles assemblies display superparamagnetic behavior above average blocking temperature (T_B) 150K, this superparamagnetic relaxation behavior is found to be modified by interparticle interactions, which depending on the applied field; size distribution; the surface magnetocrystalline anisotropy originated from exchange interaction with random anisotropy among particles assemblies. On the other hand, antiferromagnetic order occurs with a Neél temperature (T_N) of about 11K. A spin-flip transition is also observed below T_N at a certain applied field. In particular, the exchange coupling interaction between pure Ni core with NiO oxide shell layers have been responsible for their higher coercivity (H_C). Furthermore, the EPR spectra at low and room temperature reflect these magnetic order nature associated with this type of core-shell nanocomposite crystallographic character anisotropy and size distribution, coupling with the strong interparticle interaction.

4:30 PM C6.9

SYNTHESIS OF BRUSH-LIKE CONDUCTING POLYMER NANOPARTICLES AND THEIR EFFECT ON MEDIATING Li ION TRANSPORT FROM LIQUID ELECTROLYTES TO CATHODE.

Yong Pang, Ningpine Chen, Liang Hong, National Univ of Singapore, Dept of Chemical & Environmental Engineering, SINGAPORE.

A new approach to the synthesis of nano-scale particles of polypyrrole (PPy) and polyaniline (PAN) is presented. By this method, several kinds of organic molecules with polyoxyethylene (POE) chains as their polar moiety were chemically grafted to pyrrole and aniline molecules through tolylene diisocyanate (TDI). The modified pyrrole or aniline molecules, together with unmodified counter parts, were subsequently subjected to chemical polymerization in a THF / water mixture, which resulted in very stable colloidal dispersions. The particles obtained should possess brush-like architectures in the dispersing medium, and their TEM sizes fall within the range of 10 to 40 nm, which was affected by the length and the bulkiness of POE segments. A more interesting TEM examination is that a nanosized core-shell morphology was obtained when a TDI-POE urethane oligomer was employed as the seed for the polymerization of PPy. As far as the functionality of the synthesized nanoparticles is concerned, this study examined their intrinsic conductivity after separation from the dispersion medium and their effect on lithium ion conduction in an organic liquid medium. After separation the particles existed as thin membranes that showed electrical conductivity of up to 10⁻³ Scm⁻¹. When a very small portion of the nanoparticles (>0.1 wt%) was re-dispersed into a liquid electrolyte comprising a soluble lithium salt (LiX) and an aprotic solvent, e.g. DMSO, a limited change in the electrical conductivity was observed. However, the re-dispersion gave rise to a significant reduction in the electrical resistance at the electrode/electrolyte interface according to the gain-phase impedance measurement. To study this effect, the influences arising from HLB (hydrophile-lipophile balance) values of the brush chains, different types of the mono-valence anions of LiX, variation of the aprotic solvents, and the different identity of the conducting polymers were evaluated.

SESSION C7: SEMICONDUCTOR NANOPARTICLES

Chair: L. Andrew Lyon
Wednesday Morning, November 29, 2000
Liberty (Sheraton)

9:00 AM *C7.1

NANOCRYSTAL QUANTUM DOTS: RECENT PROGRESS IN SYNTHESIS AND SPECTROSCOPY. Moungi G. Bawendi, Dept of Chemistry, MIT, Cambridge, MA.

Advances in the chemical preparation of nanocrystal dots that are of high crystal quality have spurred detailed studies of their electronic, magnetic and optical properties. This talk will focus on three topics. The first topic will be the review of recent results in the synthesis of anisotropic cobalt nanocrystals. The second focus will be the study of the fluorescence properties of single nanocrystal quantum dots. Peeling away at the averaging effects inherent to spectroscopic studies of ensembles of dot, single dot experiments have uncovered an unexpectedly complex behavior, much of which remains to be fully explained on a fundamental level. The third topic addresses the question of the possibility of laser action in chemically prepared nanocrystal quantum dots. Although an initial motivation for many

optical studies, until recently and despite numerous efforts, stimulated emission from highly quantum confined chemically prepared dots had not been forthcoming.

9:30 AM C7.2

ANISOTROPIC DEFORMATION OF COLLOIDAL PARTICLES UNDER HIGH ENERGY HEAVY ION IRRADIATION.

T. van Dillen¹, A. van Blaaderen^{1,2}, W. Fukarek³, A. Polman¹.
¹FOM-Institute AMOLF, Amsterdam, THE NETHERLANDS;
²Debye Institute, Utrecht University, THE NETHERLANDS;
³Research Center Rossendorf, Dresden, GERMANY.

MeV heavy ion irradiation changes spherical colloidal silica particles into non-spherical oblates. This deformation is due to a contraction of the particle in the direction of the ion beam and a biaxial expansion perpendicular to the ion beam. We studied this anisotropic deformation effect of spherical silica colloids of both 300 nm and 1 μ m diameter as a function of ion energy, fluence and flux, using Xe, Au and I irradiation. We used ion energies ranging from 0.5 to 16 MeV and fluences varying between 0.3 and 11×10^{14} ions/cm². Size aspect ratios as high as 5 are achieved. A linear increase of the transverse diameter is observed with increasing ion fluence. For a fixed fluence the deformation increases with ion energy and is linear with the average electronic stopping power. No volume change is observed after irradiation. The deformation effect decreases with increasing temperature. When the ion range is chosen less than the colloid diameter, non-ellipsoidal shapes can be formed as well. Prolate particles can be obtained by subsequent irradiations under orthogonal angles. The deformation of TiO₂, ZnS and ZnS-SiO₂ core-shell particles will also be shown. Quite interestingly, no deformation is observed for crystalline Al₂O₃ and Ag colloids, as will be discussed. Finally, we will show several applications of these ion irradiation deformed particles. First, we find indication for nematic liquid crystalline ordering of oblate particles in solution. Second, we observe large changes in the optical transmission spectra of a three-dimensional colloidal photonic crystal upon deformation.

9:45 AM C7.3

PREPARATION AND APPLICATIONS OF MULTI-SHELLED POLYMER BEADS. Richard A. Farrer, Gregory T. Copeland, Justine Wilbur, Lindsay Woodward, Scott J. Miller and John T. Fourkas, Boston College, Eugene F. Merkert Chemistry Ctr, Chestnut Hill, MA.

Functionalized polymeric beads are important media for resin-bound synthesis, colloid chemistry, photonic bandgap materials, and many other applications in chemistry, physics and biology. A multiphoton fluorescence microscope makes it possible to study the spatially-dependent properties of the interiors of such beads with high, three-dimensional resolution. We have taken advantage of this ability to observe the interiors of beads to develop chemical techniques taking beads that are initially spatially homogeneous and patterning them with multiple, chemically-distinct shells of controllable width. Depending on the diameter of the beads, it is possible to make ten or more shells. We will discuss techniques for the preparation of such layered beads and their application in combinatorial chemistry and materials science.

10:30 AM *C7.4

COLLOIDAL QUANTUM RODS. Paul Alivisatos, Univ of California, Dept of Chemistry, Berkeley, CA.

In recent years there have been significant advances in the preparation of semiconductor quantum dots by colloidal chemistry routes. CdSe and InAs are examples of materials which can be made as nearly spherical nanocrystals of high quality. We have recently learned how to control the shapes of these particles, to yield quantum rods. This provides a new opportunity to examine the influence of shape on optical, electrical, and structural properties. Colloidal quantum dots and rods may also find some practical applications, as biological fluorescent labels, or as the active elements in photovoltaics.

11:00 AM C7.5

PREPARATION AND CHARACTERIZATION OF ONE-DIMENSIONAL CdS, CdSe AND GaN NANOPARTICLES.

Chia-Chun Chen, C.-C. Yet, Z.-H. Lang, J.-J. Lin, C.-H. Chen, M.-Y. Yu, Lee, Y.-Z., Department of Chemistry, National Taiwan Normal University, Taipei, TAIWAN.

One-dimensional nanoparticles of CdS, CdSe and GaN semiconductors with different morphologies including rod-like (nanorods), wire-like (nanowires) and cube-like (nanocubes) shapes have been prepared using several different techniques. Their structural, stoichiometry, and optical properties were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDX), absorption, emission and Raman spectroscopy. The nanorods of CdS and CdSe were synthesized via arrested

precipitation from their respective inorganic ions in a micellar solution. The materials showed straight and rodlike shapes with a narrow distribution of aspect ratios. Large-scale GaN nanowires were obtained from a VLS growth of gallium and ammonia. The SEM images indicated that almost all the resulting materials exhibited wire-like structures with diameters in the range of 20 to 50 nm and lengths up to several micrometers. The nanocubes of CdS were prepared through the crystal growth on patterned self-assembled monolayers. The TEM image showed that each individual nanoparticles dispersed well on the carbon substrate and exhibit regularly cubic-like shape. Our synthetic methods have provided new routes for the synthesis of semiconductor nanoparticles with a specific morphology. Potential applications of the nanowires in field emitting devices and single-electron transistors will be discussed.

11:15 AM C7.6

SELF-ORGANIZING PbSe QUANTUM CUBE AND QUANTUM DOT SUPERLATTICES. W. Gaschler, University of New Orleans (AMRI) and IBM T.J. Watson Research Center, Yorktown Heights, NY; C.B. Murray, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We report a high temperature (130 to 200°C) solution phase synthesis of monodisperse lead chalcogenide (PbSe, PbTe) quantum dots and quantum cubes. Organically passivated quantum dots with sizes tunable from 3 to 8 nm and quantum cubes with sizes tunable from 7 to 12 nm are isolated with <5% standard deviation. These dots and cubes show effects of quantum confinement with strong size-dependent absorption in the near IR. The dots and cubes each self-organize forming two and three dimensional superlattices (colloidal crystals, opals). The symmetry of the superlattice is determined by the shape of the nanoscale building blocks. This provides opportunities to study the effects of shape on the electronic properties of quantum confined structures from "particle-in-a-box" to "particle-in-a-sphere."

11:30 AM C7.7

TEMPLATED FABRICATION OF HEXAGONAL ZnS SINGLE CRYSTAL NANOSHEETS: A NEW MOLECULAR PRECURSOR FOR ZnS NANOPARTICLES BY A SOFT SOLUTION-PROCESSING ROUTE. Shu-Hong Yu, Jose Maria Calderon Moreno, Takeshi Fujiwara, Takahiro Fujino, Ryo Teranishi, Masahiro Yoshimura Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Low-dimensional nanostructured semiconductors have been the focus of recent scientific research due to their important nonlinear optical properties, luminescent properties, and quantum size effects, which have a wide range of fundamental applications in nanodevices. Many attempts have been made to fabricate such low-dimensional nanostructure materials by use of a variety of nanofabrication techniques. Here, highly ordered lamellar ZnS single crystal nanostructures which we called "nanosheet", were fabricated for the first time by thermal decomposition of a new molecular precursor $ZnS(en)_x$ with a composition of $2ZnS \cdot (NH_2CH_2CH_2NH_2)$ obtained via a soft-solution processing route. This new method involved either a solvothermal reaction of Zn^{2+} with thiourea or a similar reaction between Zn (or Zn^{2+}) and sulfur in ethylenediamine medium at 120-180°C. The results of small angle X-ray and HRTEM images confirmed that this new molecular precursor displayed well-defined lamellar nanostructures. The thermal stability of this molecular precursor was determined by TG-DTA analysis. After decomposed at 250-500°C in vacuum and lost the volatile part, i.e., ethylenediamine molecular, pure hexagonal ZnS single crystal nanosheets with excellent lamellar nanostructure and highly (001) orientation were obtained. To our best knowledge, this is a first report about fabrication of unusual hexagonal ZnS single crystal nanosheets by a simple soft solution-processing route. In contrast, similar reactions in other solvents such as ethanol could only produce cubic ZnS nanoparticles. The optical properties of as-prepared nanoparticles were investigated by UV-vis spectra and PL measurements. Our results demonstrated that it is possible to fabricate low-dimensional anisotropic nanoparticles selectively by a soft solution-processing route, which may add another variable to tune the optical properties of semiconductor quantum dots. This work has been supported by the Japan Society for Promotion of Science (JSPS) as part of the "Research for the Future Program" No. 96R06901.

11:45 AM C7.8

DESIGN AND MODELING OF PURPOSE-BUILT ANISOTROPIC METAL OXIDE NANOMATERIALS. Lionel Vayssieres, Jinghua Guo, Joseph Nordgren, Uppsala University, Dept of Physics, SWEDEN.

A new concept has been developed in order to achieve a new generation of smart materials (i.e. purpose-built nanomaterials), modeled and designed to match the physical and structural requirements of its applications. This concept, well sustained by a

thermodynamic model based on the monitoring of the nucleation, growth and ageing process through the control of the interfacial tension of the system allows to control the particle size and the surface morphology as well as the ability to thermodynamically stabilize metastable phases in solution. The outcome of such concept is of great interest both for fundamental and applied research purposes since the influence of parameters such as for instance, particle size, orientation and surface morphology, film texture and porosity on the electronic structure and/or catalytic activity of metal oxide materials may be probed and demonstrated. Moreover, designing well controlled materials allows to tune and optimize the physical properties of existing devices as well as creating novel improved devices. This concept, well illustrated on the controlled growth of spinel iron oxide nanoparticles in aqueous solution, has been successfully applied to the development of novel well-designed anisotropic materials such as large arrays (several centimeter squares) of oriented (perpendicular and parallel) nanorods of iron(III) oxide (Hematite), ZnO oriented microfibers and microtubes as well as star-shaped ZnO materials deposited, without any templating method, onto various substrate, such as conducting glass, Si wafers or sapphire for photovoltaic, photoelectrochemical and catalytic devices. New directions and applications such as, for instance, electrochemical capacitors, electrochromic devices and nanostructured chemical and gas sensors are currently under investigation.

SESSION C8: DIELECTRIC NANOPARTICLES

Chair: Christine D. Keating
Wednesday Afternoon, November 29, 2000
Liberty (Sheraton)

1:30 PM *C8.1

MONODISPERSE OXIDE NANOPARTICLES WITH APPLICATIONS IN FERROELECTRICS. Stephen O'Brien, Louis Brus, Columbia University, New York, NY; Chris B. Murray, IBM Corp. T.J. Watson Research Center, Yorktown Heights, NY.

The synthesis and structural characterization of relatively monodisperse nanoparticles of barium titanate ($BaTiO_3$) is presented. The nanoparticles exist as an organic ligand-stabilized suspension in organic solvents for purposes of processing. The electric properties of thin films of barium titanate nanoparticles have been investigated. The ferroelectric and dielectric properties of metal oxides with the perovskite structure are highly dependent on particle shape and size, especially approaching the nanoscale region. The spontaneous and reversible electric dipole moment, characteristic of ferroelectric metal oxides in an applied electric field, originates from ion displacement in the crystal unit cell. The behavior of this dipole moment in the bulk material is a function of ferroelectric domain size and domain-domain interactions. An understanding of this phenomenon would be considerably enhanced by the ability to study the ferroelectric properties of a material progressing from nanoscale (a limited number of unit cells) to bulk. It is therefore of importance to develop a rational synthesis of monodisperse oxide nanoparticles which would allow control of particle size and shape, and permit facile manipulation into thin films or devices using chemical techniques.

2:00 PM C8.2

RESONANT LIGHT SCATTERING PROPERTIES OF METAL NANOSHELLS. Steven J. Oldenburg, Sarah L. Westcott, Joseph B. Jackson, Surbhi Lal, Robin N. Taylor, and Naomi J. Halas, Department of Electrical and Computer Engineering and the Rice Quantum Institute, Rice University, Houston, TX.

Metal nanoshells are nanoparticles consisting of a dielectric core of nominally 100 nm diameter surrounded by a nanoscale (10-20 nm), uniform metallic shell. The plasmon-derived electromagnetic resonances of metal nanoshells are controlled by the relative dimensions of their core radius and shell thickness, while absolute size of the total particle determines whether it functions as an absorber or scatterer on resonance. Fabrication of gold nanoshells is based on functionalization of silica nanoparticles prepared by the Stober method, followed by electroless plating of gold onto the nanoparticle surfaces. For silica core-gold shell nanoshells prepared by this method, the spectral range of the optical resonances of the finished nanostructure extend from nominally 650 nm in the visible to beyond 2 microns in the infrared. In addition, the core-shell geometry gives rise to spectrally distinct multipole resonances, each with unique and strongly angular-dependent light scattering properties. The polarization and angular dependence of the light scattering from specifically designed dipole and quadrupole resonant nanoparticles has been measured, and very good comparison with theory is obtained. Further modifications of the angular dependent light scattering properties of gold nanoshells due to the presence of a conductive or dielectric layered substrate may also be discussed.

2:15 PM C8.3

ORDERING AND SELF-ORGANIZATION OF Si NANOCRYSTALS IN NANOCRYSTALLINE Si SUPERLATTICES. G.F. Grom, P.M. Fauchet, and L. Tsybeskov, Dept of Electrical and Computer Engineering, Univ of Rochester, Rochester, NY; H.J. Labbe and D.J. Lockwood, Institute for Microstructural Sciences, National Research Council, Ottawa, CANADA; B.E. White Jr., Motorola, Digital DNA Laboratories, Austin, TX; J. Diener, D. Kovalev, F. Koch, Technische Universität of Munchen, Physik-Department, Garching, GERMANY.

Additional degrees of freedom from dimensional and compositional asymmetry in nanoscale anisotropic particles inspire novel device concepts and allow exceptional flexibility in tailoring their properties for the development of commercially feasible devices. In this presentation, we report solid phase crystallization induced formation of planes of ordered Si nanocrystals within Si/SiO₂ superlattices (SLs). We show that under certain fabrication conditions, Si nanocrystals have identical sizes, brick-like shapes, and preferred [111] crystallographic orientation along the SL axis as determined by transmission electron microscopy and polarized Raman spectroscopy. The aspect ratio of this nano-object can be easily varied by changing the density of nucleation sites in amorphous Si (a-Si) layers with a specific thermal budget of rapid thermal annealing. Crystallographic anisotropy is expected to strongly effect the vertical transport through nanocrystals due to a six-fold symmetry of electron energy dispersion in Si. Si nanocrystals are very well passivated by SiO₂ vertically as follows from the geometry of the structure. On the other hand, laterally or in the X-Y plane, these as-crystallized nanocrystals are separated from each other by grain boundaries or/and a-Si residue. Lateral passivation or in other words cross-talk among charged nanocrystals can be modified by post-crystallization oxygen diffusion and oxidation. The combined effects of shape, orientation and passivation anisotropy in the ensemble of nearly identical Si nanocrystals lead to a narrower photoluminescence compared to the luminescence signal from isotropic, nearly spherical Si nanoparticles. Fabrication of anisotropic Si nanocrystals by solid phase crystallization of a-Si/SiO₂ SLs shows an abundance of unique properties and a great promise of their successful implementation in nanoelectronic devices.

2:30 PM C8.4

LAYER BY LAYER ELECTROSTATIC SELF-ASSEMBLY OF LARGE DIAMETER MONODISPERSE SILICA NANOSPHERES WITH A POLYELECTROLYTE. Thomas S. Phely-Bobin, Izabela Galeska, and Fotios Papadimitrakopoulos, Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

Recent efforts have focused on 2D and 3D assemblies with the goal of creating highly ordered supramolecular structures. We presently report results from the layer by layer electrostatic assembly of monodisperse silica spheres with particle diameter (D) from 100 to 400 nm with polyethylenimine (PEI). Our results indicate that both thickness and surface coverage are pH dependent. The average film thickness, as determined by ellipsometry, is as high as two third of the particle diameter per layer of SiO₂ /PEI. The structure and mechanical properties of these organic/inorganic superlattices have been characterized by scanning electron microscopy and quartz crystal microbalance spectroscopy. Careful control of pH and substrate quality could yield in highly uniform layers consisting of a monolayer of silica spheres. Such assemblies exhibits Bragg diffraction in the visible range. Implementation of these assemblies for semipermeable membranes with optical response could open new dimension in the conformal growth of meso-sized composites on a variety of technologically important applications.

3:15 PM *C8.5

ELECTRIC FIELD ASSISTED ASSEMBLY OF METALLIC NANOWIRES FOR CHARACTERIZATION OF MOLECULAR ELECTRONIC DEVICES. Theresa S. Mayer, Thomas N. Jackson, Department of Electrical Engineering, Penn State University, University Park, PA; Christine Keating, Thomas E. Mallouk, Department of Chemistry, Penn State University, University Park, PA.

Recent interest in molecular-scale electronics as a means to fabricate extremely dense logic and memory circuits has led to the development of molecular diodes, switches, and negative differential resistance devices. These devices have been fabricated by self assembly of the constituent molecules onto micron-scale (1 - 10 μm) metal pads defined on a planar substrate or nanometer-scale (30 - 70 nm) metal pads defined on a suspended silicon nitride membrane. In this talk, we will describe our recent research activities related to synthesis and electric field assisted assembly of nanometer-scale (15 - 200 nm) metallic wires, which provide an approach of probing molecular junctions at a smaller scale. The high aspect ratio nanowires are made using replication techniques where single or multiple layers of metals such as Au, Pt, Ag, and Pd are electrodeposited into a porous

membrane and released into a dielectric fluid for assembly. Because the nanowires are compatible with molecular self-assembly strategies, molecular junctions can be formed within the nanowire during synthesis or between two crossing wires at the time of assembly. Assembly of the nanowires is conducted by introducing a nonuniform alternating electric field between two metal electrodes defined on a SiO₂ substrate. The forces that induce alignment of the nanowires are a result of nanowire polarization in the applied electric field. Using this technique, we have successfully positioned individual and crossed nanowires between metal pads that are used for external probing. Experiments are currently underway to measure the transport properties of the metallic nanowires and molecular junctions created within nanowires and at the intersection of the crossed nanowires.