

SYMPOSIUM S

Functional Nanostructured Materials through Multiscale Assembly and Novel Patterning Techniques

April 2 – 5, 2002

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* Invited paper

SESSION S1: SURFACTANT AND POLYMER
TEMPLATING

Chair: Sarah H. Tolbert
Tuesday Morning, April 2, 2002
Metropolitan III (Argent)

8:00 AM *S1.1

SUPRAMOLECULAR TEMPLATING OF NANOPOROUS CATALYSTS. Jackie Y. Ying, Dept. of Chemical Engineering, Massachusetts Inst. of Technology, Cambridge, MA.

Nanostructured materials are of interest for a variety of applications. This talk describes the synthesis of novel nanoporous materials with tailored oxidation states, coordination chemistry and electronic structure. We have found that sol-gel processing can be combined with supramolecular templating agents in deriving well-defined porous structures of a variety of metal oxides. Through ligand interaction between metal alkoxide precursors and surfactant head groups, we have successfully derived a family of stable mesoporous and microporous transition metal oxide molecular sieves (termed TMS) with hexagonally-packed cylindrical pore structures. The compositional flexibility and pore size tailoring of the TMS system open new possibilities for catalytic applications beyond the silicate-based zeolitic materials or mesoporous MCM-41 structures. Besides surfactant templates, we have also utilized triblock copolymers for the synthesis of mesoporous tungstate metal oxides with nanocrystalline colloidal building blocks for solid acid catalysis. Lastly, the combination of triblock copolymer and oil has been introduced to derive silica mesocellular foams with open, ultralarge mesopores. These unique materials have been used to fixate metalloporphyrin and metallophosphine complexes for effective epoxidation, hydroxylation, Heck catalysis and asymmetric hydrogenation. The heterogenized catalysts provide for excellent activity, enantioselectivity and reusability. We have also devised vapor grafting techniques to create highly dispersed Pd clusters on nanoporous supports for carbon-carbon coupling reactions, with activities that rival even the best homogeneous catalysts.

8:30 AM S1.2

DESIGN OF TRANSITION METAL OXIDE AND HYBRID MESOPOROUS MATERIALS. Clément Sanchez, David Grosso, Eduardo L. Crepaldi, Galo J. de A.A. Soler-Illia, Lab Chimie de la Matière Condensée, Univ Pierre et Marie Curie, Paris, FRANCE.

Hybrid organic-inorganic nanocomposites are extremely versatile in composition, processing, and optical and mechanical properties. A striking example is given by mesostructured hybrid networks, precursors to mesoporous solids. Silica-based mesostructures can be processed as powders, monoliths, films or fibers, displaying a great mesostructural variety. Synthesis methods are being currently developed to reproducibly obtain transition metal (TM) oxide-based mesostructured hybrids. The modification of pore surface by organic functions represents the ultimate control that can be attained to create arrays of cavities presenting tailored features. Recently, we communicated the preparation and characterization of titania, zirconia and alumina mesoporous films by evaporation-induced self-assembly (EISA), using non-ionic surfactants as structure directing agents. Here, we describe the critical variables involved in the deposition method (surfactant and acid concentration, temperature, relative humidity), which are crucial for a high degree of meso-organization and film optical quality. In addition, we demonstrate that this method can be extended to the formation of mesostructured VO_x-based hybrid films. In situ SAXS and interferometry analyses were used to evaluate the mesostructure formation during dip-coating. A worm-like structure is obtained as an intermediate phase. Following elimination of residual solvent and HCl (allowing condensation), bidimensional hexagonal (p6m) and then rectangular (p2m) structures (with d-spacings in the 50-150 Å range) were finally formed. Thermal treatment in the 160-350°C range, combined with ozone/UV treatment results in stable oxide mesoporous (30-50 Å pore size) coatings. Different methods were used to graft organic functions on the pore surfaces: pre- and post-synthesis functionalisation strategies are described, using pyrrol and perfluoro derivatives for silica films. These rely on the formation of Si-O-Si bonds on the pore surface. In the case of TM oxide-based films, the organic functions are bound to the inorganic wall by carboxylate, phosphate or acetylacetonate grafting groups.

8:45 AM S1.3

ORDERED MESOSTRUCTURED GERMANIUM FROM SURFACTANT DRIVER ORGANIZATION OF ZINTL CLUSTERS. Dong Sun, Sarah H. Tolbert, Dept of Chemistry & Biochemistry, Univ of California-Los Angeles, Los Angeles, CA.

In this presentation, we describe the formation of periodic nanostructured germanium composites, synthesized via surfactant driven inorganic/organic self-assembly. The results demonstrate that

the ideas of solution phase inorganic/organic self-assembly can be extended from sol-gel type oxides to non-oxide materials. In our experiments, tetraalkyl ammonium cationic surfactants, used as the structural directing agent, and soluble anionic Zintl phase germanium clusters, used as the inorganic precursors, self assemble into lamellar or hexagonally ordered mesostructured composites. The phase of the composites formed depends upon the surfactant type and the concentrations used in the synthesis. The germanium framework can be oxidized toward neutral germanium using mild oxidants such as air or protons. This results in a more interconnected and robust framework. Ion exchange and heat treatment to remove surfactants from hexagonally ordered composite have been performed and preliminary result indicates that it is possible to at least partially remove surfactants from the cylindrical channels while retaining the nanoscale periodicity.

9:00 AM *S1.4

MULTI-SCALE SELF-ASSEMBLY AND PATTERNING OF FUNCTIONAL HYBRID NANOSTRUCTURES. C. Jeffrey Brinker, Dhaval Doshi, Hongyou Fan, and Yi Yang, The University of New Mexico/Sandia National Laboratories Advanced Materials Laboratory, Albuquerque, NM.

The use of amphiphilic molecules or polymers as inorganic structure directing agents is now a well-established synthetic route to the production of so-called mesoporous solids composed of ordered periodic networks of monodisperse pores. Less explored are self-assembly routes to form hybrid (organic/inorganic or metal/inorganic) nanocomposites. This presentation will review our progress on evaporation-induced self-assembly of thin film nanocomposites prepared by two general approaches. First beginning with a homogeneous ethanol/water mixture of hydrophilic and hydrophobic precursors plus surfactant, preferential evaporation of ethanol during dip- or spin-coating or ink-jet printing results in micelle formation and the organization of hydrophilic precursors surrounding the micellar exteriors and the sequestration of hydrophobic precursors within the micellar interiors. Continued solvent evaporation promotes the simultaneous organization of the hydrophilic and phobic moieties into composite mesophases such as organic polymer/silica nanolaminates that mimic seashell or robust 3-dimensional arrays of quantum dots. Second using functional polymerizable or photosensitive surfactants, we can directly assemble composite mesophases that are optically polymerizable, patternable, or adjustable. For example, the co-self-assembly of amphiphilic photoacid generators results in photosensitive thin film mesophases in which the pore size, pore volume, surface area, and refractive index may be continuously varied over a range depending on the UV exposure time. Alternatively the use of optically polymerizable diacetylenic surfactants as both structure directing agents and monomers provides a direct route the formation of highly ordered conjugated polymer/silica nanocomposites exhibiting thermochromic, solvatochromic, or mechanochromic responses. For both composite synthesis approaches, conventional lithography, soft lithography, or micro-printing procedures can be used to pattern additional structure and function on the meso and macroscales.

9:30 AM S1.5

"HAIRY TUBE" POLYMER TEMPLATES FROM DIBLOCK COPOLYMER THIN FILMS. Manfred Stamm, Sergeij Minko, Igor Tokarev, Institut fuer Polymerforschung Dresden, Physical Chemistry and Physics Dept, Dresden, GERMANY.

By the use of microphase separation of diblock copolymers thin ordered polymer films can be prepared. Order may be parallel or perpendicular to the surface depending on the interaction of components to the substrate. To achieve hollow nanoscale cylinders in a polymer template film a blend of the copolymer with a low molecular weight compound is used, which after film deposition can be easily removed. The majority component of the copolymer forms the matrix phase, while the minority component is located at the inner walls of the hollow tubes, thus forming so-called "hairy tubes" at nanometer diameter and distance. They may be filled with different materials or used for further functionalization.

10:15 AM *S1.6

ASSEMBLY OF INTERACTIVE FUNCTIONAL UNITS AND DOMAINS IN 3-D COMPOSITE SYSTEMS DURING SYNTHESIS AND PROCESSING. Galen D. Stucky, Dept of Chemistry and Biochemistry and Materials Dept, Univ of California, Santa Barbara, CA.

A continuing challenge in nanostructured materials device fabrication is the molecular assembly of electronic and optical units into multicomponent integrated systems that have the appropriate interconnects for the reproducible transfer of information. Signal amplification is almost always a necessary ingredient of such a system. We have explored various approaches to this problem and the talk will

present the results of recent synthetic, optical, and electronic observations made on complex inorganic/organic nanostructured materials.

10:45 AM S1.7

A NEW CLASS OF NANOSTRUCTURES: PERIODICALLY ORDERED ORGANIC-INORGANIC HYBRID NETWORKS EXHIBITING STRONG QUANTUM CONFINEMENT. Jing Li,

Xiaoying Huang, Harry R. Heulings IV, Rutgers University, Department of Chemistry, Camden, NJ; Huaxiang Fu, Rutgers University, Department of Physics, Camden, NJ; Tan Yuen, C.L. Lin, Temple University, Department of Physics, Philadelphia, PA.

Multifunctional nanomaterials are highly attractive as candidates of a new generation of materials desirable for advanced electrical, magnetic and optical applications. A new class of nanostructures with interesting optical and magnetic properties have been prepared and characterized. These nanocomposite hybrid materials are assembled as ultrathin II-VI semiconductor slabs ($M = \text{Zn, Cd; Q} = \text{S, Se, Te}$), interconnected by mono- and bi-functional organic molecules that act as linkers and spacers. The intriguing properties of these nanostructures are that they exhibit strong quantum confinement effect while possessing a perfectly periodic crystal lattice. Their optical absorption spectra show surprisingly large blue shifts in the absorption edge (1.0-1.5 eV) with respect to the II-VI parent structures. Band-structure and transition probability calculations using density functional theory within local density approximation (LDA) have confirmed that the observed large blue shifts in the optical absorption spectra are due to the quantum confinement effect (QCE) of the II-VI layers. Substitution of nonmagnetic elements M by magnetic metals leads to interesting magnetic behavior while retaining strong quantum confinement in these hybrid systems.

11:00 AM *S1.8

STRUCTURE AND SHAPE CONTROL IN SELF-ASSEMBLED FUNCTIONAL NANOMATERIALS. Uli Wiesner, Cornell Univ, Dept of Materials Science and Engineering, Ithaca, NY.

The control of the shape and the size of inorganic materials is an important feature of natural growth phenomena. For biological systems both are the result of long evolutionary optimization processes and are intimately related to specific functions. In biomineralization, complex morphologies on different length scales are usually obtained through cooperative self-assembly of organic and inorganic species. In spite of the considerable success in understanding the mechanisms of self-assembly, it remains a challenge for solid-state chemists and material scientists to mimic such natural pathways and develop simple and efficient routes to advanced materials. In the present contribution we demonstrate that unprecedented structure and shape control on the nanoscale is obtained in a synthetic self-assembly process by choice of the appropriate functional polymers as well as ceramic precursors. It is based on a unique polymer-ceramic interface. The hydrophilic parts of the polymer are completely integrated into the ceramic phase analogous to what is found in biological hybrid materials. The potential for new functional materials lies in the versatility of the polymer chemistry as well as that of the sol-gel chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructured materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. Examples will include the preparation of nanoobjects with controlled shape, size, and composition with possible biosensor applications as well as mesoporous materials.

11:30 AM S1.9

DETAILED INVESTIGATIONS OF THE MICROPOROUS CHARACTER OF MESOPOROUS SILICAS AS REVEALED BY NEW SMALL-ANGLE SCATTERING TECHNIQUES. Kui Yu, Sandia National Labs, Albuquerque, NM; Bernd Smarsly, Christine Goeltner, Markus Antonietti, Max-Planck Inst of Colloids & Interfaces, Potsdam, GERMANY; C. Jeffrey Brinker, Univ of New Mexico, Ctr for Micro-Engineered Materials, Albuquerque, NM.

In the past years, various supramolecular templating strategies have been developed to create mesoporous silica materials with a well-defined morphology of the mesopores. Applying sol-gel procedures, larger mesopore sizes are available using aqueous solutions of amphiphilic block copolymers acting as a template, in many cases with poly(ethylene oxide) (PEO) as the hydrophilic block. Although the general mechanism of the procedure has been studied extensively, the role of the PEO block has been unclear, in particular with regard to additional microporosity due to the PEO chains. In our study, mesoporous silicas based on PEO-containing amphiphiles were subject to a detailed quantitative evaluation of small-angle x-ray and neutron scattering (SAS) data. The samples were obtained from various amphiphiles (poly(styrene)-poly(ethylene oxide), etc.) and have pore diameters between 5 nm and 12 nm. The SAS data were

evaluated using modified evaluation algorithms, which shows higher accuracy in particular with regard to the presence of additional micropores. Firstly, the SAS investigations show that mesoporous silicas, obtained from these amphiphiles via sol-gel procedures, contain a large degree of additional micropores. This microporosity can be reasonably quantified by our new approach and amounts up to 50 per cent of the inner surface area, while the pore diameter is about 0.7 nm. Secondly, it is seen that the degree of additional microporosity is significantly dependent on the block-length of the PEO block. In conclusion, this microporosity has to be attributed to the PEO chains. Based on these results, a model is presented which quantitatively relates the porosity of the silicas to the block-lengths of the block copolymers. Furthermore, our investigations will allow to get deeper insights into the pore formation and the structure of the corresponding aqueous solution of the amphiphiles.

11:45 AM S1.10

ORDERED ORGANOSILICATE NANOCOMPOSITES BY

SELF-ASSEMBLY. Shu Yang, Yoichi Horibe, Cheng-Hsuan Chen, Thomas Tattray, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; Peter Mirau, Agere Systems, Murray Hill, NJ.

Nanoporous organosilicates have many potential applications including membranes, sensors, waveguides, dielectrics and microfluidic channels. To create porous materials at nanometer length scale, the microstructure and phase behavior of the nanocomposites need to be understood. A series of block copolymers were used as templates to form periodic lamella, cylinder and spheres in organosilicates at a length scale of 10 nm and thickness greater than 100 micrometer. Fundamental aspects, such as order-disorder transition, long range ordering and interface of polymer-matrix are studied with a variety of techniques.

SESSION S2: STRUCTURAL CONTROL AND CHARACTERIZATION

Chair: Uli B. Wiesner

Tuesday Afternoon, April 2, 2002
Metropolitan III (Argent)

1:30 PM *S2.1

NANOCRYSTAL PATTERNING USING GENETICALLY ENGINEERED BACTERIOPHAGE. Angela M. Belcher, Seung-Wuk Lee, Chuanbin Mao, Christine Flynn, Andrew Hayhurst, George Georgiou, Brent Iverson, The University of Texas at Austin, Departments of Chemistry and Biochemistry and Chemical Engineering, Austin, TX.

A bacteriophage systems will be discussed as a method to nucleate and organize 2,6 semiconductor nanoparticles at several length scales. Engineering the p8 major coat of M13 bacteriophage with a peptide selected to bind zinc sulfide organizes nanoparticles with conserved orientation and forms a wire of nanoparticles along the length of the phage coat. These same engineered phage grown at liquid crystal concentrations form a highly ordered self-supporting crystal hybrid film that can organize nanoparticles over centimeter length scales. Control of the lyotropic liquid crystal phase by phage length, concentration and magnetic fields will be discussed.

2:00 PM S2.2

CADMIUM SULFIDE HELICES TEMPLATED BY SELF-ASSEMBLED NANORIBBONS. Eli D. Sone¹, Eugene R. Zubarev², Samuel I. Stupp^{1,2,3}, Northwestern Univ, ¹ Dept of Chemistry, ² Dept of Materials Science and Engineering, and ³ Medical School, Evanston, IL.

The ability to control the size and shape of inorganic materials on the nanoscale could have profound technological implications as well as being important for the study of nanoscale physical phenomena. For cadmium sulfide (CdS), progress in synthesis of nano-objects has been largely limited to fairly basic shapes such as spheres and wires. Here we report on the first example of helical nanostructures of cadmium sulfide (CdS). These polycrystalline semiconductor helices have a pitch of ~50 nm, and are produced by mineralization of self-assembled organic nanoribbons. The nanoribbon templates are formed by triblock molecules containing a bulky hydrophilic dendritic head group, rigid-rod midsection, and flexible hydrophobic tail that self-assemble into one-dimensional objects. We show here that in certain organic solvents the ribbons adopt a twisted helical shape with a fairly uniform pitch and a surprisingly long persistence length. CdS can grow along one face of the twisted ribbon template to produce a single coil morphology, or along both faces to produce two intertwining coils. The helical morphologies of CdS shown here represent a step towards the goal of harnessing the power of supramolecular organic chemistry for the creation of inorganic nanostructures.

2:15 PM S2.3

COPOLYPEPTIDE-MEDIATED ASSEMBLY OF NANOPARTICLES INTO HOLLOW MICROSPHERES. Michael S. Wong, Rice University, Dept of Chemical Engineering, Houston, TX; Jennifer N. Cha, Kyoung-Shin Choi, Timothy J. Deming, Galen D. Stucky, University of California, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

Various modes are being explored for the construction of functional materials from nanoparticles. Structural complexity and multi-component ordering in such nanostructures are limited, though, by current processing methods. We report a room-temperature, wet chemical-based synthesis route to composite hollow spheres using block copolypeptides that are designed with specific recognition sites for nanoparticles of various compositions. As an example of this versatile bio-inspired approach, micron-sized hollow spheres composed of ~10-nm silica and gold nanoparticles were synthesized and characterized. The mechanism of formation and implications for technological applications will be discussed.

2:30 PM S2.4

EFFECT OF NANOPARTICLES ON PHASE TRANSITIONS IN BLOCK COPOLYMERS. Jae Youn Lee, Russell B. Thompson, Department of Chemical and Petroleum Engineering, University of Pittsburgh, PA; David Jasnow, Department of Physics, University of Pittsburgh, PA; Anna C. Balazs, Department of Chemical and Petroleum Engineering, University of Pittsburgh, PA.

Diblock copolymers can be used to direct the self-assembly of nanoscopic particles into solid nano- plains, wires or spheres. On the hand, the presence of the nanoparticles can affect the morphology of microphase-separating diblock copolymers. We use a mean field model and scaling theory to examine the effect of nanoscale, spherical particles on structure formation in diblock melts. We find that particle size and the particle-block interaction energies play a critical role in the final geometry of the system. In particular, we observe that relatively large particles (which are comparable in size to the block domains) can induce transitions between the different copolymer mesophases. For example, even when the diblock composition would dictate a cylindrical geometry, the addition of a small volume fraction of large, non-selective spheres can drive the system into the lamellar phase. However, the addition of chemically similar but smaller spheres preserves the cylindrical structure. Variations in the interaction energies can suppress or promote such phase transitions. Through the computational and theoretical analysis, we can rationalize these findings and establish guidelines for controlling the morphologies of diblock/nanoparticle mixtures.

3:15 PM *S2.5

OXIDE NANOBELTS AND NANOWIRES - A STRUCTURALLY AND MORPHOLOGICALLY CONTROLLED NANOMATERIALS SYSTEM. Z.L. Wang, Center for Nanoscience and Nanotechnology and School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

Synthesis of structurally and morphologically controlled nanomaterials is a key challenge to the transition from nanoscience to nanotechnology. Currently, carbon nanotubes have been extensively studied, but a controlled synthesis of nanotubes for a specific helical angle is still unfeasible experimentally. In this presentation, we report the success of synthesizing one dimensional nanostructure of a group of semiconductive oxides with structural and morphology control. Ultra-long belt-like, quasi-one-dimensional nanostructures (so called nanobelts or nanoribbons) have been successfully synthesized for oxides of zinc, tin, indium, cadmium and gallium, by simply evaporating the desired commercial metal oxide powders at high temperatures [1]. The as-synthesized oxide nanobelts are pure, structurally uniform, single crystalline and most of them free from defects and dislocations; they have a rectangular-like cross-section with typical widths of 30-300 nm, width-to-thickness ratios of 5-10 and lengths of up to a few millimeters. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. The nanobelts are an ideal system for fully understanding dimensionally confined transport phenomena in functional oxides and building functional devices along individual nanobelts.

[1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 291 (2001) 1947.

3:45 PM S2.6

3D PATTERNS IN POLYMER SURFACTANT NANOGELS. J.G.E.M. Fraaije, G.J.A. Sevink, A. Zvelindovsky, Leiden University, Leiden Institute of Chemistry, Leiden, THE NETHERLANDS.

Polymer surfactant gels based on Poly Propylene Oxide -Poly Ethylene Oxide block copolymers find widespread application in

various areas: health and personal care, biotechnology, cosmetics. Through mesoscopic polymer density functional simulation, we discovered a simple way to prepare tiny gel droplets (10 nm- 1 micron diameter), dispersed in aqueous solution. The self-assembled nanogels display a fascinating array of novel soft 3D 'mathematical' patterns, such as Platonic and Archimedean solids (polyhedrons), in addition to common structures such as onion phases, tubes and inverted micelles. The results are presented as a compound phase diagram, in which each point is a three dimensional density field. The phase diagram depends on two parameters: the size of the droplet and the block composition of the polymer molecule. The intriguing polyhedron structures arise when infinite 3D networks, such as perforated lamellae or gyroid phases are confined in the small droplets. The confinement leads to very fundamental geometrical selection rules, similar to those in Carbon chemistry. We also find tetrahedrons, hexahedrons, octahedrons (regular polyhedrons), and even C60-type buckyballs (truncated polyhedrons), but now on a much larger length scale in a soft material. We discuss the novel structures in the framework of soft nanotechnology applications and possibilities for experimental verification. The results clearly demonstrate that in principle, it is possible to produce highly intricate soft nanostructures by a very cheap dispersion method, with common chemicals in everyday applications.

4:00 PM S2.7

Abstract Withdrawn.

SESSION S3: POSTER SESSION

Tuesday Evening, April 2, 2002
8:00 PM

Metropolitan Ballroom (Argent)

S3.1

SYNTHESIS AND CHARACTERIZATION OF COPPER AND IRON OXIDE NANOPARTICLES WITHIN MCM-41 AND MCM-48 MESOPOROUS SILICAS. C. Minchev^a, R. Köhn^b, T. Tsoncheva^a, M. Dimitrov^a, M. Friöba^{b,c*}, Bulgarian Academy of Sciences, Sofia, BULGARIA.

In the last years the mesoporous M41S molecular sieves have gained large interest as host structures and catalytic supports for metals, metal oxides and organometallic compounds. In the present work a simple method for the synthesis of pure siliceous MCM-41 and MCM-48 silica materials, modified with copper or iron oxide nanoparticles located almost exclusively within the mesopores, is presented. The modified samples were characterized by powder X-ray diffraction, nitrogen physisorption, temperature programmed reduction, X-ray absorption (EXAFS/XANES) or Mössbauer spectroscopy and methanol decomposition as a catalytic test reaction. The existence of small, slightly disordered metal oxide nanoparticles was proved. The redox and catalytic behavior of the modified samples depending on the used metal oxide and the type of the mesoporous support are studied and compared to the corresponding bulk oxide phases.

S3.2

SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE TiNi SHAPE MEMORY ALLOY. E.G. Baburaj, Vikram Bhosle, and K. Salama, University of Houston, Department of Mechanical Engineering, Houston, TX.

Equiatomic or near equiatomic TiNi phase has CsCl type (B2) structure and exhibits shape memory effect. The martensitic and reverse transformation temperatures of these alloys in nanocrystalline form are highly sensitive to the alloy stoichiometry, the presence of phases other than TiNi, and the grain size. In the present study nanocrystalline TiNi shape memory alloy has been produced by mechanical alloying of titanium hydride and nickel, cold compaction of the ultrafine powder, and vacuum annealing at the dehydrogenation temperature of titanium hydride. During mechanical milling the pre-cursor components mix at nanoscale. Subsequent annealing at the decomposition temperature of the hydride results in the abnormal diffusion of nickel into the titanium hydride to form the intermetallic compound. Advantages in the use of titanium hydride in place of titanium are the ease of fragmentation of the hard and brittle titanium hydride, penetration of the hydride into soft nickel, extensive diffusion at the transformation temperature, and the retention of a reducing atmosphere during the formation of the intermetallic compound. Results of investigations on the martensitic and reverse transformations in the alloys in terms of processing parameters, alloy chemistry and grain size, using DTA, XRD, SEM and TEM, will be presented.

*This work was supported in part by the Office of Naval Research Grant No. M0014-99-1-1069.

S3.3

ELECTROCHROMIC WO_{3-x} AND COLOSSAL MAGNETORESISTIVE (La, Sr)MnO₃ PEROVSKITE OXIDE THIN FILMS BY PULSED LASER DEPOSITION. Fumiaki Mitsugi, Eiichi Hiraiwa, Tomoaki Ikegami and Kenji Ebihara, Graduate School of Science and Technology, Department of Electrical and Computer Engineering, Kumamoto University, Kumamoto City, JAPAN.

Perovskite (ABO₃) oxides such as WO_{3-x} (A-site deficient) and (La, Sr)MnO₃ thin films were deposited by KrF excimer pulsed laser deposition technique. The WO_{3-x} has attracted much attention due to its electrochromic property. The optical transmittance of the WO_{3-x} changes by an applied voltage. The optical property measured by the spectrometer of the WO_{3-x} thin film deposited on quartz substrate at the substrate temperature of 400° and the oxygen pressure of 200 mTorr showed high transmittance in visible region. The optical band gap of the film was 3.6 eV. The film had the triclinic crystal structure. In the case of the oxygen pressure of 10 mTorr, the transmittance of the film was less than 5% in the wavelength region of 400 - 500 nm. The amorphous film will have the oxygen deficiency (x) of 0.3 - 0.5. We have studied the potential for NO gas sensor of the WO_{3-x}. The electrical conductivity of the WO_{3-x} changes by the reaction with gas. The triclinic WO_{3-x} thin film prepared on Al₂O₃ substrate having Pt electrode had a sensitivity in NO gas (R_{NO}/R_{N₂}) of 4.2 at an relatively low operating temperature of 200°. The electrical conductivity of the (La, Sr)MnO₃ thin film also changes by an applied magnetic field. We deposited the colossal magnetoresistance (CMR) thin films on MgO(100) substrate at the laser fluence of 2J/cm² and 500mTorrO₂. The maximum magnetoresistance ratio (15%) of the La_{0.8}Sr_{0.2}MnO₃/MgO thin film appeared at the room temperature by the applied magnetic field of 0.7T.

S3.4

MASK FREE SOFT LITHOGRAPHIC FABRICATION OF SUBMICRON 2D METALLIZED ARRAYS. Cristin E. Moran, Corey J. Radloff, Dept of Chemistry, and Naomi J. Halas, Dept of Chemistry and Dept of Electrical and Computer Engineering, Rice University, Houston, TX.

We have developed a method of fabricating large area 2D arrays of discrete submicron-scale metal structures on glass surfaces without need for a lithographically-defined master template. The fabrication method uses a combination of soft lithographic techniques [1] and a variant of the functionalization-metallization chemical approach originally developed for the fabrication of metal nanoshells. [2] Commercially available diffraction gratings were used to form polydimethylsiloxane stamps by a standard molding technique. These grating stamps were used to print well-defined lines of a passivating siloxane molecule onto a glass substrate. A secondary stamping of the same passivating molecule onto the same substrate at an angle with respect to the initial stamping resulted in the formation of intersecting molecular grids or more generally "Moire patterns". The substrate is then exposed to a metallization precursor, then to an electroless plating solution. These subsequent chemical treatments are highly specific to the unpassivated region of the substrate, resulting in sharp lines and distinct submicron islands over the entire region of the multiply stamped substrate. These arrays of metallic structures are varied in size, separation and shape by using a variety of gratings to mold the polymer stamps. A variety of distinct geometrical patterns have been fabricated and imaged on a range of length scales using scanning probe, scanning electron, and optical microscopies. Differences in the functionalization-metallization chemistry specifically optimized for macroscopic surfaces, in comparison to nanoparticle surfaces, will also be discussed. We anticipate that this method will be of significant practical utility in the straightforward and inexpensive fabrication of large area 2D arrays for a variety of optical and photonics applications.

[1] Y. Xia and G.M. Whitesides, *Angew. Chem. Int. Ed.*, 37, 550-575 (1998).

[2] S.J. Oldenburg, R.D. Averitt, S.L. Westcott, and N. J. Halas, *Chem. Phys. Lett.* 288, 243-247 (1998).

S3.5

NANOPATTERNS OF DIBLOCK COPOLYMER MICELLAR MONOLAYERS WITH IN-SITU CHANGEABLE TONES AND THEIR APPLICATIONS FOR NANOPARTICLE SYNTHESIS. B.H. Sohn, S.I. Yoo, B.W. Seo, S.H. Yun, D.C. Kim, and W.C. Zin, Dept of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, KOREA.

In a selective solvent, diblock copolymers, composed of two different polymers covalently linked, spontaneously self-assemble into nanometer-sized micelles consisting of a soluble corona and an insoluble core above the critical micelle concentration. By simple spin coating of such solutions, a nanopattern of a freestanding monolayer film of diblock copolymer micelles was fabricated. The film composed of two-dimensionally compacted micelles showed mechanical stability

without a supporting substrate and was transferable to various substrates. In addition, core-corona inversion of micelles was induced in situ in the freestanding film by a selective solvent for the core without a change of micellar packing. Thus, it was possible to switch nanopatterns between positive and negative tones. Using this nanopattern for nanoparticle synthesis, we demonstrated arrayed nanoparticles including silver and zinc oxide, and characterized their optical properties.

S3.6

NANOWIRE BUILDING BLOCKS: ASSEMBLY AND FUNCTIONAL DEVICE ARRAYS. Yu Huang, Xiangfeng Duan, Charles M. Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

Miniaturization in electronics through improvements in established 'top-down' fabrication techniques is approaching the point where fundamental issues are expected to limit the dramatic increases in computing seen over the past several decades. Here we report a 'bottom-up' approach in which functional device elements and element arrays have been assembled from solution through the use of electronically well-defined semiconductor nanowire building blocks. We will also show that crossed nanowire p-n junctions and junction arrays can be assembled in over 95% yield with controllable electrical characteristics, and in addition, these nanowire junction arrays have been configured as key OR, AND, and NOR logic-gate structures with substantial gain and have been used to implement basic computation.

S3.7

NOVEL II-VI GaIn MEDIA: FROM AMPLIFIED SPONTANEOUS EMISSION TO LASING. Vikram C. Sundar, Hans J. Eisler, Mounqi G. Bawendi, Massachusetts Institute of Technology, Dept of Chemistry and Center for Material Science and Engineering, Cambridge, MA.

The advantages of three-dimensional quantum confinement have long motivated research towards the creation of color-selective lasers based on colloidal semiconductor nanocrystals (NCs). Recent observations of amplified spontaneous emission (ASE) from close-packed films of cadmium selenide (CdSe) nanocrystals have hastened efforts to develop appropriate NC-microcavity feedback structures, and demonstrate true laser action from these nanocrystals. This talk details our efforts in this regard. We describe a novel sol-gel NC/titania matrix, which provides a facile technique for spin-coating waveguides showing ASE. Some novel characteristics of these waveguides include their greater stability, processability and ability to fine-tune their refractive index: features we use to create more-complicated structures showing ASE simultaneously at different wavelengths. Lastly, we report on the successful creation of optically pumped lasers utilizing these NC-titania films as the gain media and distributed feedback (DFB) gratings as the optical feedback mechanism. Novel features of the resulting lasers are detailed, including the ability to tune the output color by simply changing the size of the constituent NC and the ability to operate these lasers at temperatures varying from 80 K to room temperature.

S3.8

OPTICAL PROPERTIES OF 2D METALLIZED ARRAYS FABRICATED VIA MASKLESS SOFT LITHOGRAPHY. Jennifer Steele, Cristin Moran, Allen Lee, Alexander J. Rumberg, and Naomi J. Halas, Rice University, Department of Physics and Astronomy, Department of Chemistry, and Department of Electrical and Computer Engineering, Houston, TX.

Using a combination of soft-lithographic techniques and variations on the functionalization-metallization chemical approach originally developed for metal nanoshells, a maskless method for the fabrication of periodic submicron long range 2D metallic patterns has been developed. The patterning strategy is based on the soft lithographic stamping of a criss-cross pattern of passivated lines onto a substrate, followed by subsequent metallization of the nonstamped areas of the pattern. Variations in the crossing angle and stamp templates permits the fabrication of a wide variety of 2D structures, such as squares, rectangles, diamonds, or rhombohedral islands, where a large range of variations in aspect ratio and inter-island spacing can be systematically controlled. This presents a nearly ideal system with which to study the dependence of the optical properties of 2D metal island arrays on the specifics of the array structure. In this talk we present studies of the optical extinction of 2D gold array films fabricated by this technique. The array films show systematic variation in their peak extinction dependent on inter-island spacing. In addition, the quality of the observed spectral features is seen to correlate to the quality of metallization of the samples. In the case of gold islands, the shape, size, periodicity and spacing of the islands control and modify the plasmon resonant properties of the island arrays.

S3.9

SELF-ASSEMBLED MONOLAYERS FOR MOLECULAR

TRANSPORT. Huilin Tu, Carla E. Heitzman, Kathryn E. Gordon, Paul V. Braun, Univ of Illinois at Urbana Champaign, Dept of Materials Science and Engineering, Urbana, IL.

Patterned self-assembled monolayers (SAMs) have been designed and assembled with the goal of forming pathways to confine and regulate the lateral transport of organic molecules and ions. The patterned SAMs on gold were fabricated by microcontact printing (μ CP) of thiol-terminated molecules onto gold followed by immersion of the patterned samples into a solution containing the second thiol to fill in the remaining space. A similar process was applied to prepare SAMs on silica surfaces with a range of silane molecules. The various monolayers were designed to have chemical and physical properties to enhance the probability that probe molecules or ions can be selectively deposited onto and diffuse through different regions in the SAMs. For example, monolayers containing ethylene oxide repeat units were designed for the transport of polar species, and monolayers containing dimethyl siloxane were designed for the transport of nonpolar species. Techniques including atomic force microscopy, scanning tunneling microscopy, laser scanning confocal microscopy, and infrared spectroscopy have been exploited to measure the properties of the monolayers and to probe for 2-dimensional transport of molecules or ions.

S3.10
SEMICONDUCTOR NANOSTRUCTURES DEFINED WITH SELF-ORGANIZING POLYMERS. Michael Haupt, Stephan Miller, Andreas Ladenburger, Rolf Sauer and Klaus Thonke, Univ Ulm, Dept of Semiconductor Physics, Ulm, GERMANY; Silke Riethmueller and Martin Moeller, Univ Ulm, Dept of Organic and Macromolecular Chemistry III, Ulm, GERMANY; Florian Banhart, Univ Ulm, Dept of Electron Microscopy, Ulm, GERMANY.

We describe a technique to create very small semiconductor nanostructures, with sizes far beyond the limit of conventional optical lithography processes, by the use self-assembling diblock copolymers as nano-lithographic masks. Quantum structures with very high aspect ratio of 1:10 were fabricated from III-V semiconductor heterostructures by dry etching. In a first step, so-called diblock copolymer micelles were generated in a toluene solution. These micelles were loaded by a noble-metal salt. After dipping a substrate into this solution, a monolayer of ordered micelles is generated, covering almost the complete surface. After treatment in a hydrogen plasma all of the organic components are removed and only crystalline metal clusters of ≈ 12 nm size remain. This metal cluster mask can be used directly in a chlorine dry etching process to etch cylinders in GaAs and its alloys of In and Al. It is also possible to etch through a quantum well layer underneath the surface in order to produce quantum dots. The resulting nanostructures were investigated by scanning force microscopy, by high resolution transmission electron microscopy, and also by low temperature photoluminescence spectroscopy.

S3.11
SYNTHESIS AND SELF-ASSEMBLY OF SILVER NANOPARTICLES COATED WITH UNIFORM SILICA. Yu Lu, Yadong Yin, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated a simple method based on sol-gel chemistry to coat silver nanoparticles (40-50 nm in diameter) with uniform layers of silica. The thickness of the silica coating could be easily controlled in the range of 10-100 nm by changing the reaction time and/or the concentration of the sol-gel precursor. These core-shell nanoparticles could be further assembled into three-dimensional periodic lattices or one-dimensional waveguide structures using procedures recently demonstrated by our group. By controlling the center-to-center distance between the silver nanoparticles, it was also possible to tune the plasmon resonance absorption of the silver nanoparticles, and thus the photonic properties of these self-assembled structures.

S3.12
BLOCK-BY-BLOCK GROWTH OF SINGLE-CRYSTALLINE Si/SiGe SUPERLATTICE NANOWIRES. Yiyang Wu, Rong Fan, Peidong Yang, Univ of California at Berkeley, Dept of Chemistry, Berkeley, CA.

Heterojunction and superlattice formation is essential for many potential applications of semiconductor nanowires in nanoscale optoelectronics. We have developed a hybrid pulsed laser ablation/chemical vapor deposition (PLA-CVD) process for the synthesis of semiconductor nanowires with longitudinal ordered heterostructures. The laser ablation process generates a programmable pulsed vapor source, which enables the nanowire growth in a block-by-block fashion with well-defined compositional profile along the wire axis. Based on this method, single crystalline

nanowires with longitudinal Si/SiGe superlattice structure have been successfully synthesized. This unique class of heterostructured one-dimensional nanostructures holds great potential in applications such as light emitting devices and thermoelectrics.

S3.13
CARBON NANOTUBE REINFORCED THREE DIMENSIONALLY ORDERED POROUS CARBON. Ji Su and Emilie J. Siochi, Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA; Ngan T. Huang, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Carbon nanotube/fiber reinforced three dimensionally ordered porous carbon was recently developed using a dynamic processing technique. The porous carbon structures offer nano-scale or sub-micro-scale pores with three-dimensional regularity and significantly improved mechanical properties such as dynamic compressive modulus due to the existence of carbon nanotubes/fibers in the structured porous carbon. Mechanical property of the structured porous carbon with carbon nanotubes/fibers exhibits more significant dependence on measurement frequency when compared to the structured porous carbon without carbon nanotubes/fibers. The high surface area, high regularity and high mechanical strength of the porous carbon structure make it a very promising material for potential application in energy storage and fuel cell technologies. This presentation will discuss the control of the dynamic processing method for fabrication of the structures, scanning electron microscope (SEM) evaluation of the structures and the characterization of other physical properties.

S3.14
CONVENTIONAL AND ATOMIC LAYER CVD IN HIGH ASPECT RATIO NANOPORES: MATERIALS AND DEVICES. Dmitri Routkevitch, Peter Mardilovich, Alexander Govyadinov, Oleg Polyakov, F. Howland Carpenter, Nanomaterials Research LLC, Longmont, CO; Jeffrey W. Elam and Steven M. George, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO.

Chemical vapor deposition (CVD) is a convenient and flexible route for thin film synthesis. One of the major challenges in applying this technique for templated nanofabrication is achieving uniform coverage inside the network of nanoscale pores with high aspect ratio (length to diameter). As an example, gas microsensors from anodic alumina developed at Nanomaterials Research require conformal deposition of metal oxides inside the pores with diameter from 10 to 300 nm and length from 10 to 500 microns. Furthermore, in many cases it is also desirable that the deposition process fills the secondary sub-5 nm pores inside the walls of anodic alumina. We will present our recent results on using both Atomic Layer Deposition (ALD) and conventional CVD to overcome this challenge. ALD uses a pair of surface-limited reactions between gaseous precursors and a solid surface. The first reaction results in a chemisorbed monolayer of the first precursor species on the surface. When the second precursor is introduced, it reacts with the first one resulting in the monolayer of the desired film and regeneration of the surface. These reactions are separated by the inert gas purging to prevent undesired reactions in the gas phase. We have demonstrated that this process is ideally suited for precision deposition of nanoscale films conforming to the nanoscale morphology of anodic alumina. It is also ideal for synthesis of nanolaminated materials with 'dialed-up' composition. Novel approaches will be also described to localize conventional CVD to the nanopores without excessive deposition on the surface of nanotemplates. Applications of these processes for batch-scale production of practical devices (e.g., gas microsensors), for the synthesis of photonic materials, as well for fine-tuning the bulk properties of anodic alumina will be presented. This work was supported by the SBIR programs of DOE (DE-FG03-00ER83053) and NIH (1R43-ES10739).

S3.15
DETERMINISTIC SYNTHESIS OF ZnO NANORODS. Young-Woo Heo, Vijayram Varadarajan, David Norton, Univ. of Florida, Department of Materials Science and Engineering, Gainesville, FL.

ZnO is a direct bandgap semiconducting oxide currently being investigated for chemical sensing and UV optoelectronics. The formation of ZnO nanoscale materials offers opportunities in probing quantum effects in low dimensional ionic semiconductor structures. It may also prove enabling in sensor applications given the large surface to volume ratio in nanoparticles and nanorods. For many applications, the in situ growth of rod-like nanostructures with spatial selectivity would be desirable. In this talk, we will describe recent results for the deterministic growth of ZnO nanorod clusters on planar surfaces. Using a catalytically-driven molecular beam epitaxy approach, we have achieved the growth of ZnO nanorods possessing diameters on the order of 20-40 nm and lengths greater than 1 μ m. Nucleation of the nanorods occurs only on catalysis particles. Selected area electron

diffraction shows these ZnO rods to be single crystals. In this talk, we will report on the synthesis and properties, including photoluminescence, microstructure, and perhaps transport.

S3.16

ELECTRODEPOSITION OF $\text{Bi}_{1-x}\text{Sb}_x$ NANOWIRES OF VARYING COMPOSITIONS. A.L. Prieto, M.S. Martin-Gonzalez, A.M. Stacy, Department of Chemistry; R. Gronsky, T. Sands, Department of Materials Science and Engineering, University of California, Berkeley, CA.

Dimensionally restricted materials present a wide range of potential applications, ranging from thermoelectric power generation to information storage and processing. In particular, nanowires are promising materials for thermoelectric applications because quantum confinement has been shown to increase thermoelectric efficiency. Bulk $\text{Bi}_{1-x}\text{Sb}_x$ is currently the best n-type thermoelectric material for low-temperature applications. Recent calculations by Dresselhaus et al. predict that an anomalously high thermoelectric figure of merit (a predictor for high efficiency in the conversion of heat and power) should be achievable for 30 nm diameter n-type wires with the composition $\text{Bi}_{0.75}\text{Sb}_{0.25}$, and for 40 nm diameter p-type wires with the composition $\text{Bi}_{0.86}\text{Sb}_{0.14}$. As a step toward experimentally verifying these predictions, we have used porous anodic alumina as a template to make nanowires of 40 nm diameter $\text{Bi}_{1-x}\text{Sb}_x$ of varying compositions by electrodeposition into the pores. Characterization of the nanowire/porous Al_2O_3 composite materials using X-Ray diffraction (XRD) to determine the phase, degree of crystallinity, and orientation of the nanowires will be presented. We have used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in conjunction with energy dispersive spectroscopy (EDS) to determine the extent of pore-filling, the morphology of the wires, and the composition of the resulting composite material.

S3.17

FUNCTIONALIZED, *SUBNANOMETER* GOLD PARTICLES: NEW BUILDING BLOCKS FOR NANOELECTRONIC APPLICATIONS THROUGH FACILE LIGAND EXCHANGE REACTIONS. Gerd H. Woehle, Marvin G. Warner, James E. Hutchison, University of Oregon, Dept of Chemistry, Eugene, OR.

Subnanometer, ligand-stabilized gold nanoparticles are of great interest as possible building blocks for nanoelectronic devices due to their well-defined electronic structure. Successful application of nanoparticles requires the introduction of functionality into the stabilizing ligand shell and control of the core size. Here, we report a new class of functionalized, thiol-stabilized gold particles with *subnanometer* core diameters ($d_{\text{CORE}} = 0.8 \pm 0.2$ nm) prepared by ligand exchange reactions of a phosphine-stabilized precursor, $\text{Au}11(\text{PPh}_3)8\text{Cl}3$, with ω -functionalized alkanethiols. This ligand exchange method is applicable for a diverse family of alkanethiols to produce both organic- and water-soluble particles that show increased stability over the phosphine-stabilized precursor. These new materials are the first potentially useful, subnanometer building blocks for optical and nanoelectronic applications. Extensive characterization indicates that the thiol-stabilized exchange products have well-defined core sizes and dispersities. Ligand exchange can be used to either produce completely exchanged thiol-stabilized particles or, if desired, produce partially exchanged particles with a mixed ligand shell. Investigation of these new materials by UV-vis spectroscopy and cyclic voltammetry revealed that these particles have defined optical transitions and show discrete charging behavior. These results confirm the presence of discrete energy levels in the electronic structure of these materials. It was also found that the optical and electronic properties show a strong dependence on the nature of the stabilizing ligand shell. Initial experiments to assemble these new particles on surfaces will also be discussed.

S3.18

MICROSTRUCTURE AND FIELD EMISSION BEHAVIOR OF DOPED AND UNDOPED MULTIWALLED CARBON NANOTUBES. Rodney Andrews, Padmakar Kichambare, David Jacques, Dali Qian, University of Kentucky, Center for Applied Energy Research, Lexington, KY.

Among the types of materials investigated for field emitters, multiwalled carbon nanotubes (MWNTs) are well suited for display applications as their structure lends itself to easy fabrication on the nanometer scale. It has been demonstrated that MWNTs exhibit excellent field emission properties and thus an investigation has been carried out to establish the effect of incorporating N_2 and / or Ru on the morphology and field emission characteristics of MWNTs. We report on the growth and field emission properties of the undoped MWNTs, nitrogen containing and Ru containing MWNTs prepared by chemical vapor deposition (CVD) on silicon (100) substrates. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed a strong effect of doping on the microstructure and

field emission behavior of the MWNTs. With xylene as hydrocarbon source and ferrocene as catalyst, a dense, uniform and aligned MWNTs that are 50 μm in length and 20-40 nm in diameter are formed. With xylene as the hydrocarbon source and a mixture of ferrocene and ruthenocene as the catalyst, cone-shaped MWNTs were produced. With pyridine as the hydrocarbon source and ferrocene as the catalyst, dense and uniform MWNTs containing nitrogen were formed. TEM analysis of the pyridine produced MWNTs showed pronounced structural modifications compared to those produced from xylene. The undoped MWNTs demonstrate superior emission current density of about 52 mA/cm^2 at an applied field of 17 $\text{V}/\mu\text{m}$ with onset of turn-on field at 10.5 $\text{V}/\mu\text{m}$, compared to the nitrogen doped MWNTs and Ru:Fe containing MWNTs which exhibit a low emission current. It is observed that the microstructure also has a strong role on the field emission behavior of these nanotubes.

S3.19

NANOENGINEERED DEFECTS FOR COUPLING OPTICAL ENERGY AT 355 NM TO SILICA. A.V. Hamza, W.J. Siekhaus, M.D. Feit, A.M. Rubinchik, L.L. Chase, S. Demos, M. Runkel, K. Neeb, M.C. Nostrand, B.W. Choi, I.D. Hutcheon, M. Staggs, and M.J. Fluss, University of California, Lawrence Livermore National Laboratory, Livermore, CA; M. Savina and M. Pellin, Argonne National Laboratory, Argonne, IL.

The coupling of optical energy at 355nm to silica was investigated by producing silica surfaces with embedded gold nanoparticles. Au particles of various diameters from 20 to 60nm were dispersed and attached on fused silica substrates. The nanoparticle-covered surfaces were coated with between 0nm and 500nm of SiO_2 by e-beam deposition. The threshold for observable change in the silica overcoat and initiation site morphology for these "engineered" surfaces was determined. The gold nanoparticle coated surfaces with the thickest (500nm) SiO_2 coating exhibited the lowest (front surface) damage threshold of $<0.7 \text{ J}/\text{cm}^2$ determined by light scattering and Nomarski microscopy. The gold nanoparticle coated surfaces with the 100nm SiO_2 coatings exhibited what nominally appeared to be the highest (front surface) damage threshold of $19 \text{ J}/\text{cm}^2$. However, the damage morphology, measured by atomic force microscopy, in the two thickness cases was completely different: silica film exfoliation versus pinpoint damage for the 100nm and 500nm thick coatings, respectively. Pinpoint damage was approximately 1 micron in diameter and 500nm deep, suggesting the nanoparticle was removed in the damage process. At higher fluences the pinpoint damage is larger (~ 2 micron in diameter) and deeper (700nm), suggesting more particle-silica energy transfer. A model, including electromagnetic coupling to the nanoparticle, heating, and possible plasma formation and mechanical coupling to the surrounding material, was developed. Comparison of the model with experimental results suggests possible damage mechanisms. In addition to giving direct evidence on the threshold, size, and morphology of damage resulting from a known initiator, nanoparticle initiation experiments allow refinement and validation of the model. For example, the importance of shock-waves and laser detonation-waves can be determined. This work was performed under the auspices of the U.S. Department of Energy at Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

S3.20

PATTERNING OF SURFACE USING MICRO-CONTACT PRINTING/ELECTROPOLYMERIZATION AND FILLING OF HYDROPHOBIC/HYDROPHILIC CHANNELS WITH CAPILLARY FLOW. Cathie Williamson, Kathy Kielyka, Rebecca Zangmeister, Neal Armstrong, University of Arizona, Tucson, AZ.

Micro-contact printing of alkanethiols, doped with additional phenyl-terminated alkanes, has been used to pattern conductive surfaces, both at the micron and sub-micron level. This patterning is followed by electropolymerization of amine-substituted phenols, to create highly contrasting regions of hydrophobic "channel bottoms" and hydrophilic "channel walls" (up to 30 nm in height), which can then be filled with rod-like aggregate or rod-like polymeric materials as a means of achieving oriented, patterned arrays of these materials. We will review the problems inherent to control of the electropolymerization process, imaging of the sub-micron patterns with AFM, and control of capillary filling of these features to achieve aligned structures.

S3.21

POSITRON ANNIHILATION IN NANOCRYSTAL QUANTUM DOTS. Robert W. Meulenber, University of California, Santa Barbara, CA, and Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, CA; P. Asoka-Kumar, Wolfgang Stoeffl, Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, CA; Mia Berrettini, C. Steven Yun, Geoffrey F. Strouse, University of California, Santa Barbara, CA.

Positron annihilation spectroscopy can provide information on the nature of local electron-electron (e-e) interactions in a material. By using two-detector coincidence Doppler broadening positron annihilation spectroscopy (COPAS), the high momentum Doppler spectra can be related to the e-e interactions with chemical specificity of the defect environment. At the nanoscale, defect levels, as well as surface and core reconstruction events can modify the e-e interactions as predicted from quantum confinement (QC). In this presentation, we report the changes in the COPAS spectra with nanoparticle (NP) size that are suspected to arise from QC effects that modulate local e-e interactions. Comparison of different NP systems (Co, Au, CdSe) allows for the investigation of magnetic effects at the nanoscale.

S3.22

PREPARATION AND CHARACTERIZATION OF THREE-DIMENSIONAL METAL MESHES AND SPHERES. Lianbin Xu, Le Duc Tung, Weilie L. Zhou, Leonard Spinu, John B. Wiley, Advanced Materials Research Institute, Dept. of Chemistry, Univ. of New Orleans, New Orleans, LA; Ray H. Baughman, Anvar A. Zakhidov, Dept. of Chemistry and Physics, Univ. of Texas, Dallas, TX.

Electrochemical methods have been used to deposit metals (such as nickel, palladium and gold) within porous opal membranes. The opal arrays act as templates for the growth of the metal arrays. Subsequent dissolution of the opal produces open three-dimensional metal mesh structures. Nickel meshes can then be oxidized in air to produce nonconducting nickel oxide meshes. This results in an inverse template that can be used for the growth of three-dimensionally periodic metal sphere arrays. Details on the preparation and characterization of these materials will be presented.

S3.23

SELF ASSEMBLY OF PLATE-LIKE PRECIPITATE STRUCTURES IN PLZT THIN FILMS. Cengiz S. Ozkan, Univ of California-Riverside, CA; Bahadır Tunaboylu, Ken Ring, Sadik Esener, Univ of California, San Diego, CA; Ali Ata, Gebze Tech Inst, Kocaeli, TURKEY.

In this paper, we discuss the self assembly of submicron sized precipitates upon phase transformation of $Pb_{0.91}La_{0.09}Zr_{0.65}Ti_{0.35}O_3$ PLZT films grown on sapphire substrates via magnetron sputtering. PLZT thin films are utilized in applications such as electro-optic and pyro-electric devices and the film microstructure influences the device properties. As-grown and annealed thin films were characterized using transmission electron microscopy and x-ray diffraction. Low temperature deposition and subsequent annealing has resulted in polycrystalline morphology with an average grain size of 600 nm. Pair-plate precipitates were formed after annealing of PLZT films deposited at high temperatures, >490C. The average size of a plate-like precipitate was 35 nm in width and 150 nm in length. The characteristic phase transformation could be related to the presence of internal stress due to the lattice mismatch and the thermal expansion mismatch of the PLZT/sapphire thin film structure.

S3.24

SURFACE RELIEF GRATING INDUCED COLLOIDAL CRYSTAL STRUCTURES. Dong Kee Yi, Eun-Mi Seo, Dong-Yu Kim, Kwang-Ju Institute of Science and Technology, Department of Materials Science and Engineering, Kwang-Ju, SOUTH KOREA.

Significant effects of the modulation depth and groove spacing on a three-dimensional colloidal self-assembly with symmetric and asymmetric one and two-dimensional templates are demonstrated. When the ratio γ of the surface modulation h to the diameter of the bead exceeded 0.35, then three-dimensional square array patterns were obtained, and when the ratio γ was from 0.28 to 0.35, pseudo {110} structure resulted. When the ratio γ was less than 0.28, the three-dimensional crystallization of colloids was not observed but regular tetragonal or hexagonal clusters were formed in a two-dimensional pattern. The surface number density of colloids, defined as the number of colloids per unit area of the top most layer, was smaller for the three-dimensional square array than the two-dimensional regular clustered structure.

S3.25

TEMPLATED ELECTRODEPOSITION OF METAL AND SEMICONDUCTOR NANO ARRAYS FOR ENERGY CONVERSION AND OTHER APPLICATIONS. F. Howland Carpenter, Alexander Govyadinov, Peter Mardilovich and Dmitri Routkevitch, Nanomaterials Research LLC, Longmont, CO; Lin Simpson, ITN Energy Systems, Littleton, CO.

This talk will present advanced electrochemical approaches for the synthesis of templated nanowire arrays with the focus on their potential for energy conversion applications. The nanotemplates have

been produced on several substrates, including aluminum foil as well as silicon wafers and glass slides. Techniques have been developed to precisely engineer the thickness and composition of the interface between the nanotemplate and the substrate. This has allowed us to fine-tune the electrodeposition inside the pores, achieve desired performance of nanowire arrays and facilitate their device integration. Electrodeposition of various metals and semiconductors into these nanotemplates was used to create novel nanostructured materials. These materials were incorporated into a number of energy conversion devices with performance characteristics defined by their nanoscale architecture. Examples include: thermophotovoltaic materials based on resonance effects in metal nanowire arrays, polarization-sensitive radiation detectors from semiconductor nanowires, and electromagnetic shielding materials. In addition, electrodeposition has been also used for the synthesis of transition metal nanoparticles, which were used for localized templated growth of carbon nanotube arrays via catalytic pyrolysis. Ongoing work involves integrating these prealigned and prepackaged carbon nanotubes into field emission devices and probe tips for scanning microscopy. This work was supported by BMDO (N00014-98-C-0354), and NSF (DMI-0060455).

S3.26

ULTRAVIOLET LUMINESCENCE EMITTED FROM ZnO NANOSTRUCTURAL FILMS BY KrF PULSED LASER DEPOSITION. Kenji Ebihara, Tamiko Ohshima, Tomoaki Ikegami and Raj K. Thareja*, Department of Electrical and Computer Engineering, and Graduate School of Science and Technology, Kumamoto University, Kumamoto, JAPAN. *Department of Physics, Indian Institute of Technology Kanpur, Kanpur, INDIA.

Zinc oxide (ZnO) is a direct wide band gap semiconductor having an energy gap of 3.3 eV and large exciton binding energy of 60meV at room temperature. For the fabrication of ZnO-based blue light-emitting diodes and short-wave length laser diodes, understanding and controlling the emitting properties of the ZnO materials including ultraviolet (UV) and green emissions have been required. The UV emission center is an exciton transition and the green emission is caused by different intrinsic defects such as oxygen vacancy, zinc vacancy, etc. Photoluminescence (PL) intensity peaks of ZnO crystallites at 380nm and 500nm have been observed. We report here UV luminescence from ZnO thin films deposited by KrF excimer laser ablation technique. The KrF excimer laser beam (Lambda Physik, COMPEX205, wavelength=248 nm, pulse duration=25nm, maximum output=650 mJ/pulse) was used to ablate stoichiometric ZnO target at oxygen pressures from 2 mTorr to 10 mTorr. Laser fluence on the target was changed in the range of 1 to 4 J/cm². Substrates heated between 500 and 700 C were placed 50 mm away from the target. The films were grown on Si(100), quartz and sapphire(0001) substrates. The optical properties of the ZnO thin films were characterized by photoluminescence using the frequency-triple mode locked (355 nm) Nd:YAG laser. PL spectra of the deposited ZnO films on the sapphire substrate exhibited a UV peak near a band gap at 395 nm(3.14eV) and a broad green-yellow emission around 550 nm (2.25 eV). Strong stimulated emission was observed when the excitation energy exceeded 466kW/cm². The c-axis oriented ZnO film has optical band gap of 3.23 eV and crystallite size of 30-40nm estimated from the Scherrer formula.

S3.27

A NOVEL TECHNIQUE FOR THE MEASUREMENT OF Ge ADATOM SURFACE MIGRATION LENGTH ON Si(001). Hyung-jun Kim, Joon-Yeon Chang, and Ya-Hong Xie, Dept of MS&E, Univ of California-Los Angeles, Los Angeles, CA.

A novel method for determining the surface migration length of Ge adatoms on Si(001) has been developed. The Stranski-Krastanov (SK) growth of Ge on a Si substrate generates Ge self-assembled quantum dots (SAQDs). A buried 60° misfit dislocation network located at the interface of a partially relaxed SiGe buffer layer and the Si(001) substrate is used as the stressor for the preferential nucleation of Ge SAQDs. When the average dislocation spacing becomes larger than the migration length of Ge adatom, a denuded zone free of Ge SAQDs appears that separates the preferentially nucleated SAQDs from the randomly nucleated ones. The width of the denuded zone is used as the Ge adatom migration length. This migration length is measured using the samples grown at a range of growth temperatures and Ge molecular beam fluxes.

All of the samples are fabricated using molecular beam epitaxy (MBE). Ge SAQDs are grown on the relaxed buffer layers consisting of a 800 Å thick Si_{0.9}Ge_{0.1} (approximate 10% relaxation after anneal) followed by a 100 Å thick Si cap layer. The growth temperatures and growth rate of Ge are varied from 650°C to 750°C and 0.05 Å/sec to 0.5 Å/sec, respectively, with a constant Ge coverage of 6 Å. A contact mode atomic force microscope (AFM) is used for surface topography of Ge SAQDs samples. Based on the fact that the migration length is proportional to the square root diffusion coefficient at the constant

diffusion time, the diffusion coefficient is determined with the measured surface migration length of Ge adatom. Surface migration lengths (L) and diffusion coefficients of Ge adatom are plotted versus the growth temperatures (T_g) in an Arrhenius plot. The activation energy of Ge adatom surface migration is obtained from the slope of the L vs T_g curve. Our approach illustrating the measurement of Ge surface migration length is not limited to Si/Ge system but can be used for other heteroepitaxial systems in SK growth mode such as InAs SAQDs grown on a partially relaxed InGaAs buffer layer on a GaAs substrate.

S3.28

AN ATTEMPT TO SYNTHESIZE HOLLOW NANO-SIZE SILICA PARTICLES BY TEMPLATE SOL-GEL PROCESS. Kenzo Susa, Youichi Machii, Hanako Yori; R&D Center Hitachi Chemical Co., Ltd. Ibaraki, JAPAN.

Nano-size hollow particles are expected to lower the dielectric constant, density, refractive index of the matrix materials in which they are dispersed. An attempt was made to synthesize such nano-size silica particles by a sol-gel method incorporated with organic templates, surfactant micelle, or dendrimer. This paper focuses on the result of the surfactant templates. Precursor sol was prepared by mixing TEOS, surfactant, ethanol, water and hydrochloric acid at room temperature; it was cast in a dish and left to dry and form porous dry gel. The dry gel was then heat-treated at 600°C in air for 5 hr to remove the surfactant. The heat-treated samples were characterized for porosity by nitrogen gas absorption and with a helium gas pycnometer. The sample prepared with CTAB as the surfactant gave a porosity of 47% for open pores and 19% for closed pores assuming the true density of silica to be 2.2 g/cm³. A pore size of 2nm was obtained from the nitrogen gas desorption isotherm using Saito-Foley method. The sample was further characterized through small angle X-ray diffraction measurement as well as by TEM observation, and was found to have a periodic character of 2-D as well as 3-D hexagonal symmetry with the periodicity of 3.25nm for $d(100)$. These results suggest that during the process nano-size silica particles with surfactant template have been self-assembled to form ordered meso-porous structure consisting of hollow particles of open as well as closed pore types.

S3.29

ASSEMBLIES OF DNA-FUNCTIONALIZED Ag/Au CORESHELL NANOPARTICLES. YunWei Cao, Rongchao Jin, Chad A. Mirkin, Northwestern Univ, Dept of Chemistry and Center for Nanofabrication and Molecular Self-assembly, Evanston, IL.

We report a two-step synthesis of Ag/Au composite core-shell nanoparticles. These core-shell nanoparticles were prepared by reduction of HAuCl₄ by NaBH₄ in the presence of Ag-nanoparticle 'templates' and characterized by UV-vis spectroscopy, transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) microanalysis. Significantly, these particles do not alloy, yielding structures with the optical properties of Ag and the surface chemistry and high stability of Au. Experimental and theoretical data support the structural characterization of these novel materials as Ag cores (~12 nm in diameter) coated with approximately one atomic monolayer of Au (~3 Å). The core-shell nanoparticles have been modified with alkanethiol-oligonucleotides forming structures that undergo reversible hybridization with complementary oligonucleotides to form extended nanoparticle network structures. By spotting aliquots of a solution containing the oligonucleotide-modified nanoparticles without and with DNA target on a reverse-phase alumina plate, a distinct colorimetric transition from yellow to dark brown can be observed by the naked eye. The optical properties of the dispersed and aggregated core-shell particles form a new colorimetric channel for nanoparticle based DNA detection.

S3.30

SYNTHESIS OF ORDERED METALLIC NANOWIRES INSIDE ORDERED MESOPOROUS MATERIALS THROUGH ELECTROLESS DEPOSITION. Zongtao Zhang and Sheng Dai, Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Recent breakthrough in nanomaterial synthesis have resulted in a novel methodology for preparing mesoporous inorganic materials with unprecedentedly large surface areas and highly ordered meso-structures. Both mesoporous silicon and transition-metal oxides have been synthesized. The essence of this new methodology is the use of molecular self-assemblies of surfactants of related substances as templates during the formation of oxides, the size of the oxide mesopores can be precisely tailored from 1.2 to 20 nm, based on the use of various surfactant or block copolymer assemblies. The perfect periodic mesoporous structures of these materials suggest that they could serve as generic nanoscale reactors for manufacturing and replicating technologically important nanomaterials. The metallic

nanowire is a key element in nanotechnology. Extensive attempts have been made recently to fabricate such nanowires inside the ordered mesoporous host, but all methodologies reported thus far have involved the direct impregnation of the mesoporous materials with precursor molecules or ions, followed by thermal or chemical reduction. Only noble metallic nanowires (such as platinum or silver) have been synthesized through this protocol. Here, we report a new method for synthesizing metallic nanowires with diameters in the range of 10-100°. This methodology is based on a combination of electroless deposition and template synthesis using ordered mesoporous materials.

S3.31

MASS-DISTANCE SCALING OF NANO-SIZED BRANCHED POLYMERS: EFFECTS OF SOLVENT QUALITY AND BACK-FOLDING. Walter G. Rothschild, Wayne State University, Dept. of Chemical Engr & Matls Sci, Detroit, MI.

We demonstrate, on the basis of internal mass-distance scaling of MD-simulated and geometrical model patterns of nanosized Poly(propylene imine)-*dendr*-DAB(CN)₆₄, that the system represents a good approximation of a mass fractal of dimension $d = 2.1$ to 2.6 depending on solvent quality (good solvent, poor solvent). The ramifications of such a finding on (a) structure and (b) dynamics are significant: (a) Concerning its structure, the average local density decreases at an accelerating rate with increasing intramolecular distances, indicating that the branching patterns widens if taken from any point within the structure and going outward (self-similarity). Such aspects can be used to predict the effect of solvent quality, points of criticality (abrupt density changes), and location of endgroups as well as their polarity effects. (b) Concerning the dynamics, transport processes and fluxes that diffuse on the dendrimer's branches are expected to show non-classical behavior, such as delayed diffusion and fracton modes in their low-frequency spectral regions. The simple scaling approach, based solely on the knowledge of the coordinates of the mass points of nano-sized pattern, is much more detailed and circumvents the requirement of mutual self-similarity for a series of different-sized objects in the classical scaling techniques between molecular mass and radius of gyration.

S3.32

SYNTHESIS AND CHARACTERIZATION OF SELF-ASSEMBLED PIEZOELECTRIC ZnO NANOSTRUCTURES AND INTEGRATION WITH Si PROCESSING. Arthur V. Cresce¹, Hasina Afroz Ali², Agis A. Iliadis², Peter Kofinas³, and U. Lee⁴. ¹Materials and Nuclear Engineering Department, University of Maryland, College Park, MD. ²Electrical and Computer Engineering Department, University of Maryland, College Park, MD. ³Chemical Engineering Department, University of Maryland, College Park, MD. ⁴Army Research Laboratory, Adelphi, MD.

The formation of 10 nm self-assembled ZnO nanoparticles on Si and SiO₂/Si surfaces, using diblock copolymers, and wet chemical processing compatible with semiconductor manufacturing, is reported. The diblock copolymer, consisting of norbornene and a norbornene-dicarboxylic acid blocks with a 400 to 50 repeat unit ratio, was synthesized by ring opening metathesis polymerization using Shrock's catalyst. The microphase separation of the block copolymer was employed to grow spherical self-assembled ZnO nanoparticles. The self-assembly of the inorganic nanoparticles was achieved at room temperature in the liquid phase by incorporating ZnCl₂ to the carboxylic acid block, or by exposure of a solid film to diethyl zinc vapors. Subsequent room temperature wet chemical processing of the doped films resulted in the formation of zinc oxide, [followed by the saturation of double bonds in the polymer backbone. The formation of ZnO was verified by x-ray photoelectron spectroscopy XPS. TEM micrographs show the size and distribution of the zinc oxide nanoclusters in the polymer matrix. This study provided information on the formation of zinc oxide structures in a self-assembled polymer matrix, with the intention of controlling the shape and distribution of zinc oxide domains. The doped diblock copolymer was applied on Si and SiO₂/Si wafers, by standard spin-on techniques, and its photolithographic patterning, metallization, and reactive ion etching using ozone was developed.

S3.33

AUTOMATIC FILM FORMATION SYSTEM FOR ULTRA-THIN ORGANIC HETERO-STRUCTURE BY MASS-CONTROLLED LAYER-BY-LAYER SEQUENTIAL ADSORPTION METHOD WITHIN ONE NANOMETER INTERFACE ROUGHNESS. Seimei Shiratori and Takahiro Ito, Keio Univ, Yokohama, JAPAN.

Mass-controlled layer-by-layer sequential adsorption process was newly developed for the fabrication of ultra-thin organic films formed by polyelectrolytes. Conventionally, the control of the film thickness in the layer-by-layer sequential adsorption process of polymer electrolytes was tried by changing the number of dippings. In the

conventional automatic dipping system, none considered the adsorption and desorption phenomena in the rinsing steps, or adsorption during the movement of the dipper arm. It was found that minor errors accumulate during the process and decrease the accuracy of control of the film deposition system. In this study, by optimization of the feedback constant of the data acquired by quartz crystal microbalance (QCM) to the dipping time, high-quality self-assembled films were produced. In order to remove the accumulation of errors from the "set value", we propose a new feedback algorithm for extending the feedback control for the "block of layers" in the hetero-structure: we applied "double mass control" by monitoring not only the frequency shift of each individual layer, but also that of the block of layers. At the same time, the saturation characteristics during deposition were also monitored to further improve the new dipping algorithm. As the results, the relationship between the number of bilayers and the film thickness showed improved linearity. In addition, by monitoring the saturating condition in each deposition step, the linearity in the relationship between the frequency shift and the deposition time was remarkably improved. This enabled control of the relationship between the frequency shift and the block or layer thickness on exactly nm-scale. From the cross-sectional images observed by TEM and thickness measurement carried out using an ellipsometer, it was found that the layer thickness was controlled with nm-scale accuracy and the interface roughness can be suppressed within one nanometer. Optical devices coatings fabricated by this method are also reported.

SESSION S4: SURFACE PATTERNING

Chair: Paula T. Hammond
Wednesday Morning, April 3, 2002
Metropolitan III (Argent)

8:00 AM *S4.1

SINGLE CRYSTAL THIN FILMS OF SPHERICAL DOMAIN BLOCK COPOLYMERS. Rachel A. Segalman, Alexander Hexemer, Edward J. Kramer, Depts of Chemical Engineering and Materials, UCSB, Santa Barbara, CA.

Bulk spherical domain A-B diblock copolymers with a large enough product $\chi(T)N_B$, where $\chi(T)$ is the Flory interaction parameter between A and B segments and N_B is the degree of polymerization of the shorter B block, order into a bcc lattice of B-block spheres in an A-block matrix. As $\chi(T)N_B$ is decreased, the bulk bcc structure melts to form a fluid of B-block spheres before a completely disordered block copolymer melt is formed. We have observed that the ordering of a disordered spun cast thin film is very sensitive to $\chi(T)N_B$ and to the presence of substrate topology. Upon annealing a film of thickness one B-sphere thick on a SiO₂ layer grown on silicon with steps 30 nm high, a single crystal film of block copolymer grows from the step edges under conditions where $\chi(T)N_B = 9$. This 2D single crystal film has hexagonal symmetry, is oriented with respect to the step edge and can extend as much as 2.3 μm from it. Within a distance of 1.5 μm (2500 spheres) from the step edge few dislocations ($\sim 1 \mu\text{m}^{-2}$) are observed. Under conditions where $\chi(T)N_B = 7.5$, a single crystal film with orientational order still forms but with a high density of paired dislocations. Finally at $\chi(T)N_B = 6.9$ a film with a fluid-like packing of spheres is observed. Under conditions where $\chi(T)N_B \sim 10$ and above, we observe grain boundaries near the step edge and the system appears to be kinetically trapped. The behavior in the range $9 > \chi(T)N_B > 7$ is similar to that seen for 2D hexatic colloid structures which have short range translational order but long range orientational order. We will discuss the implications of these results for designing block copolymer films for nanolithographic applications.

8:30 AM S4.2

DEVICE FABRICATION USING PROTEIN NANOTUBES AS BUILDING BLOCKS. Hiroshi Matsui, City Univ of New York, Dept of Chemistry at Hunter College, New York, NY.

Future development of microelectronics, magnetic recording devices, and chemical sensors will be achieved by increasing the packing density of device components. For example, high-speed electrical circuits will be produced by increasing the packing density of nanometer-scaled circuit elements. To fabricate a new generation of more densely packed three-dimensionally-assembled devices, the placement of the components in the exact positions with high reproducibility is desirable. We introduce a new method to fabricate devices such as electronics, sensors, and magnetic recording media using biological functions. Our strategy is to use protein nanotubes, which can recognize and selectively bind a well-defined region on patterned substrates, as building blocks to assemble three-dimensional nanoscale architectures at uniquely defined positions and then decorate the protein nanotubes with various materials such as metals, semiconductors, quantum dots, and/or insulators to fabricate complex device configurations. We have demonstrated that the nanotubes can

be selectively immobilized on surfaces using protein-protein interactions and functionalized with metals, quantum dots, and porphyrins. The nanotubes were also bundled as ropes for real-world applications. The nanocrystal-functionalized nanotubes were examined as a signal-enhancing nano-cuvettes for Raman microscopy.

8:45 AM S4.3

GRAFT POLYMERIZATIONS INITIATED FROM PATTERNED POLYMER SURFACES. Timothy Von Werne, Kenneth R. Carter, Craig J. Hawker, David Germack, Center for Polymeric Interfaces and Macromolecular Assemblies, IBM Almaden Research Center, San Jose, CA.

Polymeric surfaces comprised of thin films of a patterned rigid, highly cross-linked acrylate network on silicon substrates have been utilized as templates for the controlled growth of a secondary polymer layer. A thin film of a photopolymerizable resin was patterned into sub-micron sized features on a silicon wafer using a novel contact molding technique. The patterned cross-linked resin contained a tandem methacrylate / radical initiator, either 2,2,5-trimethyl-3-(1-(4//methacryloylmethyl) phenylethoxy)-4-phenyl-3-azahexane or 2-methacryloyloxyethyl-2/-bromoisobutylbromide, which was incorporated into the network upon photopolymerization. Controlled radical polymerizations were conducted from the initiating sites on the patterned surface yielding a grafted secondary polymer layer. An overview of the molding process and data including characterization of the modified surfaces and morphology will be presented.

9:00 AM *S4.4

LONG-RANGE ORDER AND REGISTRATION OF BLOCK COPOLYMER DOMAINS ON SUBSTRATES CHEMICALLY PATTERNED WITH INTERFEROMETRY. Paul Nealey, Juan de Pablo, Franco Cerrina, Xiaomin Yang, Richard Peters, Qiang Wang, Univ of Wisconsin, Dept of Chemical Engineering and Center for NanoTechnology, Madison, WI.

Block copolymer thin films have tremendous potential for nanofabrication because they self-assemble into ordered structures at the length scale of 5-50 nm. For many targeted applications (photonic band gap materials, magnetic storage media, arrays of quantum dots), long-range order and substrate registration is required, for example to create addressable arrays. We report experimental results and Monte Carlo simulations that detail techniques to guide the self-assembly of the domain structure of cylinder and lamellar forming block copolymer films such that: 1) the domains are perpendicular to the substrate, 2) the perfection of ordering of the domains extends over macroscopic dimensions, and 3) the periodic structure of the film is registered with features of the underlying substrate. Our approach relies on patterning substrates with regions of different chemical functionality. The contribution of interfacial energy between the ordered polymer film and the patterned substrate to the overall free energy of the system is sufficient to result in the amplification of the chemical pattern of the substrate into the domain structure of the polymer film. A fundamental concept of our work is that substrates can be easily patterned at the length scale of tens of nanometers with appropriate geometries using multiple beam interferometry.

9:30 AM S4.5

SELF-ORGANIZING NANOPHASES ON SOLID SURFACE. Wei Lu, Univ of Michigan, Dept of Mechanical Engr, Ann Arbor, MI.

Experimental evidence has accumulated in the recent decade that nanoscale patterns can self-assemble on solid surfaces. The ability of patterning nanostructures on a surface is very important for many modern technological applications, such as in microelectronics circuits and digital storage media. We developed a thermodynamic framework to study the remarkable phenomena. Based on our continuous phase field model, we developed the numerical technique and performed large-scale simulation of the process of formation and evolution of nanostructures on a solid surface. The simulation reveals remarkably rich dynamics and suggests a significant degree of experimental control in growing ordered nanoscale structures.

10:15 AM *S4.6

PERIODIC STRUCTURES FROM BLOCK COPOLYMERS FOR THIN FILM APPLICATIONS. Edwin L. Thomas, Cheolmin Park, Joy Cheng, Caroline Ross and Anne Mayes, Department of Materials Science and Engineering, M.I.T. Cambridge, MA.

There is great potential to employ self-assembling molecules for use in many aspects of modern technology. Block copolymers provide a route to many interesting periodic structures, and can be designed to contain very specific properties by altering functional groups on the polymer, and/or doping block copolymer systems with certain nanoparticle additives. This talk discusses directed block copolymer self assembly using graphoepitaxy and directional solidification. Graphotaxy is employed for the design of ultra-dense magnetic

recording media, and directional solidification combined with a topographically patterned substrate affords the possibility to access a periodic double orientation of the microdomains.

10:45 AM S4.7

FERROELECTRIC CELLS OBTAINED BY IMPRINT LITHOGRAPHY. C. Harnagea, M. Alexe, D. Hesse, and U. Goesele, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

The increasing need of the semiconductor industry to fabricate structures in the sub-100 nm range on the wafer scale level requires the development of simple, fast, high-resolution capability, and low-cost production techniques. Imprint lithography fulfills all these features and the remaining task is to optimize the process for each particular device. Ferroelectrics have become an important material in microelectronics due to the wide range of potential applications, especially in non-volatile memories and microelectromechanical systems. This work reports the fabrication of ferroelectric structures with lateral sizes from several microns down to the submicron range using imprint lithography. For comparison, electron beam direct writing and self-patterning methods were used to fabricate the same ferroelectric material under 100 nm lateral size. A second important task to be achieved is to demonstrate the functionality of the structures obtained in terms of their ferroelectric behavior. Using scanning probe microscopy in piezoresponse mode, a technique which allows the access of each ferroelectric cell for individual testing, switching of the ferroelectric polarization within the cells was revealed in terms of the piezoelectric hysteresis and changes of the domain structure.

11:00 AM S4.8

SINGLE CRYSTAL SURFACE TEMPLATING FOR ANISOTROPIC NANOPARTICLES. John Kitchin, Mark Barteau, Jinguang Chen, University of Delaware, Dept. of Chemical Engineering, Dept. of Materials Science and Engineering, Newark, DE.

Surface templating offers a powerful method for guiding self-assembly of structures. The dimensions of the structures are dominated by the characteristic dimensions of the surface pattern and interactions between the assembling moieties and the surface. Therefore, to achieve nanodimensions, the surface pattern should have nanodimensions. In our work, we use the intrinsic patterns of single crystal metal oxide surfaces as templates for the growth of metal particles. This represents the extreme case of feature size, as the characteristic dimensions of the surface pattern are atomic in nature in at least one direction. The strength of the interactions between the metal particles and the metal oxide surface has a significant role in controlling the ultimate particle shape and size. Finally, the distribution of defects on the surface has an important contribution to the distribution of particles. We have examined the formation and growth of molybdenum particles on the TiO_2 (110) crystal surface and its reconstructed surfaces in an ultrahigh vacuum chamber. This surface has alternating rows of titanium atoms and oxygen atoms. After annealing a surface with a sub-monolayer amount of molybdenum deposited on it, we observe the formation of anisotropic molybdenum nanoparticles by scanning tunneling microscopy. Additionally, we observe a strong correlation between the location of the particles and locations of defects on the oxide surface. The anisotropic shape of the Mo particles is in contrast with the shape of metal particles such as gold and copper on this surface, which form nearly round particles. These metals have a relatively low affinity for oxygen so there is not a strong interaction between the metal oxide surface and the metal particles. Therefore, there is not a strong guiding effect from the surface pattern of atomic rows for these metals.

11:15 AM *S4.9

INTEGRATION OF SELF-ASSEMBLED POLYMERS FOR SEMICONDUCTOR APPLICATIONS. Chuck Black, K.W. Guarini, K.R. Milkove, R.L. Sandstrom, S. Yeung, and Y. Zhang, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Self-organizing diblock copolymer thin films provide a low-cost, efficient means to engineer nanometer-scale structures over large wafer areas. In particular, these polymer systems are attractive for microelectronics applications because of their compatibility with standard silicon processing techniques. We have begun exploring semiconductor applications of diblock copolymer templates composed of polystyrene (PS) and polymethylmethacrylate (PMMA). Upon annealing, the PS and PMMA separate into a hexagonal lattice of PMMA cylinders in a matrix of PS. Thin films of ordered polymer domains may be formed on various substrates such as polysilicon, silicon dioxide, silicon nitride, and full 8-inch-diameter silicon wafers. We have been developing a variety of processing techniques for pattern transfer of the nanometer-scale template into the underlying substrate. Such processes should enable new opportunities for nanostructure fabrication. We have recently demonstrated integration of these self-assembled polymers into the fabrication of a simple MOS

capacitor, yielding devices with increased charge storage capacity over planar structures.

11:45 AM S4.10

A NOVEL PATTERNING METHOD FOR METAL-ORGANIC PRECURSORS ON A SiO_x/Si SUBSTRATE USING A LOCAL ELECTRIC FIELD. Hiroshi Fudouzi, Mikihiro Kobayashi, Norio Shinya, Toyohiro Chikyow, Parhat Ahmet, Tamami Naruke, National Institute for Materials Science, Tsukuba, JAPAN.

This paper will demonstrate a new technique to deposit metal-organic molecular in a non-polar solvent using an electrified pattern. Recently nanostructures assembled with molecular have much attention because of their potential applications in electronic, optical and biochemical devices. We have developed a novel method using an interaction between metal-organic molecular dissolved in a non-polar solvent and a local electric potential field on a substrate. The molecular were selectively deposited at the electrified region of the substrate. We used an n-type (100) Si wafer covered with SiO_x layer of 500nm thickness as a substrate. Positively electrified pattern was formed on the substrate by scanning a focused Ga^+ -ion beam at 30keV. Then the substrates were immersed in a precursor solution, $\text{Ti}(\text{O}^t\text{-C}_3\text{H}_7)_4$ alkoxide molecular dissolved in octane, for several hours at room temperature. The molecular were selectively deposited on the electrified pattern. We estimate that the transfer of molecular from the liquid phase was occurred by the attractive interaction between an induced dipole moment of a neutral molecule and the local electric field. Earlier study using a polymer film demonstrates that protein molecular selectively deposited on an electrified pattern. We can make a stable electric field and form a patterned oxide film on a SiO_x/Si substrate. Silicon wafer is important substrate because of its many useful properties in practical application. SrTiO_3 is one of the important materials because of its high dielectric constant. A commercial precursor solution (Symetrix Co., metal-organic complex dissolved in a xylene, Sr:Ti=1:1) was used in the experiment. As deposited precursors pattern on the substrate was heat-treated in air at 650°C for 5hrs. The TEM observation showed that the structure of the film was amorphous and thickness of the film was about 20nm.

SESSION S5: NANOSCALE ELECTRONICS

Chair: Robert M. Dickson
Wednesday Afternoon, April 3, 2002
Metropolitan III (Argent)

1:30 PM *S5.1

GROWTH AND PROPERTIES OF SELF-ASSEMBLED CRYSTALS OF SINGLE-WALLED CARBON NANOTUBES. A. Ilie, C. Durkan, M.S.M. Saifullah, and M.E. Welland, Engineering Department, Cambridge University, Cambridge, UNITED KINGDOM; James Gimzewski, UCLA Department of Chemistry, Los Angeles, CA.

It was recently discovered that crystals of single-walled carbon nanotubes (SWCNTs) can be produced by self-assembly during thermolysis of nano-patterned C60/catalyst precursors [1]. In this process, multilayers of C60 and Ni were evaporated into spatially confined regions, of the order of several hundred of nanometers, and then annealed at temperatures high enough to generate a catalytic breakdown of the C60. This led to the formation of carbon nanostructures, shaped in the form of rods or faceted crystals, several microns long and with widths in the range of 10-500nm. High resolution transmission electron microscopy (HRTEM) and electron diffraction revealed that these crystals had unusual and appealing properties, since in all cases they were constituted of physically identical and perfectly aligned SWCNTs. Whilst the majority of crystals were (10,10) crystals (corresponding to a SWCNT diameter of 1.36 nm), a range of crystals was also observed. Here we present an in-depth investigation performed on these crystals of SWCNTs. Various techniques, such as Raman spectroscopy, electron energy loss spectroscopy (EELS), TEM, and atomic force microscopy (AFM), were combined to gain insight into their structure, as well as into their mechanical and electrical properties. This allowed us to determine that, the geometric arguments derived from electron diffraction aside, the nano-crystals are indeed composed of SWCNTs. Moreover, a particular aspect of this study is that we characterised the nanotube crystals both in their optimal growth conditions, and also outside this regime, when (i) the crystal formation was barely initiated, and (ii) beyond optimum, when the tubes were subject to structural transformations. This approach consequently allowed us to obtain information about the crystal growth process. As a by-product of this process, other non-carbon nanostructures were obtained, allowing the possibility of producing other types of nanostructured materials by this route.

1. R.R. Schlittler, J.W. Seo, J.K. Gimzewski, C. Durkan, M.S.M. Saifullah, and M.E. Welland, Science 292, 1136 (2001).

2:00 PM S5.2**POLYMER FUNCTIONALIZATION FOR AIR-STABLE N-TYPE CARBON NANOTUBE FIELD-EFFECT TRANSISTORS.**

Moonsub Shim, Ali Javey, Nadine Wong Shi Kam, Hongjie Dai, Stanford University, Department of Chemistry, Stanford, CA.

Field-effect transistors of individual single-walled carbon nanotubes (SWNTs) are promising in developing nanoscale electronics. However, typical semiconducting SWNTs exhibit only p-type character. While n-type semiconducting SWNTs can be made by methods such as charge transfer from alkali metals, these n-type SWNTs suffer from immediate degradation upon exposure to ambient conditions. A new scheme for n-doping SWNT is presented. Functionalization of carbon nanotubes with a polymer rich in amine groups leads to air-stable n-type SWNTs with excellent FET characteristics.

2:15 PM S5.3**ROOM TEMPERATURE SINGLE ELECTRON TRANSISTOR**

BASED ON CARBON NANOTUBES. J.B. Cui, R. Sordan, M. Burghard, and K. Kern, Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, GERMANY.

Single electron transistors (SETs) are ideal devices for high precision electrometry. So far, most of the SETs can work only at low temperature, which limits the application of the devices. A small tunneling dot with size of 10 nm is generally required to get the SET device working at room temperature. However, it is a real challenge to fabricate such a small dot even with state of the art nanofabrication technologies. Single walled carbon nanotubes (SWCNTs) with diameters of a few nanometers appear to be natural candidates for SET fabrication. A single electron transistor device that operates at room temperature was realized via local chemical modification of carbon nanotubes. The mask technique used to define the tunneling dot is compatible with standard semiconductor technologies and able to create dots with a size of ~ 10 nm. Conductance oscillations as a function of gate voltage as well as differential conductance peaks versus bias voltage were observed up to room temperature. The non-equal separation of the conductance peaks is attributed to the discrete energy level splitting (~ 36 meV) of the modified carbon nanotube segment.

2:30 PM S5.4**CHARACTERISTICS OF NANO-SCALE FIELD EFFECT TRANSISTORS VIA STRUCTURE MODIFICATIONS OF SELF-ASSEMBLED MOLECULES.**

Hong Meng, Department of Chemistry and Biochemistry, University of California at Los Angeles, CA; Jie Zheng, Jan Hendrik Schön, Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

This paper demonstrates self-assembled monolayer molecular array can be used as active layer in three-terminal devices, that is, field effect transistors (FETs). The approach is an important step towards molecular-scale electronics. In order to understand the mechanism of such molecular scale devices, a series of conjugated aromatic dithiols, hyper-conjugated dithiols linked by oxygen or sulfur atom and conjugated monothiols have been studied. Contact angle and Ellipseometry measurements of the self-assembly films of the compounds on gold substrate supported the single monolayer structures. Electrochemistry measurements of the bulky materials as well as self-assembly thin films have been discussed. The performance of the FETs indicated that longer conjugation length of molecules showed higher current modulations. No saturation currents were observed in hyper-conjugated dithiols made FETs and only diode-like behavior was shown in conjugated monothiol based FETs. These results suggested that the charge transport through molecules determines the characteristics of SAMFETs rather than the transverse conduction from molecule to molecule as in the case of bulk organic crystals or thin films.

3:15 PM *S5.5**CHEMICAL SYNTHESIS OF ONE-DIMENSIONAL NANO-STRUCTURES AND THEIR PROPERTIES.**

Peidong Yang, Department of Chemistry, University of California, Berkeley, CA.

Nanowires are of both fundamental and technological interest. They not only exhibit interesting electronic and optical properties intrinsically associated with their low dimensionality and the quantum confinement effect, but also represent the critical components in the potential nanoscale electronic and photonic device applications. With the ever-decreasing sizes of these 1D nanostructures, the "bottom-up" chemical approach is playing increasing role due to its capability of making much smaller features as compared to the "top-down" approach. In this talk, I will introduce the vapor-liquid-solid crystal growth mechanism for the general synthesis of nanowires of different compositions. I will discuss some of the unique physical properties of the nanowires and their potential applications including nanolaser,

nanosensor and optical switch. Strategies towards controlled assembly of these 1D building blocks will also be discussed.

3:45 PM S5.6**SINGLE GALLIUM NITRIDE NANOWIRE DEVICE.**

Guosheng Cheng, Huaiming Wang, Youxiang Zhang, Martin Moskovits, University of California, Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

The many possible uses of the wide-band-gap semiconductor, GaN, in optoelectronic devices, such as light emitting diodes operating at blue and near-ultraviolet wavelengths, and in applications such as high-temperature and high frequency electronics has engendered a great deal of interest in this material. At the same time, much progress has been made towards fabricating pseudo-one-dimensional structures such as nanotubes and nanowires of a wide variety of materials. These are of interest largely because of the new range of physical properties that structures of that size range are expected to exhibit. Here, we report a simple synthesis, based on vapor-liquid-solid growth, for producing ultra-long GaN nanowires in large quantities. We also describe isolating single GaN nanowires for the purpose of performing single nanowire measurements and ultimately in order to produce single GaN nanowire devices. GaN was synthesized by reacting Ga_2O vapor with ammonia in a continuous flow cell in the presence of metallic indium as a nucleation catalyst. An alumina ceramic plate or a silicon wafer was used as substrate. The resulting long GaN nanowires were shown to be single crystal and their phase was determined to be hexagonal wurzite using X-ray diffraction. The majority of the wires produced had lengths in the range 50-80 μm . Nanowires with lengths of several hundred μm could be grown by allowing the growth process to continue longer. The mean diameter of the GaN nanowires could be varied in the range 10-100 nanometers, depending on the fabrication temperature, which also determined the mean size of the indium catalyst nanoparticles. The growth mechanism involved in the GaN nanowire growth is undoubtedly the, now familiar, vapor-liquid-solid (VLS) process. Scanning electron microscopy revealed the presence of the ball-shaped fluid alloy particles (likely composed of In, Ga and N) at the terminus of growing nanowires, a typical characteristic of VLS growth. Single GaN nanowires could be transferred to a sapphire substrate by mechanically removing nanowires from the large mass of nanowires produced on the alumina substrates. The GaN nanowire-covered alumina plate was sonicated in ultra-pure methanol to form a suspension. Several drops of the suspension were then placed on the sapphire substrate. After drying at room temperature, single, aligned GaN nanowires were found on the sapphire substrate using SEM imaging. The average inter-wire distance was $\sim 2-5$ μm .

4:00 PM S5.7**MANIPULATION OF GE NANOCRYSTALS IN A TRI-LAYER INSULATOR STRUCTURE OF A MIS MEMORY DEVICE.**

L.W. Teo¹, C.L. Heng¹, V. Ho², M. Tay², W.K. Choi^{1,2}, W.K. Chim^{1,2}, D.A. Antoniadis^{1,3}, E.A. Fitzgerald^{1,3}. ¹Singapore-MIT Alliance, Advanced Materials for Micro- and Nano- Systems Programme, SINGAPORE. ²Department of Electrical & Computer Engineering, National University of Singapore, SINGAPORE. ³Department of Electrical and Computer Engineering, Massachusetts Institute of Technology, MA.

A metal-insulator-semiconductor (MIS) device that consists of germanium (Ge) nanocrystals embedded in a novel tri-layer insulator structure is proposed for memory applications.¹ The tri-layer structure comprises a thin (~ 5 nm) rapid thermal oxidation (RTO) silicon dioxide (SiO_2) layer, a Ge+ SiO_2 middle layer (3-20 nm) deposited by rf co-sputtering technique, and a RF-sputtered silicon dioxide capping layer. High-resolution transmission electron microscopy (HRTEM) results show that Ge nanocrystals of sizes ranging from 3 - 20 nm were found after rapid thermal annealing of the tri-layer structure at 1000°C for 300 s. The electrical properties of these devices have been characterized using capacitance versus voltage (C-V) measurements. A significant hysteresis was observed in the C-V curves of these devices, indicating charge trapping in the composite insulator. Comparison with devices having a similar tri-layer insulator structure, but with a pure sputtered oxide middle layer (i.e. minus the Ge nanocrystals), clearly indicated that the observed charge trapping is due to the presence of the Ge nanocrystals in the middle layer. The C-V measurements of devices without the capping SiO_2 layer exhibited no significant hysteresis as compared to the embedded Ge nanocrystal tri-layer devices. The HRTEM micrographs showed that the presence of the capping oxide is critical in the formation of nanocrystals for this structure. By varying the thickness of the middle layer, it was found that the maximum nanocrystal size correlates well with the middle layer thickness. This indicates that the nanocrystals are well confined by the RTO oxide layer and the capping oxide layer. In addition, Ge nanocrystals formed using a thinner middle layer were found to be relatively uniform in size and distribution. This structure, therefore, offers a possibility of fabricating memory devices with

controllable Ge nanocrystal size.

1. W.K. Choi, W.K. Chim, C.L. Heng, L.W. Teo, V. Ho, V. Ng, D.A. Antoniadis and E.A. Fitzgerald, 'Observation of memory effect in germanium nanocrystals embedded in an amorphous silicon oxide matrix of a metal-insulator-semiconductor structure, submitted for publication in Applied Physics Letters'.

SESSION S6: ELECTRONIC, OPTICAL AND MAGNETIC ARRAYS

Chairs: Tianquan Lian and John T. Fourkas
Thursday Morning, April 4, 2002
Metropolitan III (Argent)

8:00 AM *S6.1

INORGANIC NANORODS: SYNTHESIS, ALIGNMENT, PROPERTIES. Paul Alivisatos, Univ of Calif at Berkeley, Dept of Chemistry, Berkeley, CA.

Inorganic nanocrystals with well-defined shapes are important for understanding basic size-dependent scaling laws, and may be useful in a wide range of applications. Methods for controlling the shapes of inorganic nanocrystals are evolving rapidly. This talk will focus on a strategy that involves pyrolysis of organometallic precursors in mixtures of hot organic surfactants. The surfactant mixtures can be used to control the growth rates of different facets of the nanocrystals, allowing for wide tunability of shape. This will be illustrated with CdSe and Co nanocrystals. Both of these materials show pronounced variation of fundamental properties with aspect ratio. The nanorods can be aligned in a variety of ways. For instance, monolayers of surfactant coated rod-like nanocrystals of these materials display a very rich phase diagram, analogous to the phases of liquid crystals. Block copolymers can be used to orient the rods. Finally, very special inorganic structures, tetrapods consisting of four rods at the tetrahedral angle, will always spontaneously align perpendicular to a surface. The possible application of these aligned nanorods in biological detection, photovoltaics, and light-emitting diodes will be described briefly.

8:30 AM S6.2

PROPERTIES OF ROLLED-UP InGaAs/GaAs NANOTUBES. Ch. Deneke, C. Müller and O.G. Schmidt, Max-Planck-Institut für Festkörperforschung, MBE Service Gruppe, Stuttgart, GERMANY.

Recently, it was shown that inherently strained semiconductor bilayers form into a new class of nano-objects if released from their substrate [1-3]. The fabrication process combines self-formation processes with standard semiconductor processing techniques and therefore establishes a powerful integration of top-down and bottom-up approach in nanotechnology. Here, we grow thin AlAs/InGaAs/GaAs layers pseudomorphically onto GaAs (001) substrates by molecular beam epitaxy. The AlAs layer is removed ex-situ with selective etching. As a result the InGaAs/GaAs bilayer is detached from the substrate and the intrinsically strained bilayer rolls up into a novel kind of nano-object, called free-standing nanotube. We vary the diameter of these tubes from 500 nm to 14 nm, simply by changing the built-in strain and the thicknesses of the layers. Surprisingly, we find that the tube diameter can be described by a continuum mechanical model down to the nanometer scale. The wall thickness of the tubes and the inner to outer diameter ratio is determined by the number of rotations during the roll-up procedure. We present tubes that have performed 30 full rotations. Transmission electron microscopy investigations reveal that the epitaxial structure of the layers is not altered during the roll-up process. Raman spectroscopy indicates that the translation symmetry between the layers is broken as expected from theory.

References:

- [1] V. Ya. Prinz, V.A. Seleznev, A.K. Gutakovskiy, A.V. Chehovskiy, V.V. Preobrazhenskii, M.A. Putyato, T.A. Gavrilova; *Physica E* 6, 828-831 (2000).
- [2] O.G. Schmidt, K. Eberl, *Nature* 410,168 (2001).
- [3] O.G. Schmidt, N. Schmarje, Ch. Deneke, C. Müller, N-Y. Jin-Phillipp; *Adv. Mater.* 13(10),756-759 (2001).

8:45 AM S6.3

NON LITHOGRAPHIC FABRICATION OF DENSE Sn NANOWIRE ARRAYS. Regina Ragan, Vanessa Sih, and Harry A. Atwater, California Institute of Technology, Thomas J. Watson Dept. of Applied Physics, Pasadena, CA.

Fabrication of diamond cubic Sn nanowires can enable opening of the zero direct energy band gap via quantum confinement effects, yielding a group IV direct energy bandgap semiconductor. Engineering of the nanowire radius tunes the energy bandgap as indicated by band-structure calculations. Tight binding energy band calculations performed for diamond cubic Sn indicate for wires of 40 nm in

diameter, the band gap is predicted to be 0.4 eV, which corresponds to an absorption edge wavelength of 3 microns and for wires of 10 nm in diameter, the bandgap is predicted to be 2.5 eV corresponding to an absorption edge of 500 nm. We have fabricated Sn nanowires with 12:1 aspect ratios (40 nm diameter and 500 nm length) by high pressure injection (1400 psi) of molten Sn into porous alumina templates fabricated by electrochemical anodization of Al foil. Anodically-synthesized alumina templates with pore sizes less than 10 nm and densities of 10^{11} cm² are achievable with this non-lithographic technique.

¹ Structural and optical characterization of Sn nanowire arrays will be discussed.

² A.P. Li et. al., *J. App. Phys.* 84, 6023 (1998).

9:00 AM *S6.4

SEMICONDUCTOR NANOCRYSTAL QUANTUM DOTS: FROM SINGLE DOTS TO LASING DOTS. Moungi Bawendi, MIT, Dept of Chemistry, Cambridge, MA.

Advances in the chemical preparation of nanocrystal quantum dots that are of high crystal quality and have high fluorescence quantum yields have spurred detailed studies of their electronic and optical properties. Applications in fields ranging from biology to optical devices are now also being pursued. Following a short general introduction of the optical and chemical properties of these dots, this talk will focus on two topics. The first 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 second 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. Here we review the physical processes that affect lasing action in these dots. We show that an understanding of these processes can lead to the design of structures that exhibit stimulated emission and lasing from quantum dots under optical pumping.

9:30 AM S6.5

ELECTRONIC STRUCTURE THEORY OF SEMICONDUCTOR DOTS AND DOT MOLECULES. Alex Zunger, NREL, Golden, CO.

We have developed an atomistic approach to the electronic structure of semiconductor quantum dots. The approach is based on pseudopotential theory, thus avoiding continuum-like effective-mass models. Many-body electron correlation effects are introduced via Configuration Interaction. We have applied this method to study neutral as well as charged dots of Si, CdSe, InP and InAs, revealing spectral shifts due to accumulation of a few carriers per dot, as well as deviations from Hund's rule and the Aufbau principle. This method was also applied to "Dot Molecules", predicting their excitonic spectra as a function of dot-dot distance. Experimental implications on spectroscopy and transport will be discussed.

9:45 AM S6.6

LASER OSCILLATION IN AGGREGATES OF ULTRASMALL SILICON NANOPARTICLES. M.H. Nayfeh, S. Rao, N. Barry, J. Therrien, G. Belomoin, A. Smith, Univ of Illinois, Dept of Physics, Urbana, IL; S. Chaieb, Univ of Illinois, Dept of Theoretical and Applied Mechanics and the Beckman Institute for Science and Technology, Urbana, IL.

We dispersed electrochemically etched Si into ultrabright, blue or red luminescent ultrasmall nanoparticles, with brightness higher than fluorescein or rhodamine. The emission from single particles is readily detectable. Aggregates or films of the particles exhibit emission with highly nonlinear characteristics. We observe directed blue beams at ~ 410 nm between faces of aggregates excited by femto second radiation at 780 nm. We also observe laser oscillation at ~ 610 nm from aggregates of red luminescent elemental Si nanoparticles, excited by radiation at 550-570 nm from a mercury lamp. Intense directed Gaussian beams, a pumping threshold, spectral line narrowing, and speckle patterns manifest the emission. The results are analyzed in terms of population inversion and stimulated emission in quantum confinement-induced Si-Si dimer phase, found only on ultrasmall Si nanoparticles. This microlasing constitutes an important step towards the realization of a laser on a chip, hence optoelectronics integration and optical interconnects.

10:30 AM *S6.7

REFLECTIVITY BASED OPTICAL READOUT OF STRIPED METAL NANOPARTICLES AT REST AND IN MOTION: TOWARDS HIGH THROUGHPUT NANOPARTICLE READERS.

Michael J. Natan, Chief Technical Officer, SurroMed, Inc, Mountain View, CA.

The synthesis and optical properties of a series of segmented, cylindrically-shaped metal Au and Ag nanoparticles have recently been described. The novelty of these materials stems from the variation in metal composition along the particle length. Because the reflectivity of Au and Ag are different, the appearance of the particles under white light illumination in an optical microscope is analogous to a conventional barcode, with a series of alternating light and dark regions. This presentation will focus on the synthesis, characterization, and optical properties of the particles. Early results on new approaches to particle synthesis will be presented. Progress on striping pattern readout of a planar array of stationary particles as well as a stream of flowing particles will be described.

11:00 AM S6.8

IMPRINT LITHOGRAPHY FOR LARGE-SCALE SYNTHESIS OF MONODISPERSE NANORODS. Kornelius Nielsch, Jinsub Choi, Ralf B. Wehrspohn, Herbert Hofmeister, Manfred Reiche, and Ulrich Gösele, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

Monodisperse nanorods are highly desirable for many biomedical applications ranging from diagnostics of cancer cells to drug delivery. In the recent years, self-ordered alumina pore channel arrays, based on an approach of Masuda et al. [Science 1995, 268, 1466], have attracted a lot of interest as a template material for the synthesis of anisotropic nanoparticles with a defined diameter ($\pm 10\%$). In analogy to polycrystallites, the pore channels are hexagonally self-arranged in domains. In these pore arrays, numerous lattice defects and domain boundaries exist where large deviations of the average pore diameter occurs. When we introduce imprint lithography in the fabrication process of our templates, a monocrystalline arrangement of pore channels on a cm^2 -scale is obtained and the deviation of the pore diameter is reduced to less than 5%.

We have developed a novel 4th imprint stamp consisting of hexagonal convex pyramid array based on modern VLSI processing using DUV-lithography, anisotropic etching, LPCVD Si_3N_4 deposition and wafer bonding. Using a commercial oil press the pattern of the imprint mold is directly transferred into polished aluminum substrates. Subsequently, the aluminum is anodized and a perfectly arranged array of highly monodisperse alumina pore channels is formed. The alumina templates are filled by electrodeposition or autocatalytic deposition with metals like Ag, Au, Co, or Ni and - in contrast to most publications in this field - a degree of pore filling of almost 100% was achieved. The nanorod diameter (20...400 nm) and its length (0.2...50 μm) can be adjusted precisely over a large range. TEM characterisation shows that silver nanorods are single crystalline. The nanorods might be transferred into an aqueous solution by selectively dissolving the alumina matrix. The dissolved nanorods can be further functionalized or serve as templates for hollow polymer nanococoons.

11:15 AM S6.9

INVESTIGATION OF MAGNETIC NANOWIRES FABRICATED BY USING SINGLE-WALLED CARBON NANOTUBE TEMPLATES. Thomas W. Tomblar, Hongjie Dai, Stanford Univ, Dept of Chemistry, Stanford, CA; Myles Steiner, Aharon Kapitulnik, Stanford University, Dept of Applied Physics, Stanford, CA.

Due to recent advances in nanofabrication techniques, there is much interest in the investigation of true one-dimensional systems. We present a technique for producing isolated nanowires by direct deposition onto a suspended single-walled carbon nanotube. Using the nanotubes as templates, we have made several metal and metal oxide nanowires. Here we present transport studies on nickel nanowires that were typically 5 nm thick and 1 micron long. The wires were investigated at temperatures down to 20 mK and with both perpendicular and parallel magnetic fields.

11:30 AM S6.10

METAL-ASSISTED SELF-ASSEMBLY OF LENGTH FRACTIONATED SINGLE-WALL CARBON NANOTUBES IN DENSE, ORDERED ARRAYS. Debjit Chattopadhyay, Izabela Galeska, Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Length separation of "individual" single wall carbon nanotubes (SWNTs) has been a challenge withholding their incorporation in a variety of nanoscale devices. Herein we demonstrate a shear induced "solubilization" and length separation of shortened-SWNTs by gel permeation chromatography (GPC) along with their subsequent substrate independent organization, which holds significant promise for the development of nanoscale devices. As witnessed by spectroscopic ellipsometry and Quartz Crystal Microbalance (QCM) experiments, these fractionated SWNTs can be successfully organized

in dense (up to 1.1 g/cm^3 highly oriented regular arrays on a range of substrates by a simple self-assembly process both in monolayer and multilayer formats. Tapping-mode atomic force microscopy and polarization Raman spectroscopy, point to a high degree of SWNT alignment normal to the substrate.¹ Additionally, spectroscopic characterization (UV-Vis and NIR) of the SWNT fractions, which provide the first direct observation of all the theoretically predicted interband transitions between the mirror image spikes in the density of states (DOS) of SWNTs will also be presented.²

References:

1. D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, J. Am. Chem. Soc. 2001, 123, 9451.
2. D. Chattopadhyay, S. Lastella, S. Kim, F. Papadimitrakopoulos, J. Am. Chem. Soc. 2001, In press.

11:45 AM S6.11

LAYER-BY-LAYER ASSEMBLY OF MULTILAYER THIN FILMS OF MIXED NANOPARTICLES BASED ON HYDROGEN BONDING. Jianchang Guo, Tianquan Lian, Emory University, Department of Chemistry, Atlanta, GA.

We report the layer-by-layer assembly of inorganic nanoparticles using hydrogen-bonding interaction. We synthesize nanoparticles (Au, Ag, CdSe, CdS) with carboxylic acid containing groups on the surface. Multilayers of films can be built by depositing alternating layers of nanoparticles and poly(vinylpyridine)(PVP). Multilayer films of one type of particles in all layers or with different type of particles in different layers can be assembled. The multilayer buildup is monitored by UV-Vis spectra, which showed a linear increase of the film absorbance with the number of adsorbed nanoparticle layers. The resulted films have high degree of flatness and smoothness as indicated by small angle X-ray diffraction (SAXD). Hydrogen bond interaction, the driving force for the formation of PVP/CdSe multilayer thin film, between the pyridine group of PVP and the carboxylic acid group on nanoparticle was verified by FTIR spectroscopy.

SESSION S7: OPTICAL PATTERNING AND OPTICAL MATERIALS

Chair: Robert M. Dickson
Thursday Afternoon, April 4, 2002
Metropolitan III (Argent)

1:30 PM *S7.1

DEVELOPMENT OF NANO-PHOTONIC DEVICES AND THEIR INTEGRATION BY OPTICAL NEAR FIELD. M. Ohtsu, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama, JAPAN; Also with Localized Photon Project, ERATO, Japan Science and Technology Corporation, and with Near-field Photonics Group, Kanagawa Academy of Science and Technology, JAPAN.

This paper reviews the recent progress of application of interactions between optical near-fields and nanoscale materials. Photochemical vapor deposition of nanometric Zn, Al, and ZnO are realized by using an UV optical near-field. Novel near-field effect of the deposition is also demonstrated by using a non-resonant light. Optical near-field technology offers the opportunity of modifying surfaces and developing new nanostructures that may exhibit a quantum effect due to their extremely small size. In order to confirm it, quantum size effect of ZnO dots are evaluated. Photo-emission of Si nano-dots are also evaluated by near field optical spectrometer in the UV region. Utilizing the very advanced potential of this technology, the concept of nano-photonic IC is proposed. The optical switching operation of a single InGaAs quantum dot is shown to be able to be used for nano-photonic devices. Nano-photonic switching operation utilizing optical near-field interaction is also proposed and the switching time of about 200 ps was estimated. Related spectroscopy of CuCl quantum dots are carried out to demonstrate the optical near field energy transfer. Sub-micron width plasmon waveguide for converting far-field propagating light to optical near-field is proposed in order for using as an input port of the nano-photonic IC. Guiding characteristics of the plasmon waveguide fabricated by Si anisotropic etching process are evaluated to be the mode spot size of 110 nm and propagation distance over several micron.

2:00 PM S7.2

WHISPERING GALLERY MODE EMISSION FROM HIERARCHICALLY ASSEMBLED QUANTUM DOT SPHERICAL MICROCAVITIES. Michael H. Bartl, Univ of California at Santa Barbara, Dept of Chemistry and Biochemistry and Materials Dept, Santa Barbara, CA, and Univ of Graz, Institut fuer Chemie, Graz, AUSTRIA; Jennifer N. Cha, Univ of California at Santa Barbara, Dept of Chemistry and Biochemistry, Santa Barbara, CA; Michael S.

Wong, Rice Univ, Dept of Chemical Engineering, Houston, TX; Galen D. Stucky, Univ of California at Santa Barbara, Dept of Chemistry and Biochemistry and Materials Dept, Santa Barbara, CA.

Spherical microcavities are used to confine the propagation of light in three dimensions and can be applied for nanoscale devices such as optical switches, low-threshold lasers, and photonic band-gap structures. Recently in our group, hierarchically assembled multi-composite, inorganic hollow nano- and micron-sized spheres have been successfully synthesized from nanoparticles. Here we report on the optical properties of one such hollow microsphere, in which the wall is composed of an inner layer of luminescent II-VI semiconductor quantum dots, such as CdSe, and an outer layer of silica nanoparticles. A laser-excitation photoluminescence microscope set-up was assembled to study the emission properties from individual microcavities. The room-temperature photoluminescence spectra of single spheres selected by a pinhole show a sharp periodic structure that we assign to selected whispering gallery modes of the hollow semiconductor microsphere. Since the semiconductor layer has a much higher refractive index than that of the silica, the light emitted by the quantum dots undergoes repeated total internal reflections at the spherical semiconductor/silica interface and is therefore trapped in the whispering gallery modes.

2:15 PM *S7.3

THE APPLICATION OF SILVER OXIDE THIN FILMS TO PLASMON PHOTONIC DEVICES. Junji Tominaga, Dorothea Büchel, Christophe Mihalcea, Takayuki Shima and Toshio Fukaya, Laboratory for Advanced Optical Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

RF-magnetron sputtered thin films of silver oxide (AgOx) layers have recently been applied to ultra-high density optical data storage. The AgOx films sandwiched by protection layers show very interesting characteristics in strong light-scattering, local plasmon generation and super resolution by focusing a laser beam on. Especially, the combination with a recording thin film (optical phase change or magneto-optical) used in recordable optical disks improves the storage density and overcome the diffraction limit. In this invited paper, we describe the basic characteristics of nano-scale light scattering centers generated in the AgOx films, and the interaction with ultra-high density recorded mark patterns and a second scattering center, which are both placed in a near-field region. The experiment was carried out in a dynamic condition, using specially designed optical disks with a multilayered structure consisting. The disk was rotated at a constant linear velocity of 6.0 m/s, which is the same speed as that of DVD, and two laser beams (blue and red) were focused on a same spot by the tracking control technology of rewritable DVD system. In the case of using the recording film, small mark-patterns beyond the diffraction limit scattered the incident blue laser light by the red laser power which generates and controls the light scattering center in the AgOx film. The scattering effect was strongly correlated with the mark sizes. On the other hand, in the case of applying double AgOx layers separated by a thin dielectric film for the observation of the dipole light scattering, Two transition points to scatter the evanescent light to the far-field were confirmed at the red laser powers of 2.5 mW and 3.8 mW. According to the results, it was confirmed that AgOx films decomposed due to the incident laser beam (red), resulting in the light scattering.

2:45 PM S7.4

DATA STORAGE CAPABILITIES FROM A Ag/AgO THIN FILM SYSTEM. Lynn A. Peyser, Robert M. Dickson, Georgia Inst of Tech, Dept of Chemistry, Atlanta, GA.

Fluorescence microscopy of nanoscale AgO films prepared by a chemical bath deposition technique reveals strong photoactivated emission when excited with wavelengths shorter than 520 nm. Emission intensity from the AgO films shows very little thickness dependence, indicating that the Ag clusters photochemically generated from the oxide are surface moieties. While blinking and characteristic emission patterns demonstrate single nanoparticle observation, large-scale dynamic color changes are also observed, even from the same nanoparticle. High-density, patterned data is readily written to these films with UV or blue excitation; the control of which is governed by the product of intensity and time. The stored data can be non-destructively read with the strong red fluorescence resulting from green ($\lambda > 520$ nm) excitation lasting for long periods of time without significant degradation.

3:30 PM *S7.5

MULTIPHOTON FABRICATION: MAKING THINGS WITH LIGHT. Tommaso Baldacchini, Richard A. Farrer, Huzhen Chen, Michael J. R. Preville, John T. Fourkas, Boston College, Dept of Chemistry, Chestnut Hill, MA.

We discuss recent advances that we have made in the fabrication of

three-dimensional structures using multi-photon absorption (MPA). Since the probability for the absorption of N photons is proportional to the light intensity to the Nth power, MPA allows us to localize photochemical events to a small, sub-diffraction-limited region in the focal volume of a tightly-focused laser beam. By controlling the position of this focal volume, with appropriate photochemical processes it is possible to fabricate two- and three-dimensional structures from a wide variety of materials with feature sizes that can be as small as 100 nm. We will present some of our latest results in the MPA fabrication of metallic and polymeric microstructures.

4:00 PM S7.6

LASER GUIDANCE DEPOSITION TECHNIQUE FOR PATTERNING 3D MICROSTRUCTURES MADE OF NANOPARTICLES WITH VARYING SURFACE FUNCTIONALITY. Juntao Xu¹, Changong Zhou², Sheila Grant^{1*}, Edward Nadgorny², and Jaroslav Drellich¹. ¹Dept of MS&E and ²Dept of Physics, Michigan Technological Univ, Houghton, MI. *Present address: Dept of Biological Engr, Univ of Missouri-Columbia, Columbia, MO.

In this paper, we present results on patterning three-dimensional (3D) microstructures using the laser-guidance deposition of polystyrene and gold nanoparticles from particle-in-solvent suspensions on a substrate. A weakly focused laser beam is used to axially confine and propel particles along the laser beam. The gradient forces, which arise from electrical forces on polarizable particles in a gradient optical field, provide confining the particles to the beam axis. The scattering forces, which arise from momentum conservation of scattered photons, propel particles toward the substrate. Both polystyrene particles (100-400 nm) and gold particles (20-50 nm) with different organic functionality on the surface are selected as constructive materials for fabrication of 3D microstrips. In the experiments, the laser power varies from 0.1 W to 1.6 W. The quality of microstrips produced under different deposition conditions is studied using optical microscopy and atomic force microscopy. It was found that deposited polystyrene and gold particles form nanoclusters made of at least several particles. If deposited at an appropriate rate, such clusters form multilayer microstrips of high particle density. The typical width of the microstrips fabricated in this study is less than 10 microns. Parallel arrays made of colloidal particles with different surface functionality are constructed by this technique, which seems to be especially attractive approach for developing novel chemical and biological microsensors.

SESSION S8: POSTER SESSION

Thursday Evening, April 4, 2002
8:00 PM

Metropolitan Ballroom (Argent)

S8.1

ELECTRICAL PROPERTIES AND DEVICES OF LARGE-DIAMETER SINGLE-WALLED CARBON NANOTUBES. Ali Javey, Moonsub Shim, Hongjie Dai, Stanford Univ, Dept of Chemistry, Stanford, CA.

Individual semiconducting single-walled carbon nanotubes (SWNTs) with relatively large diameters in the range of 3 to 5 nm are found to exhibit ambipolar field effect transistor (FET) behavior. Both electron and hole conduction are observed for these FETs by simple electrostatic gates. The effects of ultraviolet (UV) radiation and temperature on their electrical properties show that the ambipolar characteristic is intrinsic to the large-diameter nanotubes. The ambipolar SWNTs can be easily used as building blocks for functional nanoelectronic devices such as voltage inverters that operate under ambient conditions.

S8.2

ELECTRICAL PROPERTIES OF LONG SUSPENDED SINGLE-WALL CARBON NANOTUBES. Nathan Franklin, Thomas Tomblor, Hongjie Dai, Stanford University, Dept of Chemistry, Stanford, CA.

Suspended single-wall carbon nanotubes are grown on top of pre-deposited metal electrodes. This configuration allows investigation of the electrical properties of suspended nanotubes up to 10 microns long. Previous experiments have been limited to nanotubes less than 1 micron. Semi-conducting and metallic nanotubes are investigated at low temperatures and with a back gate. Because of their suspended nature these nanotubes show promise as MEMS (Micro Electro Mechanical Systems) devices, and it is interesting to see the electrical properties of long nanotubes not in contact with a surface.

S8.3

POTENTIAL STANDARD ULTRATHIN FILMS: IDENTIFICATION OF ISOSTRUCTURAL SELF-ASSEMBLED MONOLAYERS.

David J. Vanderah, Richard S. Gates, Diana N. Zeiger, Curtis W. Meuse, Gintaras Valincius, NIST, Biotechnology Dept., Gaithersburg, MD.

The self-assembled monolayers (SAMs) of a series of octadecyl 1-thiaoligo(ethylene oxide)_x disulfides [S(CH₂CH₂O)_xC₁₈H₃₇]₂, where x = 4 - 8, were assembled on polycrystalline gold and characterized by reflection-adsorption infrared spectroscopy (RAIRS), spectroscopic ellipsometry (SE), and electrochemical impedance spectroscopy (EIS). For x = 6 - 8, the SAMs appear to be isostructural. The EIS data indicate highly stable, highly ordered, nearly defect-free SAMs that behave as ideal capacitors in an electrochemical environment. The RAIRS data show that the 1-thiaoligo(ethylene oxide) [TOEO] segments adopt the ordered 7/2 helical conformation of the folded-chain crystal polymorph of poly(ethylene oxide)[PEO] with atom positions along the TOEO segment, oriented normal to the substrate, that correlate with the atom positions along the c axis of the unit cell of PEO. The similar structures of the TOEO segments, which provide spacings (cross-sectional area = 21.4Å²) similar to the gold itself, result in similar structures for the C₁₈ segments that the RAIRS data show are nearly identical to octadecanethiol SAMs. SE measurements show SAM thicknesses increase by 0.30 ± 0.02 nm/ethylene oxide unit, in close agreement with that expected (~0.28 nm/ethylene oxide) from the unit cell dimensions of PEO. Thus, for x = 6 - 8 the film properties, such as optical constants and dielectric constants, do not change and are constants for all three films. The similarity of the properties of these SAMs appear to make them suitable for use as ultrathin film standards for a variety of surface science techniques.

S8.4
INVESTIGATIONS OF SUBSTRATE-SELECTIVE COVALENT ATTACHMENT FOR GENETICALLY-ENGINEERED MOLECULAR INTERCONNECTS. Kenneth Bousman, Gajendra S. Shekhawat, George Sirinakis, Narendra Rana, Fred Heuchling, John Welch, Robert E. Geer, Eric T. Eisenbraun, and Alain E. Kaloyeros, Albany Institute for Materials, Albany, NY.

The utilization of individual molecules for digital device structures, so-called moletronics, holds the promise for orders of magnitude increase in the level of device integration compared to today's integrated circuits (ICs). Similar advances in the area of on-chip interconnects may also benefit from a molecular approach wherein individual molecular structures can serve as signal conduits between IC devices. Self-assembling, genetically-derived molecular arrays, essentially one-dimensional molecular crystals, are under investigation for applications as such interconnects at the University at Albany Institute for Materials. These materials consist of polypeptide beta sheets chemically modified for template-driven immobilization on patterned silicon-oxide test structures. Successful template-driven, or directed, self-assembly relies on the selective covalent attachment of the molecular interconnect to the patterned silicon oxide substrate. Consequently, we present recent experimental investigations of selective, covalent molecular self-assembly on silicon oxide/silicon nitride blanket and patterned structures using monochloroalkylsilanes as the molecular attachment groups between the substrate and beta-sheet molecular interconnect. Monolayer deposition protocols will be discussed in addition to scanning probe microscopy (SPM) and x-ray photoelectron spectroscopy (XPS) investigations of self-assembled films. It is shown that appropriate cleaning procedures and deposition schedules can be used to produce selective molecular attachment to silicon oxide compared to silicon nitride with a selectivity exceeding 10:1. Demonstrations on patterned silicon oxide/silicon nitride will also be presented.

S8.5
LIGATION AND SELF-ASSEMBLY OF INORGANIC COLLOIDS. Frank E. Osterloh, Hiroki Hiramatsu, Jason S. Martino, Daniel P. Hewitt, University of California at Davis, Department of Chemistry, Davis, CA.

The directed self-assembly of ligand-modified colloidal particles is a promising method for the bulk synthesis of three-dimensional inorganic nanostructures. Important challenges within this biomimetic strategy are the identification of ligand systems that ensure efficient binding between nanoparticles, and the development of methods for the site-selective covalent attachment of these ligands to the surfaces of individual particles. In order to achieve these goals, ligand exchange reactions on inorganic particles with 0D spherical (gold, cadmium sulfide, silica), 1D wire-like (trimolybdenumtrisulfide), and 2D sheet-like (KCa₂Nb₃O₁₀ perovskite) morphologies have been investigated. Ligands contained trimethoxysilyl- and mercapto-groups for covalent attachment to the inorganic particle, and amine, carboxylate, and alkane head groups for chemical recognition. This afforded homogeneously coated particles with mutual binding affinities based on electrostatic and van-der-Waals interactions, which undergo aggregation reactions to form oligomeric nanostructures, a

silica-gold composite for example. Refined ligation protocols, which lead to particles that carry two different types of ligands on different areas of their surfaces, will also be discussed. Further, a colloid based surface patterning method is demonstrated, which allows to produce nano- to microscale rectangular pits on a silicon surface using soluble colloidal perovskite sheets as nanoscale masks.

S8.6
OPTICAL ENCODING OF MICRON-SIZED NANOPOROUS SILICON PARTICLES. Thomas A. Schmedake, Frederique Cunin, Jamie R. Link, Michael J. Sailor, University of California - San Diego, Dept of Chemistry and Biochemistry, La Jolla, CA.

A new method for optically encoding particles for high throughput screening applications will be presented. Encoding is accomplished by generating multi-layer films in porous silicon through controlled etching conditions. Light reflected at each layer boundary interferes with light from the other boundaries generating an interference pattern in the reflection spectrum. This pattern can be used as a fingerprint for identification purposes. Methods of encoding that have been demonstrated so far include Bragg stacks and rugate filters and mismatched multi-layer films. Bragg stacks generated by alternating layers with matched optical thickness (refractive index times metric thickness) produce peaks in reflectivity spectrum with FWHM ~15 nm and are not limited to the optical visible range. Alternatively, multi-layer films with mismatched optical thickness can be designed. The Fourier transform of the resulting interference spectrum gives a series of peaks corresponding to the optical thickness of each layer. Additionally, the intensity of each peak can be adjusted by changing the refractive index contrast at each boundary. Encoded films can be removed from the silicon substrate by electropolishing, then diced (through ultrasonication or mechanical agitation) into micron sized particles, maintaining the original optical signature. Efforts to control the size distribution of the particles will be discussed along with comparisons with alternative encoding methods.

S8.7
ORDERED ARRAYS OF NANOSTRUCTURED (II,Mn)VI SEMICONDUCTORS: FORMATION WITHIN MCM-41 SILICA. Felix J. Brieler, Michael Froeba, Justus Liebig Univ, Institute of Inorganic and Analytical Chemistry, Giessen, GERMANY; Limei Chen, Peter J. Klar, Wolfram Heimbrot, Philips Univ, Dept of Physics and Materials Science Centre, Marburg, GERMANY; Hans-Albrecht Krug von Nidda, Alois Loidl, Univ of Augsburg, Dept of Physics, Augsburg, GERMANY.

We present a novel way of synthesising highly ordered arrays of hollow (II,Mn)VI semiconductor quantum wires by forming the A_{1-x}Mn_xB semiconductor (0 ≤ x ≤ 1) inside the pore system of mesoporous MCM-41 and SBA-15 silica host structures [1]. Therefore mesoporous hosts with different pore diameters in the form of powders and monoliths as well as variable loadings of the host structure with the semiconductor compounds were examined. X-ray diffraction and TEM studies reveal the hexagonal symmetry of these arrays (space group p6m) and confirm the high degree of order. Physisorption measurements show the filling of the pores of the silica host structure. XANES, EXAFS, EPR and Raman studies confirm the good crystalline quality of the incorporated guest species. The effects of the reduction of the lateral dimensions on magnetic and electronic properties of the diluted magnetic semiconductor were studied using PL and PLE spectroscopy as well as SQUID and EPR measurements. A blue shift in the band gap energy by about 200 meV and a stronger band gap bowing compared to bulk is observed. Curie-Weiss parameters are reduced and the paramagnetic to antiferromagnetic phase transition of the Mn-system is suppressed. [1] F.J. Brieler, M. Fröba, L. Chen, P.J. Klar, W. Heimbrot, H.-A. Krug von Nidda, A. Loidl, Chem. Eur. J. 2001, in press.

S8.8
ORIENTED GROWTH OF BORON NITRIDE NANOTUBES FROM SINGLE SOURCE PRECURSORS. Xu Zhang, Dept of Chemistry, National University of Singapore, Ming Lin, IMRE, SINGAPORE and Dept of Chemistry, National Univ of Singapore, Kian-Ping Loh, Dept of Chemistry, National Univ of Singapore, SINGAPORE; Mark Yeardon, IMRE, Singapore and Dept of Materials Science, National Univ of Singapore, SINGAPORE.

The growth chemistry and atomic structure of BN nanotubes have attracted attention recently because the wide band gap suggests interesting novel applications in optoelectronic devices. BN nanotubes may be advantageous compared to carbon nanotubes since they are predicted to display insulating properties independent of their chirality. This property is paired with enhanced ultimate strength and oxidation resistance. Oriented growth of nanotubes on a substrate is an area of active research since there are potential application of aligned nanotube assemblies in, for example, flat-panel type field emission displays. In the case of carbon nanotube synthesis,

significant improvements in terms of oriented growth on substrates have been achieved by growth methods employing catalyst-embedded substrate or overgrowth on molecular sieves. We have succeeded in growing BN nanotubes and thin films on Si(111) in an ultrahigh vacuum growth chamber using a remote discharged atom beam generated from a single-source precursor. Our experiments have been performed in parallel with in-situ UHV TEM investigations using the MERLION system.

S8.9
POLYCATION BEARING Os COMPLEXES DIRECTLY ENCAPSULATED INTO MESOPOROUS SILICA FSM-16 AND ITS ELECTROCATALYTIC REDUCTION OF NITRITE. Wenjiang Li, Youwei You, Zichen Wang, Wing Ying Tam, Department of Physics, Hong Kong University of Science & Technology, HongKong, CHINA; Department of Chemistry, Jilin University, Changchun, CHINA.

Recently functional mesostructured materials containing conductive polymer have been considerable interest because of their especial optical and electrical properties. The application of the functional mesostructured materials is anticipated as sensors, photo conversion or luminescent materials because mesostructured silica offer great advantages over silica gels in shape-selective. We have investigated the assembly of conductive mesostructured composite for electrochemical device application where the redox polymer (PVP-Os) is doped in the mesochannels by a direct self-organizing process. The large specific surface area and porous structure of the mesoporous FSM-16 result in stability of PVP-Os entrapped in this matrix. The mesoporous composite modified-electrodes had the capability of catalyzing the reduction of nitrite, which has high toxicity to human bodies on our environment, and could be expected as amperometric sensors for nitrite. It is found that redox polymer bearing Os complexes adsorbed in mesoporous materials as electron shuttle was able to transfer electrons successfully and improve the response of the modified electrode. The electrochemical behavior of the as-made electrode not only showed much apparently voltammetric peak currents compared to that of an unmodified electrode but also reduced the largely negative potential needed at a bare electrode.

S8.10
QUANTUM INTERFERENCE AND BALLISTIC TRANSMISSION IN NANOTUBE ELECTRON WAVE-GUIDES. Jing Kong, Erhan Yenilmez, Thomas W. Tomblar, Woong Kim, Hongjie Dai, Stanford University, Department of Chemistry and Laboratory for Advanced Materials, Stanford, CA; Robert B. Laughlin, Stanford University, Department of Physics, Stanford, CA; Lei Liu, C.S. Jayanthi, and S.Y. Wu, University of Louisville, Department of Physics, Louisville, KY.

The electron transport properties of well-contacted individual single-walled carbon nanotubes are investigated in the ballistic regime. Phase coherent transport and electron interference manifest as conductance fluctuations as a function of Fermi energy. Resonance with standing waves in finite length tubes and localized states due to imperfections are observed for various Fermi energies. Two units of quantum conductance $2G_0=4e^2/h$ are measured for the first time, corresponding to the maximum conductance limit for ballistic transport in two channels of a nanotube.

S8.11
SPATIALLY CONTROLLED DEPOSITION OF PEPTIDES BY AN ATOMIC FORCE MICROSCOPE USING THE DIP-PEN NANOLITHOGRAPHY TECHNIQUE. Laura Sowards, Gunjan Agarwal, Rajesh Naik, Morley Stone, Materials and Manufacturing Directorate, Air Force Research Labs, Wright-Patterson Air Force Base, Dayton, OH.

Dip-pen nanolithography has been used as a novel patterning technique to deposit materials onto a substrate. Our goal is to use this technique to precisely deposit biological molecules in specific patterns which become the building blocks for structures formed by "bottoms-up" fabrication. Our method involves using a peptide which binds to the substrate on one end and has structurally determined properties on the other end for detection, additional binding, etc. We began our work with a synthetic peptide which has a His-tag that binds to nickel substrate on one end and a Myc-tag which can be tested by immunofluorescence on the other end. The compound was successfully deposited in multiple patterns and verified by both lateral force microscopy and immunofluorescence. The next step is to alter the Myc-tag end of the peptide to incorporate further binding sites and/or desired properties. The main advantage of using the dip-pen nanolithography technique is that it allows for a "bottoms-up" approach to nanoscale structure fabrication by allowing the placement of compounds in specific patterns.

S8.12
TEM ON SELF-ASSEMBLING OF Ni-Di-SILICIDE PRECIPITATES IN A Si(001) MATRIX. M. Falke, H.-J. Hinneberg, Institute of

Physics, Technical University Chemnitz, GERMANY; St. Teichert, Freiburger Compound Materials GmbH, Freiberg, GERMANY; A.L. Bleloch, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

NiSi₂ is a cubic metallic silicide with a lattice constant close to that of Si and therefore inviting for epitaxial growth of thin films and sub-micron structures. We present a TEM study of NiSi₂ precipitate self-assembling in a Si(001) matrix. The samples were prepared by MBE depositing different amounts of Ni applying a trapezoidal or rectangular rate profile together with a constant Si rate. This growth method leads to a certain silicide precipitate distribution in a Si matrix and is known as the first step of Allotaxy for producing metal silicide films in and on Si in a second annealing step. In the samples with a trapezoidal concentration profile of Ni-amounts around 25 at% in the Si matrix a 3-dimensional assembling of nm-sized A-type NiSi₂ precipitates underneath a broad distorted layer of bigger A- and B-type NiSi₂ precipitates was observed. The 2-dimensional assembling of silicide precipitates in several layers parallel to the substrate surface is known from literature for other metal/Si systems and caused by special diffusion phenomena appearing in inhomogeneous precipitate distributions. But, the observed assembling in an additional third dimension - one above each other perpendicular to the Si matrix surface was not reported by other research groups up to now. A detailed study of this special kind of assembling was carried out investigating the samples containing small Ni-amounts of around a few at% deposited applying the rectangular rate profile. In this case under certain deposition conditions only the nm-sized A-type precipitates appear assembled one above each other in chains perpendicular to the Si matrix surface without arranging in layers parallel to this surface. Cross-section HRTEM and electron diffraction in [001] zone axis proved the A-type NiSi₂ lattice of the precipitates. Their tetrahedral like shape (as concluded from the [110] zone axis images) is difficult to determine exactly. EELS measurements with high spatial resolution confirmed the location of Ni inside the precipitates. Lateral TEM investigations revealed radial lattice distortions around them. We conclude that local strain which can be responsible for energetically favoured nucleation positions one above each other (as known e.g. from strained Si/Ge systems) and matrix defects are important factors influencing the Ni diffusion and thus the silicide precipitate assembling in the investigated samples.

S8.13
THE FABRICATION AND CHARACTERIZATION OF CARBON NANOTUBE NANO-ELECTRODE ENSEMBLE FOR CHEMICAL/BIOSENSOR APPLICATIONS. Jun Li, Ramsey Stevens, Bin Chen, Alan Cassell, Cattien Nguyen, Jie Han, ELORET Corp., NASA Ames Research Center, Moffett Field, CA; Lance Delzeit, Meyya Meyyappan, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, CA.

Nanoelectrode ensembles are very attractive electroanalytical tools with greatly improved sensitivity for the application as chemical and biosensors. So far nanoelectrode ensembles were prepared by template synthesis using nanoporous membranes or nanoscale defects created in the self-assembled organic monolayers on a Au surface. We report here on a new approach to fabricate solid-state nanoelectrode ensemble by bottom-up scheme using well-aligned multi-walled carbon nanotube arrays on a conducting substrate. Carbon nanotubes have many unique physical and materials properties. For our application, they are expected to present the similar properties as other carbon electrodes which are the most popularly used electrodes for electroanalytical applications. We manipulated the carbon nanotube arrays in two ways for different applications. They can be electropolymerized with a uniform polypyrrole film which modifies their surface and mechanical properties. This approach stabilizes the carbon nanotube array electrode in liquid solution and can be adapted for the applications which need large surface area. The nanotube arrays can be also filled up with dielectrics and polished to a smooth surface with only the end of the individual carbon nanotubes exposed. This novel approach provides an easy way in which the electronic properties of individual carbon nanotubes can be investigated with current sensing AFM and IV measurements. We will present our preliminary results on the electronic and electrochemical characterization of thus prepared nanoelectrode ensemble and discuss the future application as chemical and biosensors.

S8.14
THE RESTRUCTURING OF NANOPARTICLE CHAIN AGGREGATES. Adamos Dalis, Sheldon Friedlander, University of California-Los Angeles, Dept of Chemical Engineering, Los Angeles, CA.

Previous electron microscope studies in our laboratory have shown that nanoparticle chain aggregates (NCA) of inorganic oxides have elastic properties. Measurements were made with titania, alumina, and iron oxide NCA generated by laser ablation (Ogawa et al., 2000).

Primary particles were 5 to 10 nm in diameter, and the lengths of the NCA were of the order of 0.5 microns. Chain stretching took place by generating holes in the formvar films of an electron micrograph grid on which NCA had been deposited. NCA stretching appears to begin with the rotation and/or sliding of adjacent nanocrystals. Most of the NCA lengthening results from the separation of kinked chain segments held together by weak, probably van der Waals forces. NCA strains up to 90% were observed. NCA elastic behavior could be associated with aggregate substructures that unravel under tension and reform when tension is relaxed. We simulate by means of a Monte Carlo algorithm the formation of these substructures in a gas process starting from a straight chain. The algorithm is a modified version of one used in simulating polymer dynamics. The dynamic behavior of chain aggregates may have applications to the properties of composite materials that incorporate NCA, such as commercial rubber, and to the biological (health) effects of inhaled NCA such as diesel soot.

References:

K. Ogawa, T. Vogt, M. Ullmann, S. Johnson and S.K. Friedlander, (2000) "Elastic Properties of Nanoparticle Chain Aggregates of Titania, Alumina and Iron Oxide Generated by Laser Ablation", *J. Appl. Phys.*, 87, 63.

S8.15

TWO-DIMENSIONAL MOLECULAR GRIDS ON MERCURY.

Natalia Varaksa, Lubomir Pospisil, Zbynek Janousek, Bohumir Gruner, Bing Wang, Jaroslav Pecka, Thomas Magnera, and Josef Michl; Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO; J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, CZECH REPUBLIC.

We have constructed a Langmuir-Blodgett trough for measurement of compression isotherms on a mercury-electrolyte interface under conditions of controlled potential, and used it for an examination of two-dimensional networks formed from star-shaped connectors and linear couplers. The ultimate objective is to construct sturdy assemblies with a minimum of defects and a maximum domain size for purposes such as size-based molecular separation and assembly of regular arrays of surface-mounted dipolar rotors. We have therefore used readily reversible coupling reactions and attempted to work under thermodynamic control, with the expectation that it may be possible to use a slow exchange reaction later to replace the initial "phantom" couplers with covalently bound sturdy couplers later without disturbing the order in the initially equilibrated grid. For the formation of square grids, we used the cross-shaped lanthanum(III) bis(meso-tetrapyrrolylporphyrin) sandwich anion as the connector and hydrogen-bonding hydroquinone derivatives as linear couplers. For hexagonal grids, we used trigonal connectors derived from 1,3,5-tris-carboranylbenzenes by attachment of thioether-carrying alkane chains. In this instance, the linear couplers are mercury cations delivered from the mercury interface at sufficiently positive applied potentials as monitored by cyclic voltammetry (frequently, the open circuit potential is adequate). The coupling interaction is believed to be the ligation of the thioether sulfur atoms to the mercury cations. These grids are very sturdy, show no tendency to dissolve in the electrolyte even under compression on the LB trough, and yield ordinary LB isotherms from which molecular areas are readily deduced. In contrast, at more negative potentials, the merely physisorbed connectors are removed from the surface easily under moderate compression and their LB isotherms yield nominal molecular areas of zero. We have observed hysteretic behavior in that once formed, the surface networks remain on the surface until the applied potential reaches a value much more negative than needed for the reduction of the mercury cations; the nature of the coupler and of the connector linking interactions under these circumstances is not known. A clear distinction between physisorption and grid formation and evidence for hysteresis are also provided by impedance measurements. Only indirect evidence for the structure of the grids is available at this time: molecular area from the LB isotherm, area per redox center (mercury ion) from coulometry, and molecular modeling. This work has been supported by the US Army Research Office.

S8.16

A STUDY OF THE CRYSTALLOGRAPHY AND GROWTH MECHANISM OF GOLD NANORODS SYNTHESIZED USING A SEED MEDIATED STEP BY STEP GROWTH PROCESS.

Christopher Johnson, Erik Dujardin, Sean Davis, Stephen Mann, University of Bristol, School of Chemistry, Bristol, UNITED KINGDOM; Catherine Murphy, University of South Carolina, Department of Chemistry and Biochemistry, Columbia, SC.

Symmetry breaking and the associated introduction of anisotropy in nanoparticle systems creating complex structures have been achieved by two distinct approaches. Firstly lower symmetries can be obtained by assembling spherical particles in anisotropic environments. The synthesis of anisotropic nanoparticles that are capable of transferring their anisotropy to superstructures even by isotropic interactions

constitutes the second strategy [1]. A wide variety of materials have recently been shown to grow anisotropically in the form of rods including FCC metals. To rationally design these superstructures it is necessary to understand and control the formation of the nanorod building blocks. This requires an appreciation of their structure and growth mechanism. Here we present a HRTEM and electron diffraction structural study of mature gold nanorods prepared by a seed mediated step by step process [2], as well as a thorough morphological and statistical study of the nanorods during earlier stages of growth. This gave an understanding of the involvement of five-fold twinning in the anisotropic growth of cubic crystals on a nanometre scale [3]. [1] E. Dujardin, L. Hsin, C.R. Wang, S. Mann, *Chem. Commun.*, 2001, 1264. [2] N.R. Jana, L. Gearheart, C.J. Murphy, *J. Phys. Chem. B.*, 2001, 105, 4065. [3] C. Johnson, E. Dujardin, S. Davis, C.J. Murphy, S. Mann, In preparation.

S8.17

THE CURVATURE ENHANCED ACCELERATOR COVERAGE MECHANISM BEHIND SUPERCONFORMAL ELECTRODEPOSITION: MODEL AND EXPERIMENT.

Daniel Josell, Thomas Moffat and Daniel Wheeler, NIST, Gaithersburg, MD.

We explain the mechanism by which changes of surface area during electrodeposition lead to local variations in coverage of adsorbed additives, inducing location-dependent metal electrodeposition rates and superconformal filling of features. Simulations from a model based on this mechanism are compared to filling experiments for trenches as small as 90 nm wide and ~0.45 microns deep. We first identify electrolytes that yield superconformal electrodeposition of metal in trenches [1]. All kinetic parameters describing the rate of additive accumulation on metal surfaces as well as the impact of the accumulation on metal deposition rate are obtained from studies of deposition on flat metal specimens. The dilute additive that accelerates metal deposition accumulates on the metal surface, displacing a deposition-inhibiting additive. Kinetic parameters are found to be linear in the fractional coverage of the accelerator, which saturates at one monolayer coverage [2,3]. Accumulation of the dilute accelerator is described by diffusion across a boundary layer and deposition voltage dependent interface kinetics. Where specimens are not flat (i.e., non-zero curvature), area change during deposition causes additional change of local accelerator coverage through mass conservation. Accumulation of accelerator, and thus the deposition rate, at the bottoms of superfilling features is found to be dominated by this area change effect. The model, with no free parameters, is used to predict filling behavior of lithographically patterned features. Predictions are in excellent agreement with experimental results; initial period of conformal growth, subsequent superfill, and development of overfill bump are all observed and explained as is fill versus void formation for different deposition voltages, electrolyte compositions and feature dimensions [2-4]. Insufficient accelerator in the electrolyte results in minimal accelerator accumulation on all surfaces, conformal growth and failure to fill higher aspect ratio features. Near optimal electrolyte concentration results in limited accumulation on the sidewalls coupled with rapid increase of coverage on the bottom surface due to area-reduction and superconformal filling. Excessively high electrolyte concentration leads to saturation on all surfaces and reversion to conformal deposition.

1. T.P. Moffat, J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelly, G.R. Stafford and D. Josell, *J. Electrochem. Soc.*, 147, 4524 (2000).
2. T.P. Moffat, D. Wheeler, W.H. Huber, and D. Josell, *Electrochem. Solid-State Lett.* 4, C26 (2001).
3. D. Josell, T.P. Moffat, D. Wheeler and W.H. Huber, *Phys. Rev. Lett.* 71, 016102 (2001).
4. D. Josell, D. Wheeler, W.H. Huber, J.E. Bonevich and T.P. Moffat, A Simple Equation for Predicting Superconformal Electrodeposition in Submicron Trenches, *J. Electrochem. Soc.* (in press).

S8.18

CHEMICAL PRECURSOR ROUTES TO NANOSTRUCTURED NONOXIDE CERAMICS.

Kersten M. Forsthoefel, Mark J. Pender, Larry G. Sneddon, Univ of Pennsylvania, Dept of Chemistry, Philadelphia, PA.

Porous alumina templates have recently been widely used to generate nanostructures from a variety of materials including polymers, carbon, metals, semiconductors and ceramics. We report here an efficient route to boron carbide, boron nitride, and silicon carbide ceramic nanofibers and nanotubes employing these templating methods in conjunction with newly developed molecular and polymeric precursors. Thus, dip-coating or vacuum filtration of solutions of 6,6-(CH₂)-(B₁₀H₁₃)₂ or polyhexenyldodecaborane through alumina templates followed by pyrolysis and etchback in 48% HF yields boron carbide nanofibers or nanotubes. Boron nitride nanotubes have

been generated in a similar fashion by employing the precursor polyborazylene, while silicon carbide nanotubules have been generated from commercially available polymeric precursors. In all cases, SEM and TEM analyses show aligned, monodispersed ensembles of nanofibers and nanotubules. Structural control of the end-products can be varied through changes in concentration of the precursor solution, the number of alumina membrane treatments and pore size of the alumina template.

S8.19
COMPOSITE NANOPARTICLES FOR OPTICAL APPLICATIONS. Virginie Hornebecq, Sebastian Polarz, Markus Antonietti, Max-Planck-Institute of Colloids and Interfaces, Dept of Colloids, Potsdam, GERMANY; Mona Treguer-Delapierre, Thierry Cardinal, Institut de Chimie de la Matière Condensée de Bordeaux, Pessac, FRANCE.

The simultaneous increase of both, the luminescence and the non-linear optical properties is one of the main current challenges for optical devices (commutation, optical storage?). Recently, some works have shown that composite materials based on the interaction of metal nanoparticles and a luminescent center (semi-conductor or metal ion) are able to exhibit such optical behavior. The problem is first to control the size, the distribution and the distance of the two components of the composite materials and, secondly, to include these composite materials in an amorphous matrix in order to make the original properties accessible for the applications. In order to solve those problems, the idea is to induce the synthesis of the composite materials inside ordered mesoporous silica with well controlled pore size and pore topology. In the present study, we have first synthesized Ag-nanoparticles in the porous silica matrix. Starting from a porous silica matrix with different type and size of pores (from 2 to 10 nm) -in order to control the homogeneity of the dispersion and the concentration of these Ag-nanoparticles- and from a silver sulfate solution, the radiation chemical method is used to reduced silver ions and to obtain Ag-nanoparticles. The resulting materials are characterized, from a physico-chemical point of view, using electronic microscopy (TEM and HRTEM), absorption spectroscopy and vibrational spectroscopy (Infra-red and Raman). Optical properties of these materials are investigated using time resolved luminescence spectroscopy (in visible and in near infra-red). Non-linear optical properties are also investigated using interferometry. A particular attention is focused on the understanding of the confinement effect of particles on the optical properties.

S8.20
FABRICATION OF LOW-DIMENSIONAL SUPERLATTICES OF GOLD NANOPARTICLES. Toshiharu Teranishi, Japan Adv Inst of Sci and Tech, School of Materials Science, Ishikawa, Japan Sci and Tech Co, PRESTO, Fukuoka, JAPAN; Akira Sugawara, Takami Shimizu, Takuhiro, Hayashi, Mikio Miyake, Japan Adv Inst of Sci and Tech, School of Materials Science, Ishikawa, JAPAN; Masa-aki Haga, Chuo Univ, Dept of Applied Chemistry, Tokyo, JAPAN.

Low dimensional (1D and 2D) superlattices of gold (Au) nanoparticles are the promising materials for future nanoelectronic and nanooptical devices. The 2D superlattices of Au nanoparticles larger than 2 nm would be applied to the nonlinear optical devices, while those of smaller particles as well as 1D chains of nanoparticles would be done to the single electron tunneling devices using Coulomb blockade phenomenon at room temperature. Recently, we have developed the methods to control the size of alkanethiol-protected Au nanoparticles larger than 2 nm with quite narrow size distributions by the heat-treatment of 1.5 nm Au nanoparticles in the solid state. The particle sizes could be controlled from 3.4 to 9.7 nm by varying the heat-treatment temperature from 150 to 250°C. These Au nanoparticles easily formed 2D superlattices with hexagonal packing by self-assembly or LB technique on various flat substrates. Then we have successfully prepared the Au nanoparticles smaller than 2 nm by using a newly-synthesized ligand, 2,6-bis(1-(thioalkyl)benzimidazol-2-yl)pyridine (TC_nBIP, n: the number of methylene groups in alkyl chain), which was designed to have disulfide group and 2,6-bis(benzimidazol-2-yl)pyridine (BIP) group, the former serving to produce small Au nanoparticles and the latter inducing the interaction between the ligands or serving as a tridentate ligand. The 2D superlattices of TC_nBIP-protected Au nanoparticles with various interparticle spacings were fabricated by the self-assembly or the bridging complexation of Fe(II) with two TC_nBIP ligands. Furthermore, planar arrays of 1D chains of 3.4 nm alkanethiol-protected Au nanoparticles were fabricated on nanoscale ridge-and-valley structured carbon substrates with the valley depth and period of a few and ~20 nm, respectively, which were prepared from the faceted (110) planes of sodium chloride crystals by a vacuum process.

S8.21
GROWTH OF CARBON NANOTUBES WITH CONTROLLED

PROPERTIES FOR FIELD EMISSION AND NANOELECTRONIC APPLICATIONS. Lifeng Dong, Jun Jiao, Catherine L. Mosher, and Sean Foxley, Physics Department, Portland State University, Portland, OR.

Due to their unique electrical properties and extremely high aspect ratios, carbon nanotubes are promising candidates for applications in field emission and nanoelectronics. However, these potential applications have not yet been actualized, due to an inability to synthesize carbon nanotubes with controlled properties. Using chemical vapor deposition (CVD) it was found that controlling the catalyst deposition and growth parameters could influence the alignment, orientation and morphologies of nanotubes. For field emission applications, a liquid catalyst was directly spin-coated onto a porous silicon substrate. Carbon nanotubes grew in well-aligned bundles perpendicular to the substrate surface, which is beneficial for such applications. For nanoelectronic applications, it will be useful to have carbon nanotube connections between electrodes. Therefore, in another approach, the liquid catalyst was spin-coated onto a patterned piece of polydimethyl siloxane (PDMS), and then stamped onto a porous silicon substrate. The resulting growth was an array of nanotube columns, with orientation parallel to the substrate. Some nanotube bridges were formed between columns. It is desirable to control aspects of carbon nanotubes aside from their alignment and orientation, such as their internal structures and morphologies. Through characterization and analysis of samples with High Resolution Transmission Electron Microscope (HRTEM), Scanning Electron Microscope (SEM), Selective Area Diffraction (SAD) and X-ray Diffraction Spectrum (XDS), it was found that these aspects varied with the type of hydrocarbon gas used in the CVD process. The use of CH₄ yielded many single-walled nanotubes, as well as several double-walled and some multi-walled nanotubes. The use of C₂H₂ resulted in only multi-walled nanotubes. Experimental results demonstrated that H₂ plays an important role in the formation of carbon nanotubes. The use of H₂ during the CVD process has three effects: it dramatically reduces the average carbon nanotube diameter, prevents the formation of amorphous carbon particles, and increases the growth rate of carbon nanotubes. A possible growth mechanism, including the effect of a high ratio of H₂ to C₂H₂, is suggested for the growth of well-aligned carbon nanotubes with uniform diameters.

S8.22
Abstract Withdrawn.

S8.23
Abstract Withdrawn.

S8.24
NANOSCALE ELECTRONICS FROM ASSEMBLED NANOWIRE BUILDING BLOCKS. Xiangfeng Duan, Charles Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

One-dimensional structures, such as nanowires, are ideal building blocks for nanoscale electronics due to their unique physical dimension and electronic properties. To fully exploit the potential of such structures, we first present a rational approach for the synthesis of a wide range of semiconductor nanowire materials with controlled chemical composition, physical dimension and electronic properties. Electrical characterizations of individual nanowires by two terminal, gate-dependent transport measurements demonstrate that these nanowires can be doped as either n- or p-type semiconductors in a controlled way. We will then present a rational approach for orthogonal assembly of nanowires into multi-terminal devices such as field effect transistors, crossed p-n junctions, light emitting diodes and tunneling diodes. In addition, when combined with redox molecules, these nanowires can also be assembled into non-volatile memory device and device arrays. Lastly, The implication of use nanowires as building blocks for high-density integrated device arrays will be discussed.

S8.25
NANOSCALE SELF-ASSEMBLY IN RIGID-ROD CONJUGATED POLYMER THIN. Tianxi Liu, Bin Liu, Wuiwui Chauhari Tjiu, Kee Chua Toh, Ailin Ding, Wei Wang, Molecular and Bio-Materials Laboratory, Institute of Materials Research and Engineering, Singapore, SINGAPORE.

Conjugated polymers are organic semiconductors possessing a number of features (such as solution processability, band gap tuning by chemical structure and self-organization) which make them very attractive as potential replacements for conventional inorganic semiconductors. Recently, some conjugated rigid-rod polymers received increasing attention mainly due to the shape-persistent character and optical and electronic applications. Of particular interests are cases where thin films of conjugated polymers on different substrates self-assemble into "nanopatterns" for the long-term goal of nanodevice construction.

In this study, a blue light emitting material, poly[2,7-(9,9-dihexyl-fluorene)-co-alt-2,5-dihexyloxy-para-phenylene] ($M_n=21400$; PD=1.6) was synthesized via the Suzuki coupling reaction. The polymer possesses two hexyl chains on each rigid phenylene ring, which makes it soluble in common organic solvents, such as chloroform and xylene, and it exhibits lyotropic liquid crystalline (LC) behavior by polarized light microscope. Both AFM and TEM images show that the supramolecular structure self-assembled during evaporation of solvent consists of continuous LC phase and isolated crystalline (spherulite) phase. The thickness of individual lamellae in LC phase is not uniform. Most lamellae are tapered, i.e., they end in sharp wedges. Typically, the average thickness of lamellae in LC is approximately 60-70 nm, while that in crystalline phase is around 20-30 nm. The existence of the two ordered domains was also confirmed by SAXS results. Since the length of repeating unit is about 1.26 nm by modeling, the average molecular length is about 44.1 nm, indicating that extended-chain lamellae are developed in the LC state. Hence, the distribution of lamellar thickness reflects the distribution of molecular length owing to an extended-chain conformation in the lamellae. Among conjugated polymers, liquid crystallinity is common for the "hair rod" polymers which have rigid backbones and flexible side chains. The feature of liquid crystallinity allows fabrication of an EL device that emits highly polarized light by forming highly ordered PL films and that is of potential for use as a backlight for LC display devices. Also, it may be expected that the control of the side-chain lengths via synthesis opens the way to fine tuning the LC and/or crystalline behavior. The effects of the length of side segments and molecular weight on the formation of (liquid) crystalline morphology are currently being investigated.

S8.26

NOVEL NANOSIZED PATTERNING TECHNIQUES USING AN ELECTROPULSED SCANNING PROBE MICROSCOPE.

Pedro Brogueira, Physics Dept. and ICEMS, Instituto Superior Tecnico, Lisboa, PORTUGAL; Luis Viseu Melo, Physics Dept., Instituto Superior Tecnico, Lisboa, PORTUGAL.

Scanning Probe Microscopes (SPM) have been used to change surfaces at nanometer scales. We report the deposition of user defined patterns in a controlled manner using an electropulsed SPM. The patterns were fabricated by applying -12V electrical pulses in the 10 to 40Hz range between a commercial CoCr conductive tip and a crystalline n-doped Si wafer. The tip damage during deposition is negligible as measurements on the same surface region before and after deposition show no detectable differences. Immediately after deposition the same tip is used for measuring the fabricated patterns. Applying one isolated electrical pulse results in a pixel with a typical size of the order of 30nm. By combining the scanning ability of the SPM with the atmospheric deposition induced by electrical pulses on the tip, patterns can be fabricated. For example, by applying electrical pulses during a 25nm x 800nm tip scan in AFM tapping mode, at 40Hz, lines with 65nm width by 828nm length were obtained (in good agreement with the expected dimensions of 55nm x 830nm derived from the pixel size and the scan range). The height of the deposited patterns is of the order of 2 to 3nm, and was found to increase with the density of scan lines. The RMS roughness of the deposited material is shown to be strongly dependent on the electrical pulse frequency. The smoother pattern surface results from the 40Hz pulse frequency. No deposition was observed at higher frequencies.

S8.27

SILVER SELENIDE NANOWIRE ARRAYS AND THEIR MAGNETORESISTANCE. Ruizhi Chen, Peking Univ, Institute of Physical Chemistry, Beijing, PR CHINA; Dongsheng Xu, Peking Univ, Institute of Physical Chemistry, Beijing, PR CHINA; Guolin, Guo, Peking Univ, Institute of Physical Chemistry, Beijing, PR CHINA; Weilie Zhou, Advanced Materials Research Institute, Univ. of New Orleans, New Orleans, LA; Yuehua Chen, Peking Univ, Dept, of Chemistry, Beijing, PR CHINA.

Silver selenide is a well-known superionic conductor. Its low-temperature phase is a semiconductor with a narrow direct band gap and high carrier mobilities which could be applied in various fields of microelectronics. Recently, it was reported that nonstoichiometric silver selenide show large positive magnetoresistance (MR). The significant MR effect at room temperature and its linear dependence on magnetic field will make it a promising material for applications in the magnetic field sensing devices. The nanowires of large positive MR materials will show promise in exploring new fundamental phenomena in transport properties and technological applications in magnetic nanodevices. The purposes of this paper are 2-fold:(1) To prepare silver selenide nanowire arrays and to provide detailed structural characterization of the nanostructured materials. (2) To study relationship between their functional properties, especially magnetoresistance, with nanostructures. Silver selenide nanowires were prepared by a dc electrodeposition process in anodic aluminum oxide(AAO) templates

from an aqueous acid electrolyte at room temperature. The XRD, EDAX, TEM, and HRTEM have been employed to characterize the nanowires arrays. The results showed that the structure of silver selenide nanowires is a uniform crystalline with a (002) growth direction. The resistivity measurement were carried out by standard four probe method using a ac bridge technique. The magneto-resistance of the nanowires with diameters from 20 to 100nm in magnetic field have been investigated. The experimental details and results will be described and discussed in this paper.

S8.28

SPONTANEOUS FORMATION OF NANOCRYSTAL MONOLAYER FILMS AT AIR/WATER INTERFACE. Harumi Asami^{1,2}, Itaru Kamiya², Masahiko Hara^{1,3}. ¹Tokyo Institute of Technology, Dept of Electronic Chem, Yokohama, JAPAN. ²Mitsubishi Chemical Corp, Yokohama, JAPAN. ³RIKEN, Frontier, Wako, JAPAN.

Chemically synthesized semiconductor nanocrystals (NCs), also known as colloidal quantum dots, are small clusters whose size is ca. 1 to 10 nm in diameter. The self-assembled structure of NCs in low dimensions has attracted much attention both from the scientific and the technological points of view. However, controlling self-assembled NC structures has not been an easy task. In an attempt to achieve such goal, we have performed investigation on fabrication of self-assembled films of tri-n-octylphosphine oxide-capped CdSe NCs. NC monolayer films formed spontaneously at the air/water interface were transferred onto Si wafers using a horizontal lift-off technique while changing the surface area, or lateral compression, by Langmuir trough and the choice of organic solvent to disperse the NCs on water surface. We observed that the use of CHCl₃ as solvent resulted in larger surface pressure in the weak compression (large area) regime with respect to the case with hexane. This result suggests that submonolayer films with different structures can be prepared by the choice of solvent. To confirm this, fluorescence microscopy and atomic force microscopy were performed to observe the self-assembled structure of submonolayer NC films transferred onto Si wafers. NC monolayer film formed with CHCl₃ solution showed arabesque-like structure. While densely packed domains and many cracks between were observed with hexane solution when the surface was compressed to the same area. The difference in the structure of the NC monolayer films will be discussed in terms of solubility, interfacial interaction of NCs with solvent and water, etc.

S8.29

STRUCTURAL ANALYSES AND MAGNETIC PROPERTIES OF MULTIPLE-STRUCTURE MULTILAYERED Co/Au FILMS.

Rimika Koiwai, Masanobu Kobayashi, Chiba Institute of Technology, Dept of Material Science, Chiba, JAPAN; Yoshinori Maeno, Oki Electric Industry Co., Ltd, Advanced Device Lab, Tokyo, JAPAN.

We have studied the multilayered Co/Au and Co/Pd films known as perpendicular magnetization films. Both films showed some different changes at the interfaces between Co and noble metals with annealing, since Co-Au is a eutectic system while Co-Pd is an isomorphous system. Multiple-structure multilayered Co/Au films (MSM Co/Au), which consists of periodic piles of multilayered Co/Au film layers and Au thin film layers, are expected to show more interesting characters than former Co/Au films. Structural analyses and magnetic properties of these samples were analyzed by XRD, profile fittings, and VSM. The MSM Co/Au films showed the peculiar XRD peaks based on two kinds of periodic thicknesses, Λ_M and Λ_T . Λ_M paired a Co layer and a Au layer. This periodic thickness is the same period as Co/Au films. Λ_T paired a Au layer and Λ_M which was piled a few times. For profile fittings, we assumed the extended 3-step model. This model includes two fluctuations of periodic thickness and alloyed layer thickness at the interface. The detailed changes of alloyed layers at the interfaces with annealing were obtained by this profile fitting. The perpendicular magnetizations are influenced by periodic thicknesses or pile numbers. However MSM Co/Au films have the perpendicular magnetizations as former Co/Au films. Moreover it was found that the magnetization curves of MSM Co/Pd have multi-stage shapes. Therefore it is expected that the similar magnetization curves should obtain in MSM Co/Au films.

S8.30

STRUCTURAL AND OPTICAL PROPERTIES OF VERTICALLY WELL-ALIGNED ZnO NANOWIRES GROWN BY METALORGANIC VAPOR PHASE EPITAXY. W.I. Park, D.H. Kim, S.-W. Jung, Gyu-Chul Yi, H.M. Jang, Pohang University of Science and Technology (POSTECH), Dept of Materials Sci. and Eng., Pohang, KOREA ROK.

One-dimensional semiconductor nanowires have attracted increasing interest due to their novel physical properties and diversity for potential electronic and photonic device applications. Many nanowires including Si, Ge, InP, GaAs, GaN, and ZnO have been fabricated for applications since Si submicron whiskers were grown using a

catalysis-assisted vapor-liquid-solid (VLS) growth method. In VLS nanowire growth, impurities act as catalysts and play an essential role in forming liquid alloy droplets for deposition on a preferred site. Meanwhile, during the catalysis-assisted growth, the catalyst might be incorporated into nanowires, and generate unintentional defect levels. However, even low defect concentrations affect physical properties of semiconductors, and hence unintentionally doped impurities are detrimental to device fabrication. In this letter, we report MOVPE growth of ZnO nanowires without employing any metal catalysts usually needed in other methods. More importantly, nanowires grown in this research are vertically well-aligned and exhibit uniform thickness and length distributions, which are very useful for many device applications. The nanowires were grown on $\text{Al}_2\text{O}_3(00\bullet 1)$ substrates at growth temperatures of 400-600°C using MOVPE. Electron microscopy revealed that nanowires with uniform distributions in their diameters, lengths, and densities were grown vertically from the substrates. The mean diameter of the nanowires is as narrow as 20 nm. In addition, X-ray diffraction measurements clearly show that ZnO nanowires were grown epitaxially with homogeneous in-plane alignment as well as a c-axis orientation. More importantly, from photoluminescence spectra of the nanowires strong and narrow excitonic emission and extremely weak deep level emission were observed, indicating that the nanowires are of high optical quality. Further structural and optical properties of the nanowires will be presented.

S8.31

STRUCTURE AND FIELD ELECTRON EMISSION OF CARBON NANOTUBES DEPENDENT ON GROWTH TEMPERATURE.

Yoon Huh, Jeong Yong Lee, Korea Advanced Institute of Science and Technology, Dept of Materials Science and Engineering, Daejeon, KOREA; Tae Jae Lee, Seung Chul Lyu, Cheol Jin Lee, Kunsan National Univ, School of Electrical Engineering, Kunsan, KOREA.

The growth of carbon nanotubes (CNTs) using chemical vapor deposition (CVD) methods has attracted much attention because of many advantages such as high purity, high yield, selective growth, and vertical alignment. It has been found that the structure of carbon materials is dependent on the growth parameters such as reaction temperature, catalyst, reaction gas, etc. A strict control of growth condition allows to design the structure of carbon materials in the nanometer regime. Especially the growth temperature is crucial for selective and controlled growth of CNTs, which is necessary for many applications. A number of research groups reported that the growth of CNTs could be controlled by varying the growth parameters of CVD process. However, there are not many systematic studies on the temperature-controlled growth of CNTs using thermal CVD. This present work deals with the temperature dependence on the growth and structure of CNTs grown by thermal CVD. The vertically aligned CNTs are synthesized on iron (Fe)-deposited silicon oxide substrate by thermal CVD using acetylene gas at temperatures in the range 750-950°C. Configuration and structural characteristics of CNTs have been investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo gravimetric analysis (TGA), and Raman spectroscopy. As the growth temperature increases from 750 to 950°C, the growth rate and the average diameter increase while the density decreases by a factor of about 2. TEM images show that the relative amount of crystalline graphitic sheets increases with increasing the growth temperature and a higher degree of crystalline perfection can be achieved at 950°C. The HRTEM images, TGA data, and Raman spectra reveal consistently that the degree of crystalline perfection increases progressively as the growth temperature increases. This result demonstrates that the growth rate, diameter, density, and crystallinity of carbon nanotubes can be controlled with the growth temperature.

S8.32

Abstract Withdrawn.

S8.33

SYNTHESIS OF MESOPOROUS TITANIA. T.Y. Kim, S.K. Lee, W.I. Lee, Inha Univ, Dept of Chemistry, Incheon, KOREA.

Differently from silicate-based mesoporous materials, the synthetic route of mesoporous titania, which might have promising applications for photocatalysis or solar energy conversion, has not been established, so far. In this work, we synthesized mesoporous titania with two different liquid crystal templating methods (neutral templating method and charge-matched templating method), applying several Ti-precursors and surfactants. The structure of prepared materials were characterized by XRD and TEM, and BET. We have found that the transformation of hexagonal mesoporous structure to lamellar structure is dependent the on titanium/surfactant molar ratio, and pH of solution.

S8.34

TI-ISLAND-CATALYZED Si NANOWIRE GROWTH BY

GAS-SOURCE MBE: MORPHOLOGY, ORIENTATION, AND TWINNING. Qiang Tang¹, Xian Liu¹, Ted Kamins², Glenn S.

Solomon¹, James S. Harris¹. ¹Stanford University, Stanford, CA. ²Hewlett-Packard Laboratories, Palo Alto, CA.

We have grown silicon nanowires catalyzed by Ti islands by molecular beam epitaxy (MBE) using Si_2H_6 as the gas source with in situ reflection high-energy electron diffraction (RHEED). Approximately one monolayer of Ti was deposited on Si(001) wafers at 550°C and then annealed above 800°C to form TiSi_x islands. The Si nanowires were then grown at 500°C~600°C by directing a Si_2H_6 molecular beam toward the wafer, with the TiSi_x islands as seeds. After annealing, but before Si growth, the stoichiometric TiSi_2 (C49) phase was observed with RHEED. The silicon nanowires are typically between 20 and 40 nanometers in diameter and several hundred nanometers long. RHEED patterns indicate that the growth directions are $\langle 112 \rangle$, consistent with some previous results. The nanowires changed their growth direction several times during growth, resulting in complex RHEED patterns. The experimental RHEED patterns perfectly match simulated RHEED patterns calculated assuming that the nanowires change their direction by twinning along (111) planes. When we grew long (hundreds of nanometers) nanowires, we observe RHEED patterns of epitaxial silicon nanowires, first-order twinned nanowires (twinned relative to the substrate orientation), second-order twinned nanowires (twinned relative to the first-order twin), and TiSi_2 simultaneously. Since each twinning creates 3 new crystal orientations, third- and higher-order twins have many orientations, which makes the intensity of the RHEED pattern from each orientation too weak to be observed. When we grew short nanowires (tens of nanometers long), we could not see RHEED patterns of the second-order twin. Nanowire growth without substrate rotation also results in the reduction or elimination of the second-order twin components of the RHEED pattern, while scanning-electron microscopy indicates less change of the nanowire growth direction.

S8.35

HEAT-INDUCED SIZE EVOLUTION OF GOLD NANOPARTICLES IN SOLID STATE AND FABRICATION OF LB MONOLAYER FILM.

Takami Shimizu, Toshiharu Teranishi, Satoshi Hasegawa, Mikio Miyake, Japan Adv Inst of Sci and Tech, School of Materials Science, Ishikawa, JAPAN.

Two-dimensional (2D) superlattices of metal nanoparticles have been fabricated as promising materials for optical and nanoelectronic devices. Especially, the 2D superlattices of gold (Au) nanoparticles larger than 2 nm would be applied to the nonlinear optical devices. For not only fabricating the perfect superlattices of Au nanoparticles but also investigating their size-dependent physical and chemical properties, a precise control of particle size is very important. Recently, we have developed a simple method to control the size of alkanethiol-protected Au nanoparticles by the heat-treatment of 1.5 nm Au nanoparticles in the solid state. The nanoparticles uniformly grow until they become stable at the heat-treatment temperature because the smaller nanoparticle has a lower melting point. The particle sizes could be controlled from 3.4 to 9.7 nm with quite narrow size distributions by varying the heat-treatment temperature from 150 to 250°C. These Au nanoparticles easily formed self-assembled 2D superlattices with hexagonal packing covering the area of a few μm^2 on the flat carbon substrates, though the larger domain size of 2D superlattices is required for the optical devices. Then we adopted LB technique to achieve wide-range 2D superlattices of Au nanoparticles. When the chloroform solution of alkanethiol-protected Au nanoparticles was spread onto water subphase, the monolayer of Au nanoparticles was formed at a proper surface pressure. This monolayer with hexagonal packing could be easily transferred to the glass substrate, resulting in the covering area of $\sim 1 \text{ cm}^2$.

S8.36

INTEGRATION OF FUNCTIONAL MATERIALS BY SOFT LITHOGRAPHY: ADDITIVE PATTERNING OF ELECTROCERAMICS. Erik A. Mikkelsen, David A. Payne, Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL.

The integration of functional materials, e.g., electrical, mechanical, and optical, with various substrates (including semiconductors), is achieved by chemical-solution deposition (CSD) methods. Soft lithography is used to pattern the surface features through use of self-organizing molecular resists and microcontact printing. Differential surface forces and shrinkage that take place in drying and firing of the CSD film lead to residual stresses and additive patterning by a novel lift-off process. Details are reported for the directed deposition of functional materials on planar and non-planar surfaces, with special emphasis on materials chemistry, thin film mechanics, and the influence of processing parameters on pattern resolution and limitations.

S8.37

MAGNETIC NANOSTRUCTURES OF IRON AND COBALT OXIDES WITHIN MESOPOROUS MCM-48 AND MCM-41 SILICA HOST STRUCTURES. Ralf Köhn^a and Michael Fröba^{a,b}. ^aInstitute of Inorganic and Applied Chemistry, University of Hamburg, GERMANY. ^bInstitute of Inorganic and Analytical Chemistry, Justus-Liebig-University Giessen, GERMANY.

Transition metal oxide nanoparticles were synthesized within mesoporous MCM-48/-41 silica phases. By wet impregnation, drying, and calcination procedures, it was possible to form iron, iron/cobalt, cobalt oxide nanoparticles almost exclusively within the pore system. Nitrogen physisorption measurements still revealed mesoporosity for the host/guest compounds accompanied by a reduction of the surface area and pore radius, both indications of a decoration/coating of the inner surface of the silica walls. X-ray absorption spectroscopic measurements proved the existence of small, slightly disordered metal oxide nanoparticles. High resolution transmission electron microscopy investigations showed that the mesoporous host structure is still intact after the treatment. Thermogravimetric investigations revealed differences in the reduction/oxidation behavior of the metal oxide nanoparticles compared to their corresponding bulk phases. The reduction of the nanostructures leads to a change of the paramagnetic to a ferromagnetic behavior.

S8.38

MESOPOROUS CARBON/IRON OXIDES: A NEW HOST-GUEST-SYSTEM. Holger Huwe, Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University Giessen, Giessen, GERMANY; Michael Froeba, Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University Giessen, Giessen, GERMANY.

Within the pore system of mesoporous silica (MCM-48, SBA-1) different carbon precursors were pyrolyzed in order to synthesize mesoporous carbon, designated as CMK-1 and CMK-2. Characterization of the pristine host structures were carried out by using XRD, physisorption, TEM and electron energy loss spectroscopy (EELS). By multiple wet impregnation with iron nitrate, drying and calcination procedures it is possible to form iron oxides within the pore system of the CMK-1 and CMK-2. The XRD measurements show that the iron oxide is almost exclusively within the pore system and not on the outer surface. Nitrogen physisorption measurements show a reduction of the inner surface and the pore diameter of the guest system in dependence of the loading with iron oxide. Variations by the wet impregnation with e.g. the iron nitrate concentration show effects in the reduction of the inner surface and the pore diameter. These host-guest-systems show great potential for application in catalysis and can be used for synthesizing nanostructured magnetic materials.

S8.39

PATTERNED ANODIC OXIDATION OF ALUMINUM THIN FILMS BY NANO-INDENTATION. Qiyu Huang, Whye-kei Lye, Michael Reed, University of Virginia, Department of Electrical and Computer Engineering, Charlottesville, VA.

Porous aluminum oxide formed by the anodic oxidation of bulk aluminum is known to have near vertical sidewalls. It has been widely studied and used in industries as nano-fabrication templates, filters or lighting-emitting arrays. Little work has been done on the patterned anodic oxidation of deposited aluminum thin films. In this study, we explore the nano-scale patterning of aluminum thin films by indentation, observe the anodization progress of patterned aluminum thin films; with the goal of facilitating the integration of this technique with established microfabrication tools. An anodization barrier, comprising a layer of Polymethylmethacrylate (PMMA) or SU-8, is cast onto 300 nm thick aluminum films. The barrier is subsequently patterned and the exposed aluminum anodized in a 10% sulphuric acid solution. Traditional photolithography and nano-indentation are explored as techniques for patterning the polymeric barrier layer. Sharp edge definition on micron scale patterns has been achieved. Extension of this technique to smaller dimensions is presented. We further report on the observation of contrast reversal of anodization, tentative explanation is presented. Potential applications and challenges will be discussed.

S8.40

QUANTUM SIZE EFFECT SILICON STRUCTURES VIA MOLECULARLY SELF-ASSEMBLED HYBRID TEMPLATES. Elena A. Guliants, Don C. Abeysinghe, Taitech, Inc., WPAFB, OH; Moises A. Carreon, Vadim V. Guliants, University of Cincinnati, Department of Chemical Engineering, Cincinnati, OH; Chunhai Ji, Wayne A. Anderson, State University of New York at Buffalo, Dept of Electrical Engineering, Buffalo, NY.

A novel approach for the synthesis of advanced functional inorganic materials with the atomic-scale control over the size of periodic features on the sub-30 nm scale is presented. The key innovative

aspect of this technique is the direct, bottom-up formation of a two-dimensional periodic array of spatially separated nanostructures in a self-organized thin-film porous template. This thin-film template is fabricated via biologically inspired hierarchical self-assembly of organic surfactant molecules in the presence of inorganic charged silicate species. The removal of an organic molecules from such an organic/inorganic hybrid system creates a periodic array of pore channels of ~3-30 nm diameter inside the thin-film silica template. This porous template is employed as a shadow mask to directly grow various functional nanostructures inside the confined environment of the periodic pore arrays. In the present study, silicon nanostructures were grown inside the templates by both chemical and physical (sputtering) vapor deposition. Their structural properties such as Si atomic packaging inside the pores and crystallinity were carefully examined by electron microscopy. Quantum size effect in the nanostructures was clearly pronounced in the photoluminescence spectra taken at both low and room temperature, which makes the approach highly promising for the fabrication of nanoscale optoelectronic devices.

S8.41

RESOLUTION LIMITING DEFORMATION IN ELASTOMERIC STAMPS FOR MICRO-CONTACT PRINTING. Kenneth Sharp, Anand Jagota, Greg Mitchell, Dave Kristunas, The DuPont Company, Wilmington, DE.

Micro-contact printing is a method for pattern transfer in which an inked elastomeric stamp with surface relief features is pressed into contact with a substrate. Deformation of the stamp during printing limits the precision and scale of features that can be printed. Theoretical analysis has proposed combinations of materials properties (such as modulus and adhesion), external load, and geometrical parameters that influence some of the modes of deformation that limit performance. We report on an experimental investigation into these modes, including roof collapse resulting in unwanted contact, and buckling of slender relief features. We employ both conventional and novel elastomeric materials, both as a way to obviate deformation-based limitations, and as a test of the theoretical predictions.

S8.42

SELF-ORGANIZED SI NANOWIRES WITH ROOM-TEMPERATURE PHOTO-EMISSION. Chunhai Ji, State University of New York at Buffalo, Dept of Electrical Engineering, Buffalo, NY; Elena A. Guliants, Don Abeysinghe, Taitech, Inc., WPAFB, OH; Wayne A. Anderson, State University of New York at Buffalo, Dept of Electrical Engineering, Buffalo, NY.

Two-dimensional arrays of self-organized Si nanowires were synthesized using the metal induced growth (MIG) method. In MIG processing, the thermally evaporated 25 ~ 100 nm thick Ni films serve as prelayers for magnetron sputtered Si. When sputtering at 550°C, the Si crystallization occurs via the formation of nickel disilicide followed by subsequent epitaxial growth of Si crystals on nickel disilicide due to an extremely small lattice mismatch. Scanning electron microscopy study showed that the nanowires originated from the Si thin film and grew upwards in bundles. The diameter of nanowire was measured on the 10 ~ 20 nm scale. The length of nanowire was typically 1 μm. Transmission electron microscopy and electron diffraction analysis revealed the single crystal structure of nanowires. Quantum-size effect in the produced wires was investigated by measuring the photoluminescence spectra at both low and room temperature. An intense room temperature PL peak centered around 690 nm with FWHM of 180 nm showed promise of MIG-Si nanowires for the red light-emitting diode applications. In addition, self-aligned silicide film on the bottom provides an ultimate back Ohmic contact, which significantly simplifies the fabrication of optoelectronic devices.

S8.43

STUDY OF FIELD EMISSION ON CARBON NANOTUBES WITH DIFFERENT SOURCES. Mark Ching-Cheng Lin, M.S. Lai, H.J. Lai, M.H. Yang, P.Y. Wei, A.K. Li, Material Research Laboratories, ITRI, Hsinchu, JAPAN.

The field emission properties of carbon nanotubes (CNTs) from various sources are investigated for the application of field emission display. Comparisons are made between graphite with Ni metal as catalyst and polycyclic aromatic hydrocarbon as precursor by arc discharge method. Cathode deposits are examined using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) to determine microstructure. Carbon structure is studied using Raman spectroscopy. Electron field emission characteristic is measured with diode method. In this study, SEM micrograph of cathode deposit shows dense random fiber-like carbon nanotubes. HRTEM image clearly exhibits characteristic feature of multiwalled carbon nanotube. Microstructural investigation provides evidence that both metal catalyst and precursor can be used to

synthesize carbon nanotubes. Raman spectrum shows a strong peak at about 1580 1/cm indicating formation of well-graphitized carbon nanotube. The degree of carbon nanotube graphitization is high and is in good agreement with HRTEM result. From field emission measurement, the lowest onset field is about 1.0 V/um and can be attributed to highly sharp tips and high density of carbon nanotubes. Based on microstructure characterization and field emission measurement, influence on field emission properties including turn on voltage, threshold voltage, and field enhancement factor of carbon nanotube synthesized from different sources is discussed.

S8.44

SURFACE ALIGNMENT OF PURIFIED SINGLE-WALLED CARBON NANOTUBES BY ELECTRIC FIELD. Jessica Koehne, Jabulani Barber, Michelle Di Leo, M. Meyyappan, NASA Ames Research Center, Moffett Field, CA; Cattien V. Nguyen, ELORET Corp./NASA Ames Research Center, Moffett Field, CA.

Purification of surfactant-free, unmodified single-walled carbon nanotubes suspended in 2-propanol by size-exclusion chromatography was demonstrated. To evaluate the ultra diluted carbon nanotubes in solution, the chromatographed fractions were concentrated by electric induced deposition on microfabricated metal electrodes. Characterization by atomic force microscopy on the deposited fractions demonstrated that indeed this technique separated carbon nanotubes from impurities. In addition, preliminary results are also presented to demonstrate that this technique can be employed to align carbon nanotubes to bridge the gap of metal electrodes by applying an alternating-current electric field between the metal electrodes. This offers a simple technique for fabricating single-walled carbon nanotube devices that can also be easily scalable.

S8.45

CARBON NANOTUBES PREPARED BY A SPINNING AND CARBONIZING OF POLYMER CORE/SHELL MICROSPHERES. Denisa Hulicova, Asao Oya, Katsuhiko Hosoi, Shin-ichi Kuroda, Gunma Univ, Fac of Engineering, Dept of Chemistry, Kiryu, JAPAN; Hiroaki Abe, Japan Atomic Energy Research Institute, Dept of Materials Development, Takasaki, JAPAN.

Multi-wall carbon nanotubes (MWCNTs) were prepared by a technique based on the spinning and carbonizing of fine core/shell (C/S) microspheres, the core and shell of which is made from polymer without and with carbon residue, respectively after heating in an inert atmosphere. C/S microspheres were synthesized by two-step soap-free emulsion polymerization of methylmethacrylate MMA and acrylonitrile AN. The diameter of PMMA microspheres and PMMA core/PAN shell microspheres prepared by use of 4ml AN is ca. 330 nm and 370 nm, respectively. The polymer blend formed by mixing the water emulsions of PMMA core/PAN shell microspheres and PMMA microspheres was subjected to continuous melt-spinning at 310-320°C, stabilizing of PAN at 250°C in air and finally carbonizing at 1000°C in nitrogen. MWCNTs with diameters of 10-20nm were left from the elongated PAN shells after removal of core and matrix PMMA at carbonization. TEM and HRTEM studies of product show that MWCNTs are characterized by being straight with narrow hollows and having the closed tips. The walls of CNTs consist of oriented graphene layers in spite of relatively low carbonization temperature. The reason of this phenomenon is probably the intensive mechanical stretching during spinning resulting in a preferred orientation of PAN molecules along the fiber axis. In order to increase the CNTs yield and to simplify the preparation procedure, the PMMAcore/PANshell1/PMMAshell2 (C/S1/S2) microspheres ca. 600nm in diameter were synthesized by three-step soap-free emulsion polymerization and were directly melt-spun. The outer PMMA layer played the role of matrix polymer. MWCNTs prepared in higher yield are having the similar structure and diameters as the one prepared from C/S microspheres. Presented method provides the possibility of MWCNTs mass production and also the preparation of MWCNTs with a wide variety of crystalline structures and textures. Moreover, the synthesis is no-catalyzed and further purification procedure of product is eliminated.

S8.46

NANOSTRUCTURED CARBON CAPSULES WITH HOLLOW CORE/MESOPOROUS SHELL STRUCTURE. Jong-Sung Yu¹, Suk Bon Yoon¹, Kwonnam Sohn², Jeong Yeon Kim¹ and Taeghwan Hyeon². ¹ Department of Chemistry, Hannam University, Taejeon, KOREA. ² School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Seoul, KOREA.

There has been great deal of interest to create core-shell composite materials and capsules with tailored structural, optical and surface properties using spherical nanoparticles as molds. Various procedures have been applied to fabricate uniform coated and stable colloidal particles. Herein we would like to report the fabrication of carbon capsules with hollow core/mesoporous shell (HCMS) structures using

sacrificial submicrometer-size solid core/mesoporous shell (SCMS) silica spheres as templates. The structure of the HCMS carbon capsules is an inverse replica of the SCMS silica sphere templates. The carbon capsules have bimodal pore systems consisting of uniform tunable hollow macroscopic core and of mesopores in the shell, thus leading to wide range of applications including catalysts, adsorbents, sensors, electrode materials, and advanced storage materials.

S8.47

SYNTHESIS OF NANOSTRUCTURED UNIFORM POROUS CARBON NETWORKS: MORPHOLOGY CONTROL. Soonki Kang, Suk Bon Yoon, Geunsuk Chai and Jong-Sung Yu, Department of Chemistry, Hannam University, Taejeon, KOREA.

New ordered nanoporous materials are a blooming subject of fundamental and technological interests. In this work, two different ordered uniform porous carbon frameworks with interesting morphology alteration were synthesized against sacrificial colloidal silica crystalline templates through simply controlling acid-catalyst sites for acid-catalyzed polymerization of phenolic resin. The resulting carbon networks can be fabricated to have controllable uniform pores and interesting altered morphologies. These highly ordered uniform porous carbons have a high thermal stability and electronic conductivity, and as a catalyst supporter showed much improved catalytic activity for methanol oxidation in a direct methanol fuel cell. The nanostructured uniform carbon networks can find many advanced applications such as catalysts, adsorbents, sensors, electrode materials, and photonic materials.

SESSION S9: PHOTONIC MATERIALS

Chairs: Mohan Srinivasarao and David J. Norris
Friday Morning, April 5, 2002
Metropolitan III (Argent)

8:00 AM *S9.1

ON-CHIP ASSEMBLY OF SILICON PHOTONIC BAND GAP CRYSTALS. David J. Norris, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; Yurii A. Vlasov, IBM TJ Watson Research Center, Yorktown Heights, NY; Xiang-Zheng Bo and James C. Sturm, Dept. of Electrical Engineering, Princeton University, Princeton, NJ.

Photonic crystals, structures that are periodic on an optical length scale, can reflect light for any direction of propagation. Since this property, known as the photonic bandgap, can be utilized to confine, manipulate, and guide photons, photonic band gap crystals should enable a variety of optical devices all combined on an ultra-compact optical chip. For this goal, conventional semiconductor nanofabrication techniques have been adapted to make photonic crystals. However, a potentially simpler and cheaper approach for creating three-dimensionally periodic structures is the natural assembly of colloidal microspheres. Unfortunately, despite recent successes in achieving semiconductor photonic crystals with this approach, strong skepticism remains whether such crystals will ever be useful. Natural assembly not only yields irregular, polycrystalline photonic crystals that are impossible to incorporate into a device, but more importantly, it leads to many defects that destroy the photonic band gap. Here, these issues will be addressed by exploring high-quality silicon inverted opals that are assembled directly 'on-chip'. Optical results show that the defect densities in these structures are sufficiently low that the photonic band gap survives. Further, since the photonic crystal is grown directly onto a Si wafer, we demonstrate that it can be subsequently patterned for a desired device application with straightforward post-growth processing. Thus, our approach, while retaining the simplicity of natural assembly, provides structures that reclaim many of the advantages of conventional nanofabrication.

8:30 AM S9.2

FABRICATION AND OPTICAL PROPERTIES OF MULTILAYER METAL NANOSHELLS. Corey Radloff, Dept of Chemistry; Naomi J. Halas, Dept of Chemistry, Dept of Electrical and Computer Engineering, Rice University, Houston, TX.

Nanoparticles with dielectric-metal, core-shell compositions have been shown to possess optical resonances with frequencies that are a sensitive function of the relative thickness of their constituent layers. For the case of silica-gold and silica-silver core-shell nanoparticles, demonstrated fabrication methods have been shown to produce nanoparticles with resonance frequencies spanning the visible and near infrared range of the optical spectrum. Modifications of this simple two-layer geometry permit the expansion of this spectral range. One such modification is the development of 4-layer nanoparticles with a dielectric core, secondary metal layer, tertiary dielectric layer and a terminating metal coating. This "nanoshell in a nanocavity" construction results in additional optical resonances obtainable at longer wavelengths, providing a strategy for the synthesis of resonant

nanoparticles in the mid- and eventually the far-infrared frequency ranges. We have developed a fabrication method for this multilayer nanoshell structure. Following synthesis of a silica-gold nanoshell, the nanoparticle is then functionalized using an aminoalkoxysilane for subsequent encapsulation in a silica shell of controllable thickness. This silica layer has the additional feature of stabilizing the nanostructure against thermal destruction by more than 300 degrees relative to the pristine nanoshell. Once this silica encapsulation layer has been formed, its surface is then functionalized and metallized using a chemical approach consistent with the initial shell layer fabrication. Multilayer nanoshells with strong, multi-peaked resonances in the infrared region of the spectrum have been synthesized by this method. The infrared extinction spectra of these nanostructures are in quantitative agreement with the predicted Mie response for a multilayer nanostructure of the same dimensions. The extent to which this approach is practical for the fabrication of resonant nanoparticles in the mid and far infrared region of the spectrum will be critically addressed.

8:45 AM *S9.3

ON-CHIP COLLOIDAL ASSEMBLY OF ELECTRICALLY FUNCTIONAL STRUCTURES VIA DIELECTROPHORESIS.

Orlin D. Velev, North Carolina State University, Dept. of Chemical Engineering, Raleigh, NC; Eric W. Kaler, Simon O. Lumsdon, Kevin D. Hermanson, University of Delaware, Dept. of Chemical Engineering, Newark, DE.

We present three examples of electrically functional devices assembled from colloidal components by dielectrophoresis, the mobility of particles via alternating electric fields. The microstructures are interfaced with electrically addressable patterns on glass substrates. Microscopic electronically readable biosensors are assembled in situ from the latex particles used in agglutination assays by combining dielectrophoresis with tuning of the colloidal forces. A similar concept has been applied to form electrically switchable 2D photonic crystals. Single, specifically oriented, crystals of area $>25 \text{ mm}^2$ have been obtained by a simple procedure without prior expensive templating. Finally, we report a novel colloidal process for the collective dielectrophoretic assembly of microwires from suspensions of metallic nanoparticles. The metallic wires of micrometer diameter and millimeter lengths have good Ohmic conductance for both AC and DC. We show that the method allows making rudimentary self-assembled and self-repairing "wet" circuits. The simple process, the high surface-to-volume ratio and the possibility for facile functionalization make these unique structures promising for application as sensors or in bioelectronic circuits. Dielectrophoresis is a powerful tool for the assembly of functional microstructures, with large potential for future advances.

9:15 AM S9.4

MULTISCALE 3-D MATERIALS HIERARCHY WITH ANODIC ALUMINA NANOTEMPLATES. Dmitri Routkevitch, F. Howland Carpenter, Peter Mardilovich and Alexander Goyadinov, Nanomaterials Research LLC, Longmont, CO.

The number of publications on templated nanofabrication using self-organized anodic aluminum oxide (AAO) skyrocketed during the last decade. This presentation will overview our latest results on using this fascinating material for three-dimensional multiscale engineering of materials and their integration into devices. The heart of the approach is based on self-organized anisotropic morphology and chemistry of AAO. Uniform and parallel primary nanopores of AAO provide the main level of nanoengineering at the scale of 3 to 300 nm in pore diameter and 0.5 to 500 micrometer in pore length. Optional annealing of AAO forms secondary sub-5 nm pores in the walls of the primary pores, thus further decreasing the scale of structuring of templated materials. Furthermore, techniques recently developed by the authors for pore diameter modulation enable 3-D nanotemplate morphology engineering and open additional opportunities for the synthesis of novel electronic and photonic materials. Various techniques, such as electrodeposition, polymerization, sol-gel, and CVD could then be used for templated deposition of pre-aligned and pre-packaged nanoarrays. Finally, due to its intrinsic anisotropy anodic alumina could be micromachined in a hybrid process, resembling both surface and bulk MEMS. This process provides the micrometer-scale engineering capabilities and was extensively used to form 2- and 3-D ceramic microcomponents and microdevices. These devices incorporate templated nanostructured components, which define the system response and performance. We will present case studies for several types of such devices, including energy conversion materials, photonic crystals, field emission cathodes and gas microsensors.

This work was supported by BMDO (N00014-98-C-0354), NSF (DMI-9983511) and NIH (1R43-ES10739).

9:30 AM S9.5

POROUS SILICON MATCHED MICROCAVITIES FOR

SELECTIVE SENSING APPLICATIONS. Thomas A. Schmedake, Jamie R. Link, Michael J. Sailor, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, CA; Rong Liu, Yeshiahu Fainman, University of California, San Diego, Department of Electrical and Computer Engineering, La Jolla, CA.

Porous Si microcavities have been constructed by electrochemically etching periodic multilayered structures. The creation of a defect mode in the photonic bandgap allows for a narrow ($\sim 10 \text{ nm FWHM}$) region of transmission in the center of the stopband in the reflection spectrum. Optically matched pairs of these notch filters have been used to obtain enhanced selectivity for chemical sensing. Exposure of the films to analyte causes the pores of the PSi structure to become partially filled. This results in a change in the refractive index, leading to a change in the transmission frequency. When white light is allowed to pass through two of these filters that are tuned to slightly different wavelengths ($\sim 5 \text{ nm}$ apart), most of the light is reflected by one film or the other resulting in an overall transmission level that is very low. One of the two films is chemically modified to provide a differential affinity towards a selected analyte. A pronounced increase in transmission is then observed in the presence of the analyte because the transmission notch for the modified film shifts relative to the unmodified microcavity. This sensing scheme is relatively insensitive to fluctuations in temperature, humidity or the presence of nonspecific analytes because these effects cause a shift in both microcavities. Results will be presented demonstrating the detection of ethanol vapor at concentrations ranging from 0-1.3ppm in the presence of heptane vapor at concentrations of 0-17ppm. This technique is amenable to the sensing of analytes in complex matrices, such as is required for biological sensors.

10:15 AM *S9.6

BUILDING COMPLEX STRUCTURES FROM MONODISPERSED SPHERICAL COLLOIDS. Younan Xia, Yadong Yin, Byron Gates, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have been actively exploring the use of spherical colloids as the building blocks in fabricating complex, functional structures through self-assembly. In one example, we have assembled polymer beads and silica colloids (with sizes in the range of 50 nm - 2 microns) into crystalline lattices over large areas that exhibit interesting photonic bandgap properties. In another demonstration, we have assembled colloids into well-defined aggregates by templating against cavities patterned on solid substrates. This talk will outline the detailed procedure for each approach, together with a brief discussion on their advantages, disadvantages, and possible extensions.

10:45 AM S9.7

NANOCUPS: REDUCED SYMMETRY METAL NANOSHHELLS. R.K. Bradley and N.J. Halas, Rice University, Departments of Chemistry and Electrical and Computer Engineering, Houston, TX.

Metal nanoshells are spherical layered nanoparticles comprised of a dielectric core and a metallic shell, typically silver or gold. These nanoparticles are fabricated using a multistep process involving functionalization of a dielectric core nanoparticle and subsequent metallization of the nanoparticle surface via seeded electroless plating. This procedure results in macroscopic quantities of highly uniform and highly symmetric layered nanoparticles. By combining electrophoretic deposition with the chemical functionalization and metallization of nanoshells it is possible to break this growth symmetry for a macroscopic quantity of nanoparticles and to produce uniform reduced-symmetry nanoparticles in high yield. Electrophoretic deposition results in the selective masking of one portion of the nanoparticle surface, so that when metallization of the shell layer is complete the nanoparticle forms a nanocup structure. These particles can be subsequently straightforwardly dislodged from the substrate for further chemical functionalization, if desired.

11:00 AM S9.8

THE EFFECT OF ELECTROSTATIC INTERACTIONS ON CRYSTALLIZATION IN BINARY COLLOIDAL FILMS.

Alessandro Rugge, Sarah H. Tolbert, University of California, Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA.

Colloidal crystals are unique building blocks for materials displaying complex nanoscale structures. The realm of architectures obtained through colloidal assembly may potentially be greatly expanded by utilizing two different types of colloidal particles. The controlled assembly of a binary system requires the ability to tune interparticle interactions and understand how these affect the order of the films that can be produced upon solvent evaporation. In this study we utilize two sets of monodisperse colloidal particles in the production of drop-coated array films: silica and polystyrene modified with amphoteric groups. The relative magnitudes of the surface charge on the two types of particles can be tuned continuously with pH allowing control over the electrostatic interactions. A correlation is established

between the surface charge on the particles and the degree of order in the colloidal films that can be produced under different conditions. When both particles are highly charged, the particles self-assemble into polycrystalline close-packed arrays in which the two components are thoroughly mixed. More interesting results are obtained from binary films containing one weakly charged colloid, which will not order on its own, and one highly charged colloid. In this case, the highly charged silica particles act as a templating agent, forcing the weakly interacting polystyrene particles into an ordered crystalline lattice. Results for both low and high charge colloids can be explained based on simple electrostatic calculations, which show that the average interaction in a mix system still favors ordering.

11:15 AM *S9.9

IRRATIONAL SELF-ASSEMBLY OF THREE-DIMENSIONAL STRUCTURES IN A POLYMER FILM. Mohan Srinivasarao, Jung Ok Park, School of Textile and Fiber Engineering & School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

We report the formation of a three dimensionally ordered array of air bubbles of monodisperse pore size in a polymer film through a templating mechanism based on thermocapillary convection. Dilute solutions of a simple, coil-like polymer in a volatile solvent are cast on a glass slide in the presence of moist air flowing across the surface. Evaporative cooling and the generation of an ordered array of breath figures, leads to the formation of multilayers of hexagonally packed water droplets that are preserved in the final, solid polymer film as spherical air bubbles. The dimensions of these bubbles can be controlled simply by changing the velocity of the airflow across the surface.

11:45 AM S9.10

FABRICATION OF PERIODIC ARRAYS OF NANOSCALE SQUARE HELICES. Martin O. Jensen, Scott R. Kennedy, Michael J. Brett, Dept of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, CANADA.

We demonstrate fabrication of periodic arrays of nanometer scale square helices, with potential applications in three-dimensional photonic band gap crystals (PBC). Processing is reproducibly performed using a thin film deposition method known as Glancing Angle Deposition (GLAD) [1]. Through advanced substrate motion, this technique allows for controlled growth of square helices in a variety of inorganic materials. Organization of the helices into periodic two-dimensional geometries is achieved by prepatterning the substrate surface with e-beam lithographically defined seeds. The regular turns of the helices yield periodicity in the third dimension, perpendicular to the substrate. We present studies of tetragonal and hexagonal helix arrays in Si and SiO₂, with lattice constants as low as 300 nm. The typical diameter of the helix arms is 100 nm. By deliberately adding or leaving out seeds in the substrate pattern, we have succeeded in engineering point and line defects. Our periodic nanoscale structure closely matches ideal photonic band gap architecture, as recently proposed by Toader and John [2]. While our fabrication technique is simpler than most suggested PBC schemes, it is highly versatile. A wide range of materials can be used for GLAD, manipulation of lattice constant and helix pitch ensures optical tunability, and the GLAD films are robust to micromachining.

[1] K. Robbie, M.J. Brett: "Sculptured thin films and GLAD (Glancing Angle Deposition): growth mechanics and applications", J. Vacuum Science and Technology A15, 1460-1465 (1997).

[2] O. Toader, S. John: "Proposed Square Spiral Microfabrication Architecture for Large Three-Dimensional Photonic Band Gap Crystals", Science 292, 1133 - 1135 (11 May 2001).

SESSION S10: NANOSCALE MATERIALS

Chair: Younan Xia

Friday Afternoon, April 5, 2002
Metropolitan III (Argent)

1:30 PM S10.1

UNIQUE BEHAVIOR OF NEGATIVE-DIFFERENTIAL-RESISTANCE MOLECULES ATTACHED TO Au-NANOPADS AS ADDRESSED BY STM AND AFM. Ganesh K. Ramachandran, Xiaodong Cui and Stuart Lindsay, Department of Physics and Astronomy, Arizona State University, Tempe, AZ; Adam M. Rawlett, Theresa Hopson, Larry Nagahara and Ray Tsui, Motorola Labs, Tempe, AZ.

The observation of negative differential resistance (NDR) and conductance switching (CS) in a class of conjugated nitro-amines, **1** [see Z.J. Donhauser et al., *Science* **292**, 2303 (2001) for details], has sparked the promise that molecular electronic devices (when embedded in appropriate matrices) become alternatives to traditional

solid-state devices. In this work we extend these findings using a new technique developed by us [X.D. Cui et al., *Science* **294**, 571 (2001)] to reproducibly measure single-molecule conductivities by attaching gold nanocrystals as nano-contact pads addressed by an Au-coated AFM tip. We have reproduced the STM observation of CS in the monothiolated molecule **1**, and extended it to the corresponding dithiol species of **1**. However, we observe that Au-capped dithiolated **1** molecules do not exhibit the expected CS. Instead, a predominantly bimodal distribution of particle-sizes is observed in STM experiments. It is possible that the contacts play a role in the observed switching and NDR. A discussion of these results and its relation to the observed conductance spectra (collected using the conducting-AFM) will be reported.

1:45 PM S10.2

REVERSIBLE CHARGING OF CdSe NANOCRYSTALS IN A SIMPLE SOLID STATE DEVICE. Wing Woo, Kentaro Shimizu, Mirna Vitasovic, Robert Neuhauser, Catherine Leatherdale, Mounqi Bawendi, MIT, Dept. of Chemistry, Cambridge, MA; Michael Rubner, MIT, Dept. of Materials Science and Engineering, Cambridge, MA.

The physical and chemical properties of colloidal semiconductor nanocrystal (NC) quantum dots are being extensively explored for their potential applications in a variety of fields. The application of these NCs into novel optoelectronic, nanoelectronic, and biological applications could be significantly enhanced by understanding the physical processes that can controllably and reversibly modify their properties. One possibility to drastically change NC electrical and optical properties is by charging them. Hence, there is a growing interest in preparing stable, charged NCs. We report a novel, solid-state, thin-film device that allows reversible switching of NCs between charged (both positive or negative) and uncharged states at room temperature with a high degree of reproducibility and stability. Reversible fluorescence quenching and absorption bleaching of NCs are directly observed. Our basic design can be scaled both down to the sub-micron scale, and up to macroscopic scales, indicating the feasibility of using NCs as the active material in optical modulators and in tunable fluorescent or photochromic displays.

2:00 PM S10.3

A SOFT SOLUTION-PHASE APPROACH TO THE LARGE SCALE SYNTHESIS OF CRYSTALLINE NANOWIRES OF METALS. Yugang Sun, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated a soft solution-phase approach to the large-scale synthesis of metallic nanowires. For example, silver nanowires as long as 50 micrometers have been synthesized by reducing silver nitrate with ethylene glycol in the presence of an appropriate polymer coordination compound. The diameter of these nanowires could be easily controlled in the range of 30-60 nm by changing the reaction conditions such as the temperature and the ratio between polymer compound and silver nitrate. By employing different coordination compounds, this method could be potentially extended to other metals such as gold, platinum, and palladium. This talk will give a detailed description on the mechanism, as well as full characterization of the nanowires.

2:15 PM S10.4

PROPERTIES OF Bi₂Te₃, Bi_{2-x}Sb_xTe₃ AND Bi₂Te_{3-x}Se_x NANOWIRES. M.S. Martin-Gonzalez¹, A.L. Prieto¹, S. Huxtable³, A. Abramson³, D. Li³, A. Majumdar³, R. Gronsky², T. Sands², A.M. Stacy¹. ¹Department of Chemistry. ²Department of Materials Science and Engineering. ³Department of Mechanical Engineering University of California, Berkeley Berkeley, CA.

Thermoelectric materials are of interest for applications as heat pumps and power generators. There is a renewed interest in those materials lately because they appear to offer a significant enhancement in the figure of merit when quantum confined compared to bulk. Among them, Bi₂Te₃, especially its doped phases Bi_{2-x}Sb_xTe₃ and Bi₂Te_{3-x}Se_x, are the best thermoelectric materials for application at room temperature. Moreover, if we take into account that in order to make a thermoelectric device, both n-type (Bi₂Te_{3-x}Se_x) and p-type (Bi_{2-x}Sb_xTe₃) legs are needed. The measurement and the understanding of the properties of these alloys in nanowire form is crucial. In this work we are presenting a comparison of the electrical and thermal conductivity of nanowires (starting at 200 nm diameters) of these three compounds obtained by electrodeposition into porous alumina. The elemental composition, the degree of filling, and morphology of several samples was determined by SEM in conjunction with EDS. TEM of single nanowires will also be shown.

2:30 PM S10.5

NANOSCALE TEXTURING AND SHAPING OF ELECTROSPUN POLYMER FIBERS. Jean S. Stephens, Silke Megelski, John F. Rabolt, Univ of Delaware, Dept of Materials Science and

Engineering and Delaware Biotechnology Institute, Newark, DE; D. Bruce Chase, Central Research and Development, Experimental Station, DuPont, Wilmington, DE, and Univ of Delaware, Dept of Materials Science and Engineering, Newark, DE.

The ability to add texture while shaping materials would reduce, if not eliminate, post-processing protocols thus saving energy and reducing cost. Our research has focused on the formation of polymer fibers with micro- and nanoscale pores using the electrospinning process. Nanoporous fibers were formed from a series of volatile solvents and characterized by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and Raman spectroscopy (1). Pores ranging in size from 20 - 1000 nm (having depths ranging from 50 - 70 nm) have been observed on the surface of both amorphous (e.g., polystyrene, poly(methyl methacrylate)) and semicrystalline (e.g., polycarbonate, synthetic spider silk) polymer fibers. The size and density of the nanopores can be varied simply by changing the processing conditions. In some cases we have been able to fill these nanopores with metallic nanoparticles and polymer vesicles in order to explore their electronic, photonic, and biomedical properties.

(1) J.S. Stephens, S. Frisk, S. Megelski, D.B. Chase, J.F. Rabolt, Applied Spectroscopy, 55, Oct 2001.

3:15 PM S10.6

PROBING ENERGY TRANSFER IN SELF-ASSEMBLED POLYELECTROLYTE FILMS USING NEAR-FIELD OPTICS. Geoffrey Lowman, Natalie Daoud, Paul Carson, Steven Buratto, University of California, Santa Barbara, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

Polyelectrolyte layer-by-layer (LbL) self-assembly constructs thin films with predictable overall thickness, but the internal layer structure is far less distinct. Neutron reflectivity studies have demonstrated interlayer mixing that can extend at least one full polycation / polyanion bilayer, which may have consequences in the bulk material properties of LbL films. Radiationless energy transfer between chromophores incorporated into specific layers in LbL films has been employed as a complementary optical tool for characterizing this internal layer structure. We present near-field scanning optical microscopy (NSOM) measurements of local energy transfer in an LbL film consisting of poly(*p*-phenylene vinylene) (PPV) and poly(allylamine hydrochloride) (PAH) doped with Texas Red (Sulforhodamine 101 acid chloride) (TR-PAH) as donor and acceptor layers respectively. We observe drastic differences in ET efficiency in localized regions of LbL films. We also track the average energy transfer efficiency as the donor and acceptor layers are separated by varying the thickness of optically inactive polycation layers of PAH and polyanion layers of poly(styrene sulfonate) (PSS). In addition, we present preliminary results in isolating single dye molecules in LbL films imaged with confocal microscopy.

3:30 PM S10.7

PLASMON SCANNED SURFACE-ENHANCED RAMAN SCATTERING EXCITATION PROFILES. Christy L. Haynes and Richard P. Van Duyne, Northwestern University, Department of Chemistry, Evanston, IL.

Since the discovery of surface-enhanced Raman spectroscopy (SERS) in 1977, scientists have come to understand the enhancement mechanism, but have been unable to consistently optimize the weak signals inherent in Raman experiments. The enhanced Raman signals originate from excitation of the localized surface plasmon resonance (LSPR) of a nanostructured metal surface, thus producing concentrated electromagnetic fields at the surface of the nanostructure. Design of the nanostructured metal substrate plays an important role in understanding and optimizing SERS experiments. In this research, the size-dependent optical properties accessible by nanosphere lithography (NSL) are exploited to fabricate topographically predictable SERS-active substrates with systematically varying LSPRs. Correlated micro-extinction and micro-Raman measurements, as well as quantitative implementation of a Raman standard, allow significant improvements over the current method used to optimize SERS experiments. The knowledge gained in the novel plasmon scanned excitation profiles clearly indicates the substrate parameters necessary for experimental optimization and promotes further understanding of the SERS enhancement mechanism. Data presented herein probes the correlated extinction and SERS spectra of benzenethiol adsorbed to NSL-fabricated silver substrates. The plasmon scanned excitation profile plots of LSPR λ_{max} versus the SERS intensity of any vibrational band demonstrate that SERS experiments are optimized when the LSPR λ_{max} is at slightly lower energy than the excitation wavelength. Enhancement factors as large as 4.5×10^8 are measured from the optimized SERS substrate. A plasmon scanned excitation profile was also performed using silver island film surfaces, a conventional SERS substrate. This experiment indicates the optimum film thickness for SERS experiments at a given

excitation wavelength, achieving enhancement factors as high as 8×10^6 . In this investigation, exploitation of substrate design is used in an innovative new method to probe the SERS excitation profile; this method is simple to implement experimentally and provides both practical and fundamental insights into SERS experiments.

3:45 PM S10.8

LYOTROPIC LIQUID CRYSTALLINE PHASE OF CdSe QUANTUM ROD SOLUTION. Liang-shi Li, Joost Walda, Liberato Manna, A. Paul Alivisatos, Department of Chemistry, University of California, Berkeley, Materials Science Division, Lawrence Berkeley National Lab Berkeley, CA.

It has been shown that rodlike CdSe nanocrystals (also known as 'quantum rods') have linearly polarized photoluminescence with tunable wavelength. These novel properties make CdSe quantum rods a good candidate component for devices such as polarized light emitting diodes. The method of aligning them in a large scale, however, is not yet available. On the other hand, objects such as rodlike viruses, polymer and inorganic colloidal particles have been extensively studied to test theories about the formation of lyotropic liquid crystals. When these rodlike objects are dispersed in solvent with a high enough concentration, the solution will spontaneously turn into a liquid crystalline phase in which the particles have an orientational but no or partial positional order. Here we show the lyotropic liquid crystalline phase of concentrated CdSe quantum rod solution in organic solvent. The formation of liquid crystalline phase of CdSe quantum rod solution enables us to take advantage of the highly developed processing techniques in LCD industry to align the rods in a large scale, e.g. with pretreated surface or external field. At the meantime, because CdSe quantum rods can be made with excellent monodispersity and variable width and length, and they can be dispersed in organic solvent, they may prove to be a model system for lyotropic crystal study superior to all the ones presently studied.

4:00 PM S10.9

LANGMUIR-BLODGETT ASSEMBLY OF NANORODS.

Franklin Kim, Peidong Yang, University of California, Berkeley, Dept. of Chemistry, Berkeley, CA.

Techniques for directing the assembly of metal or semiconductor quantum dots into novel superstructures have been extensively pursued over the past decades. Recent interest has been drawn toward one-dimensional (1D) nanoscale building blocks such as nanotubes, nanowires, and nanorods. If these anisotropic building blocks can be ordered and rationally assembled into appropriate 2-dimensional (2D) architectures, they will offer fundamental scientific research opportunities of their collective optical, magnetic, and electronic properties, as well as many other technologically important applications. Langmuir-Blodgett process is a very promising technique for these studies since a large area of ordered monolayer can be easily produced, and also the interparticle distance and the superstructures formed can be controlled with an appropriate selection of ligand and surface pressure. Monolayer assemblies of different nanorods have been studied using Langmuir-Blodgett technique. Generally, a 2D isotropic, 2D nematic, 2D smectic, to 3D nematic transition could be observed during the compression of the monolayer. This ordering occurs to maximize the entropy of the self-assembled structure by minimizing the excluded volume per particle in the array as first proved by Onsager. The results also show close relation with the Monte Carlo simulation results done by Dr. Frenkel's group in Netherlands. Providing suitable surface passivation chemistry, this Langmuir-Blodgett technique should be generally applicable to many other nanorods, which promise interesting, tunable collective physical properties and functional 2-dimensional nanodevices. The effect of ligand, aspect ratio of the nanorods, and various interparticle forces to the monolayer assembly will be discussed. The physical properties of the monolayers will also be briefly mentioned.