

## SYMPOSIUM Q

### Unconventional Approaches to Nanostructures with Applications in Electronics, Photonics, Information Storage, and Sensing

April 21 – 25, 2003

#### Chairs

**Younan Xia**

Department of Chemistry  
Univ of Washington  
Seattle, WA 98195-1700  
206-543-1767

**Peidong Yang**

Dept of Chemistry  
Univ of California-Berkeley  
B68 Hildebrand Hall  
Berkeley, 94720  
510-643-1545

**Orlin D. Velev**

Chemical Engineering  
North Carolina State Univ  
113 Riddick Engineering Labs  
Raleigh, NC 27695-7905  
919-513-4318

**Timothy J. Bunning**

Air Force Research Laboratory  
AFRL/MLPJ Bldg 651  
WPAFB, OH 45433  
937-255-3808 x3167

#### Symposium Support

3M Company  
Air Force Research Laboratory  
CW Group  
Duke Scientific Corporation  
General Electric Company  
Industrial Technology Research Institute (Taiwan)  
Kodak  
Nanomix, Inc.  
Nanosys

Proceedings to be published in both book form and online  
(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))  
as Volume 776  
of the Materials Research Society  
Symposium Proceedings Series

\* Invited paper

SESSION Q1: QUANTUM DOTS AND  
NANOPARTICLES I

Chair: Daniel R. Gamelin  
Monday Morning, April 21, 2003  
Metropolitan II (Argent)

**8:30 AM Q1.1**

**PHOTOLUMINESCENCE PROPERTIES OF NANO-SCALE GAN PARTICLES AND CLUSTERS.** Leah Bergman, Xiang-Bai Chen, Joel Feldmeier, and Misti D. Fowler, University of Idaho, Department of Physics, Moscow, ID; Andrew Purdy, Naval Research Laboratory, Chemistry Division, Washington, DC; Fran Adar, Emmanuel Leroy, JYHoriba Group, Edison, NJ.

We present a study of the sub-micron UV photoluminescence (PL) from GaN nano-particles and clusters as a function of size and morphology. GaN nano-particles are excellent candidates for wide ranging UV optical applications. Our GaN nano-particles exhibit strong and sharp luminescence even at room temperature. The GaN nano-particles were grown via an ammonothermal process and exhibit growth-condition dependent morphology as well as varying degrees of clustering. It was found that the PL emission lines of some of the examined samples are  $\sim 3.2$  eV, corresponding to the cubic-zincblende structure of GaN, while other samples exhibit PL  $\sim 3.4$  eV, corresponding to the Hexagonal-Wurtzite structure. Additionally, some of the samples emit light at  $\sim 3.2$  eV as well as at 3.4 eV implying the cluster to be of a mixed cubic-hexagonal structure. Moreover, we study the PL of small size clusters  $\sim 200$  nm and large size  $\sim 600$  nm the latter which is the diameter of our probing spot size. A cluster contains nano-particles of a characteristic shape and of varying size, both of which are a function of the growth condition. We found that the PL energy and the line broadening is a function of the cluster size, as well as its morphology. Our experimental findings will be discussed in terms of the confinement effect and energy transfer mechanisms among the nano-particles in a given cluster.

**8:45 AM Q1.2**

**SYNTHESIS AND ENHANCED LUMINESCENT PROPERTIES OF CdS:Mn/ZnS CORE/SHELL QUANTUM DOTS.** Heesun Yang and Paul H. Holloway, Department of Materials Science and Engineering, University of Florida, Gainesville, FL.

The high surface-to-volume ratio of semiconductor nanocrystals has profound effects on their luminescent properties. Compared to conventional organically capped II-VI undoped semiconductor nanocrystals, undoped semiconductor nanocrystals capped with inorganic material of wider band gap have been reported to have much higher bandedge photoluminescence (PL) quantum yield and better photostability, due to the significant reduction of nonradiative recombination paths and photodegradation sites. Enhanced PL is reported here from Mn<sup>2+</sup>-doped CdS nanocrystals capped with ZnS (CdS:Mn/ZnS core/shell) that were prepared using a reverse micelle route. Compared to organically (n-dodecanethiol) capped CdS:Mn nanocrystals, CdS:Mn/ZnS core/shell nanocrystals exhibited much stronger and sharper Mn<sup>2+</sup> <sup>4</sup>T<sub>1</sub>-<sup>6</sup>A<sub>1</sub> yellow PL emission. This is presumably the result of effective passivation of CdS surface states by the ZnS shell and consequent suppression of nonradiative recombination transitions. The dependence of PL emission intensity has been observed as a function of UV exposure (treatment) time for both organically and inorganically capped CdS:Mn nanocrystals. While organically capped CdS:Mn nanocrystals exhibit a significant reduction of PL emission intensity with time (rapid initial decrease, followed by a steady decrease), CdS:Mn/ZnS core/shell nanocrystals exhibit an increased PL intensity with UV exposure (rapid increase, followed by a steady increase and saturation). The core/shell nanostructure was confirmed using XPS (x-ray photoelectron spectroscopy) and EDS (energy dispersive spectroscopy) data. The effects of UV exposure on PL emission will be discussed based on XPS analysis. In addition, the PL quantum yield of CdS:Mn/ZnS core/shell nanocrystals will be reported and compared to organically capped CdS:Mn nanocrystals.

**9:00 AM \*Q1.3**

**THEORY AND MEASUREMENT OF NANOCRYSTAL ELECTRONIC STRUCTURE.** Louis Brus, Chemistry Department, Columbia University, New York, NY.

We describe recent developments in two areas of nanocrystal electronic structure: (1) ab initio DFT calculation with complete geometrical optimization, with application to understanding the difference between oxide shell and hydrogen passivation for 1-2 nm Si nanocrystals, and (2) quantitative Electric Force Microscopy, with application to determining the magnitude and location of charges and dipoles in single CdSe and PbSe nanocrystals at 23 C.

**9:30 AM \*Q1.4**

**UNDERSTANDING DOPING AND INTERPARTICLE**

**INTERACTION IN NANOMATERIALS.** Jin Z. Zhang, T.J. Norman Jr., C.D. Grant, A.M. Schwartzberg, D. Magana, T. Wilson, C. Burns, Univ of California, Dept. of Chemistry, Santa Cruz, CA; D. Cao, F. Bridges, Univ of California, Dept. of Physics, Santa Cruz, CA.

Doping of semiconductors is of fundamental importance. Uniform doping of semiconductor quantum dots on the individual particle basis is challenging. In an attempt to achieve uniform doping of semiconductor nanoparticles, we have explored the use of a molecular cluster seed approach for growing larger nanoparticles using Mn-doped ZnSe as an illustration. Mn<sup>2+</sup> doped ZnSe nanoparticles were synthesized from molecular cluster precursors, (Me<sub>4</sub>N)<sub>4</sub>[Zn<sub>10</sub>Se<sub>4</sub>(SPh)<sub>16</sub>], and characterized using a variety of techniques including spectroscopy, fs transient absorption, ESR, and XAFS, HRTEM. Correlation between local structure of Mn ions and optical properties has been established. Two Mn sites have been identified with one on the surface and the other one in the interior. While the interior Mn has characteristic 580 nm emission, the surface site acts to significantly quench the ZnSe fluorescence but gives no Mn emission at 580 nm. It is unclear from these ensemble measurements if the doping is uniform on a per particle basis. Single nanoparticle experiment is underway to determine the doping uniformity. In a separate effort, we have been interested in probing the fundamental interaction between nanoparticles that is critical to assembly of nanomaterials. Strongly interacting Au nanoparticle aggregates have been found to be an excellent system for this study. We have performed extensive characterization of the structure of the aggregates using different techniques. We also observed, for the first time, coherent vibrational oscillations of such nanoparticle aggregates based fs laser spectroscopy. The oscillation period was found to depend on probe wavelength, suggesting that the broad extended plasmon band (EPB) contains contributions from aggregates with different sizes and/or fractal structures. The vibration of the aggregates appears to be "softer" than that of hard spherical gold nanoparticles. Persistent spectral hole burning yielded a hole in the EPB, further supporting that this near-IR band is inhomogeneously broadened by different sized/structured aggregates.

**10:30 AM \*Q1.5**

**SMART DUST: PHOTONIC CRYSTALS DERIVED FROM NANOCRYSTALLINE POROUS SILICON.** Michael J. Sailor, Thomas A. Schmedake, Frederique Cunin, Jamie R. Link, University of California, San Diego, Dept of Chemistry and Biochemistry, La Jolla, CA; Jennifer Koh, Sangeeta Bhatia, University of California, San Diego, Dept of Bioengineering, La Jolla, CA.

A method to construct small particles of silicon, each smaller than the diameter of a human hair, that contain photonic codes will be described. We refer to this material as smart dust because each particle can be chemically programmed to perform simple tasks such as filtering liquids, concentrating gases, testing for toxic chemicals, or detecting biological chemicals in a Petri dish. Use of such materials should in high-throughput screening applications and in remote sensing of toxins or pollutants will be discussed. A silicon smart dust particle is encoded by generating sinusoidal layers of nanometer-scale porous structures in a silicon wafer using a programmed electrochemical etch. The film is released from the silicon wafer and small particles are produced by ultrasonic fracture. The layered nanostructure acts as a one-dimensional photonic crystal, or rugate filter, reflecting light of very sharp frequencies. Multiple spectral lines can be etched into a single particle, and the codes are read using a small low powered laser or with a hand-held spectrometer.

**11:00 AM \*Q1.6**

**IN VIVO IMAGING OF QUANTUM DOTS ENCAPSULATED IN PHOSPHOLIPID MICELLES.** B. Dubertret, Rockefeller Univ, Center for Studies in Physics and Biology, New York, NY; P. Skourides, Rockefeller Univ, Laboratory of Molecular Embryology, New York, NY; D.J. Norris, Univ of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN; V. Noireaux, Rockefeller Univ, Center for Studies in Physics and Biology, New York, NY; A.H. Brivanlou, Rockefeller Univ, Laboratory of Molecular Embryology, New York, NY; A. Libchaber, Rockefeller Univ, Center for Studies in Physics and Biology, New York, NY.

While fluorescent semiconductor nanocrystals (quantum dots) promise to revolutionize biological imaging, their use has been limited by difficulties in obtaining nanocrystals that are bio-compatible. To address this problem, we encapsulate individual nanocrystals in phospholipid block-copolymer micelles, and demonstrate both in vitro and in vivo imaging. When conjugated to DNA, the nanocrystal-micelles act as in vitro fluorescent probes to hybridize to specific complementary sequences. More importantly, when injected into *Xenopus* embryos, the nanocrystal-micelles are stable, non-toxic, cell autonomous, and slow to photobleach. Nanocrystal fluorescence can be followed to the tadpole stage, allowing lineage tracing experiments in embryogenesis.

**11:30 AM \*Q1.7**

SOLUTION SYNTHESIS AND SURFACE TERMINATION OF Si AND Ge NANOPARTICLES. Susan M. Kauzlarich, University of California, Davis, CA.

Interest in the synthesis of semiconductor nanoparticles has been generated by their unusual optical and electronic properties arising from quantum confinement effects. We have synthesized silicon and germanium nanoclusters by various solution methods with the primary goal of being able to control both the size and the surface chemistry. We have prepared Si nanoparticles that photoluminesce in the blue, green, and red. We have prepared Ge nanoparticles with complex functionalized surfaces. These nanoparticles have been characterized by TEM, FTIR, photoluminescence, fluorescence microscopy, and NMR. I will briefly present work to date and some new directions in synthesis.

SESSION Q2: QUANTUM DOTS AND NANOPARTICLES II

Chair: Jin Z. Zhang  
Monday Afternoon, April 21, 2003  
Metropolitan II (Argent)

**1:30 PM Q2.1**

QUANTUM DOT - ORGANIC OLIGOMER NANOSTRUCTURES: ELECTRONIC EXCITATION MIGRATION AND OPTICAL MEMORY DESIGN. Artjay Javier, C. Steven Yun, Geoffrey F. Strouse, University of California, Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

Energy, in the form of an electronic excitation, can be directed within an inorganic-organic composite of semiconductor quantum dots and organic oligomers by manipulating the structural conformations of the organic component or the size of the inorganic component. Continuous-wave and time-resolved photoluminescence studies indicate that weak electromagnetic resonant coupling between discrete intra-chain and inter-chain excitations of the oligomer and quantum dot excitations can be used to produce a potentially useful optical display material. Thin film blends demonstrate a thermally-induced luminescence-detected chain-melting phenomenon that has the potential for writable optical memory.

**1:45 PM Q2.2**

COLLOIDAL MAGNETIC SEMICONDUCTOR QUANTUM DOTS: POTENTIAL BUILDING BLOCKS FOR NANOSCALE SPINTRONICS APPLICATIONS. Pavle V. Radovanovic and Daniel R. Gamelin, University of Washington, Department of Chemistry, Seattle, WA.

Diluted magnetic semiconductors (DMSs) are currently the focus of intense applications-oriented research in the emerging area of spin-based electronics, or "spintronics." DMS quantum dots (DMS-QDs), quantum wells, quantum wires, and crystalline thin films are pivotal architectural elements in many proposed spintronics devices including spin-dependent LEDs, field-effect transistors, resonant tunneling diodes, quantized magnetic disks, and quantum computers. A central challenge facing the development of this technology at this time is the identification of materials that combine the necessary properties of conductivity and magnetic ordering at temperatures above room temperature. This seminar will present our group's recent advances in the development of direct solution-based synthetic routes for preparation of freestanding high-quality nanocrystalline DMSs, and will present the results of various spectroscopic and magnetic measurements performed on these materials.

**2:00 PM \*Q2.3**

SYNTHESIS, PROCESSING AND APPLICATIONS OF COLLOIDAL NANOCRYSTALS. Xiaogang Peng, University of Arkansas, Department of Chemistry and Biochemistry, Fayetteville, AR.

Rational approaches of synthesis and processing of high quality colloidal nanocrystals are explored. Green chemistry principles and growth mechanisms are used as the guidelines for the design of synthetic schemes. The processing chemistry of colloidal nanocrystals will be addressed from the understanding of the interface chemistry and the development of their ligand chemistry.

**2:30 PM \*Q2.4**

CRYSTALLINE PHOTOLUMINESCENT SUPERLATTICES FROM CHALCOGENIDE SUPERTETRAHEDRAL CLUSTERS. Pingyun Feng, Nanfeng Zheng, Xianhui Bu, Department of Chemistry, University of California at Riverside, CA.

The self-assembly of chalcogenide supertetrahedral clusters into covalent superlattices will be presented. Supertetrahedral clusters are nanometer-sized tetrahedrally shaped regular fragments of the zinc blende type lattice. These single-sized nanoclusters can grow into crystalline superlattices. The structural analysis based on single crystals reveals detailed structural information that could serve as a basis for the elucidation of larger colloidal nanostructures. The diversity of superlattices is achieved by modifying the cluster size, the cluster composition, and the inter-cluster linkage mode. Nanoclusters investigated in this research include those larger than previously known supertetrahedral clusters so that the size gap between colloidal nanoclusters and small molecular clusters could be bridged.

**3:30 PM \*Q2.5**

SYNTHESIS AND CHARACTERIZATION OF PBSE NANOCRYSTALS AND NANOWIRES. Kyung-Sang Cho, AMRI University of New Orleans, LA and IBM Corp; C.B. Murray, IBM Corp; K.L. Stokes, AMRI University of New Orleans, LA.

We present a combination a high temperature solution phase synthesis with size selective processing techniques to produce organically passivated PbSe nanocrystals spheres and cubes with size distributions less than 5%. These monodisperse nanocrystals self-organize during controlled evaporation to produce 2D and 3D superlattices (colloidal crystals, opals). The nanocrystals resemble "artificial atoms" sitting on regular close-packed superlattice sites, each separated by a selected organic spacer. The inter-particle spacing can be varied from intimate contact up to  $\sim 40 \text{ \AA}$  separation. The superlattices retain and enhance many of the desirable mesoscopic properties of individual nanocrystals and permit the first systematic investigation of new collective phenomena. Our goal is to study the properties of both the dispersed nanocrystals and assemblies as all major structural parameters are varied (composition, size, and spacing). The one dimensional self-organization of these nanocrystals into nanowires will also be presented.

**4:00 PM \*Q2.6**

PREPARATIONS AND BIOLOGICAL APPLICATIONS OF SEMICONDUCTOR AND METAL NANOPARTICLES. Chia-Chun Jay Chen, National Taiwan Normal University, Dept of Chemistry, and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, TAIWAN.

Different types of metal and semiconductor nanoparticles such as Au nanorods, II-VI semiconductor nanocrystals, and III-V semiconductor core-shell nanowires are prepared by catalytic vapor-liquid-solid growth and solution synthesis. Several synthetic strategies are applied to control the growths of those materials. High-resolution transmission electron microscopy is used to reveal their structural properties and also growth mechanism. Temperature dependencies of photoluminescence and cathodoluminescence, reflectance and Raman spectra are performed to investigate their optical properties. The nanoparticles functionalized with peptides and carbohydrates are synthesized for bio-labeling and diagnostics purposes. The bindings or interactions between the functionalized nanoparticles and specific receptors are investigated, and some important effects are observed. New applications of those functionalized nanoparticles in a living cell will be also discussed.

**4:30 PM Q2.7**

SYNTHESIS OF GOLD NANOSHELLS AND THEIR USE IN SENSING APPLICATIONS. Yugang Sun and Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

A general approach involved template-engaged replacement reaction has been developed to prepare metallic nanostructures with hollow interiors through reacting solutions of appropriate salts with metallic solid nanoparticles. The reaction between aqueous chloroauric acid and silver nanoparticles demonstrated a typical example to generate gold nanoshells. The morphology, void space, and wall thickness of these hollow structures were all determined by the silver templates, which were completely converted into soluble species during the replacement reaction. The extinction peaks of these gold nanoshells were considerably red-shifted as compared to solid gold colloids having approximately the same dimensions. In addition, the surface plasmon resonance of gold nanoshells exhibited a much more sensitive response toward environmental changes even when compared with solid colloids with a mean size much smaller than that of gold nanoshells. Such enhanced sensitivities should make gold nanoshells particularly useful as optical probes for chemical or biological binding events at solid-liquid interfaces.

**4:45 PM Q2.8**

SYNTHESIS, SELF-ASSEMBLY AND MAGNETIC PROPERTIES OF CoPtAg NANOPARTICLES. Xiangcheng Sun and D.E. Nikles,

Center for Materials for Information Technology, University of Alabama, Tuscaloosa AL; X.D. Bai, J. Li, Z.L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

CoPt and FePt alloy films with a face-centered tetragonal  $L1_0$ -ordered structure have been attractive as ultrahigh-density magnetic recording media due to their very large magnetic anisotropy. In this study, high temperature chemically reduction of cobalt chloride, platinum acetylacetonate and silver acetate was employed to synthesize  $Co_xPt_yAg_{100-x-y}$  nanoparticles in the presence of stabilizers oleic acid and oleyl amine. The relative amounts of cobalt, platinum and silver in the nanocomposite particles depended on the amount of cobalt, platinum and silver charged to the reaction. As prepared the particles possessed a disordered face-centered cubic (fcc) lattice with an average diameter of 3.5-11 nm and were superparamagnetic. XRD data and TEM images provided direct evidence of the formation of chemically disordered fcc structure. These particles were well dispersed in hydrocarbon solvents and spontaneously self-assembled into particles arrays with two or three-dimensional close-packing arrangements when colloidal solution of CoPtAg particles were spread on to solid substrates (such as, carbon coated Cu TEM grids or single crystal Si) with subsequent slow evaporating of the carrier solvent. The local structure of these arrays was also examined by using a combination of TEM and image simulations. Self-assembled magnetic arrays were heated at temperatures ranging from 550°C to 700°C under a 5%  $H_2$  in Ar atmosphere, whereupon the particles transformed into the tetragonal ( $L1_0$ ) phase, and the Ag was separated from the particles. The coercivity of the annealed magnetic particles arrays increased with increasing annealing temperature, while the particles size and arrays domain (or assembly dimension) were still kept the same due to the controlled organic surfactant layer (organic capping). It is worthy noting that the addition of Ag elements into CoPt alloy particles is demonstrated to be effective way to promote the tetragonal ( $L1_0$ ) phase ordering compared with the bulk CoPt alloys ( $L1_0$ -ordered phase above 800°C). The possible mechanism of the reduction of the ordering temperature was also given.

SESSION Q3: TEMPLATE-DIRECTED  
SELF-ASSEMBLY  
Chair: Orlin D. Velev  
Tuesday Morning, April 22, 2003  
Metropolitan II (Argent)

#### 8:30 AM Q3.1

DIRECTED ORGANIZATION OF NANOPARTICLES IN ULTRATHIN POLYMER FILMS. Rastislav Levicky and Zhen Liu, Columbia Univ, Dept of Chemical Engineering, New York, NY.

Prospective applications for nanometer-sized inorganic particles include information storage, sensing, nanoelectronics, and catalysis. Often, the principal aim is to use nanoparticles as surface-modification agents for bestowing specific desired properties onto a solid support. In these instances, the ability to tailor nanoparticle distribution on the (potentially macroscopic) surface of interest can be crucial, for example to ensure lateral homogeneity of surface properties. This talk will discuss the use of extremely thin, 10 nm and thinner, films of end-tethered commercial polymers for tuning the lateral organization of nanoparticles via thermodynamic and kinetic means. For certain values of polymer film thickness and particle diameter, macroscopic phase separation of particles and polymer is suppressed, leading to "modulated phase" behavior as a consequence of the frustrated phase separation. In this regime, particle-rich domains in the shape of disks are observed at lower particle coverages. In marked contrast, higher surface coverages lead to elongated, asymmetric stripe-like structures. In addition, it is demonstrated that nanorings with adjustable diameter in the few tens of nanometers can be fabricated by adjusting particle deposition conditions. Larger, micron-scale rings attributed to surface-tension induced instabilities, as previously shown in work of other groups, are also observed.

#### 8:45 AM Q3.2

ORDERED NANOPARTICLE QUANTUM DOT ARRAYS FORMED USING CRYSTALLINE PROTEIN TEMPLATES. Andrew McMillan, Chad Paavola, Jeanie Howard, Suzanne Chan, Jonathan Trent, NASA Ames Research Center, Center for Nanotechnology and Astrobiology Technology Branch, Moffett Field, CA; Nestor Zaluzec, Argonne National Laboratory, Materials Science Division, Argonne, IL.

Proteins that self-assemble into intricate crystalline structures are of interest to the Materials Science community because the crystalline lattice can be viewed as a nanoscale template. Using microbial genetics, proteins can be produced on a large scale with sequences tailored for specificity. We have formed nanoscale ordered arrays of metal and semiconductor nanoparticle quantum dots by binding

slurries of preformed nanoparticles onto crystalline protein templates made from genetically engineered chaperonins. Chaperonins are hollow double-ring structures composed of 60-kDa protein subunits called heat-shock proteins (HSP60s). Using structural information as a guide, we genetically engineered a thermostable recombinant HSP60 to form chaperonins with variably sized apical pores surrounded by chemically reactive thiols. These engineered chaperonins can be crystallized into two-dimensional templates up to 100 microns in diameter. The periodic solvent exposed thiols within these crystalline templates are used to size-selectively bind and organize metal and semiconductor quantum dots (1 to 10 nm) into arrays driven by the affinity of thiol for soft metals. The interparticle spacing and order within arrays formed in this manner are defined by the lattice of the underlying protein crystal. Ordered arrays can also be formed by first covalently attaching quantum dots to HSP60 subunits prior to assembly into rings and into two-dimensional crystals, thereby individually maneuvering QDs into arrays based on the self assembling properties of the subunits. These arrays have order that extends throughout the protein crystal template. Arrays formed by these methods may find use in the development of new electronic and photonic devices. This talk will focus on recent developments in the formation of inorganic nanostructures using engineered chaperonin templates.

#### 9:00 AM \*Q3.3

THIN FILMS DERIVED FROM COMPOSITE COLLOIDS AND COLLOIDAL ASSEMBLIES FOR BIOSENSING. Frank Caruso, The University of Melbourne, Department of Chemical and Biomolecular Engineering, Victoria, AUSTRALIA; Amin Yu, Thierry Cassagneau, Max Planck Institute of Colloids and Interfaces, Potsdam, GERMANY.

Ultrasensitive, highly specific biosensors have the potential to impact the fields of medical diagnostics, pharmaceuticals, and agriculture. This paper will demonstrate the applicability and versatility of using colloid particles as building blocks or as templates for the fabrication of thin film biosensors. The first type of biosensors is based on enzyme multilayers prepared from polyelectrolyte-encapsulated catalase microcrystals. Encapsulated catalase microcrystals were assembled onto planar supports through electrostatic interactions by the sequential deposition with oppositely charged polyelectrolytes. These stable, high enzyme content films display biocatalytic activities up to fifty times higher than those prepared by conventional sequential deposition of solubilized enzyme. The second type of films makes use of ordered arrays of spherical colloids as templates for the fabrication of highly sensitive polymer inverse opal biosensors for both potentiometric and optical affinity detection. The porous sensors were applied for the potentiometric detection of creatinine, an enzyme related to kidney function, and for monitoring biospecific avidin-biotin interactions through the Bragg-diffraction of electromagnetic waves within the inverse opal structure. The inverse opals described represent a new class of versatile transducers for biosensing.

#### 9:30 AM \*Q3.4

MESOSTRUCTURED ORGANIC-INORGANIC SYSTEMS FOR PHOTONICS: LIGHT LOCALIZATION & AMPLIFICATION. Rachel Jakubiak, Dean Brown, Fatma Vatansever and Timothy J. Bunning, Richard A. Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Coherent localization of light associated with multiple elastic scattering events underlies many aspects of the photophysics of emerging nano- and mesoscale material concepts that have potential application in opto-electronic components. Applications range from photonic band-gap systems (PBGs) to random particle lasers. Organic-inorganic hybrids combine the design flexibility and large-scale, low cost processing afforded by organics with superior opto-electronic properties and large refractive index contrast of inorganics. Success requires development of synergistic approaches to tailor interfacial properties and to provide rapid, large scale, multidimensional processing. In this regard, surface initiated ring opening metathesis polymerization from quantum dots (QDs) enables tailoring, including molecular weight, polydispersity, and composition, of the organic corona surrounding the QD. These tailored QDs are utilized in holographic photopolymerization to fabrication one-, two- and three-dimensional organic-inorganic hybrids. The resulting periodic composition leads to grating structures which can be modulated by an external electric field and exhibit controlled reflectivity and coherent localization of light (stimulated emission).

#### 10:30 AM \*Q3.5

VIRUS TEMPLATES FOR FORMING THREE-DIMENSIONAL METALLIC NANOSTRUCTURES. Mary Turner, Josh Faulkner, Katy Bosworth, Tim Trentler, Vicki Colvin, Rice University, Department of Chemistry, Houston, TX; Tianwei Lin, Jack Johnson, Scripps Institute, San Diego, CA.

The organization of nanoscale materials in three dimensions is a major challenge for nanochemistry. Here we show that virus crystals provide an ideal template for building organized metallic nanostructures. Biomolecular crystals are first formed via conventional crystallization methods. They are stabilized with standard cross-linking agents which result in robust and macroscopic crystals for processing. A variety of infiltration chemistries can be used to fill the large pore volume with materials as diverse as polymers and metals. In the case of the CPMV virus, the porous architecture results in a cross-bar mesh of nanostructured metals with potentially interesting optical and electronic applications.

#### 11:00 AM \*Q3.6

NEW OPTICAL AND MAGNETIC MATERIALS ASSEMBLED THROUGH HOST/GUEST CHEMISTRY USING TEMPLATED NANOPOROUS SILICAS. Sarah H. Tolbert, Adam F. Gross, Ashley Cadby, Andrew P.Z. Clark, and William Molenkamp, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA.

Polymer and surfactant templating provides a powerful method to produce periodic nanostructured materials. While these methods are often applied to template insulating oxides such as silica, the method can be used to produce optically and magnetically active materials using host/guest chemistry. In this talk, we first explore the formation of optical materials based on combinations of semiconducting polymers and templated silica. Both diffusive incorporation and direct synthesis are used to incorporate the polymer into the silica host. The effects of spatial confinement and orientation on the optical and electronic properties of the composite are then explored. In particular, confinement is used to limit or encourage polymer-polymer interactions. In the second part of the talk, we examine how host/guest chemistry can be used to control magnetic interactions between cobalt nanocrystals incorporated into the pores of a polymer templated silica host. The results indicate that the net magnetic properties of the composite can significantly altered by using nanoscale confinement to limit interactions between colloids.

#### 11:30 AM Q3.7

FAST DEPOSITION OF COLLOIDAL CRYSTAL AND NANOPARTICLE COATINGS FROM MICROLITER DROPLETS. Brian G. Prevo and Orlin D. Velev, Dept. of Chemical Engineering, North Carolina State University, Raleigh, NC.

In view of future technological applications of micro- and nanoparticle coatings and structures, it is important to develop assembly procedures that are fast, inexpensive and easy to control. Current methods of convective assembly of crystalline arrays on substrates take a long time and use large volumes of slowly evaporating colloidal suspensions. We report here a robust and technologically feasible technique for quick deposition of micro- and nanoparticle coatings of controlled thickness. Coatings of several square centimeters could be produced in minutes from colloidal suspension volumes of approximately 10 microliters. Three different types of particle coatings were investigated: (1) 2D colloidal crystals of polystyrene microspheres, (2) thin films of metallic nanoparticles, and (3) hierarchically structured metallic nanoparticle films formed via colloidal templating. The mechanism for coating, convective assembly at high volume fraction, is directly related to several controlling parameters: the speed of deposition, the particle concentration, and evaporative flux of the solvent. These parameters allow control of the structure and thickness of the particle layers. In the case of metallic nanoparticle coatings, varying the speed of deposition yields tunable optical reflectance and transmission spectra. With latex crystal coatings, the same tunability allows efficient control over the crystal thickness from submonolayers to multilayers.

#### 11:45 AM Q3.8

CONTROL OF MORPHOLOGY OF NANOPARTICLES-LIQUID CRYSTAL COLLOIDS. John L. West, Ke Zhang, Anatoliy Glushchenko, Liquid Crystal Institute, Kent State University, Kent, OH.

Liquid crystal colloids are of a great scientific and practical interest<sup>1-2</sup>. They can significantly enhance the performance of pure liquid crystals<sup>3</sup> and isotropic colloids<sup>4</sup>. While behavior of a single particle in a liquid crystal matrix is well understood theoretically and studied experimentally, the collective behavior in a system of many colloidal particles suspended in a liquid crystal is only now beginning to be explored. Our work takes a fresh approach toward the research and development of structured liquid crystal colloids. We were able to control complex 3-D particle structures using moving isotropic-nematic interface and patterned electric field. By adjusting a speed of the interface and magnitude of the field, we were able to create a variety of particle structures within a liquid crystal layer. We also investigated the affect of the liquid crystal boundary conditions and the particles size and shape on their spatial distribution. These complex structures may be used in a wide variety of liquid crystal and

related devices. 1. Poulin, P., Stark H., Lubensky, T., Weitz, D. *Science*, Vol. 275, 1770-1773 (1997). 2. Anderson, V.J., Terentjev, E.M., Meeker S.P., Crain, J., Poon, W.C.K. *Eur. Phys. J. E*, Vol. 4, 11 (2001). 3. Russel, W.B., Saville, D.A., Schowalter, W.R. *Colloidal Dispersions* (Cambridge University Press, New York, 1989). 4. de Gennes, P.G., Prost, J. *Physics of Liquid Crystals* (Clarendon Press: Oxford, 1993).

#### SESSION Q4/P2/J1: JOINT SESSION SELF-ASSEMBLY

Chair: David J. Norris  
Tuesday Afternoon, April 22, 2003  
Metropolitan II (Argent)

#### 1:30 PM \*Q4.1/P2.1/J1.1

MULTICOMPOSITIONAL ASSEMBLY AND FUNCTION IN THREE DIMENSIONS. Galen D. Stucky, University of California, Dept of Chemistry & Biochemistry and Materials Dept.

Numerous examples exist, both biological and synthetic, of composite materials that are structurally organized on multiple length scales and dimensions. The 3-d organized molecular assembly of components that are both functionally and compositionally unique into an integrated system remains a challenge, albeit exciting advances in this area are being made, as evidenced by presentations in this symposium. In biogenesis the components of the system are created via non-linear parallel multivalent synthesis and processing. On the benchtop, a first approximation to this is to use a 3-d "living polymer" approach with distinctly defined chemical potential domains in which specific molecular assembly processes can be carried out on specified time scales. The overall system organization is then determined by the molecular definition of the interfaces between the domains. This talk will review some selected recent observations made on the 3-d molecular assembly of two or more inorganic species with distinct functionalities. The a priori simpler configuration of homogeneous solution-like phases makes possible electro-optic or magneto-optical composite arrays that are otherwise not easily accessible. An alternative is to carry out the molecular assembly of species with different composition and function into phase separated extended domains. An example of this is the use of block polypeptides to co-assemble capped CdSe(CdS) quantum dots and silica nanoparticles into a microcavity configuration. In this case the electronic states of the three-dimensional confined semiconductor nanocrystallites are coupled to the photonic states of the spherical microcavity to give single mode lasing.

#### 2:00 PM \*Q4.2/P2.2/J1.2

COLLOIDAL SELF-ASSEMBLY, MULTI-BEAM INTERFERENCE LITHOGRAPHY, AND PHOTONIC CRYSTALS. Pierre Wiltzius, University of Illinois, Beckman Institute for Advanced Science and Technology, Dept. of Materials Science and Engineering, Dept. of Physics, Urbana, IL.

Photonic crystals are materials that allow us to manipulate light in new and unexpected ways. Semiconducting materials played a tremendous role in microelectronics and we expect photonic crystals to revolutionize the world of microphotonics in a similar way. Colloidal self-assembly and multi-beam interference lithography are great tools to build crystals with interesting optical properties. I will review some recent progress towards constructing photonic band-gap materials and switchable 3D Bragg gratings.

#### 2:30 PM \*Q4.3/P2.3/J1.3

FORMATION OF 2D COLLOIDAL MONOLAYERS AT LIQUID SURFACES UNDER THE ACTION OF LONG-RANGE ELECTROSTATIC AND CAPILLARY INTERACTIONS. Vesselin Paunov, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM.

Recent progress on preparation of 2D structured micro-particle monolayers has demonstrated the potential application of non-specific colloid interactions between particles trapped at liquid surfaces or into liquid layers for fabrication of high technology coatings and materials. The characterization of the long-range colloidal forces operating between particles at liquid surfaces is a major step towards understanding and controlling of the self-assembly of the particle monolayers by fine-tuning of the interparticle interactions. This presentation summarizes our findings on the long-range lateral capillary interactions between particles in several different configurations, including freely floating particles and particles trapped in a liquid film. We reveal the formal analogy between the lateral capillary interaction between particles at a liquid-fluid interface and the DLVO-type of electrostatic interaction between charged surfaces in electrolyte solution. We also analyze the super long-ranged electrostatic repulsion between charged micron-sized latex particles

adsorbed at an oil-water interface. It was found that latex particle monolayers at octane-water interface remain highly ordered as a result of long-range repulsion, even on concentrated electrolyte solution. In the case of air-water interfaces, the lateral electrostatic repulsion between the particles was found to be sensitive to the electrolyte concentration in the aqueous phase. Using a laser tweezers method, we have determined the long-range repulsive force as a function of separation between two charged polystyrene micro-spheres trapped at the oil-water interface. At large separations the force is found to decay with distance to the power 4 and is insensitive to the ionic strength of the aqueous phase. The results are consistent with a model in which the repulsion arises primarily from the presence of a very small residual electric charge at the particle-oil interface. We discuss how super-structured 2D mixed monolayers of different particles can be assembled by using such long-range interactions.

**3:30 PM \*Q4.4/P2.4/J1.4**

**TOWARDS PHOTONIC INK (P-INK): A POLYCHROME COLLOIDAL CRYSTAL DEVICE.** Andre C. Arsenault, Vladimir Kitaev, Geoffrey A. Ozin, and Ian Manners, University of Toronto, Chemistry Department, Toronto, CANADA; Hernan Miguez, Universidad Politecnica de Valencia, Centro Tecnológico de Ondas, Valencia, SPAIN.

We demonstrate here a planarized colloidal photonic crystal device whose optical stop-band position, width and intensity can be reversibly redox and solvent tuned over a broad wavelength range by an anisotropic expansion of the photonic lattice. The material is composed of silica microspheres in a matrix of crosslinked polyferrocenylsilane, a metallopolymer network with a continuously variable state of oxidation. Optical data was fitted using scalar wave theory, with a congruence to experimental data, allowing facile extraction of information concerning polymer swelling behaviour. The chemo-mechanical polychrome optical response of the material was exceptionally fast, attaining its fully swollen state from the dry shrunken state on a sub-second time-scale.

**4:00 PM \*Q4.5/P2.5/J1.5**

**COLLOIDAL CRYSTAL TEMPLATING OF POROUS SOLIDS FOR APPLICATIONS BEYOND PHOTONICS.** Andreas Stein, Hongwei Yan, Sergey Sokolov, Justin C. Lytle, Mohammed Al-Daous, University of Minnesota, Department of Chemistry, Minneapolis, MN.

A variety of colloidal crystal templating methods have been developed to produce three-dimensionally ordered macroporous (3DOM) or "inverse opal" structures. Many studies have focussed on photonic crystals as target materials, with interesting projected applications involving confinement and control of electromagnetic waves. Structural requirements on such photonic crystals are rigorous, and strict control of defects is necessary to obtain photonic bandgaps. A number of other applications of 3DOM materials pose less rigorous requirements on structural periodicity, but benefit from the 3D arrays of relatively large interconnected pores, highly accessible surfaces, and compositional flexibility of the synthesis. Such applications include optical sensing, catalysis, battery materials, and bioactive materials. This presentation will provide a general overview of relevant issues of structural control in these applications and will then focus on 3DOM materials for nanostructured electrodes ( $V_2O_5$ ,  $LiNiO_2$ ,  $LiCoO_2$ ,  $LiMn_2O_4$ , and  $SnO_2$ ) and bioactive glasses ( $SiO_2/CaO$ ).

**4:30 PM \*Q4.6/P2.6/J1.6**

**SELF-ASSEMBLY OF NANOSTRUCTURED LIQUID CRYSTALS.** Takashi Kato, The Univ of Tokyo, Dept of Chemistry and Biotechnology, School of Engineering, Tokyo, JAPAN.

Self-assembly of liquid crystalline (LC) materials with functional moieties is one of versatile approaches to obtain functional molecular soft materials. Here we show two of our approaches to the fabrication of functional LC materials built by non-covalent interactions such as hydrogen bonding and ion-dipolar interactions. The combination of self-assembly through such non-covalent interactions and nanophase segregation behavior is the key for the formation of these functional structures. (1) Low-Dimensional Ion-Conductors: Phase-segregated nanostructures formed by self-assembly processes are useful for the design of functional materials such as ion and electron conductors. Macroscopically oriented one- and two-dimensional ion-conductive materials have been obtained by self-assembly of ionic liquids and hydroxyl-functionalized aromatic molecules. They are partially incompatible and their mixtures form columnar and smectic phases. For one-dimensional conductors, macroscopic homogeneous orientation of the columnar structures is easily achieved by shearing the materials for those assembled materials at room temperature, which leads to high anisotropic ion-conductivity. (2) Ion-Induced Chiral Supramolecular Assemblies: We have designed LC folic acid derivatives having oligo(amino acid) moieties. These materials exhibit columnar and cubic phases due to the formation of hydrogen-bonded tetramers. The addition of a sodium salt induces and stabilizes the

cubic phases. Moreover, the addition of the salt has induced the formation of supramolecular chiral LC assemblies. This materials design might lead to the fabrication of materials that are responsive to stimuli such as ions and environments.

SESSION Q5: POSTER SESSION  
QUANTUM DOTS AND COLLOIDAL PARTICLES  
Chair: Orlin D. Velev  
Tuesday Evening, April 22, 2003  
8:00 PM  
Golden Gate (Marriott)

**Q5.1**

**ELECTROLESS COATING OF Ag NANOPARTICLES ON NANOSTRUCTURED VOID-COLUMN Si FILMS AND ITS APPLICATION TO MOLECULAR DETECTION BY SURFACE-ENHANCED RAMAN SCATTERING.** Kaan Kalkan, Stephen J. Fonash, The Pennsylvania State University, Nanofabrication Facility, PA.

Ag nanoparticles were coated on nanostructured void-column Si films simply by film immersion into pure  $Ag_2SO_4$  or  $AgNO_3$  solutions. Synthesis of Ag nanoparticles occurs without the need for an external reducing agent, complexing agent, or electric bias. Despite a controllable enhancement of the surface plasmon absorption band (up to an absorption coefficient of  $\sim 300,000$  l/cm) with immersion time the peak persists to be at 3.0 eV indicative of non-aggregating Ag nanospheres with a size range not exceeding a few tens of nanometers. Furthermore, the increase of plasmon absorption with the Si film thickness implies the Ag particles are synthesized throughout the thickness of the Si film in a 3D array fashion. Indeed, scanning electron microscope study confirms the presence of monodispersed Ag particles spaced uniformly along the Si nanocolumns whose average size is on the order of columnar spacing. Therefore, the nanostructured Si films not only enable easy synthesis of 3D arrays of Ag nanoparticles, but also their monodispersion and narrow size distribution without the use of a surfactant. The Ag-nanoparticle/Si-nanocolumn array films obtained were found to serve as surface-enhanced Raman scattering active substrates. Detection and identification of various organic molecules such as rhodamine, fluorescein, and perylene at trace concentrations was achieved.

**Q5.2**

**SELFASSEMBLING AROUND TEMPLATES - CREATING NANO DOTS AND PITS FOR CHEMICAL SENSING.** Franz L. Dickert, Peter Lieberzeit, Oliver Hayden, Roland Bindeus, Karl-Jürgen Mann, Vienna Univ, Inst of Analytical Chemistry, Vienna, AUSTRIA.

Organic Polymers and sol gel phases were structured by different analytes ranging from simple molecules up to more complex biological particles as enzymes and viruses acting as templates. Thus, dots of approximately 1 nm in bulk material and pits on surfaces in dimensions up to 300 nm could be created. Nanopatterned polyurethanes and polystyrenes as coating on QCM-arrays with six electrode pairs allow the monitoring of complex emissions during composting. The QCMs make possible a detection of typical volatile analytes, such as propanol, butanol, ethyl acetate and limonene. The highly selective dots are interactions centers in the smart materials and enable us in combination with artificial neural networks to perform a quantitative analysis with detection limits down to some ppm. Bioanalytes such as enzymes or viruses were incorporated by pits on the sensor surface from aqueous solutions. For this purpose the gold coatings of QCM- or SPR-devices were flattened by a polymer with a roughness lower than one nm. The enzymes and the viruses were applied to a amylose stamp and pressed on a prepolymerized sensor coating. In the case of rod like viruses, as the tobacco mosaic virus the temperature was lowered near to the freezing point. A highly ordered pattern on the stamp coating similar to nematic liquid crystals results in this way. Another possibility is the precipitation polymerization around the bioanalytes in aqueous phase using ultra thin layers. The adhesion of enzymes and viruses can be described by a concentration dependence which resembles that of the BET model. The sensor effect can also be followed by AFM measurements and thus non-gravimetric sensor effects can be evaluated which result from movable bioanalytes in the sensor pits.

**Q5.3**

**NEW WAY TO MAKE NANOPOROUS STRUCTURE FROM CONVENTIONAL DIELECTRIC MATERIALS.** Sun-Young Lee<sup>a</sup>, Hyun-Dam Jeong<sup>b</sup>; <sup>a</sup>Manufacturing Technology Center, Samsung Electronics Co., Ltd., Yongin-city, Kyungki-do, KOREA; <sup>b</sup>E-Polymer Lab., Samsung Advanced Institute of Technology, Suwon-city, Kyungki-do, KOREA.

The industry has used BPSG films as interlayer dielectric materials,

which is formed usually by using Atmospheric Pressure Chemical Vapor Deposition (APCVD) method. The BPSG films treated at a water vapor condition were characterized by using FT-IR spectroscopy, Auger electron spectroscopy, TEM, and AFM. The water molecules from the vapor were penetrated into the BPSG film and the concentration of boron and phosphorous atoms were concurrently decreased at the surface of the film. One of the most interesting results was that a porous layer in the BPSG films was observed in TEM image. The water molecules adsorbed at the film surface react with boron and phosphorous atoms of the film to produce the H<sub>3</sub>BO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> out of the surface. In case of the BPSG films damaged by dry etch process, the water absorption was found to make pores more efficiently in the films, whose diameter was in the range of 3 ~ 15 nm. In addition, the pore size was controlled by varying the concentration of the boron and phosphorous dopants. This is newly simple way to make nanoporous structure from conventional dielectric materials, which is possibly applied in the electronic and bioengineering fields

#### Q5.4

ATOMIC ORDERING IN SELF-ASSEMBLED EPITAXIAL IV-VI AND II-VI COMPOUND SEMICONDUCTOR QUANTUM DOT STRUCTURES. Peter Moeck and Armando Acha, Portland State University, Department of Physics; Teya Topuria and Nigel D. Browning, University of Illinois at Chicago, Department of Physics; Klaus Pierz, Physikalisches Technische Bundesanstalt Braunschweig, F.R. GERMANY; Patrick J. McCann and Huizhen Wu, University of Oklahoma, School of Electrical and Computer Engineering, OK.

Transmission electron microscopy (TEM) in both the parallel illumination and scanning probe mode revealed atomically ordered entities of the order of magnitude 10 nm in IV-VI and II-VI compound semiconductor quantum dot (QD) structures. While the II-VI system were [001] oriented ZnSe/(Cd,Mn)Se/ZnSe structures with varying Mn content and embedded QDs, the IV-VI system consisted of PbSe island on a [111] PbTe<sub>0.22</sub>Se<sub>0.78</sub> buffer layer that its lattice matched to the BaF<sub>2</sub> substrate, i.e. was a QD predecessor structure. Photoluminescence (PL) spectra from the II-VI structures revealed peaks at approximately 2 eV, which we attribute to the atomically ordered entities, as identified by TEM. This assignment is supported by an extensive review of the literature on the position of luminescence peaks in the (Cd,Mn,Zn)(Se,S) system.

#### Q5.5

A METAL OXIDE CLUSTER-BASED APPROACH TO NANOSTRUCTURED DIELECTRIC OR MAGNETIC INORGANIC-ORGANIC HYBRID POLYMERS. Ulrich Schubert, Viktoria Torma, Nicola Huesing, Silvia Gross, Ivan Mijatovic, Institute of Materials Chemistry, Vienna University of Technology, Austria Vito di Noto, Department of Inorganic Chemistry, University of Padova, ITALY; Fernando Palacio, CSIC, University of Zaragoza, SPAIN.

Metal oxide clusters of different size, shape and chemical composition, capped by covalently bonded polymerizable organic groups, were obtained by controlled hydrolysis of metal alkoxides in the presence of unsaturated carboxylic acids or by ligand exchange reactions. Radical polymerization of the clusters with organic co-monomers resulted in inorganic-organic hybrid materials in which the clusters, as nanosized inorganic objects, efficiently crosslink the organic polymer. The distribution of the clusters was investigated by Small Angle Scattering and ranges from a statistical distribution to weak aggregation, depending on the cluster / polymer combination. Several distribution models are proposed. Dielectric and Impedance Spectra show that polymers reinforced by zirconium or tantalum oxide clusters are interesting dielectric materials in which the dielectric constant is lower than in the undoped polymer. Incorporation of paramagnetic manganese clusters results in polymers, which show strong frequency dependence below a blocking temperature indicative of superparamagnetic behavior.

#### Q5.6

PORE-SIZE CONTROLLED SYNTHESIS OF MESOPOROUS SILICON CARBIDE. Guo-Qiang Jin and Xiang-Yun Guo, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Taiyuan, CHINA.

Mesoporous silicon carbide materials have widespread applications in many fields such as catalysis, separation, sensor technology and others. The key problem is to synthesize silicon carbide materials with high surface area and suitable pore distribution. The present work will give an improved sol-gel route to prepare mesoporous silicon carbide. In the present route, nickel nitrate was added into a binary carbonaceous silica sol to prepare a xerogel containing nickel pore-adjusting reagent. The silicon carbide was synthesized after the xerogel was heated to 1200-1300°C. The mesoporous silicon carbide was finally obtained by further purification. The XRD analysis

indicated that the samples obtained by the present route were  $\beta$ -SiC, and no other crystallites were detected from the XRD patterns. The surface area and pore distribution were measured by the Micromeritics ASAP-2000. The results showed that the samples obtained under different conditions had surface areas ranging from 40 to 200 m<sup>2</sup>/g and pore diameters varying from 40 to 3.5 nm. The synthesized silicon carbide had the largest surface area and the smallest pore diameter when Ni/Si atomic ratio in the xerogels was about 0.01. Increase or decrease in nickel content resulted in the samples with lower surface areas and larger pore diameters. Summarily, the present work gave an improved sol-gel route to synthesize mesoporous silicon carbide materials. The silicon carbide materials with high surface area can be synthesized by adding nickel nitrate to binary carbonaceous silica sols. Furthermore, the pore size of the silicon carbide can be controlled by adjusting nickel content in the sols.

#### Q5.7

EFFECT OF QUANTUM CONFINEMENT FROM AMORPHOUS GaN NANOPARTICULATE FILMS SYNTHESIZED BY LASER ABLATION. Jong-Won Yoon, Takeshi Sasaki, Naoto Koshizaki, Nanoarchitectonics Research Center (NARC), National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki, JAPAN; Seung Hwan Shim, Kwang Bo Shim, Hanyang Univ, Dept of Ceramic Engineering, Seoul, KOREA.

Nanoparticulate thin films of GaN were prepared by pulsed laser ablation without substrate heating. Target under various Ar pressures was irradiated using an ArF<sup>+</sup> excimer laser with an pulse energy of 34 mJ/pulse. The off-axis configuration of target and substrate was used to synthesize the thin films. Transmission electron microscopic (TEM) measurements indicated that the GaN thin films consisted of nanoparticles with size less than the exciton Bohr radius for GaN (11 nm). The particle size and morphology of the deposited films were strongly dependent on the processing Ar gas pressure. Under low pressure (below 10 Pa), the morphology showed a continuous film. With increasing Ar pressure from 50 to 200 Pa, the mean diameter of nanoparticles tended to decrease from 7.9 to 4.4 nm. From selected area electron diffraction (SAED) rings and X-ray diffraction (XRD) peaks, the deposited films were identified as amorphous GaN. The [Ga]/[N] ratio calculated from the XPS results was nearly unity from 50 to 200 Pa. The optical gap of these films obtained from an absorption spectra showed a large blueshift with respect to bulk GaN (3.4 eV). Furthermore, photoluminescence (PL) spectra revealed peak near 4.0 eV. The large blueshift of the absorption and PL could be due to effect of strong quantum confinement in these small particles of GaN. This pressure-controlled PLD process is suggested to be effective for control of particles size as nano-meter scale in GaN films without substrate heating.

#### Q5.8

DEEP-LEVEL EMISSION-FREE ZnO NANODOTS FORMED VIA LOW TEMPERATURE OXIDATION OF METALLIC Zn NANODOTS. Tae-Won Kim<sup>a</sup>, Tadashi Kawazoe<sup>a</sup>, Shunsuke Yamazaki<sup>b</sup>, Jungsik Lim<sup>b</sup>, Takashi Yatsui<sup>a</sup>, and Motoichi Ohtsu<sup>a,b</sup>. <sup>a</sup> Japan Science and Technology Corporation, Tokyo, JAPAN; <sup>b</sup> Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, JAPAN.

Recently, researches on the nanostructures of wide-band gap materials has been intensively carried out for the applications to nanophotonic devices. In particular, ZnO has attracted much attention to fabricate the high efficient UV light emitting devices at room temperature (RT) via excitonic recombination process. However, most of the ZnO nanostructures previously reported have been suffered from the deep-level emission, which might be attributed to intrinsic defects such as ionized oxygen vacancies or interstitial Zn. Such deep-level emission deteriorates the excitonic emission at the near band edge and leads to the low efficiency of UV light emission. In the present study, we report high-quality ZnO nanodots of deep-level emission-free fabricated at the low temperature of 380°C. We employed a simple method of fabrication, in which metallic Zn nanodots are transformed to ZnO nanodots by thermal oxidation process. From SEM and AFM images, ZnO nanodots having the diameter ranged from 10 nm to 60 nm was observed. XRD measurements revealed the mean diameter of the ZnO nanodots was about 30 nm. From the RT photoluminescence measurements using a cw He-Cd laser (325 nm in wavelength), the strong peak was observed at 3.28 eV, which is ascribed to the free exciton recombination. However, the deep-level emission intensity around 2.5 eV was negligibly weak, i.e., two orders of magnitude lower than that of the near band emission. From the results, we believe that oxygen can sufficiently diffuse into the metallic Zn nanodots even at such low temperature as 380°C, and then pure ZnO nanodots could be successfully fabricated. Therefore, we can conclude that the obtained ZnO nanodots possess extremely low defect concentration associated with the deep-level emission, and hence of sufficiently high-quality as a nanoscale UV light emitter which is one of the key components in nanophotonic devices.

#### Q5.9

##### DEVELOPMENT AND BENEFITS OF DISORDERED MICROSPHERE ASSEMBLIES FOR USE AS TEMPLATES.

Nathan L. Mitchell, Materials Department, University of California, Santa Barbara, CA; John H. Harreld, Galen D. Stucky, Department of Chemistry, University of California, Santa Barbara, CA; Yasushi Tsurita, Mitsubishi Chemical Corporation, Yokohama, JAPAN.

We report the fabrication of disordered arrays of polystyrene microspheres by utilizing polydispersity and mixtures of different sized spheres in the range of 60-260 nm. These disordered template structures have a tunable thickness and are suitable for the fabrication of high surface area, porous materials for a variety of applications. Although colloidal crystals obtained from monodisperse microspheres are commonly used as templates for porous materials, in many electrochemical or catalytic applications a high degree of crystalline order is often unnecessary or undesired. The inherent anisotropy of crystalline colloidal crystals, combined with induced stresses associated with the drying of these templates, often produces large cracks in these arrays, but by utilizing isotropic structures the degree of cracking is significantly reduced. Large areas ( $>1 \text{ cm}^2$ ) of crack free films are obtained.

#### Q5.10

##### MICROPATTERNED ORIENTED ZEOLITE MONOLAYER FILMS ON SILICON WAFER BY DIRECT IN-SITU CRYSTALLIZATION.

Shuang Li, Cori Demmelmaier, Yushan Yan, University of California, Riverside, Dept of Chemical and Environmental Engineering, Riverside, CA.

A simple way to micropattern oriented zeolite monolayer on silicon wafer substrate by direct in situ crystallization method has been demonstrated. Well-defined gold pattern on silicon wafer is produced by simply pasting TEM grid to substrate before e-beam vacuum deposition. Continuous *b*-oriented zeolite film can selectively grow between gold islands by direct in-situ hydrothermal crystallization of gold patterned silicon wafer substrate in solution with molar composition of 0.32TPAOH:TEOS:165H<sub>2</sub>O. Well-defined interface between zeolite and gold is observed. The advantages of this method are its simplicity and the strong adhesion of zeolite crystals to substrate. The controlled crystal orientation and zeolite monolayer formation result in special structural configuration in the film: a set of straight nanometer channels of zeolite crystals is perpendicular to the substrate and throughout the whole film from top to the bottom. This feature is expected to enhance the gas permeation and therefore improve the efficiency of the thin-film related to its application as size-selective chemical sensors, and separation membrane et al, in which process mass transport and shape-selective principle are crucial. This preferred orientation nanostructure can also be reflected in other properties of film such as: optics and electronics. This patterned zeolite film with oriented nanometer channel structure is potentially useful in fabrication of various patterned nanostructured materials and designing of novel zeolite-based devices. By modifying the gold islands with self-assembled monolayers(SAMs), it is expected to increase the extendibility of its application.

#### Q5.11

QUANTUM SIMULATIONS OF THE SYNTHESIS OF CdSe NANOSTRUCTURES. A. Puzder, A.J. Williamson, N. Zaitseva and G. Galli, Quantum Simulation Group, Physics and Advanced Technologies, Lawrence Livermore National Laboratory.

During the last decade, significant progress has been made in the chemical synthesis of a variety of semiconductor nanoclusters. In particular, II-VI nanostructures such as CdSe can now be synthesized with a remarkably high level of control over both their size and geometry. Recently, it has been demonstrated [1] that by altering the relative concentration of solvents used in the synthesis process it is possible to synthesize either spherical, rod or tetrapod shaped CdSe nanostructures. We present the results of first principles, density functional calculations designed to understand the mechanisms controlling the growth process of CdSe nanostructures. We first determined the relaxed atomic geometries of a set of prototype CdSe clusters ranging in size from 0.5 to 2nm. We then calculated the binding energies of a series of candidate solvent (e.g. TOPO and phosphonic acid) and passivant molecules to each of the facets of the clusters. We find strikingly different binding energies which depend on both the geometry of a facet and the atomic species (either Cd or Se) present on that facet. These results enable us to explain the recently observed dependence of nanostructure geometry on the solvent used in the synthesis process, as well as to predict the effect of alternative solvents, not yet tried experimentally.

Work done in collaboration with L. Manna and A.P. Alivisatos, Lawrence Berkeley Laboratory [1] Manna L, Scher EC, Alivisatos AP J AM CHEM SOC 122 (51): 12700-12706 DEC 27 2000.

#### Q5.12

##### SURFACTANT-ASSISTED SELF-ASSEMBLY OF ORDERED GOLD/SILICA NANOSTRUCTURES AND THEIR ELECTRICAL PROPERTIES.

Hongyou Fan, Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM; Daniel M. Boye, Physics Dept, Davidson College, Davidson, NC; Kevin J. Malloy and Thomas Sigmon, The Univ of New Mexico, Center for High Technology Materials, Albuquerque, NM; C. Jeffrey Brinker, The Univ of New Mexico/NSF Center for Micro-Engineered Materials, Dept of Chemical and Nuclear Engineering, and Sandia National Laboratories, Chemical Synthesis and Nanomaterials Dept, Albuquerque, NM.

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

#### Q5.13

UNCONVENTIONAL NANOTECHNOLOGY OF SUPERCONDUCTOR CERAMIC ARTICLES. Anatoly Rokhvarger and Lubov Chigirinsky, Polytechnic University, Chem. Eng., Chem. & Materials Sc. Dept., Brooklyn, NY.

This paper introduces recently discovered, patented, and proven in laboratory experiments an unconventional nanotechnology of silicone polymer additive supported assembly of superconductor ceramic nano-particles into functional architecture of the usable electrical or electronic articles. Developed specific methodology comprises of: a) performing and usage of nano-size high temperature superconductor (HTS) ceramic powder and b) interdisciplinary approach including Condensed Matter Physics and Materials Science with advanced methods of Ceramics and Polymer Chemistry and Engineering. The novel HTS nanotechnology, named Ceramic-Silicone-Processing or HTS-CSP, consists of the set of innovations including: 1) formulation of colloid suspension intermixture in toluene of market available ultra-fine HTS YBCO ceramic powder with silicone-polymer-resin additive and silver and/or another dope; 2) ultrasonic dispersion of ceramic particle aggregates and homogenization of the multi-component nano-suspension; 3) versatile and high workable material forming, such as adhesion coating of metal or ceramics or quartz glass substrate and extrusion or dry pressing of the condensed ceramic mass; 4) consequent polymerization and magnetic field impacts to induce uniform YBCO grain aggregation and their desirable orientation, 5) multi-step thermal treatment including incongruent melting causing super high dense ceramic sintering; and 6) thermal oxygenation to fix and rebuild YBCO orthorhombic crystal structure. HTS-CSP allows to manufacture nano/micro/macro superconductor materials of any size, shape and form with required engineering level of electrical current carrying capacity about 20kA/cm-sq at 77K at practically acceptable level of material heat/energy dissipation, such it was achieved in some laboratory experiments. Achievable now engineering cost/performance index C/P for HTS-CSP wire should be less than for copper wire having C/P=\$10/kA-m. HTS-CSP also makes possible to yield cost-competitive advanced, traditional, and innovative electrical and electronic materials including continuous-length multi-strand wire, various small and large-size coated surfaces and bulk products with especially high reliability, durability, ductility and flexibility.

#### Q5.14

NANOSCALE PROCESS ENGINEERING AND SYNTHESIS OF CARBON-ENCAPSULATED MAGNETIC NANOPARTICLES BY GRAIN-BOUNDARY-REACTION. Qixiang Wang, Guoqing Ning, Fei Wei, Guohua Luo, Department of Chemical Engineering, Tsinghua University, Beijing, CHINA.



Carbon-encapsulated metal particles, with a particle diameter less than 100 nm, exhibit properties which make them valuable for many applications, including novel catalytic, structural, electric, magnetic materials, sensors, membranes, and biomaterials applications. The mass-production of carbon-encapsulated metal particles at low cost is widely desired. Nanocrystalline materials are known as polycrystals with the size of individual crystallites in the order of several nanometer. The chemical properties of the interfacial and surface atoms of the nanocrystallines are more active than those of the grains, which lead to the grain-boundary-reaction. In this paper, combining with the theories of nanoscale process engineering (NPE), which mainly study the structural physics of nanocrystalline, nanoporous and microemulsion systems and nanoscale manufacturing process, we have accomplished the mass production of the carbon-encapsulated ferric magnetic nanoparticles by using the particles grain-boundary-reaction in a fluidized bed reactor. The starting materials of ultra fine acicular hematite particles with the length and aspect ratio of 300 nm and 10, respectively, reacted with carbon containing gases such as methane, ethylene, etc., in the temperature range of 673-953 K. The mechanism of the grain-boundary-reaction is studied with the methods of high-resolution transmission electronic microscope (HRTEM), X-ray diffraction (XRD) and thermo gravimetric analyze (TGA), etc. The magnetic properties are measured with vibrating sample magnetometer. A higher yield, commercially viable (continuously, effective and at a low cost) process in the fluidization bed reactor is well established by studying the parameters affects the magnetic properties of carbon-coated nanoparticles. The diameter of carbon-encapsulated ferric magnetic nanoparticles is about 30-60 nm, and the coercive force and saturation magnetization are 315 Oe and 30 emu / (g powder), respectively. The nonmagnetic graphite surface of the nanocomposites weight of the total particles can be well controlled in the range of 20-70%.

#### Q5.15

**SYNTHESIS OF DIELECTRIC BARIUM TITANATE POWDER BY USING HOMOGENEOUS COPRECIPITATION CHEMICAL REACTION FOR EMBEDDED CAPACITOR APPLICATION.**  
Hwu Jyh-Ming, Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu, TAIWAN, R.O.C.

Integral passive components can reduce assembly cost and enhance electrical performance more than conventional discrete passive components can. Developing a suitable material that satisfies electrical and reliability requirements is a major challenge of incorporating passives into a print circuit board. The perovskite structure of BaTiO<sub>3</sub> material has excellent dielectric and ferroelectric properties that can be adopted in diverse applications such as passive and memory devices and detectors. Although the solid reaction that has been used mainly in industry for ceramic materials can be easily processed, the chemical compositions of products are not uniform. Using the homogeneous coprecipitation reaction can produce a high purity, controllable particle size and morphology and uniform composition BaTiO<sub>3</sub> powders. Using this BaTiO<sub>3</sub> powders in a polymer-ceramic composite provides excellent dielectric properties for embedded capacitor application.

#### Q5.16

**PREPARATION AND CHARACTERIZATION OF IRON-NITRIDE NANOPARTICLES BY GAS-SOLID NITRIDATION OF IRON NANO-PARTICLES.** Jinwkon Kim and Jeong-Mi Moon, Kongju National University, Dept of Chemistry, Kongju, Chungnam, KOREA.

Nano-scale crystalline iron-nitride particles have been produced by a nitridation of mono-disperse nano-particles. The iron nano-particles were prepared by a thermal decomposition method of iron pentacarbonyl in the existence of organic stabilizer. The subsequent thermal treatment of these iron nano-particles under a continuous flow of ammonia-hydrogen gas in a quartz tube resulted in the formation of 10 nm sized Fe<sub>4</sub>N nano-particles without increasing of particle size. FT-IR and element analyses indicate no further existence of the organic stabilizer. X-ray diffraction (XRD), transmission electron microscope (TEM) and superconducting quantum interference device (SQUID) were used to characterize phase structure, particle size and magnetic properties of these nanoscale nitride particles.

#### Q5.17

**RAPID FABRICATION OF PATTERNED SELF-ASSEMBLED COLLOIDAL CRYSTALS BY INK-JET PRINTING ON STRUCTURED SURFACES.** Hwayoung Ko, Yonsei University, Department of Ceramic Engineering, Seoul, KOREA; Hyunjung Shin, Kookmin University, School of Advanced Materials Engineering, Seoul, KOREA; Jooho Moon, Yonsei University, Department of Ceramic Engineering, Seoul, KOREA.

Self-organized patterned microstructure has been fabricated on a

substrate using inkjet printing with an ink of submicron-sized monodispersed colloidal particles. At the substrate, self-assembled monolayer (SAM) molecules has been deposited by microcontact printing to generate a structured surface that exhibit lateral patterns of varying wettability consisting of hydrophobic stripes on a hydrophilic substrate. Well-dispersed suspension of 10 wt% monodispersed silica colloids was selectively deposited on such substrates using a drop-on-demand type inkjet printer. Patterned self-organized colloidal crystals of < 10 μm in sizes on the structured surfaces are rapidly fabricated, which would rather be difficult to be achieved by inkjet printing on an ordinary substrate. The modulated wettability present on the substrate induces instability of the printed droplets of suspension, breaking into much finer droplets and preventing excess spreading. Subsequent solvent evaporation leads to a colloidal crystallization confined within hydrophilic region of the strips of controlled sizes. Spatial arrangement and its dimension of the modulated wettability as well as the volume and printing speed of the colloidal suspension play an important role in production of microstructure of the self-organized colloid crystal and its resolution.

#### Q5.18

**THE DESIGN AND SYNTHESIS OF NOVEL METAL COMPLEXES FOR USE AS NANOPARTICLE PRECURSORS.**  
Scott D. Bunge, Timothy J. Boyle, Mark A. Rodriguez, Michael B. Sinclair, Nelson Bell, Sandia National Laboratories, Advanced Materials Laboratory, Albuquerque, NM.

One area that has accumulated a large amount of consolidated knowledge on precursor chemistry for the formation of thin metal films is chemical vapor deposition (CVD). It is our intention to take the conceptions of CVD precursor development (i.e., the synthesis of metal alkyls, metal alkoxides, metal amides, etc.) to solution-based approaches involving metal colloids. Since colloids can be considered as soluble surfaces it appeared rather reasonable to transfer the conceptions of CVD precursor development to solution-based approaches. For our nascent investigations, we have developed a reaction system composed of a coordinating solvent for the synthesis of nanoparticles via pyrolysis of a molecularly designed precursor. This approach takes not only advantage of the concepts of CVD, but offers control over both parameters that dictate the features of nanoparticles, the starting material, and the reaction system. Our results related to the synthesis of metal nanoparticles and II-VI semiconductor nanoparticles will be reported.

#### Q5.19

**A NEW FABRICATION METHOD OF ANTIREFLECTION LAYER USING NANO STRUCTURED SURFACE RELIEF GRATINGS ON AZOBENZENE POLYMER FILMS.** Sung-Jong Yoo, Dong Kee Yi, Mi Jeong Kim, Seung-Hwan Oh, Dong-Yu Kim, Kwang Ju Institute of Science and Technology, Department of Materials Science and Engineering, Gwangju, KOREA.

Low-cost and high-performance anti-reflection (AR) surfaces and coatings are useful for various optical and display devices. A mothe-eye-structured surface provides an alternative to traditional anti-reflection coatings with low reflection over wide spectral ranges. In this work, we report the reduction of surface reflection losses on azobenzene containing polymer films by fabricating an AR structure with nano structured mothe-eye surface patterns on the polymer films. The mothe-eye AR patterning works by creating a region of gradually varying effective refractive index between air and the azobenzene polymer layer. Mothe-eye structures were created by exposing to the interference patterns of argon ion laser beams on the surface of the azobenzene polymer films. The photo-fabricated mothe-eye structures were confirmed by measuring the AFM images and the antireflection effect was characterized.

#### Q5.20

**COLLOIDAL TEMPLATE METHOD FOR ANTIREFLECTING POROUS SURFACES.** Hye Young Koo, Dong Kee Yi, Sung Jong Yoo, Hwa Sub Shim, Dong Yu Kim, Department of Materials Science and Engineering, Kwang-Ju Institute of Science and Technology, Kwang-Ju, REPUBLIC OF KOREA.

Antireflection coatings (AR) are indispensable requirement for many optical applications. These optical coatings improve the light transmission by destructive interference of reflected light at the air-film and film-substrate interfaces. The ideal average refractive index of the coatings for glass and common polymeric substrates is about 1.2 - 1.3. And for broad-band AR coatings, we need a sequence of layers that have gradual change of refractive indices. In this work, we attempted to design the AR coatings by depositing the polymeric porous films in sequence which have gradual pore size change. The arrays of spherical air voids embedded in a host polymer matrix can reduce the average refractive index of the coatings. As the pore size is gradually changed through the layers, the coatings with gradual

refractive indices can be made. The porous film fabrication method is analogous to the general inverse opal preparation method for photonic crystals. We used polystyrene colloids which have diameters of 30 - 100 nm for the fabrication of the sacrificial template. The voids between the particles were filled with polymers by capillary action. After the original colloidal templates were removed, the porous polymeric materials were obtained. Various optical measurements were carried out including UV/Vis spectra and scanning electron microscopy. Detailed characteristics and optical properties of these structures will be discussed.

#### Q5.21

**SYNTHESIS AND CHARACTERIZATION OF COPPER/SILVER BIMETALLIC NANOPARTICLES.** Ang Thiam Peng, Chin Wee Shong, National Univ of Singapore, Dept of Chemistry, SINGAPORE.

Dodecanethiol-derivatized copper/silver bimetallic nanoparticles were prepared with different copper to silver feed ratio. The nanoparticles are characterized with x-ray diffraction (XRD), transmission electron microscopy (TEM), infrared spectroscopy (IR), variable temperature infrared spectroscopy (VT-IR), x-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and carbon-13 cross-polarization magic angle spinning NMR (carbon-13 CPMAS NMR). TEM results indicated the crystalline nature of the copper/silver bimetallic core and its nanometer size. On the other hand, the IR, XPS and TGA results suggested that all sulphur groups are chemisorbed onto the nanoparticles. The chain conformation alkanethiol has also been intensively studied by IR and carbon-13 CPMAS NMR. Both techniques clearly show that the alkanethiol exist as an all-trans conformation. On increasing temperature, VT-IR depicts the appearance of the gauche conformations and disruption of the lateral interaction between the alkyl chains which leads to melting. The enthalpy of melting was further estimated by DSC.

#### Q5.22

**NOVEL METAL ALKOXIDES FOR USE AS PRECURSORS TO COMPLEX CERAMIC NANOPARTICLES.** Timothy J. Boyle, Mark A. Rodriguez, Nicholas L. Andrews, Scott D. Bunge, Sandia National Laboratories, Albuquerque, NM.

While the development of semi-conductor nanomaterials has been extensively researched, there is relatively little research for the development of ceramic nanoparticles. Using commercial and novel metal alkoxides we have developed several routes (hydrolytic and non-hydrolytic) to generate simple and complex nanoparticles from single-source precursors. We have also investigated the structural and electronic effects that the starting materials have on the morphology of the final nanomaterials. Our results related to the synthesis of precursors and the subsequent ceramic nanoparticles will be presented. [Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.]

#### Q5.23

**SYNTHESIS AND CHARACTERIZATION OF COBALT FERRITE NANOPARTICLES IN AOT REVERSE MICELLES.** Kerk Wai Tat, Chin Wee Shong, National Univ of Singapore, Dept of Chemistry, SINGAPORE; Huan Cheng Hon Alfred, Li Jian Min, Institute of Materials Research and Engineering, SINGAPORE.

Nanoscale cobalt ferrite particles were prepared in reverse micelles (water-in-oil) of AOT/water/isoctane at room temperature. Besides controlling the size of these nanoparticles, stoichiometric of cobalt ferrite can be well adjusted by varying the ammonia contents in the water pools during synthesis. Pure cobalt ferrite powders or a mixture with maghemite can be achieved by tuning this parameter. Structural and chemical analysis of these nanopowders by x-ray diffraction (XRD), inductively coupled plasma (ICP) emission spectroscopy and electron dispersive x-ray (EDX) had confirmed the effect of ammonia concentrations. The size and shape had also been determined by transmission electron microscopy (TEM). The magnetic properties of nanocrystalline cobalt ferrite had been studied by vibrating sample magnetometer (VSM). The corresponding saturation magnetization (Ms) values increase with ammonia concentration and Co/Fe molar ratio.

#### Q5.24

**SYNTHESIS OF SUPERPARAMAGNETIC IRON-OXIDE NANOPARTICLES PROTECTED WITH ALKANETHIOLALTE MONOLAYERS.** Kaori Kamata and Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently developed a synthetic route to  $\gamma$ -iron-oxide nanocrystallites protected with self-assembled monolayers of alkanethiolates. Spherical nanoparticles of  $\sim 12$  nm in diameter could

be obtained via chemical reduction of an iron (II) precursor in the presence of alkanethiols. The surfaces of these nanoparticles could be derivatized as oil-soluble or water-soluble by using thiols with appropriate terminal groups, i.e., 1-hexadecanethiol and 16-mercaptohexadecanoic acid, respectively. The iron-oxide particles showed strong magnetization with superparamagnetic features in SQUID studies. This talk will discuss the detailed procedure (e.g., the effects of different experimental parameters such as the ratio between the metal ion source and alkanethiol and the content of solvents), as well as the stability of their suspensions.

#### Q5.25

Abstract Withdrawn.

#### Q5.26

**PROCESSING OF BARIUM TITANATE NANO-CERAMICS WITH NOVEL DIELECTRIC PROPERTIES.** Guo-Dong Zhan, Joshua D. Kuntz, Department of Chemical Engineering and Materials Science, University of California, Davis, CA; Rong-Jun Xie, Smart Structure Research Center, National Institute of Advanced Industrial Science and Technology, JAPAN; Amiya. K. Mukherjee, Department of Chemical Engineering and Materials Science, University of California, Davis, CA.

Barium titanate (BaTiO<sub>3</sub>) is one of the most widely used and studied ferroelectric materials in the electro-ceramics industry and has a promising application in modern electronics technology, such as thermistors, multilayer capacitors, and electro-optic devices. Recently, research interest has been focused to its application as a capacitor material in down-sized portable machines and dynamic random access memories. However, these applications are required BaTiO<sub>3</sub> materials to have high electrical properties. It has shown that grain size plays an important role in controlling the dielectric properties of BaTiO<sub>3</sub>. In the present study, we will report spark-plasma-sintering processing of nanocrystalline BaTiO<sub>3</sub> materials with novel dielectric properties. Fully dense nanocrystalline BaTiO<sub>3</sub> with average grain size of  $\sim 200$  nm has been produced by using the SPS method at sintering temperature as low as 1273 K for three minutes along with a high heating rate of 673 K/min. The measured room temperature dielectric constant at 1 kHz was  $\sim 10,000$  and the Curie temperature is  $\sim 400$  K. The nanocrystalline materials showed an unusual dependence of dielectric properties on frequency within 50  $\sim 1,000,000$  Hz over temperature range 297  $\sim 673$  K.

#### Q5.27

**CHEMICAL VAPOR SYNTHESIS OF MAGNETIC NANOPARTICLES.** Vijay K. Vasudevan<sup>a,b</sup>, J.M. Vetrone<sup>a,c</sup>, G.-R. Bai<sup>a</sup>, L.J. Thompson<sup>a</sup>, and J.A. Eastman<sup>a</sup>. <sup>a</sup>Argonne National Laboratory, Materials Science Division, Argonne, IL; <sup>b</sup>University of Cincinnati, Department of Chemical and Engineering, Cincinnati, OH; <sup>c</sup>Hinsdale Central High School, Science Department, Hinsdale, IL.

Iron and iron oxide nanoparticles were synthesized by chemical vapor decomposition of n-butylferrocene precursor gas in a hot-walled deposition system. The effects of variations in reactor chamber pressure, temperature, precursor flow-rate, and oxygen:nitrogen supply gas ratio on the structure, composition, size and size distribution of the particles were studied. The nanoparticles produced in the reactor chamber were dispersed directly into ethylene glycol without exposure to air. The particles were characterized by x-ray and electron diffraction, nanoprobe energy-dispersive x-ray spectroscopy, and HRTEM. The results indicate that nanoparticles with diameters ranging from 3 to 40 nm can be produced controllably. Of the different processing variables studied, oxygen content in the flow gas was observed to have the most dominant effect on the structure, composition, and size of the particles. Without oxygen,  $\gamma$ -iron nanoparticles with an fcc structure and diameters of 3-10 nm were observed. The presence of even a small amount of oxygen in the flow gas led to the formation of fcc Fe<sub>3</sub>O<sub>4</sub> (magnetite) nanoparticles, together with core-shell structures consisting of a  $\gamma$ -iron metallic core surrounded by a shell of iron oxide. With increasing oxygen flow, the nanoparticles were observed to increase in size. Concomitantly, for larger particles the metallic core was found to exhibit the bcc  $\alpha$ -iron structure. Magnetic properties of nanoparticles synthesized under different conditions were measured. The mechanisms of the synthesis of the nanoparticles and their structure, composition, and magnetic properties will be discussed, as will the potential for self-assembly of these particles into functional architectures.

#### Q5.28

**NANOCRYSTALS IN DENDRON BOX: SUPER CHEMICAL, PHOTOCHEMICAL, THERMAL STABILITY AND BIOACCESSIBILITY.** Wenzhuo Guo, J. Jack Li, Y. Andrew Wang, Xiaogang Peng, Dept. of Chemistry and Biochemistry, University of Arkansas, AR.

A novel method is described to functionalize and stabilize the semiconductor nanocrystals with dendron ligands. The G3-OH dendron modified nanocrystals were activated and further globally cross-linked through G2-NH<sub>2</sub> dendrimer. The global cross-linking of the dendron ligands sealed each nanocrystal in a dendron box. This procedure not only provides water-soluble nanocrystals with amine groups pointing outward but also improves the overall stability of the resulting nanocrystals. The reactivity of amine terminated nanocrystals is demonstrated by the traditional amine coupling reaction like Schiff base formation, EDC carboxylic acid coupling reaction, as well as NHS ester activation and ring opening reaction toward anhydrides. Furthermore, the amine coated nanocrystals were successfully biotinlated and picomole amounts of avidin caused the formation of nanocrystal-biotin-avidin conjugates which precipitated out from the solvent. The sensitivity and easy chemistry of the nanocrystal-avidin-biotin system encourages further exploration of the potential applications of this new type of nano assembly in biological science.

#### Q5.29

**ELECTROCHEMICAL REACTIONS WITHIN PATTERNED SELF-ASSEMBLED NANOCOMPOSITES.** Dhaval A. Doshi<sup>a</sup>, Timothy Stachowiak<sup>b</sup>, Darren R. Dunphy<sup>b</sup>, Adam Cook<sup>b</sup>, C. Jeffrey Brinker<sup>a,b</sup>; <sup>a</sup>University of New Mexico/NSF Center for Micro-Engineered Materials; <sup>b</sup>Sandia National Laboratories.

Reactions within nanostructures provides with opportunities of making new functional materials and discovering novel phenomena. Amphiphilic structure directing agents such surfactants and block-co-polymers have been utilized to self-assemble inorganic precursors on the 1-50 nm length scale. Evaporation induced self-assembly (EISA) approaches are used to form thin-film nanostructures with various morphologies and framework chemistry. During EISA the hydrophobic core of the surfactant micelle can solubilize monomers (oily reactants), and along with the pre-positioning of the hydrophilic inorganic precursors allows multi-component self-assembly of functional nanocomposites. We have demonstrated the self-assembly of photoresist/silica nanocomposites thin-films via EISA. Patterned UV exposure allows selective resist polymerization that after a solvent extraction (develop) step results in patterned open and closed (resist filled) nanopore networks. When such a patterned nanocomposite thin-film is deposited onto an ITO electrode, selective electrochemical reactions in the accessible open pores result in patterned deposition of metals or conductive polymers. Results from cyclic voltametry of polyaniline grown in mesoporous films and the electrochromic behavior via UV/Vis experiments are used to understand the growth mechanisms within self-assembled nanostructures. Ability to perform electrochemistry in selective regions of a nanostructured film is attractive for various device and sensors applications.

#### Q5.30

**FABRICATION OF LARGE-AREA, HIGH ASPECT RATIO, PERIODIC NANOPILLAR ARRAYS BY NANOSPHERE LITHOGRAPHY.** Peilin Chen, Chiung-wen Kuo, Inst of Applied Science and Engineering Research, Academia Sinica, TAIWAN.

Nanopillar arrays are one of the most studied nanostructures because of their potential applications in photonic crystals, data storage, and sensors. To fabricate nanopillar arrays with feature size less than 100 nm, normally it requires e-beam lithography. However, it is time consuming and costly to use e-beam lithography for large-scale fabrication. In this paper, we report the fabrication of large-area nanopillar arrays by an alternative low-cost, parallel process: nanosphere lithography. Nanosphere lithography, which utilizes two dimensional close packed structure formed by monodispersed polystyrene beads as template, has been demonstrated capable of producing well-ordered nanoparticle arrays up to 1 cm<sup>2</sup>. When these nanoparticle arrays were used as etching mask, large-area nanopillar arrays have been fabricated. Because only single layer polystyrene templates were used, the fabricated nanopillar arrays reported so far were in hexagonal arrangements, which limit their applications. In our experiment, we have prepared double layer polystyrene templates on silicon substrates. After depositing 100 nm of aluminum on top of templates and dissolving away polystyrene beads, periodic nanoparticle arrays with periodicity equal to the diameter of polystyrene beads were obtained. To make pillar structures, these samples were further placed in a reactive ion etcher. By controlling the etching mixture and etching time, we have fabricated large-area period nanopillar arrays with feature size of 65 nm, aspect ratio as high as 7 and periodicity of 400 nm.

#### Q5.31

**TUNING COLLOIDAL MASKS FOR THE CREATION OF ORDERED NANOPARTICLES.** Dirk L.J. Vossen<sup>a,b</sup>, Damir Fific<sup>a</sup>, Teun van Dillen<sup>a</sup>, Albert Polman<sup>a</sup> and Alfons van Blaaderen<sup>a,b</sup>.

<sup>a</sup>FOM Institute for Atomic and Molecular Physics, Amsterdam; <sup>b</sup>Soft Condensed Matter, Debye Institute, Utrecht University, THE NETHERLANDS.

We present easy-to-use and inexpensive techniques that extend the use of colloidal masks in lithography. The size of the individual nanoparticles as well as the inter particle distances and the symmetry of the array of nanoparticles can be precisely controlled. Examples include the fabrication of particle lines, corners and tee structures with both the nanoparticles dimensions and inter-particle distances down to tens of nanometers. These structures are interesting for plasmonic applications such as waveguides and switches and (single molecule) detection schemes. We create masks with single-particle position control using optical tweezers and critical point drying. The use of optical tweezers extends the geometry of the masks from (self-organized) hexagonal to any desired symmetry. To achieve control over the hole size two methods were developed: 1) by MeV ion irradiation the colloids plastically deform, expanding in the plane perpendicular to the ion beam, thus shrinking the size of the holes, 2) using a wet chemical process a layer of silica can be grown on the mask. In this way the hole dimensions can be controlled with nm-precision and it is decoupled from the size of the colloidal particles in the mask. Evaporation of different materials under different angles with respect to the mask gives additional control over structure and inter-particle distances.

#### Q5.32

**SELF-ASSEMBLING PROCESS OF COLLOIDAL PARTICLES INTO TWO-DIMENSIONAL ARRAY DURING DRYING - A STUDY OF NUMERICAL SIMULATION.** Hiroyuki Nishikawa, Shinya Maenosono, Yukio Yamaguchi, and Tatsuya Okubo, The University of Tokyo, Department of Chemical System Engineering, Tokyo, JAPAN.

Two-dimensional arrays of colloidal particles can be fabricated by drying colloidal dispersion under proper conditions. Capillary immersion force is predominant during drying. We modeled self-assembling process of colloidal particles induced by capillary immersion force, and examined the influences of substrate, drying rate and zeta-potential of suspension on two-dimensional structure with various analyses. Discrete Element Method (DEM) was applied to simulate the self-assembling process. The motion of each particle was numerically solved based on Newton's equation of motion. Voigt model was applied to express viscoelastic properties of colloidal particles. Considering capillary immersion force as well as van der Waals force and electrostatic repulsive force, a set of equations of motion was solved under periodic boundary condition. Coverage, drying rate, pattern of substrate and zeta-potential of suspension were varied. In any situation, colloidal particles were self-assembled very rapidly because of capillary immersion force. At lower coverage, colloidal particles mostly formed chain-like clusters with some branches. At higher coverage, however, they mostly formed hexagonal-closest-packed structures. Mechanisms of the formation of chain-like clusters and/or hexagonal-closest-packed structures were clarified with pair correlation functions and coordination number distributions. The influences of drying rate, type of substrate and zeta-potential on two-dimensional structures were examined with disordering factor defined from Voronoi polygon analysis. We clarified that electrostatic repulsion improves the quality and the quantity of hexagonal-closest-packed structures. Various patterned monolayers of colloidal particles were obtained by tuning the patterns on the substrates.

#### Q5.33

**SELF-ASSEMBLED MONOLAYER FORMATION OF NANOPARTICLES BY ADSORPTION PROCESS.** Sang-Hyun Park, Vienna Kim, Ki-Bum Kim, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA; Tae-Sik Yoon, Seoul National University, Research Institute of Advanced Materials, School of Materials Science and Engineering, Seoul, KOREA; Byung-Gil Jung and Seok-Hong Min, Kangnung National University, Department of Metal and Materials Engineering, Kangnung, KOREA; Jongnam Park and Taeghwan Hyeon, Seoul National University, School of Chemical Engineering, Seoul, KOREA.

The nanoparticles chemically synthesized by homogeneous nucleation and controlled growth in solution have advantages of a narrow size distribution, a high stability by surface-passivation surfactant, and a self-assembly to an ordered-packed array upon evaporation of solvent. For the practical application to device structure, it is necessary to deliver nanoparticles onto substrate with a uniform distribution and a wafer-scale high throughput. In this talk, we reported the investigation of the adsorption behavior of nanoparticles driven by the interaction between nanoparticle and substrate. It was found that the adsorption of nanoparticles in solution follows the competitive adsorption based on Langmuir isotherm with a maximum coverage < 50%. In addition, we proposed the multiple adsorption process by

repeating the adsorption of nanoparticles and drying the solvent. With this process, it is obtained that the surface monolayer coverage increases up to > 70% with increasing the number of adsorption process. The maximum coverage is limited by the possible adsorption of surfactant preventing the nanoparticle adsorption and the swelling of self-assembly in solution.

#### Q5.34

**DIELECTROPHORETIC ASSEMBLY OF SWITCHABLE TWO-DIMENSIONAL PHOTONIC CRYSTALS WITH SPECIFIC ORIENTATION.** Simon O. Lumsdon, DuPont Central Research and Development, Experimental Station, Wilmington, DE; Eric W. Kaler, Department of Chemical Engineering, University of Delaware, Newark, DE; Orlin D. Velev, Department of Chemical Engineering, North Carolina State University, Raleigh, NC.

The mobility and interactions of colloidal particles under the influence of alternating electric fields, which is called dielectrophoresis, is a powerful tool for the assembly of electrically functional devices. We show that switchable 2D photonic crystals can be assembled from suspensions of latex particles subjected to an electric field in a planar cell. These crystals of area > 25 nm<sup>2</sup> are specifically oriented without the need for prior expensive templating. The particles align into horizontal rows along the direction of the field and eventually crystallize due to lateral interactions between the rows. The ordering is lost as soon as the field is removed but is restored within seconds when it is reapplied. The orientation and spacing of the crystals has been examined quantitatively by observing the diffraction pattern of laser light shone through the crystal. The lattice spacing between the particles in the crystal array is highly dependent on the concentration of electrolyte in the surrounding aqueous media, and the diffraction through the cell can be used as a tool to study interactions in particle ensembles. The phase transitions from disordered system to a structure of 1D chains to 2D crystals can be controlled via the field and liquid viscosity. The fast, inexpensive and reproducible fabrication and the ability to control the structure and crystallographic orientation are important characteristics of this new assembly technique.

#### Q5.35

**NON-SPHERICAL ZnS COLLOIDAL BUILDING BLOCKS FOR DIAMOND-ANALOG PHOTONIC CRYSTAL STRUCTURES.** C.M. Liddell and C.J. Summers, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

The asymmetry introduced by a complex or non-spherical basis promotes photonic band gap formation in three-dimensional photonic crystals. However, relatively few techniques have been demonstrated to produce uniform non-spherical colloids for use as photonic crystal bases. Here we expand the menu of basis types with high refractive index by preparing non-spherical zinc sulfide colloids of uniform size and shape. We present a map of population domains that displays the effects of synthesis parameters— seeding time, seeding temperature, and growth time— on the particle size and morphology distribution of the colloids. Dimers, trimers, planar tetramers ca. 1-6.5 microns, were precipitated from aqueous solution by the thermal decomposition of thioacetamide in the presence of zinc nitrate, manganese nitrate, and nitric acid. Nanoparticle seeds were grown by aging at 26-32°C for 4-6 hrs. These agglomerated to form well-defined larger particles during high temperature aging for 20-35 min. at 85°C. Stereological techniques were used to analyze SEM images and determine the percentage of each particle shape species. For example, the quantitative characterization of a particle population prepared at 29°C for 6 hrs. and 85°C for 22 min. had the composition: 59±3% spheres, 31±2% dimers, 7±1% trimers, 0.4±0.2% tetramers, and 2.5±0.8% complex clusters (encompasses all other varieties of shape). X-ray diffraction and energy dispersive spectroscopy confirmed the particles stoichiometric composition. Their refractive index was estimated as 2.25 (413 nm)-2.09 (709 nm) by fitting the experimental absorption spectra to curves derived from Mie scattering calculations. This indicated an average porosity ~24%. Such colloids offer the potential to form diamond-analog lattices with large, stable photonic band gaps.

#### SESSION Q6: ONE-DIMENSIONAL NANOSTRUCTURES I

Chair: Younan Xia  
Wednesday Morning, April 23, 2003  
Metropolitan II (Argent)

#### 8:30 AM Q6.1

**GENERALIZED SOLUTION SYNTHESIS OF LARGE ARRAYS OF ORIENTED NANOWIRES AND THEIR APPLICATIONS.** Zhengrong R. Tian, Jun Liu, James A. Voigt, Sandia National Laboratories, Albuquerque, NM; Huifang Xu, University of New

Mexico, Albuquerque, NM; Liang Liang, eVionyx, Hawthorne, NY.

Oriented nanowire structures are important for microelectronic devices, chemical and biological sensing and diagnosis, energy conversion and storage, light emitting display devices, catalysis, drug delivery, separation, and optical storage. Here we present a generalized solution route to prepare a range of extended and oriented nanostructures, including large arrays of oriented ZnO nanowires, TiO<sub>2</sub> nanowires, and soft conductive polymer nanowires. Although the detailed chemistry for growing ZnO, TiO<sub>2</sub>, and polymers is quite different, the fundamental principles involved are similar. This approach depends on controlling the nucleation and growth events by controlling the concentration of the soluble precursors, and increasing the number of nucleation density on the interfaces. The oriented nanowires were prepared through heterogeneous nucleation, in which a large number of nucleation seeds were either pre-coated onto the substrate, or created in-situ. The new solution route allowed us to control the microstructure and the morphology over a wide range. The large arrays of oriented nanowire structures are investigated for several applications, including microsensors for chemical and biological agents, and energy storage and conversion devices.

#### 8:45 AM Q6.2

**A SONOCHEMICAL APPROACH TO 1D SELENIUM NANOSTRUCTURES.** Brian Mayers and Younan Xia, University of Washington, Seattle, WA.

We have demonstrated a sonochemical solution phase synthesis for the generation of 1-dimensional nanostructures of Selenium. This self-seeding, templateless reaction could be carried out at ambient temperature in a variety of solvents, benefitting from the inherent anisotropy of the crystal structure of selenium. The dimensions and morphology of these nanostructures could be directly controlled (length ~1-100 um, width ~20-100 nm) by selection of solvent, temperature, and concentration of precursors. Selenium has an array of interesting properties including inherent chirality, high photoconductivity, and high reactivity to form other functional materials. Here we present the synthesis and characterization (through electron microscopy, spectroscopy, and electrical transport measurements) of single nanowires, as well as the self-assembled 2D and 3D networks that can be generated by this technique.

#### 9:00 AM \*Q6.3

**NANOCRYSTAL AND NANOWIRE SYNTHESIS IN HIGH PRESSURE SOLVENTS.** Brian A. Korgel, Dept of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, University of Texas at Austin, Austin, TX.

We have been developing new methods for synthesizing metal and semiconductor nanocrystals and nanowires in a variety of solvents heated and pressurized above their critical points, including CO<sub>2</sub>, water and hexane. In some cases, like silicon and germanium nanocrystal and nanowire formation, this enables solution-phase synthesis of nanostructured materials at temperatures ranging from 400C to 500°C temperatures well above the boiling points of conventional solvents. In other cases, such as in ethane, the pressure and temperature of the supercritical solvent can be tuned for size-sensitive hydrophobic steric stabilization of nanocrystals ranging in size from 2 to 10 nm in diameter. Steric stabilization in these systems is a strong function of solvent density, due to the size-dependent van der Waals attraction between cores, which requires varying degrees of steric stabilization in order to prevent their aggregation and precipitation from solution. CO<sub>2</sub> presents a particularly challenging solvent for stabilizing nanocrystals and as a medium for nanocrystal synthesis. The key to using CO<sub>2</sub> has been to identify suitable capping ligands that enable their dispersal. Perfluorocarbons and thiolated PTFE have proven effective, and particles can either be synthesized in conventional solvents, like an acetone/water mixture and then redispersed in CO<sub>2</sub>, or synthesized by arrested precipitation in CO<sub>2</sub> through a precursor reduction in the presence of the ligands. Supercritical solvents provide a unique solvating medium for both nanocrystal and nanowire processing and synthesis.

#### 9:30 AM \*Q6.4

**NOVEL SOFT CHEMICAL ROUTES TO SPECIAL NANOSTRUCTURES.** Yi Xie, Structure Research Laboratory, Department of Chemistry, University of Sciences & Technology of China, Hefei, Anhui, P.R. CHINA.

It's known that the optical and electronic properties of nanostructures are dependent on both the initial particle sizes and the manner they organize. Therefore, synthesis methods are needed not only to prepare the starting building particles but also to coax them into desired structures in one step. Comparing with the physical methods, chemical methods (or the so called bottom-up approach) seem to

provide a more promising strategy for the formation of nanostructures in terms of cost, throughput, and potential for large-scale production. More important and interesting, chemical systems provide a changeable and adjustable microenvironment which can induce the formation of nanostructures with special morphologies. Our research on a simple three-component system CS<sub>2</sub>-water-ethylenediamine (CWE) find that nanostructures with different morphologies such as nano spheres, nano hollow spheres, nanopeanuts, nanowires and nanotubes can be obtained independently in the above one-pot system. An interesting feature is that each component of the system plays a manifold role and different chemical processes get involved in the formation of nanostructures. For example, metal sulfide nano hollow spheres can be prepared in an in-situ source-template interface reaction route based on the reaction between CS<sub>2</sub> and ethylenediamine and the source CS<sub>2</sub> itself served as the reaction template, thus can avoid the extra template materials and sophisticated operation. Modified reaction results in a more interesting structure the peanut like nanostructures, in which metal sulfide cores are self-encapsulated in metal sulfide shells, with a shell-like interstice between them. And other modified routes in the similar system result in metal sulfide nanowires, nanotubes and the spherical assemblies of nanoparticles, respectively.

#### 10:30 AM \*Q6.5

LANTHANIDE OXIDES SINGLE CRYSTAL NANOTUBES AND NANOWIRES. Yadong Li, Department of Chemistry, Tsinghua University, Beijing, PEOPLE'S REPUBLIC OF CHINA.

I was invited by Prof Younan Xia. Recent years have seen considerable interest in the fabrication of one-dimension (1D) nanostructure materials for their potential applications in mesoscopic research and in the development of nanodevices. Up to now, many important materials have been reexamined in terms of nanorods/nanowires, such as MX<sub>2</sub> (M: Mo or W, X: S or Se) nanotubes, II-VI, III-V nanorods, semiconducting oxides nanobelts, etc. Herein we report a kind of novel Lanthanide oxides single crystal nanotubes and nanowires. The synthesis of Lanthanide oxides nanotubes and nanowires was based on the preparation of Lanthanide colloidal particles at room temperature, and the subsequent hydrothermal treatment. The phase purity and the single crystal nature of the final products have been characterized by XRD, TEM, HRTEM and ED analysis. By controlling the chemical potential and ions moving rate in the reaction system, the dimensions of these materials can be tailored. And with the decreasing of the ion radii (from La to Lu), the morphologies of the Lanthanide oxides nanotubes and nanowires will gradually change, which mean that crystal structures are the inherent decisive factors for the formation of these nanotubes or nanowires. Due to their unique electronic structures and the rich transition modes within the 4f shell of the ions, Lanthanide compounds usually have outstanding optical, electrical and magnetic properties. As enrichment to Lanthanide compounds materials and 1D nanostructure, Lanthanide oxides nanotubes and nanowires should be of great significance for their possible novel properties induced by reduced dimensionalities, and may have many potential applications, such as biological label field, high-quality phosphors, etc. Reference 1. Duan, X.F.; Huang, Y.; Cui, Y.; Wang, J.F.; Lieber, C.M., *Nature*, 2001, 409, 66. 2. Huynh, W.U.; Dittmer, J.J.; Alivisatos, A.P., *Science*, 2002, 295, 2425. 3. Sun, Y.G.; Gates, B.; Mayers, B.; Xia, Y.N., *Nano Lett.*, 2002, 2, 165. 4. Huang, M.H.; Mao, S.; Feick, H.; Yan, H.Q.; Wu, Y.Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P.D., *Science*, 2001, 292, 1897. 5. Law, M.; Kind, H.; Messer, B.; Kim, F.; Yang, P. D., *Angew. Chem. Int. Ed.* 2002, 41, 2405. 6. Peng, Z.A.; Peng, X.G., *J. Am. Chem. Soc.* 2001, 123, 1389. 7. Wang, X.; Li, Y. D., *Angew. Chem. Int. Ed.*, in press.

#### 11:00 AM \*Q6.6

1D GOLD SURFACE PLASMON NANOMATERIALS. Cheng-Dah Chen, Wei-Cheng Lai, Ser-Sing Chang, and C.R. Chris Wang, National Chung Cheng University, Department of Chemistry and Biochemistry, Min-Hsiung, Chia-Yi, TAIWAN.

The properties of the nanomaterials possessing surface plasmon resonance has shown many potential applications. Electrochemical method has been successful for synthesizing the 1D gold nanoparticles suspended in aqueous solution. Their formation of the gold nanowhiskers is believed to be under a micelle-mediated growth. The fcc (100) lattice planes are largely conserved during the 1-D growth and are attributed to the growth direction. The diameters of the polydispersed nanowhiskers are roughly 3.0 nm and the aspect ratios can be as high as ca. 50. The evolution of longitudinal surface plasmon (SP) resonances indicates a VIS-NIR-IR shift for gold nanorods to nanowhiskers. We demonstrate that other type of unique structures from these 1D gold nanoparticles can be created via the photoannealing process. Nanostructures containing a string of either spherical Au nanoparticles or short Au nanorods embedded in dielectric 1D silica can be fabricated via sol-gel process following by the photoannealing with controlled laser fluences. The absorption feature of the Au nanorod@silica core-shell nanocomposites in the VIS/NIR wavelength range exhibits a sensitive red-shift as increasing

the thickness of the dielectric silica layer. This dependence of the SP resonance on the surface dielectric constant can be readily applied to the sensing. For example, the NIR spectral feature of gold nanorod has proven to be sensitive tool for the biomolecular sensing.

#### 11:30 AM Q6.7

SEED-MEDIATED GROWTH APPROACH TO METALLIC NANORODS AND NANOWIRES IN AQUEOUS SOLUTION. Catherine J. Murphy, University of South Carolina, Dept of Chemistry and Biochemistry, Columbia, SC.

Gold and silver nanorods and nanowires of controllable aspect ratio have been synthesized via seed-mediated growth in aqueous solution. The presence of surfactant during the growth steps (at room temperature) is necessary to produce nanorods. The growth mechanism seems to involve preferential adsorption of surfactant to different crystal faces of the growing material, rather than a templating effect of any micellar structure of the surfactant. Exceptions to the synthetic procedure at higher temperatures will be discussed, as will the chemical reactivity of nanorods compared to nanospheres.

#### 11:45 AM Q6.8

PREPARATION AND CONTROLLED GROWTH OF GOLD NANORODS NRs AND THEIR USE IN SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS). Babak Nikoobakht and Mostafa A. El-Sayed, Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

A method is used for preparing gold NRs with aspect ratios ranging from 1.5 to 10 for which the surface plasmon absorption maxima are between 600 to 1300 nm. This method has been adapted from previously published seed-mediated growth method [1]. The disadvantages and the limitations of the earlier method such as formation of ellipsoidal NRs,  $\phi$ -shaped particles and formation of a large fraction of spherical particles have been overcome. In a single component surfactant system, the silver content of the growth solution was used to reproducibly grow NRs with aspect ratios ranging from 1.5 to 4.5. To grow longer NRs with aspect ratios ranging from 4.6 to 10, a binary surfactant mixture composed of benzyltrimethylhexadecylammoniumchloride and CTAB was used. NRs are grown in this mixture either by aging or by addition of a suitable growth solution to shorter NRs. In SERS studies, by controlling the NR aspect ratio, it is shown that the longitudinal plasmon band can be tuned to the excitation wavelength, which results in larger Raman enhancement. By moving away the NR plasmon band from the excitation wavelength, the enhancement decreases although remains stronger relative to that of gold nanospheres.

1) Jana, N.R.; Gearheart, L.; Murphy, C.J., *Adv. Mater.* (2001), 13, 1389.

SESSION Q7: ONE-DIMENSIONAL NANOSTRUCTURES II  
Chair: Peidong Yang  
Wednesday Afternoon, April 23, 2003  
Metropolitan II (Argent)

#### 1:30 PM Q7.1

SYNTHESIS AND CHARACTERIZATION OF CADMIUM OXIDE NANONEEDLES. Xiaolei Liu, Chao Li, Song Han, and Chongwu Zhou, University of Southern California, Dept. of E.E.-Electrophysics, Los Angeles, CA; Jie Han, NASA Ames Research Center, Moffett Field, CA.

Single crystalline needle shaped CdO nanostructures were synthesized and then analyzed with X-ray diffraction, transmission electron microscope and selected area electron diffraction to confirm its crystal structure. CdO nanoneedle devices fabricated with individual nanoneedle showed high conductivity with high carrier concentration of  $1.29 \times 10^{20} \text{ cm}^{-3}$ . The temperature-dependence of the conductance revealed thermal excitation as the dominating transport mechanism. The devices exhibited sensitivity to infrared light and photo excitation via indirect band gap was confirmed. With suppressed conductance when exposed in 200ppm NO<sub>2</sub> gas, our CdO nanoneedle devices also showed a potential applications in gas sensing.

#### 1:45 PM Q7.2

HELICAL CRYSTALLINE SiC/SiO<sub>2</sub> CORE-SHELL NANOWIRES. Hai-Feng Zhang and Lai-Sheng Wang, Department of Physics, Washington State University, Richland, WA, and W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA; Chong-Ming Wang, W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA.

Helical crystalline silicon carbide nanowires covered with a silicon oxide sheath (SiC/SiO<sub>2</sub>) have been synthesized by a chemical vapor deposition technique. The SiC core typically has diameters of 10-40 nm with a helical periodicity of 40-80 nm and is covered by a uniform layer of 30-60 nm thick amorphous SiO<sub>2</sub>. A screw-dislocation-driven growth process is proposed for the formation of this novel structure based on detailed structural characterizations. The helical nanostructures may find applications as building blocks in nanomechanical or nanoelectronic devices. The screw-dislocation-induced growth mechanism suggests that similar helical nanostructures of a wide range of materials may be synthesized.

#### 2:00 PM \*Q7.3

##### NOVEL NANOSTRUCTURES OF FUNCTIONAL OXIDES - A NEW MATERIALS SYSTEM FOR NANOTECHNOLOGY.

Zhong Lin (ZL) Wang, Center for Nanoscience and Nanotechnology, 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. We have synthesized a wide range of nanomaterials, including nanobelts of functional oxides [1], self-assembled junction arrays of ZnO, diskettes of SnO<sub>x</sub> [2] and aligned silica nanowires [3]. The nanobelts have been 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 of 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 nano-size sensors [4] and field effect transistors [5] using individual nanobelts. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, *Science*, 291 (2001) 1947. [2] Z.R. Dai, Z.W. Pan and Z.L. Wang, *J. Am. Chem. Soc.*, 124 (2002) 8673. [3] Z.W. Pan, Z.R. Dai, C. Ma and Z.L. Wang, *J. Am. Chem. Soc.*, 124 (8): (2002) 1817. [4] E. Comini, G. Faglia, G. Sberveglieri, Z.W. Pan, Z.L. Wang *Applied Physics Letters*, 81 (2002) 1869. [5] M. Arnold, P. Avouris, Z.L. Wang "Field-Effect Transistors Based on Single Semiconducting Oxides Nanobelts", *J. Phys. Chem. B*, in press (2002).

#### 2:30 PM \*Q7.4

##### CATALYZED GROWTH OF SOLUBLE III-V QUANTUM WIRES AND ANALYSIS OF 2D QUANTUM CONFINEMENT IN THEM.

Heng Yu, Richard A. Loomis, William E. Buhro, Washington University, Department of Chemistry, St. Louis, MO.

The difference in the quantum-confinement effects in InP quantum wires and dots, arising from the differing dimensionality of confinement, is experimentally determined. We report the solution-liquid-solid growth of soluble InP quantum wires having diameters in the 3 - 11-nm range and narrow diameter distributions ( $\pm 13 - 21\%$ ). The absorption spectra of the InP quantum wires are compared to those previously published for InP quantum dots, from which the quantum-wire and quantum-dot band gaps are measured. Simple particle-in-a-box calculations predict linear plots of the increase in the band gap vs. the inverse square of the wire or dot diameter. These calculations also predict the slopes of the quantum-wire and quantum-dot lines to have the ratio 0.585. Our experimentally measured value is  $0.62 \pm 0.03$ , leading to the conclusion that quantum confinement in InP is weakened in quantum wires relative to quantum dots to the expected extent by the loss of one confinement dimension. We propose an analysis based on such experimentally determined wire/dot slope ratios to generally distinguish quantum-wire from quantum-dot behavior. Soluble GaAs quantum wires having narrow diameter distributions are similarly prepared.

#### 3:30 PM Q7.5

THE THERMOMECHANICAL BEHAVIOR OF BILAYER NANOCANTILEVERS. Matthew Law, Tevye Kuykendall, Peidong Yang, University of California, Berkeley, Dept of Chemistry, Berkeley, CA; Xiao-feng Zhang, Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.

The recent demonstration of bilayer nanoribbons, in which individual metal oxide nanoribbons are used as substrates for the deposition of a second functional material, is extended here to metal-on-nanoribbon bilayer structures. We coat single faces of SnO<sub>2</sub> nanoribbons with 5-50 nm of copper at room temperature and find two distinct structural

types among the resulting dual-beam nanocantilevers. Copper coating the (101) face of a SnO<sub>2</sub> nanoribbon forms a polycrystalline layer, while deposition on the (010) face yields a (010)SnO<sub>2</sub> || (111)Cu epitaxial relationship and a nearly single-crystalline film. The large difference between the Cu and SnO<sub>2</sub> thermal expansion coefficients results in a significant thermomechanical response for the composite structures. In-situ TEM techniques allow us to monitor the mechanical behavior of individual bilayer nanoribbons as a function of temperature. We find that the epitaxial bilayers bend reversibly as the temperature is cycled between 298 K and 473 K, while the polycrystalline samples show a damped bending behavior across the same temperature range. Above 550 K the copper layer melts in regions of high strain, leading to nanocantilever failure. The data show that large structures (total thickness 50-120 nm) obey the same deflection equations that describe microcantilevers. However, below a critical size ( $\sim 25$  nm) deviations from macro behavior are seen as the particular details of the interface begin to dominate the bending response. We conclude by demonstrating a thermal switch based on a single Cu-SnO<sub>2</sub> nanoribbon. Beyond their thermomechanical properties, these metal-oxide bilayer nanoribbons are interesting systems for fundamental interfacial studies and as ultrasensitive chemical detectors.

#### 3:45 PM Q7.6

##### GALLIUM NITRIDE NANOWIRES: TAILORING OF STRUCTURE AND PROPERTIES TOWARD NANO DEVICE APPLICATIONS.

Heon-Jin Choi, Sang-Kwon Lee, Justin C. Johnson, Rongrui He, Peidong Yang, Department of Chemistry, University of California, Berkeley, CA.

Wide band gap semiconductors from group III-nitrides are important materials for electronic-, optoelectronic-, and electromagnetic devices. Fabrication of these materials into one-dimensional (1D) nanoscale structures (i.e., nanowires) further fuel their power and versatility for device applications. It evolves novel properties intrinsically associated with low dimensionality and size confinement as well as makes it possible to "bottom-up" construction of nano devices by utilizing them as building blocks. Meanwhile, engineering of individual nanowires such as controlled doping or hetero-interface formation is needed to exploit the potential of these 1D building blocks. This talk will focus on the engineering of individual GaN nanowires toward fabrication of nanowire-based nano devices. Following a brief introduction of the figure of merits of GaN nanowires, an approach to fabricate n- and p-type GaN nanowires by in-situ doping as well as pure GaN nanowires will be presented with their optical-, magnetic- and electronic properties including lasing action with Fabry-Perrot cavity modes, hole-mediated ferromagnetism up to room temperatures, and field-effect conductance. Some properties from the nanowire-based device structures will also be illustrated as an example of the feasibility of these nanowires as device building blocks. A spontaneous phase separation approach will be suggested to create hetero-interfaces within the nanowires. This will be illustrated using 1D carrier and photon confinement in heterostructure nanowires fabricated from the Ga-Al-N ternary system with self-organization mode. Lastly, the possible application of GaN nanowires in electronic-, optoelectronic- and electromagnetic devices will be discussed.

#### 4:00 PM Q7.7

##### Si/SiGe SUPERLATTICE NANOWIRES: DESIGNED SYNTHESIS AND ENGINEERING FOR MANAGEMENT OF PHONON TRANSPORT.

Yiyang Wu, Rong Fan, Deyu Li, Arun Majumdar, Peidong Yang.

During the past ten years, a great deal of work has been done invariably on homogeneous nanowires. However, only a few studies have focused on the heterostructure formations. But the success of semiconductor integrated circuits relies greatly upon the capability of heterostructure formation through carefully controlled doping and interfacing. Thus, a controlled general fabrication of heterostructures within an individual nanowires is still called for. The present work has developed a general process — pulsed laser ablation assisted chemical vapor deposition (PLA-CVD) technique to synthesize well-controlled longitudinal heterostructures within single nanowires. Si/SiGe superlattice nanowires are synthesized by periodical feeding in Ge vapor during a normal SiNW growth by local laser ablation. As-made Si/SiGe superlattice nanowires are dislocation free single crystalline nanowires with modulated longitudinal elemental distribution. Both 1-D system and superlattice structure are important model for high performance thermoelectrics because of their ability in confining phonon thermal conductivity. Here, we first combine these two unique structures together for the management of phonon transport and expect to make better thermoelectric materials. Thermal conductivity (TC) measurement of single Si/SiGe nanowires shows a greatly reduced TC than bulk Si, 2-D Si/Si<sub>0.7</sub>Ge<sub>0.3</sub> superlattice thin film<sup>2</sup> and pure Si nanowires due to the multiple effects of alloy and boundary scattering mechanism and are promising in real thermoelectric applications.

#### 4:15 PM Q7.8

**ELECTRICAL CIRCUITS VIA NANOPARTICLE ASSEMBLY - SINGLE MICROWIRES AND PARALLEL ARRAYS.** Orlin D. Velev and Ketan Bhatt, Department of Chemical Engineering, North Carolina State University, Raleigh, NC; Simon O. Lumsdon, DuPont Central Research and Development, Wilmington, DE.

We have shown that suspensions of metallic nanoparticles in water spontaneously assemble via the action of alternating electric field into wires of micrometer thickness (Science, 294:1082). The key to using these new structures in electrical circuits lies in developing tools to control and modify the assembly process. We have identified two modes of microwire assembly, one through the bulk of the suspension, and one as half-cylinders on the surface between the electrodes. The mode of growth, bulk or surface, can be controlled via the AC frequency and the viscosity of the media. The surface microwires can be assembled as massively parallel arrays on the chip, which can be extracted in dry shape. The microwire growth can be guided by introducing conductive islands in the liquid and by switching the field to different electrodes. The growth pattern can be predicted by calculations of the electric field gradient. The wires grow in the direction of the highest gradient and "automatically" form electrical connections to conductive islands or particles between the electrodes. The results allow the controlled formation of a wide variety of self-assembled electrical circuits in liquid such as connectors, switches, networks, and chemiresistance sensors. One potential application of particular interest is formation of bioelectronic circuits via in situ connecting biological cells to on-chip electrodes.

#### 4:30 PM Q7.9

**GROWTH AND CHARACTERIZATION OF ZnO NANOWIRES AND COLUMNS.** Jason Baxter and Eray Aydil, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Feng Wu, Univ of California Santa Barbara, Dept of Materials, Santa Barbara, CA.

ZnO nanowires and hexagonal columns have been grown through chemical vapor deposition, using either metallic zinc or organometallic precursors and oxygen with and without plasma. By evaporating zinc in air plasma, hexagonally faceted columns grow in the [0001] direction on the oxidized zinc surface. The columns range from 50 nm to several 100 nm in diameter. Electron micrographs at different stages of growth show that the columns grow by repeated nucleation and growth of pyramidal islands on the (0001) surfaces. This preferential nucleation on the c-plane gives rise to the anisotropic growth of columns. The high index surfaces of such islands grow faster than the (0001) and {10-10} planes and eventually run themselves out of existence, leaving behind hexagonal columns. Nanowire growth can be catalyzed by monodisperse gold nanoparticles (5 or 20 nm diameter) dispersed on a substrate from a colloidal solution. The nanowires have monodisperse diameters determined by the gold particle diameter and can grow to several microns in length. Transmission electron microscopy and electron diffraction show that single crystal wurtzite ZnO nanowires grow from the gold particles in the direction perpendicular to the {10-10} or {10-11} planes. Nanowires with monodisperse diameters can also be grown from zinc acetylacetonate without the use of the gold catalyst. Cathodoluminescence experiments show that both wires and columns luminesce with the columns emitting most of the light through the top face. Emission intensity increases sharply with electron current and exhibits a threshold indicating a possibility that the columns might be lasing. Dense ZnO nanowires with high surface area can be grown on various oxide substrates, making them suitable for replacing the mesoporous semiconductor in dye sensitized solar cells. Single crystal ZnO nanowires offer improved conduction pathways compared to sintered nanoparticles used currently, where electron transport occurs by a hopping mechanism.

#### 4:45 PM Q7.10

**CATALYTIC GROWTH OF SEMICONDUCTING ZINC OXIDE NANOWIRES BY REACTIVE EVAPORATION PROCESS.**

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

Semiconducting ZnO nanowires for applications in nanoscale electronic and optoelectronic devices were synthesized by a simple reactive thermal evaporation process at growth temperature ranging from 500°C to 850°C. This process was based on the thermal evaporation of zinc metal source onto a silica/silicon substrate with the presence of metallic nanocluster catalysts. The structural, optical, chemical and physical properties of the as-grown ZnO nanowires were characterized in this research. From the observations using field emission scanning electron microscope and transmission electron microscope, ZnO nanowires were grown with the diameter ranging from 20 nm to 100 nm and the length up to several micrometers. It was observed that the diameter of ZnO was also dependent on the size

of metallic catalyst and the growth temperature. XRD measurements showed that the ZnO nanowires exhibited wurtzite (hexagonal) structures with a preferred c-axis (0002) orientation. The photoluminescence (PL) characteristics of ZnO nanowires were also investigated.

#### SESSION Q8: POSTER SESSION ONE-DIMENSIONAL NANOSTRUCTURES

Chair: Younan Xia  
Wednesday Evening, April 23, 2003  
8:00 PM  
Golden Gate (Marriott)

#### Q8.1

**LARGE-SCALE SYNTHESIS AND CHARACTERIZATION OF SILVER NANOWIRES.** Yugang Sun and Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

A soft, solution-phase approach has been developed to the large-scale synthesis of uniform nanowires of bicrystalline silver whose lateral dimensions could be controlled in the range of 30-60 nm, and lengths up to ~50  $\mu\text{m}$ . The first step of this procedure involved the formation of platinum (or silver) nanoparticles by reducing platinum chloride (or silver nitrate) with ethylene glycol heated at ~160°C. Due to their close match in crystal structure and lattice constants, these platinum (or silver) nanoparticles could serve as seeds for the heterogeneous nucleation and growth of silver that was produced in the solution via the reduction of silver nitrate with ethylene glycol. With the assistance of poly(vinyl pyrrolidone) (PVP) present in the reaction system, the silver could be directed to grow into uniform nanowires with aspect ratios as high as ~1000. The lateral dimensions and aspect ratios of the silver nanowires could be tuned by adjusting the reaction conditions, including the ratio of PVP to silver nitrate, reaction temperature, and seeding conditions. Measurements of the transport properties at room temperature indicated that these silver nanowires were electrically continuous with a conductivity (~10<sup>5</sup> S/cm) approaching that of bulk silver.

#### Q8.2

**EFFECTS OF DOPING ON THE MORPHOLOGIES OF ZnO NANOSTRUCTURES.** Yanfa Yan, Ping Liu, and M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

One-dimensional ZnO nanostructures have attracted great interest because their promising applications in electronic and optoelectronic nanodevices. The growth of one-dimensional ZnO nanostructures has been demonstrated by various techniques. For device applications, these ZnO nanostructures would often need to be doped. Here we report the effects of doping on the morphologies of ZnO nanostructures. We find that the incorporation of dopants, such as Si, Li, and Na, usually lead to reduced quality of ZnO nanostructures. While doping of Li and Na results in formation of facets on ZnO nanostructures, the doping of Si often reduces dramatically the quantity of ZnO nanostructures. The mechanisms of such effects are being investigated.

#### Q8.3

**SINGLE CRYSTALLINE GALLIUM NITRIDE NANOTUBES.** Joshua E. Goldberger, Rongrui He, Haoquan Yan, Heon-Jin Choi, Peidong Yang, UC Berkeley, Dept of Chemistry, Berkeley, CA.

Uniform GaN nanotubes were synthesized using a chemical vapor deposition process. Well-faceted single crystalline ZnO nanowires were used as templates for the epitaxial growth of thin GaN layers, and were subsequently removed via thermal reduction and evaporation in NH<sub>3</sub> and H<sub>2</sub> environments. These GaN nanotubes have inner diameters ranging from 30 to 200 nm and wall thicknesses between 5 and 50 nm. Transmission electron microscopy studies show the nanotubes to be single crystalline with a wurtzite structure and oriented along the < 0001 > direction. This is the first example of single crystalline nanotubes made from materials without a layered crystal structure. Similar vanishing-template approaches could be used to produce single crystalline nanotubes for other semiconductors.

#### Q8.4

**FABRICATION AND CHARACTERIZATION OF IRON-COBALT ALLOY MAGNETIC NANOWIRES BY THERMAL DECOMPOSITION METHOD INSIDE MAGNETIC FIELDS.** Heesung Moon, Changhun Nam, Changwook Kim, Bongsoo Kim, Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, KOREA; Gangho Lee, Department of Chemistry, Kyungpook University, Daegu, KOREA.

In recent years, spintronics or magnetoelectronics, the concept using the alignment of the electron spins), transpires as a breakthrough for

the existing technology. The perpendicular FeCo magnetic alloy nanowires are advantageous for several applications such as the high density magnetic storage device, where the single nanowire can be used as only a bit. So far, these nanowires are made by e-beam lithography and electrochemical deposition using template, but we present the perpendicular FeCo alloy nanowires fabricated by new preferential method. The advantages of this are simple, less expensive, and saving of time. In a vacuum chamber, the gas, which is vaporized from a solution of dicobalt octacarbonyl and iron pentacarbonyl mixture, is thermally decomposed by using a nichrome wire. The silicon substrate is placed inside a homogeneous magnetic field which is produced by two permanent magnets (4000gauss), so that the nanowires easily grow in the direction of the magnetic flux at same times. By measuring X-ray diffraction, scanning electron microscope and transmission electron microscope, we confirmed that these have a body-centered-cubic structure with the magnetization easy axis of [110] direction, and a diameter in the range from 4 to 6nm with a few micrometers at length. Also, we investigated that the squareness of the hysteresis loop is 61% for magnetic fields parallel to the wires and the coercivity along the easy axis is 670 oersteds by using vibrating scanning magnetometer.

#### Q8.5

VARIATION OF ELECTRIC FIELD EFFECT IN THIN Bi WIRES. D.V. Gitsu, L.A. Konopko, and A.A. Nikolaeva, Institute of Applied Physics, Academy of Sciences, Chisinau, MOLDOVA.

The electrical field effect (EFE) in bismuth monocrystal wires at various temperatures (2.1 - 300 K), elastic stretch (up to  $\xi = 2 - 3\%$  relative elongation) and magnetic fields (up to 14 T) was investigated. The cylindrical Bi crystals ranging in size from 0.1 to 3  $\mu\text{m}$  with glass coating were fabricated by Ulitovsky method. All the samples were similarly oriented: the cylinder axis made an angle of  $19.5^\circ$  with the bisectrix axis in the bisector-trigonal plane. Owing to the coaxial geometry of our samples the highest electric field value about  $10^7$  V/cm on the surface of Bi wire was achieved. The influence of EFE on thermoelectric power in thin Bi and Bi-alloys wires was studied. The following important features were observed. The EFE depends on wire diameter and value of EFE  $\Delta R/R_0$  reaches the magnitude of about 13% in a thinnest wires. The temperature dependencies of carrier mobilities were defined. In a thin Bi and Bi-Te alloy nanowires EFE alter the value of thermoelectric power, increasing positive polarity at the gate electrode leads to the increasing of thermoelectric power. Probable mechanisms of the observed effects are discussed. This work is supported by Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) # MP2 - 3019.

#### Q8.6

PATTERNING POLYMER THIN FILMS USING NANOCONTACT PRINTING. Yin He, D. Bruce Chase, John F. Rabolt, Univ of Delaware, Dept of Materials Science and Engineering, Newark, DE.

Microcontact and nanocontact printing has been used to produce patterned self-assembled monolayers (SAMs) of short chain molecules on a variety of substrates. In our work, an elastomeric stamp, fabricated from poly(dimethylsiloxane) (PDMS) using a polymer "master", is wetted with a polymer liquid ink and transferred by conformational contact to a metallic substrate. In this work, we will describe the formation of PDMS stamps from commercially available read-write compact disks (master) that have already been patterned with submicron features. SAMs of sulfur derivatized (end group and side chain functionalized) PDMS were deposited on gold surfaces using this nanocontact printing technique and it was found that the time required for deposition was 2 orders of magnitude lower than that observed for spontaneous assembly. By varying the structure of the polymer architecture, the thickness and properties of the polymer film can be controlled. Utilizing atomic force microscopy (AFM), these patterned surfaces were characterized and analyzed to determine the fidelity and the aspect ratio of the features produced. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) were used to obtain the orientation and depth profiling information of the polymer thin films formed.

#### Q8.7

EXCITON-PHONON COUPLING OF SELECTIVE GROWN ZnO NANORODS ON PRE-COATED-ZnO BUFFER LAYER. Hsu-Cheng Hsu, Wen-Feng Hsieh, Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, TAIWAN.

Hexagonal ZnO nanorods have been successfully synthesized via vapor-solid process without gold catalysis on a pre-coated ZnO buffer layer but they cannot be formed directly on the sapphire substrate. The presence of nanometer-sized pits or hills on the surface of ZnO buffer layer provides nucleation sites where the zinc vapor is transferred to and condensed. Followed by immediate oxidation the ZnO nanorods were grown on the buffer layer. However, the SEM

images show hardly growth of irregular ZnO nano-sized products on the sapphire substrate. The emission properties of nanorods have been investigated at various temperatures. In addition to a strong ultra-violet emission at 3.26 eV observed at room temperature, within a Franck-Condon model, we deduced the coupling strength of the radiative transition to LO-phonon polarization field in use of the Huang-Rhys factor from low temperature photoluminescence spectra. The observation of LO-phonon replicas provided an additional way to characterize the polarity and impurity of the ionic semiconductor.

#### Q8.8

PLASMA POLYMERIZED PHOTONIC FILMS. Hao Jiang, Anteon Co., Dayton, OH; Scott Tullis, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLP, Wright-Patterson Air Force Base, OH; Kristi O'Neill and Eric Johnson, TMCI, Dayton, OH; Kurt Eyink, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLP, Wright-Patterson Air Force Base, OH; John Grant, Research Institute, Univ Dayton, Dayton, OH; Walter Johnson, Paul Fleitz, and Timothy Bunning, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLP, Wright-Patterson Air Force Base, OH.

Spatially grading of the refractive index profile on length scales commensurate with light is the basis for high performance optical filters. Recently we fabricated an optical interference stack made of wavelength high-low refractive index layers using plasma enhanced chemical vapor deposition (PECVD), with benzene as the high-refractive index precursor ( $n = 1.65$ ) and octafluorocyclobutane as the low refractive index precursor ( $n = 1.39$ ). This work has been extrapolated here as an optical film with a gradient variation of refractive index has been studied. This ability to control microstructure on the nanoscale length scale is the basis for the fabrication of a rugate filter based on organic components. These types of optical films, stacks and rugates, have been pioneered using inorganic materials, such as  $\text{SiO}_2$  and  $\text{TiO}_2$ . The previous limitation in organic based systems was the inability to obtain any value of refractive index between those afforded by the plasma polymerized pure components, benzene ( $n = 1.65$ ) or octafluorocyclobutane ( $n = 1.39$ ). Previous attempts at controlling the refractive index by controlling the relative deposition rates in a co-deposition scheme failed. Even with a large excess flow rate of the low refractive index component, films with a high refractive index were obtained. By adjustment of critical processing parameters including precursor flow rates, plasma power, monomer input environment, and reactor geometry, we have successfully controlled the variation of the refractive indices in the deposited films for the first time. An AR coating film has been prepared to demonstrate the effectiveness of this technique. Spectroscopy, ellipsometry, and atomic force microscopy have been applied to explore relationships among the processing parameters, the structure and the optical properties of the resulting thin films and these results will be presented.

#### Q8.9

CONTROLLED PHOTOCATALYTIC GROWTH OF PLATINIZED-MICELLE NANOSTRUCTURES. Yi Yang<sup>a</sup>, Eulalia Pereira<sup>b</sup>, Yujiang Song<sup>c,d</sup>, Craig J. Medforth<sup>d</sup>, Frank van Swol<sup>d</sup>, C. Jeffrey Brinker<sup>a,d</sup>, John A. Shelnutt<sup>d</sup>. <sup>a</sup>Univ. of New Mexico, Dept of Chemical & Nuclear Engineering/NSF Center for Micro-Engineered Materials, Albuquerque, NM; <sup>b</sup>Universidade do Porto, Porto, PORTUGAL; <sup>c</sup>Univ. of New Mexico, Dept of Chemistry, Albuquerque, NM; <sup>d</sup>Sandia National Laboratories, Albuquerque, NM.

The synthesis of platinum nanoparticles has received considerable interest in recent years due to their importance in catalysis, sensors, optoelectronic, and magnetic devices, but there are few reports of Pt nanostructures other than nanoparticles and nanowires. Here, we report that certain porphyrins photocatalyze the reduction of metal complexes in aqueous solution to the zero-valent metal, leading to new Pt-composite nanostructures as well as Pt nanoparticles. Unlike chemical or photochemical reductants, a single photocatalyst molecule when illuminated reduces metal ions continuously, thus repeatedly generating zero-valent metal atoms that under appropriate conditions are deposited only in the vicinity of the photocatalyst molecule. In this way, the location at which metal is deposited is determined by spatially arranging the photocatalyst molecules in a desired manner. In this work, by pre-positioning the Sn(IV) octaethylporphyrin photocatalyst molecules inside of sodium dodecylsulfate micelles along with ascorbic acid and  $\text{K}_2\text{PtCl}_4$  at pH=3, we have synthesized uniform nano-assemblies composed of the porphyrin-containing detergent micelles probably coated on the outer micellar surface with a shell of Pt nanoparticles. The Pt nanocrystals in the mature assemblages are crystallographically aligned and joined to give a robust, rigid, porous, single-crystalline Pt superstructure. Intense tungsten lamp irradiation for 15 minutes gives a uniform size distribution. The diameter of these globular nanoparticle assemblies



increases by addition of more layers of Pt nanoparticles and is determined by the porphyrin-to-platinum concentration ratio. Thus, the size distribution of the particle assemblies is controlled by porphyrin concentration and also the intensity of the light. The Pt-nanoparticle-cluster/micelle/porphyrin assemblies are nanoreactors which efficiently catalyze the reduction of water to  $H_2$ , giving a turnover rate ( $H_2$ /Pt atom) of 390 hr<sup>-1</sup> in tungsten light. This general porphyrin-based photocatalytic approach makes possible a wide variety of functional nanostructured metals, alloys, semiconductors, and metal-composite assemblies.

#### Q8.10

##### OPTICAL CONTROL OF Zn NANOPARTICLE GROWTH.

T. Yatsui and T. Kawazoe, Japan Science and Technology Corporation, ERATO, Tokyo, JAPAN; S. Takubo, J. Lim, M. Kouroggi, and M. Ohtsu, Tokyo Institute of Technology, Interdisciplinary Graduate School of Science and Engineering, Kanagawa, JAPAN.

We have proposed a nano-scale photonic integrate circuit (IC) to realize ultrahigh integration of photonic switching arrays for future optical transmission systems. It is composed of sub-100 nm scale dots, which must be fabricated by depositing nano-scale dots with nano-scale controllability in size and position. We demonstrate here this level of controllability by a nonresonant light to regulate the size of Zn nanoparticles in the photo-chemical vapor deposition (PCVD). We first deposited Zn nanoparticles by PCVD. Gas-phase diethylzinc (DEZ) at a partial pressure of 5 mTorr was used as a gas source. A He-Cd laser (wavelength = 325 nm; its photon energy is higher than absorption band edge energy of adsorbed DEZn and thus, it is resonant to the electronic transition of a DEZn molecule) was used as the light source for the photodissociation of DEZ. An SEM image showed the grain size in the range of 100-200nm. Next, in addition to the He-Cd laser, we deposited Zn with an illumination of Ar<sup>+</sup> laser (wavelength = 488 nm) or He-Ne laser (wavelength = 633 nm). They are nonresonant light sources because their photon energies are lower than absorption band edge energy of DEZn. The respective grain size were found to be less than 50 nm (illuminating Ar<sup>+</sup> laser and He-Cd laser) and less than 10 nm (illuminating He-Ne laser and He-Cd laser). These results are due to the acceleration of dissociating ethylzinc or due to the desorption of deposited Zn by the nonresonant light, which are originated from the size-dependent resonance of nanoparticles. Since the Zn deposition technique reported here is applicable to near-field PCVD and high-quality ZnO nanocrystallites can be obtained by oxidizing Zn, it could be used to fabricate and position-controlled ZnO nanocrystallites; a promising material for use in nano-scale light-emitters and switching devices in nanophotonic ICs.

#### Q8.11

SINGLE CRYSTALLINE BORON NANOWIRES. Zhongke Wang, Takeshi Sasaki, Yoshiki Shimizu, Kenji Kawaguchi, Naoto Koshizaki, Naonoarchitectonics Research Center, AIST Central 5, Tsukuba, Ibaraki, JAPAN; Kaoru Kimura, Dept of Adv Mater, Graduate School of Frontier Science, The Univ Tokyo, Tokyo, JAPAN.

Single crystalline boron nanowires have been synthesized under 25 Pa of Ar ambient at the flow rate of 5 sccm in a quartz glass tube by ablation a compressed boron pellet using the third harmonic of Nd:YAG laser (355 nm in wavelength). The temperature at the center of the target was controlled to be 600 to 1100°C by using an electric furnace that surrounded the tube. The SEM images revealed that the products on the quartz glass substrate placed near the target after the ablation were dense entanglements of nanowires in large amounts. The nanowires are generally at least several micrometers to the order of mm in length, and several tens nm to 150 nm or above in diameter, appearing to grow both in long straight fibrils and in curly tufts from SEM images. Low magnified TEM observation suggested the wire products are classified into three types, the aggregates, ones that join to particle, and individual ones. The typical form is the aggregate of nanowires without particles at the tips of nanowires. By the detailed analysis of transmission electron diffraction (TED) pattern, nanowires are in tetragonal structure. All the characterized nanowires grew in the direction of [001], and the wire surface was coated with a thin amorphous phase. From the analysis of parallel electron energy loss spectroscopy (PEELS), only a peak corresponding to K-shell ionization edge of boron was clearly detected at about 188 eV. No other impurities such as O, C, Si etc. was observed in the interior of boron nanowires.

#### Q8.12

##### CONTROLLED GROWTH OF SILICON CARBIDE NANOWIRES.

Han-Kyu Sung, Kwang-Ryul Lee, June-Gunn Lee, Heon-Jin Choi, Department of Materials Science and Engineering, Korea Institute of Science and Technology, Seoul, KOREA.

Nanowires have a great potential as building blocks toward fabrication of electronic-, optoelectronic-, electromechanic-, and sensor devices in

nano meter scale. To exploit the potential, it is desirable to grow nanowires in a controlled manner such as self-aligned growth, creation of interfaces within the nanowires and/or controlled doping. In this presentation, we will illustrate the preparation of silicon carbide (SiC) nanowires in a controlled manner. We will describe the growth of SiC nanowires by using chemical vapor deposition (CVD) process with methyltrichlorosilane (MTS) as precursor, and their structural characteristics. The resulting SiC nanowires were randomly grown on the silicon or graphite substrates by vapor-liquid-solid or vapor-solid growth mechanism. We will then illustrate the growth of vertically self-aligned SiC nanowires on the substrates by controlling the processing conditions. We will also illustrate the structurally or compositionally modulated SiC nanowires, i.e., SiC nanowires having coaxial homo-interfaces within the nanowires or *in-situ* doped with aluminum (Al). We will discuss our results with a point of view of the preparation of nanowires in a controlled manner for device applications.

#### Q8.13

Abstract Withdrawn.

#### Q8.14

##### FABRICATION OF POROUS SiC-BASED CERAMICS WITHIN MICROCHANNEL NETWORKS FOR HIGH TEMPERATURE MICROREACTORS.

In-Kyung Sung, Hao Wang, Xiadong Li, Michael Mitchell<sup>†</sup>, Paul Kenis<sup>†</sup>, Dong-Pyo Kim, Chungnam National University, Dept of Fine Chemical Engineering and Chemistry, Daejeon, KOREA; <sup>†</sup>University of Illinois-Urbana-Champaign, Dept of Chemical and Biomolecular Engineering, Urbana, IL.

A new challenge is the development of microreactors, which are capable of performing complete chemical processes. Ceramic microreactors are desirable for the operation not only at ambient conditions, but at high temperatures and pressures as well. Resistive heating or combustion of a fuel can provide the heat necessary for the reaction. Potential applications of high temperature microreactors include reforming of fuels to hydrogen, typically a heterogeneous process. The highly endothermic process is needed to maintain at temperature range 700-900°C. Here we will show our efforts in the fabrication of porous SiC microchannels that are compatible with operation at high temperatures. The channels were incorporated by two types of high surface-area structures; inverted beaded bed, foam-like microstructure. At first, microchannels with 100µm high inlet were patterned on Si wafer using photolithographic process. An aqueous solution of monodispersed polystyrene (PS) beads with 10-1µm diameters was injected along channel with a specially designed cell and assembled into array under sonification. The vacuum-dried packed channels were infiltrated by low viscous ceramic precursors such as polysilazane and polycarbosilane. Finally, inverted beaded SiC matrix was prepared by pyrolysis at inert atmosphere at 1000°C with removal step of PS template. And foam-like SiC network was alternatively produced by filling the channels with mixed pastes of the polymers and carbon nanotube or carbon nanofiber templates which can be burned off in air after ceramization. Moreover, we will extend to investigate on catalytic activity at various temperatures in the microreactor systems.

#### Q8.15

EPITAXIAL CrO<sub>2</sub>@SnO<sub>2</sub> CORE-SHEATH NANOTAPES. Rong Fan, Rongrui He, Yiyang Wu, Matthew Law, Peidong Yang, Dept of Chemistry, University of California, Berkeley, CA.

Recently, controlled fabrication of 1-D heterostructures such as bimorph nanotapes were achieved to give a general methodology to synthesize various complex structures in order to achieve well-designed multi-functions over the traditional homogenous systems. SnO<sub>2</sub> nanoribbons were proposed as nano-substrates for epitaxial growth of various lattice-matched oxide bilayer nanotapes in our group, employing the concept of thin film epitaxy. In the present work, CrO<sub>2</sub> epitaxial growth on SnO<sub>2</sub> nanoribbons was studied using chemical vapor deposition technique. As-made CrO<sub>2</sub>@SnO<sub>2</sub> hybrid nanotapes has core-sheath structure with single crystalline CrO<sub>2</sub> sheath coating on SnO<sub>2</sub> ribbon cores. SEM and TEM images reveal the uniform morphology for as-made hybrid CrO<sub>2</sub>@SnO<sub>2</sub> nanotapes. X-ray diffraction analysis shows there are two sets of diffraction patterns corresponding to CrO<sub>2</sub> and SnO<sub>2</sub> with only traces of impurities. High resolution TEM indicates a sharp interface between two kinds of oxides. CrO<sub>2</sub> is becoming a central material in the field of spintronics due to its nearly complete spin polarization, and possesses great promise for lots of uses such as giant magnetoresistance material, spin-valve and spin tunneling junction devices. Herein, magnetization measurements show that the as-made CrO<sub>2</sub>@SnO<sub>2</sub> nanotapes are ferromagnetic at room temperature, which provide a good model to study 1-D magnetic and magnetotransport properties. Meantime, the CrO<sub>2</sub>@SnO<sub>2</sub> nanotapes are important building blocks for making nanoscale spin-dependent electronic devices.

#### Q8.16

SYNTHESIS OF TUBULAR GRAPHITE CONES. Guangyu Zhang and Xin Jiang, Fraunhofer Institute for Surface Engineering and Thin Films, Braunschweig, GERMANY; Enge Wang, State Key Laboratory for Surface Physics and International Center for Quantum Structures, Institute of Physics, Chinese Academy of Sciences, Beijing, P.R. CHINA.

Due to their high aspect ratios and unique atomic structures, carbon nanotubes (CNTs) have potential applications as biological and scanned probes, field electron-emitting sources, etc. Their hollow interiors can also serve as nano-channels for liquid-state materials. However, their extremely small size results in difficulties to mount and mechanically handle individual nanotubes and a high susceptibility to lateral bending and vibration, which largely prevent the realization of technological applications. Here we report the synthesis of a new material, called "tubular graphite cone" (TGC), that possesses the advantages associated with CNT but free of the technical difficulties. These TGCs have nanometer size tips at one end and micron size roots at the other. They are made of inner cylindrical graphite sheets (just like nanotubes) and outer helical and faceted graphite sheets. Continuous shortening of the graphite layers from inner to outer make them cone-shaped. Most interestingly, all layers are stacked by identical zigzag types of graphite sheets.

#### Q8.17

GROWTH AND CHARACTERIZATION OF COBALT-FILLED CARBON NANOTUBES PREPARED BY A SIMPLE CATALYTIC METHOD. Xicheng Ma, School of Chemistry and Chemical Engineering, Shandong University, P.R. CHINA; Yuanhua Cai, Xia Li, Ning Lun, Shulin Wen, School of Material Science and Engineering, Shandong University, P.R. CHINA.

Filling materials into the inner hollow cavity of carbon nanotubes (CNTs) have brought great attention because the new filled one-dimensional structure are expected to exhibit different physical properties than those of empty nanotubes. In this presentation, we demonstrated a simple catalytic method for preparation of Co-filled CNTs. This method provides a new way for encapsulating ferromagnetic materials into the cavity of CNTs. In this method, high-quality Co-filled CNTs were prepared in situ in the decomposition of benzene over Co/silica-gel nano-scale catalysts, which were formed by sol-gel process from cobalt nitrite and silica gel as the catalysts precursor. Unlike the previous reports, the catalysts need not be pre-reduced prior to the forming of Co-filled CNTs, thus the advantage of this method is that Co-filled CNTs can be produced in one step, at a relatively low cost. Control over the composition and structure of the as-made Co-filled CNTs was accomplished by changing experimental parameters. Under appropriate conditions, aligned Co-filled CNTs were formed. Both high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the morphology, microstructure and composition of the as-made products. Experimental results showed that ~80% yield of CNTs with high quality were obtained and almost nearly 100% of them were filled with cobalt nanorods or nanowires, the extent of the filling inside the CNTs is in excess of 60%. The encapsulated cobalt was further identified always as high temperature alpha-Co phase with fcc structure. Furthermore, the encapsulated cobalt were found consists of abundance of twinned boundaries and stacking faults, which were presumed to be responsible for some novel properties of these encapsulates. Magnetic properties of these encapsulates were measured, experimental results showed that these encapsulates possessed excellent magnetic properties. Further experiments to investigate the relationship between microtwins and magnetic properties of these encapsulates are still being pursued.

#### Q8.18

REMOTE GROWTH OF LARGE AREA CARBON NANOTUBES/FIBERS BY ANTENNA-EDGE PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION. Guofang Zhong, Hiroshi Kawarada, Iwao Ohdomari, Waseda University, Center of Excellence of Waseda University, Tokyo, JAPAN.

In this paper, the remote growth of large area carbon nanotubes/fibers (CNTs) is performed on a new apparatus based on an antenna-edge plasma assisted chemical vapor deposition (CVD), which has been successfully used for the hetero-epitaxial growth of diamond<sup>[1]</sup>. In the remote plasma, the deposition area of CNTs was much larger, and the uniformity and reproducibility of CNTs were also better than those in an immersed plasma. In our experiments, the diameter of discharging ball was within 2cm, while the growth area of CNTs at a substrate distance of 5-10cm away from the discharging ball was 5cm, which was limited by the size of a resistive substrate heater. From the configuration of the plasma and the substrate distance, the deposition area of 10-15cm is expected to be possible.

Vertically aligned, very thin CNTs (~500nm in length) were successfully prepared at low temperature around 500 degree Celsius in 3 minutes. This low temperature was suitable for direct growth of CNTs on glasses. It is a key point for the large scale industrial application of field emission displays. Since the antenna-edge microwave plasma assisted CVD system could be easily scaled up by adopting multiple antennae positioned in an appropriate distance, the controlled growth of large area, oriented CNTs at low temperature could be obtained. The scaling up of this system is just under constructing. [1] M. Tachiki, T. Fujisaki N. Taniyama, M. Kudo and H. Kawarada, J. Crystal Growth. 237-239. (2002)1277.

#### Q8.19

NANOSCALE SURFACE PATTERNING. Meng Yu and Alben Ivanisevic, Purdue University, Department of Biomedical Engineering, W. Lafayette, IN.

We describe a new method for nanoscale surface patterning based on our ability to tune relative adhesion forces. In this approach, we use a modified Atomic Force Microscope (AFM) tip as a tool to either remove or deposit molecules on a biomimetic surface. One can control the relative strength of the adhesion forces between two different interfaces by choosing among different chemical functionalities. During our patterning we move the tip in a specified location and control the adhesion force throughout the process, which allows us to fabricate a template on a chosen interface. We use this lithographically defined template to guide complex nanoscale building blocks. Due to the flexible nature of this patterning method, 2-D and 3-D features can be interfaced within micron size prototype architectures with high spatial resolution. The application of this novel method can be potentially recognized in the areas of electrical device fabrication, biosensor implementation and DNA-protein engineering.

#### Q8.20

DIRECTED GROWTH OF METAL NANOTUBULE ARRAYS. Feng Li, Weilie Zhou, Jibao He, Andriy Vovk, John B. Wiley, University of New Orleans, Advanced Materials Research Institute and the Department of Chemistry, New Orleans, LA.

An electrochemical method has been developed that readily allows the growth of nanotubules. Similar to other methods used in tubule fabrication, this one exploits the porous structure of anodic alumina membranes (AAM). By selective coating of one side of the AAM, it is possible to control the extended growth of the nanotubules along the walls of the template pores. Long tubules, 10's of microns, can be readily fabricated with this approach. Furthermore, modifications of the technique make it possible to produce solid nanowires with hollow tips as well as to produce wires with varying diameters along the length of the wire.

#### Q8.21

3-D STRUCTURING OF InP BY MAGNETIC FIELD ASSISTED ANODIC PORE FORMATION. M. Christophersen<sup>a,b</sup>, M. Haurylau<sup>a</sup>, S. Langa<sup>b</sup>, H. Föll<sup>b</sup>, P.M. Fauchet<sup>a</sup>; <sup>a</sup>Department of Electrical & Computer Engineering, University of Rochester, NY; <sup>b</sup>Materials Science, University of Kiel, GERMANY.

Pore crystals can be used as a 2-D photonic crystal. Periodic two-dimensional arrays of electrochemically etched macropores have been fabricated in *prestructured* Si with diameters and lattice constants limited to feature sizes larger than 0.5  $\mu\text{m}$ . The pores in InP form *self-organized* pore crystals with feature sizes from 500 nm down to 50 nm [1]. InP and aluminum oxide are the only two materials which exhibit self-organized pore crystals. In contrast to aluminum oxide, self-organized pore crystals produced in InP can form single crystals (i.e., exhibit long range order). We will present results on a new fabrication technique leading towards 3-D photonic crystals in InP. The electrochemical etching cell is placed in a magnetic field with strength of the order of several kG. We will present the first results obtained upon the application of magnetic fields of different strength and orientations. Our results show that bending of the pores within a radius of curvature of the order of the pore diameter is attainable. It is known, for example in GaAs, that applying a magnetic field can slightly increase the etch rate. Our results show for the first time that the *nanostucture* of a porous semiconductor layer can be controlled by magnetic field assisted electrochemical etching. Since the thickness of the porous layers can reach up to several hundred microns, the use of a magnetic field during electrochemistry can lead to controllable 3-D structures. [1] H. Föll, S. Langa, J. Carstensen, M. Christophersen, I. Tiginyanu, K. Dichtel, Pore Etching in Compound Semiconductors for the Production of Photonic Crystals, L6.4, MRS Proceedings Vol. 722, 2002.

#### Q8.22

NANOWIRES AND QUANTUM DEVICES FABRICATED BY 2D DOPANT PATTERNS IN Si. J.C. Kim, J.S. Kline, J.R. Tucker,

University of Illinois, Department of Electrical and Computer Engineering, Urbana, IL; J.-Y. Ji, T.-C. Shen, Utah State University, Department of Physics, Logan, UT; R.-R. Du, University of Utah, Department of Physics, Salt Lake City, UT.

A novel 2D electron system in Si has been achieved recently by depositing a submonolayer of P onto Si(100) surfaces followed by low temperature Si overlayer growth.<sup>1</sup> If the surface P coverage is greater than 0.05 ML, overlapping of the donor wavefunctions renders the delta-layer conducting even at 0.3 K. The resistivity of the delta-layers is in the range of 1-4 k $\Omega$ /sq, depending on P density. We intend to employ the patterned delta-layers as the epitaxially incorporated source and drain, and thus many material defects which are detrimental to nanoscale devices can be eliminated. We will report our progress in making some of the simplest dopant pattern devices: nanowires and lateral tunnel junctions made from these wires. Starting from Si(100)-2 $\times$ 1 monohydride surfaces with prefabricated contact regions, a scanning tunneling microscope is used to desorb H to define the wire between two contacts. After P exposure and Si epitaxial overlayer growth in UHV, a layer of dielectric material and top metal gate are deposited ex situ. Transport measurements with gate biases are carried out at low temperatures. The significance of this approach to Si based quantum devices will be discussed. This work is supported by NSF, ARO and DARPA. <sup>1</sup> T.-C. Shen et al., Appl. Phys. Lett. 80, 1580-1582 (2002).

#### Q8.23

CONTROL OF InAs QUANTUM DOT NUCLEATION USING INTERFERENCE OF OPTICAL WAVES. S. Oktyabrsky, M. Yakimov, and V. Tokranov, School of NanoSciences and NanoEngineering, University at Albany-SUNY, Albany, NY.

With a goal of development of a semiconductor quantum dot (QD) medium with uniform coverage and narrow size distribution, we have studied the nucleation of InAs and InGaAs QDs grown by molecular beam epitaxy (MBE) with in-situ exposure to the UV interference pattern. Single beam (interference with scattered surface wave) and double beam interference from N<sub>2</sub> laser (wavelength 337nm) has been applied. The MBE growth parameters were adjusted to obtain low density (<10<sup>10</sup> cm<sup>-2</sup>) of the self-assembled QDs, to be comparable with the periodicity of the interference pattern. The resultant surface QD ensembles were analyzed using scanning electron microscopy and atomic force microscopy, and by transmission electron microscopy for the capped QD layers. The unidirectional periodic QD patterns were formed as a result of the laser beam interference at pulse energy density of  $\sim 0.1$  J/cm<sup>2</sup>, just few times lower than the ablation threshold. We discuss the possible mechanisms for nucleation control: pulsed substrate temperature modulation, destroying the nucleation clusters in the antinode of the standing wave pattern; energy transfer to the surface adatoms through absorption of UV photons, causing evaporation of adatoms from the surface; and undulation of the surface by laser ablation that controls the surface energy.

#### Q8.24

SUBMICRO MAGNETIC NANOSTRUCTURE PRODUCED BY ELECTRON BEAM DIRECT WRITING ON CoC AND Co(TaC) SYSTEM. J.P. Wang, MINT & Electrical and Computer Engineering Department, University of Minnesota, MN; Y. Zhao, T.J. Zhou, T.C. Chong, Data Storage Institute, SINGAPORE; T. Thong, Electrical and Computer Engineering Dept, National University of Singapore, SINGAPORE.

In this paper, we present a novel method to fabricate sub-micro magnetic nanostructure by electron beam radiation induced nano-scale phase transition. The CoC films with thickness of 30 nm and Co concentration of 40%-80% were co-sputtered onto C-buffered glass substrate at room temperature using DC magnetron sputtering system. The X-ray diffraction results show that the as-deposited films are amorphous with the cobalt concentration less than 60 at% and the magnetic measurements reveal that these films are nonmagnetic. Ta was selected to improve the magnetic properties of the films because it can enhance the segregation of Co and C. The (Co<sub>60</sub>C<sub>40</sub>)<sub>x</sub>Ta(1-x) films were prepared where x varied from 0%-10%. It was found that the film with Ta doping could obtain the coercivity of 822 Oe, which was 45% higher than the films without Ta doping could, after annealing under the same condition. Magnetic patterning of the as-deposited Co<sub>60</sub>C<sub>40</sub> and (Co<sub>60</sub>C<sub>40</sub>)<sub>x</sub>Ta(1-x) films film was realized by subjecting it to electron beam radiation using a focused 30keV beam with a current of 7.1 nA and a dwell time of 0.75 seconds and longer. For CoC thin films, the magnetic dot were not formed until the dwell time increased to 3.8 seconds, and the dot size increases almost linearly with the square root of the dwell time per dot. While for Co(TaC) thin films, the weak magnetic line was produced with the dwell time of 0.75 seconds, and the tripe domain is very clear with the dwell time of 1.9 seconds. It is clear that the time of magnetically patterning (Co<sub>60</sub>C<sub>40</sub>)<sub>x</sub>Ta(1-x) films is much shorter than that of magnetically patterning Co<sub>60</sub>C<sub>40</sub> films. The presented

method of magnetically patterning a nonmagnetic film has the potential application for nanoscale solid magnetic devices.

#### Q8.25

Abstract Withdrawn.

#### Q8.26

CONTROLLED GROWTH OF GALLIUM NITRIDE SINGLE CRYSTAL NANOWIRES USING A CHEMICAL VAPOR DEPOSITION METHOD. Song Han, Wu Jin, Tao Tang, Chao Li, Daihua Zhang, Xiaolei Liu, Jie Han, Chongwu Zhou, University of Southern California, Department of Electrical Engineering-Electrophysics, Los Angeles, CA.

Nitride nanowires have stimulated enormous interest for their potential to be used in nanoscale electronic and optoelectronic devices. High-quality single crystalline gallium nitride (GaN) nanowires were grown for the first time using gold nanoparticles as the catalyst using a chemical vapor deposition (CVD) method. Our method enables control over several important aspects of the growth including the diameter, the position and the orientation. By using mono-dispersed gold nanoparticles of 10 nm, 20 nm and 30 nm in diameter, GaN nanowires of different diameters were grown. Histograms of the nanowire diameters revealed Gaussian distributions peaked at 10 nm, 20 nm and 30 nm, respectively. Furthermore, a controlled CVD method has been developed to grow GaN nanowires at desired sites by using ebeam lithography to pattern the catalyst islands. Very often we can get a single GaN nanowire bridging two adjacent catalyst islands. Such a position control can pave the way for the fabrication of nanowire devices and integrated systems. In addition, control of GaN nanowire orientation via epitaxial growth on a-plane sapphire substrates has also been achieved. Careful scanning electron microscope inspection revealed most of the nanowires grew vertically in the patterned catalyst region. Our work opens up new ways to use GaN nanowires as nano-building blocks and has great potential for the construction of integrated nanowire systems.

#### Q8.27

GALLIUM CATALYZED GROWTH OF ALIGNED SILICON OXIDE NANOWIRES. Zhengwei Pan, Sheng Dai, David B. Beach, Oak Ridge National Laboratory, Chemical Science Division, Oak Ridge, TN; Douglas H. Lowndes, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

Silicon oxide, as a good candidate for photoluminescence materials, has been studied extensively [1,2]. Silicon oxide in the form of nanowires was successfully fabricated by various techniques (such as chemical vapor deposition and laser ablation) [3-5] and high brightness blue light emission was observed [3,4], suggesting the potential application of silicon oxide nanowires in future integrated optical devices. The growth of silicon oxide nanowires were usually controlled by a vapor-liquid-solid process, in which a small size (5 to 100 nm in diameter), high melting point metal catalyst (such as Co [5], Fe [4] and Au [3]) controls the nanowire's growth direction and diameter. Recently, a new synthetic route, in which large size (5 to 50 nm in diameter), low melting point gallium droplets were used as the catalyst, was developed to the large-scale growth of highly aligned, closely packed silicon oxide nanowire [6,7]. In these gallium-catalyzed silicon oxide nanowire growth, silicon wafers were used as the silicon source. Here, we report that aligned silicon oxide nanowires can also be fabricated in high yield by using silane gas or SiO powders as the silicon source with the presence of gallium. In both cases, gallium droplets were obtained by thermal decomposition of gallium nitride powders at high temperature (1150°C for silane and 1350°C for SiO). Scanning electron microscope (SEM) investigations show that the silicon oxide nanowires tend to grow in bunches, in which numerous nanowires with diameters of 10-100 nm simultaneously grow out from the lower hemisphere surface of a large liquid gallium droplet (5 to 50 nm in diameter) to form comet-like or badminton-like structures, regardless the source material is silane or SiO. Many SEM and transmission electron microscope (TEM) images will be shown to illustrate the morphology and structures of the as-synthesized materials. References [1] G.G. Qin, J. Lin, J.Q. Duan and G.Q. Yao, Appl. Phys. Lett. 69, 1689 (1996). [2] L. Liao, X. Bao, X. Zheng, N. Li and N. Min, Appl. Phys. Lett. 68, 850 (1996). [3] Z.Q. Liu, S.S. Xie, L.F. Sun, D.S. Tang, W.y. Zhou, C.Y. Wang, W. Liu, Y.B. Li, X.P. Zhou and G. Wang, J. Mater. Res. 16, 683 (2001). [4] D.P. Yu, Q.L. Hang, Y. Ding, H.Z. Zhang, Z.G. Bai, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong and S.Q. Feng, Appl. Phys. Lett. 73, 3076 (1998). [5] Y.Q. Zhu, W.K. Hsu, M. Terrones, N. Grobert, H. Terrones, J.P. Hare, H.W. Kroto and D.R.M. Walton, J. Mater. Chem. 8, 1859 (1998). [6] Z.W. Pan, Z.R. Dai, C. Ma and Z.L. Wang, J. Am. Chem. Soc. 124, 1817 (2002). [7] B. Cheng, Y.Y. Wu, P.D. Yang and J. Liu, Adv. Mater. 14, 122 (2002).

### Q8.28

CATALYTIC FUNCTIONALIZATION OF NANOPOROUS GOLD MEMBRANES. Yi Ding and Jonah Erlebacher, Johns Hopkins Univ, Dept Materials Science and Eng, Baltimore, MD.

Selective electrochemical dissolution of silver from silver/gold alloys exhibits an unusual three-dimensional pattern-forming instability, a kind of self-assembly that can be used to produce pure gold in the form of a sponge with open porosity, ligament width/spacing tunable between 5 nm and several microns, and extremely high surface area. We report a method to create free-standing nanoporous gold films with thickness of order 100 nm by dealloying silver/gold leaf, "gildable" onto a variety of planar and non-planar substrates. We further report an electroless plating technique to coat the surface of nanoporous gold leaf with a variety of catalytically important metals via a gas-phase electroless reduction of metal salts confined in the aqueous layer absorbed within the leaf. The reaction is self-limiting to a great extent and results in a conformal and uniform coating of the gold with an ultrathin (less than 5 nm) layer of the reduced metal. Microstructure and surface area characterization of platinum, nickel, cobalt, and silver-coated nanoporous membranes are reported. These nanoporous metal structures combine the high-surface area advantages of nanoparticles with the in-plane electrical conductivity of thin films, good characteristics for high sensitivity in sensing.

### Q8.29

SELF-CATALYTIC FORMATION OF ZnO NANOWIRES BY SIMPLY HEATING ZINC FILMS IN OXYGEN. Y.G. Wang, S.P. Lau, B.K. Tay, Nanyang Technological University, School of Electrical and Electronic Engineering, SINGAPORE; K.Y. Tse and H.H. Hng, Nanyang Technological University, School of Materials Engineering, SINGAPORE.

Nanowires, a kind of nanostructured materials, are of interest for its potential applications in nanoscale electronic and optoelectronic devices, various synthesis methods have been explored. In this presentation, a simple method for synthesis of ZnO nanowires is reported. ZnO nanowire was observed to grow directly from metallic zinc film through heating them in oxygen atmosphere at relatively low temperature (~673K) without the need of catalysts. Detailed investigations indicated that the formation of nanowires was influenced mainly by three factors: surface morphology of zinc film, annealing temperature and oxygen partial pressure. Nanowire appeared on film surface in a wide of temperature range around melt point of metallic zinc (693K) from 600-800K, however the optimum temperature was found to be 673K, longer and higher density of nanowires were formed under this temperature. Suitable surface roughness was acquired for formation of nanowires, very few nanowires appeared on films with roughness of several nanometers. Low oxygen partial pressure favored the growth of longer nanowires. The obtained nanowires were characterized by TEM and PL spectrum. The PL showed intense band edge emission peak and relatively low deep level emission intensity as compared with nanowires prepared by other methods. According to our experiments, the formation of ZnO nanowire here was different from other methods, a kind of self-catalytic process controlled the growth of nanowire from metallic zinc films. At optimum growth temperature, a liquid zinc phase existed between the nanowire and films acted as catalyst for the continuous growth of nanowire.

### Q8.30

NEW FACILE AND BIOLOGICAL ROUTES FOR THE SYNTHESIS OF CARBON NANOTUBES. Mark J. Pender, Laura Sowards, Rajesh Naik, Benji Maruyama, Richard Vaia, Morley Stone, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

While carbon nanotubes can be synthesized in a variety of ways and on large scales, further ease and control in the synthesis of these technologically important structures is desired. Herein we report two new routes for the synthesis of carbon nanotubes that offer these advantages. Using a simple polymer/metal formulation, SWNTs can be easily grown and characterized. Dissolving metal salts (e.g. iron, cobalt, nickel) in a commercially available siloxane polymer solution allows one to coat a number of different substrates with smooth, uniform layers of the polymer/metal blend. A high temperature oxidation yields a smooth silicon oxide film with islands of metal oxides that act as the sites of initiation and growth at high temperatures in an appropriate atmosphere. Additionally, we have investigated the use of common iron-sequestering proteins as catalyst precursors for the growth of carbon nanotubes. Such proteins may be patterned with dip-pen nanolithography and, thus, yield discrete, well-defined patterns of carbon nanotubes on a substrate at scales smaller than those offered by common lithographic techniques.

### Q8.31

ONE-STEP AND SELF-MASKED DRY ETCHING METHOD FOR

FABRICATING NANOTIP ARRAYS OVER LARGE AREA AT LOW TEMPERATURE. C.H. Hsu and C.F. Chen, National Chiao Tung University, Department of Materials Science and Engineering, Hsinchu, TAIWAN; H.C. Lo, J.S. Hwang, and K.H.Chen, Academia Sinica, Institute of Atomic and Molecular Science, Taipei, TAIWAN; L.C. Chen, National Taiwan University, Center For Condensed Matter Sciences, Taipei, TAIWAN.

Well-aligned nanotip arrays were fabricated by electron cyclotron resonance plasma process using gas mixtures of silane, methane, argon and hydrogen. Nanotip arrays with high aspect ratios (~100) and sharp apexes (~1 nm) were achieved by direct etching from a variety of substrates such as silicon, gallium nitride, gallium phosphate and aluminum with the simultaneous formation of silicon carbide (SiC) protecting caps on the tips. High-resolution transmission electron microscopy and Auger depth profile analyses revealed that the SiC cap exhibited 3C-SiC microstructure and a Si:C composition ratio of 1:1. This one-step self-masked dry etching technique makes it possible to fabricate uniform nanotip arrays on various substrates over large area at low process temperatures, therefore, possesses a high potential for practical industrial application.

### Q8.32

NANO-FABRICATION BY TWO-PHOTON LITHOGRAPHY. Tae-Woo Lee, Oleg Mitrofanov, John A. Rogers, Christopher A. White, and Julia W. P. Hsu, Bell Laboratories, Lucent Technologies, NJ.

We demonstrate the applications of two-photon lithography in nano-fabrication. Our two-photon microscope setup includes a 130 fs, 76 MHz, 710 nm mode-locked Ti:sapphire laser as the light source and a modified Nikon microscope with piezo scanner to move sample with respect to the laser beam. Using the two-photon microscope, we fabricated two-dimensional (2D) photonic crystal structures in commercially available SU-8 films. The laser beam power, writing speed, focal depth, line spacing and writing angles determine the line width, aspect ratio, and symmetry of the photonic crystals. We have obtained 2D photonic crystals with circle, elliptical round, square, or diamond unit cells in hexagonal or square lattice. An aspect ratio as high as 6.9 with 250 nm line width was achieved. Thus, two-photon lithography is a good technique for fabricating photonic structures with sub-diffraction-limit resolution. In addition, we can controllably place defects of specific patterns, e.g. lines, dots, Y-splitters, can be placed in the otherwise perfect photonic crystal. We also demonstrate the fabrication of 2D photonic crystals by two-photon lithography between waveguides made using conventional UV photolithography. The combination of these two lithography methods was done on a single polymer film, significantly simplifying the processing steps. Furthermore, the nanostructures made by two-photon lithography can be used as masters for microcontact printing and replica molding. Since we can easily control the aspect ratio of the two-photon fabricated structures, we fabricated structures with different aspect ratio and used them to test the limit of using commercially available polydimethylsiloxane elastomeric materials (Sylgard 184 and Gelest) for nanofabrication.

### Q8.33

CONTROLLED ARRAY MATRICES OF NANOWIRES BY NANO-CONTACT SOFT LITHOGRAPHY. Hou Tee Ng<sup>†</sup>, Jessica Koehne, Jun Li<sup>†</sup>, Alan Cassell<sup>†</sup>, Jie Han<sup>†</sup> and M. Meyyappan, National Aeronautics and Space Administration Ames Research Center Moffett Field, CA.

The ability to fabricate and replicate structures and devices on the micrometer to the nanometer length scales using simple, efficient, and cost-effective approaches presents one of the major challenges toward miniaturization of future electronic, optoelectronic, biomedical, and magnetic devices. Compared to the more sophisticated but expensive advanced lithographic techniques such as electron-beam and X-ray lithography, current nonphotolithographic approaches (such as micromolding, nanoimprinting, lithographically induced self-construction, and electrostatic lithography) of fabricating and replicating structures certainly provide attractive alternative means to meet these objectives. Here we demonstrate rapid, efficient and reliable fabrication and replication of high density arrays of polymeric structures using ultrathin layer-mediated processes. Highly controllable dry surface treatment has been used to create a chemically inert and stable interfacial zone between two polymers of the same chemical identities to allow simple replica molding and rapid intact release of highly flexible molded polymeric structures. These structures could then be used to pattern, via nano-contact soft lithography, arrays of catalysts for the controlled growth of single crystalline nanowires. Novel device architecture has been successfully employed based on these nanowires to realize nanoelectronics.

## SESSION Q9: MOLECULAR SYSTEMS

Chair: Timothy J. Bunning

Thursday Morning, April 24, 2003

Metropolitan II (Argent)

### 8:30 AM Q9.1

#### PRESSURE EFFECTS ON BLOCK COPOLYMER TEMPLATES.

Metin H. Acar, Juan Gonzalez, Anne M. Mayes, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA.

The microphase separation of block copolymers has been an ongoing matter of study because of the potential application of these as self-assembling materials as templates for the fabrication of devices on the nanometer scale. A thermodynamic parameter that is usually overlooked in the design of such systems is pressure. Pressure can have a dramatic effect on the order-disorder behavior of block copolymers, which is responsible for the formation of the characteristic morphologies exhibited by these systems. We have developed a novel class of block copolymers called baroplastics, which exhibit pressure induced order/disorder transitions. This property may have an important application in controlling the order and orientation of block copolymer films, as pressure can be applied locally and instantaneously. Baroplastic block copolymers have been synthesized by atom transfer radical polymerization (ATRP) and shown to disorder at room temperature under applied pressure. The morphologies of baroplastics on a silicon substrate have been studied using AFM. The pressure modification of these microstructured templates is explored.

### 8:45 AM Q9.2

POLYANILINE NANOFIBERS: FACILE SYNTHESIS AND CHEMICAL SENSORS. Jiaying Huang, Shabnam Virji, Richard B. Kaner, University of California, Los Angeles, Department of Chemistry and Biochemistry, Exotic Materials Institute and California NanoSystems Institute, Los Angeles, CA; Bruce H. Weiller, The Aerospace Corporation, Materials Processing and Evaluation Department, Space Materials Laboratory, Los Angeles, CA.

Conducting polymer polyaniline nanofibers with uniform diameter between 30-50 nm can be made in bulk quantities through a facile aqueous/organic interfacial polymerization method at ambient conditions. The nanofibers have lengths varying from 500 nm to several microns and form interconnected networks. This synthesis has the following advantages: (i) Both the synthesis and purification are simple with no template-removing steps needed. (ii) Uniform nanofibers comprising >95% of each sample are readily produced. (iii) The synthesis is easily scalable and reproducible. Multiple syntheses performed from millimolar to molar quantities yield nanofibers of the same morphology, size distribution and uniformity. (iv) The nanofibers are readily dispersed in water, which could facilitate environmentally friendly processing and biological applications. (v) The diameter of polyaniline fibers is at the nanoscale, which dictates their superior performance as chemical sensors. For example, thin films made of the nanofibers have excellent performance as resistive type sensors in both sensitivity and time response upon exposure to acid (HCl) and base (NH<sub>3</sub>) vapors. Surprisingly, the nanofiber films show essentially no thickness (0.22.5 μm) dependence in their performance.

### 9:00 AM \*Q9.3

BIOPHOTONICS BASED ON LIQUID CRYSTALS AND NANOSTRUCTURED SURFACES. Nicholas L. Abbott, Department of Chemical Engineering, University of Wisconsin, Madison, WI.

Recent advances in the capability to control the structure of organic surfaces over a wide range of length scales offers new opportunities to design the interactions between liquid crystalline materials and surfaces, and thus to orient liquid crystals through these interactions. This presentation will report on the balance of intermolecular forces acting at interfaces between thermotropic liquid crystals and solids that possess well-defined chemical functionality and nanometer-scale topography. This understanding will be used to describe the design surfaces that permit a variety of interfacial phenomena ranging from acid-base reactions to complex biological interactions (e.g., antibody-virus binding)- to be amplified and imaged by using liquid crystals.

### 9:30 AM \*Q9.4

CONJUGATED POLYMER NANOWIRES FOR NANO-ELECTRONICS AND NANOPHOTONICS. Samson A. Jenekhe, Maksudul M. Alam, Yan Zhu, University of Washington, Departments of Chemical Engineering and of Chemistry, Seattle, WA.

In bulk thin film form, conjugated polymers are being exploited in a range of electronic and photonic devices including light emitting devices for displays, lasers, photovoltaic cells, photodetectors, and thin film transistors. Single chains of conjugated polymers are

envisioned as molecular wires and potential building blocks for fabricating molecular-level electronic devices. However, major barriers to investigating conjugated polymer molecular wires include the difficulty of isolating and manipulating a single polymer chain and in making contacts to it. We will present the synthesis, self-organization, nanoscale morphology, and electronic and optical properties of a novel class of conjugated polymer nanowires. The initial results suggest that these conjugated polymer nanowires with diameters on the order of 5-50 nm and lengths of up to 250-1000 nm are promising building blocks for nanoelectronics and nanophotonics.

### 10:30 AM \*Q9.5

NANOSCALE ARCHITECTURAL CONTROL OF ORGANIC FUNCTIONAL MATERIALS FOR PHOTONICS AND MOLECULAR ELECTRONICS. Alex K-Y. Jen, Hong Ma, Jingdong Luo, Sen Liu, Marnie Haller, Larry Dalton, Hadi Zareie, Bryn Reed, and Mehmet Sarikaya Department of Materials Science and Engineering, University of Washington, Seattle, WA.

We have recently introduced dendritic structures to NLO chromophores and polymers, and investigated the role of the site isolation effect in determining the material properties. Our efforts are aiming at systematically tuning of the molecular topology of organic E-O materials in nanoscale. We will highlight our latest progress in design, synthesis, and properties of different material systems for this purpose, varying from 3-D shaped dendritic chromophore, fully-functionalized dendrimers with the center core of NLO chromophores and crosslinkable groups on the periphery, to side-chain dendronized NLO polymers. The results obtained by using this approach are extremely encouraging and it may help to launch a new paradigm of molecular engineering for next generation of high performance E-O materials. We will also discuss our recent results in molecular electronics. We have developed a design criterion and, based on which, chemically synthesized conducting molecules with controlled molecular architectures. The size, shape, orientation and ordered patterns of molecular wires can be engineered through a delicate interplay of the intermolecular p-p stacking and chemisorptive substrate-linker interactions. Through scanning tunneling spectroscopy, we have demonstrated changes in electronic behavior of single molecules that form into different long-range ordered assemblies. The ability to assemble predictable two-dimensional molecular crystals and understand the order-related electronic behavior of single molecular components could allow future design of nano-patterned arrays as a controlled platform towards further miniaturization of electronic devices.

### 11:00 AM \*Q9.6

BIOLOGICALLY-BASED NANOSTRUCTURES FOR CATALYSIS AND OPTICS. Rajesh R. Naik, Lawrence L. Brott, Mark J. Pender, Laura A. Sowards, Morley O. Stone, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

A hallmark of biological systems is their ability to self-assemble. This self-assembly can occur on the molecular, macromolecular, and meso scale. In this work, we have chosen to exploit biology's ability to self-assemble by incorporating additional functionality within the final structure. In previous work, we have demonstrated how peptides can be selected from a combinatorial library that possess catalytic activity with respect to inorganic nucleation and deposition. We have engineered some of these peptide sequences into self-assembling protein structures. The goal of this project was to create an organic/inorganic hybrid that retained the "memory" properties of the organic, but possessed the superior optical and electronic properties of the inorganic. Data will be presented that examines hybrid structures based on viral and metal-transport protein structures.

### 11:30 AM \*Q9.7

MIRRORLESS LASING IN LIQUID CRYSTALLINE PHOTONIC BANDGAP MATERIALS. Wenyi Cao, Peter Palffy-Muhoray, and Bahman Taheri, Liquid Crystal Institute, Kent State University, Kent, OH; Antonio Munoz, Dept. of Physics, Universidad Autonoma Metropolitana, Mexico City, MEXICO.

Liquid crystals (LC) are promising photonic band gap (PBG) materials. Certain LC phases have spatially modulated ground states; these materials effectively form self-assembled PBG structures. These structures can also be made permanent by photopolymerization. Typically, LCs respond readily to applied fields, enabling modulation and switching of the bandgap. Since classical light propagation is forbidden, fluorescent emission in the bandgap can lead to population inversion and stimulated emission at the band edges. Mirrorless lasing experiments provide an effective probe of the bandgap. We discuss the underlying physics, and present the results of mirrorless lasing experiments in a variety of cholesteric LC materials. We present recent results of 3-D lasing in blue phases as well as lasing from defect modes. We discuss possible applications, including remote sensing.

**1:30 PM Q10.1**

**FORMATION, PATTERNING, AND POLYMERIZATION OF SURFACE ADLAYERS USING SELF-ASSEMBLED MONOLAYERS AS TEMPLATES.** David W. Mosley, Mark A. Sellmyer, Joseph Jacobson, Massachusetts Institute of Technology, Media Laboratory, Cambridge, MA.

Ordered surface adlayers of diacetylene-containing molecules were formed using amide hydrogen-bonding interactions with a pre-formed self-assembled monolayer on gold. Photopolymerization of the diacetylene molecules in the adlayer results in enhanced solvent and processing stability of the adlayer. Patterning of the base monolayer allows patterning of the adlayer as well, and may lead to methods for templating soluble two-dimensional monolayer sheets.

**1:45 PM Q10.2**

**NANOPATTERNING OF INORGANIC/ORGANIC HYBRID COMPOSITES: TOWARDS MINIATURIZED CHEMICAL SENSORS.** Ming Su and Vinayak P. Dravid.

Miniaturized chemical and biochemical sensors have the potentials to change the current analytical science, as the miniaturization of computer chip has done in computer industry. A critical element to fabricate miniaturized sensor is the ability to the site- and shape-specific patterning of functional nanostructures with controllable chemical and structural properties, but at nanoscale dimension. The newly developed approach of dip pen nanolithography (DPN) is ideally suited for nanopatterning. However, until recently DPN was limited to the patterning of small organic molecules that can form covalent bonds with substrates. We have recently extended the DPN technology beyond the organic molecules by the nanopatterning of inorganic/organic composite materials. This abstract describes the use of sol-precursor for the patterning of semiconductor sensor elements between metallic electrodes. The sensing properties are demonstrated by exposure to low concentration of chemical vapors such as methane and acetic acid. Combined with the highly spatial-controlled DPN, the versatile and matured sol-gel technology is potentially important to construct integrated sensors with low energy consumption, high selectivity and sensitivity for the detection of multiple chemical vapors.

**2:00 PM \*Q10.3**

**"SOFT" MATERIALS AND PATTERNING TECHNIQUES FOR FLEXIBLE AND NANOSCALE ELECTRONICS.** John A. Rogers, Jana Zaumseil, Vikram Sundar, Yueh-Lin Loo, Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Organic and molecular materials hold great promise for the future of electronics, photonics and nanotechnology. New additive printing and lamination techniques can be used directly with these classes of "soft" materials to build electronic devices with near-molecular dimensions: the electrical contacts in both cases are formed at ambient conditions that do not degrade or disrupt the often chemically and mechanically fragile organics. This talk describes these methods and their use in fabricating organic transistors, circuits that incorporate them and prototype systems, such as electronic paperlike displays, that illustrate some of their potential applications.

**2:30 PM \*Q10.4**

**TOWARD ELIMINATION OF SOLVENTS IN MICRO/NANOFABRICATION: SOLVENTLESS POLYMERIZATION AND ITS APPLICATIONS.** Hongwei Gu, Degang Fu, Chenjie Xu, Jun Tang, Bing Xu, Hong Kong University of Science & Technology, Department of Chemistry, Clear Water Bay, Hong Kong (SAR), CHINA.

We have recently developed a solventless polymerization process, based on catalytic polymerization and soft lithography. This process involves adding catalysts on the surface of solid substrate and polymerizing volatile monomers at the gas/solid interface. It provides an alternative to other thin-film-making processes—spin coating, cold plasma polymerization, and layer-by-layer deposition—and may serve as an approach to ultimately eliminate solvents in micro/nanofabrication. In this paper, we will discuss the details of this solventless polymerization process and the exploration of its applications. The activity of the catalysts and constant exposure of them to the monomers determines the effectiveness of the solventless polymerization. In the process of patterning the catalyst, we found that the catalysts always adhere to the hydrophilic regions regardless of the polarity of the organic solvents used to dissolve the catalysts. The morphology of these thin films depends on catalyst concentrations,

time of catalyst exposure to monomers, and type of monomers, which all can be easily controlled. The thin films, generated by solventless polymerization, on the surface can be used for a range of applications. This process works well on silicon and silicon dioxide substrates, and is complementary with reactive ion etching (RIE) process, in which the polymeric thin film acts as an etching resistant. Using this process in microchannels produces thin films with better smoothness. It also offers a simple route to generate microstructures when solvent disturbs the microstructure formation. In addition, this solventless polymerization process provides a simple and fast protocol to screen the catalysts in parallel mode since many catalysts can be checked simultaneously without interferences of solvents.

**3:30 PM \*Q10.5**

**MICRO TO NANOSCALE ORGANIC AND INORGANIC FUNCTIONAL SYSTEMS VIA POLYMER STAMPING TECHNIQUES.** Paula T. Hammond, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Research directions in materials and polymer science include the development of surface-directed assembly that can guide the placement of molecular to micron-scale objects onto substrates in pre-determined arrangements for sensors, electrical and optical devices, MEMs, and 2-D photonic systems. Nonlithographic approaches to these goals such as nano to microscale printing, molding, and templating, will be key to driving the technologies toward application and commercialization. We have used these techniques to build up complex, laterally patterned microstructures on the surface, in which more than one materials system can be selectively placed on a surface. A new approach to patterning surfaces, polymer-on-polymer stamping, extends these techniques to a number of different surfaces. This approach involves the microcontact printing of graft and block copolymers on a range of materials, including common plastic substrates and the surfaces of polyelectrolyte multilayers, to obtain patterned functional surfaces of multiple level layer-by-layer thin films. These films may then be used to template materials deposition, including other layer-by-layer thin films, metals, and colloidal particles. The use of this approach in the patterning of electro-optical polymers on various substrates, including polymers with electrochromic or ion transport properties, will be discussed. The ease and simplicity of the technique make it an accessible means of incorporating a number of passive and active organic multilayer systems into devices. New developments in this work include the ability to pattern a variety of conducting and electro-optical thin films, organic oxides such as TiO<sub>2</sub>, and most recently the modification and patterning of polydimethylsiloxane surfaces. Especially interesting results have been obtained by the direct transfer of entire multilayer films from a stamp surface, allowing the placement of complex nanostructured thin film "objects" on surfaces. Ongoing work on multilayer thin films for sensors will also be included.

**4:00 PM \*Q10.6**

**NONLITHOGRAPHIC PATTERNING METHODS AND THEIR APPLICATIONS IN ORGANIC ELECTRONICS USING MOLECULAR SELF-ASSEMBLY MATERIALS.** Zhenan Bao, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Nonlithographic patterning methods present attractive alternatives to conventional optical lithography and e-beam lithography for the fabrication of micrometer and nanometer features. We have demonstrated several new patterning methods that allow the formation of a broad range of feature sizes enabled by molecular self-assembled materials. Here the self-assembled materials are used for various functions, such as the interfacial transfer layer, spacing layer between electrodes, surface initiation layer for metal or polymer growth, or the protecting layer from etching and other chemical reactions. The application of the above methods in the fabrication of organic thin film transistors will be discussed.

**4:30 PM Q10.7**

**PATTERNED LANGMUIR-BLOGETT FILMS OF MONODISPERSE MAGNETIC NANOPARTICLES USING SOFT LITHOGRAPHIC TECHNIQUE.** Hong Yang, Qijie Guo, Saifur Rahman, Xiaowei Teng, University of Rochester, Department of Chemical Engineering, Rochester, NY.

Recently several types of monodisperse magnetic nanoparticles such as FePt, Co, Fe, Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> have been made through solution phase syntheses. Some of these nanoparticles show superior magnetic properties and have been studied as materials for ultra high density magnetic storage media and magneto-optical devices. It becomes increasingly important to develop strategies to fabricate these nanoparticles into patterned thin films in order to further explore their application potentials. Langmuir-Blodgett (LB, vertical lift) technique is one of the flexible and promising methods because it allows the fine control of thickness and homogeneity of monolayer, and ease for multilayer depositions. In this presentation, I describe a

method to make patterned LB films of nanoparticles of iron oxides and to transfer these patterned films on solid substrates such as silicon wafer using soft lithographic technique. We used monodisperse iron oxide nanoparticles dispersed in hexane ( $\sim 1 \text{ mg mL}^{-1}$ ) as spreading solution. LB films of iron nanoparticles were made using a KSV 3000 Langmuir trough in a Class 10,000 clean room. The monodisperse nanoparticles were first compressed into Langmuir film to target pressure ranges and subsequently lifted onto patterned polydimethylsiloxane (PDMS) surface. Thin films of nanoparticles were transferred to silicon wafer and other substrates using micro contact printing ( $\mu$ -CP). Dots, wells and other patterns on PDMS were examined for making monodisperse iron oxide nanoparticles on native silicon wafer. Field emission scanning electron microscope (SEM), transmission electron microscope (TEM), atomic force microscope (AFM), powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS) were used in the characterization. The effects of particle quality, surface properties and other factors on the transfer efficiency of the patterns will be discussed.

#### 4:45 PM Q10.8

THE PHYSICS OF PLASMON PRINTING – MASK OPTIMIZATION AND EXPERIMENTS. Pieter G. Kik, Stefan A. Maier, and Harry A. Atwater, California Institute of Technology, Thomas J. Watson Laboratory of Applied Physics, Pasadena, CA.

We have proposed a new approach to optical lithography that could be used to print patterns with feature sizes below 50 nm using standard positive photoresists and broad beam illumination with visible light. The method relies on the plasmon resonance occurring in nanoscale metallic particles. The nanoparticle surface plasmon oscillation can be excited resonantly, producing a strongly enhanced dipole field around the particle. We have shown that this enhanced near field can be used to locally expose a thin resist layer in experiments and calculations involving isolated Ag nanoparticles. In this talk we experimentally and theoretically assess the feasibility of using plasmon printing for the reproduction of large areas containing complex nanoparticle patterns. Using Finite Difference Time Domain (FDTD) simulations we evaluate the influence of particle-particle interactions and mask composition on the resonance frequency. The surface plasmon resonance of isolated 50 nm diameter Ag particles on a glass mask in index matched surroundings is predicted to occur at 418 nm. The presence of a 15 nm thick ITO coating - necessary in the mask preparation process - is found to redshift the resonance by 30 nm. It is shown that the deposition of a 5 nm thick SiO<sub>2</sub> spacer layer on the ITO completely recovers the resonance frequency. This resonance wavelength falls within the sensitivity range of commercial AZ photoresist. For our experiments we have fabricated plasmon printing masks on ITO covered glass substrates on 0.25 mm<sup>2</sup> areas using e-beam lithography. The masks contain thousands of arrays of closely spaced Ag nanoparticles (diameter 30-50nm) at various center-to-center spacings ranging from 25 nm to 1  $\mu\text{m}$ . Transmission spectroscopy reveals a clear extinction features related to the Ag surface plasmon resonance in these arrays, providing a direct measure of the required exposure wavelength. In masks without a spacer layer, resonances occur around 500 nm. The location of the absorption maximum is found to depend on the polarization of the incident light due to particle-particle interactions. Printing experiments using exposure in the near UV ( $\lambda > 400 \text{ nm}$ ) on ultrathin resist layers with these masks will be presented.

#### SESSION Q11: POSTER SESSION PROPERTIES AND APPLICATIONS

Chair: Peidong Yang  
Thursday Evening, April 24, 2003  
8:00 PM  
Golden Gate (Marriott)

#### Q11.1

SELF-ORGANIZED LATERAL BRIDGING OF CARBON NANOTUBES BETWEEN ELECTRODES USING THERMAL CHEMICAL VAPOR DEPOSITION. Takashi Ikuno, Shin-ichi Honda, Norihiro Yamauchi, Winadda Wongwiriyanan, Shigeharu Ohkura, Mitsuhiro Katayama and Kenjiro Oura, Dept. of Electronic Eng., Graduate School of Osaka Univ., Osaka, JAPAN.

Carbon nanotubes (CNTs) are molecular wires exhibiting controllable electrical properties which depend on the chirality and the diameter. However, the industrial applications of the CNTs to nanodevices have not been realized because of difficulties in the assembly and integration of CNTs and also the high contact resistance between CNTs and the electrodes. Accordingly, it has been necessary to utilize self-organized synthesis of CNTs to achieve high throughput and reliability of the CNT nanodevices. In this study, we synthesized directly self-organized CNT bridges between the electrodes. The

self-organized CNT bridges were successfully synthesized by thermal chemical vapor deposition with pure C<sub>2</sub>H<sub>4</sub> gas of 100 Pa at 900°C. Fe thin films deposited on the SiO<sub>2</sub>/Si wafers were used as substrates. The Fe thin films were transformed into the assembly of Fe nanoparticles with 57 nm in average diameter and  $2.2 \times 10^9 \text{ cm}^{-2}$  in number density by thermal annealing. From SEM results, it has been found that the CNTs, which have about 10 nm in diameter and over several  $\mu\text{m}$  in length, were laterally bridged between Fe nanoparticles in a self-organized manner. The yield of the CNT bridges depended on both the gas pressure and the reaction temperature. TEM revealed that some of the resultant CNTs consist of bundles of double or triple walled CNTs with high linearity. Furthermore, on the optimal conditions, CNTs were bridging between the Ta electrodes (10  $\mu\text{m} \times 10 \mu\text{m}$ ) on SiO<sub>2</sub>/Si wafers in a self-organized manner, which has a gap of 1  $\mu\text{m}$  between Ta electrodes formed by lithographic technique. More detailed results on the CNT bridges as a function of synthesis parameters will be presented.

#### Q11.2

NANOELECTRODE ARRAYS BASED ON LOW SITE DENSITY ALIGNED CARBON NANOTUBES. Yi Tu, Boston College, Dept of Chemistry, Chestnut Hill, MA; Yuehe Lin, Pacific Northwest National Laboratory, Richland, WA; Zhifeng Ren, Boston College, Dept of Physics, Chestnut Hill, MA.

Nanoelectrode arrays (NEAs) were fabricated from the low site density ( $10^6/\text{cm}^2$ ) aligned carbon nanotubes (CNTs). The CNTs were grown by plasma enhanced chemical vapor deposition (PECVD) on Ni nanoparticles made by the electrochemical deposition. Each nanotube is separated by several microns from the nearest neighbor that is important for preventing the diffusion layer overlap between nanoelectrodes. The NEAs consisting of up to million of nanoelectrodes with diameter of 100 nm for each one can be made in 1 cm<sup>2</sup> area by this non-lithography method. It can greatly improve the detection limit and signal to noise ratio.

#### Q11.3

LOW TEMPERATURE SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOTUBES APPLICABLE FOR FIELD EMISSION DISPLAY BY INDUCTIVELY COUPLED PLASMA CHEMICAL VAPOR DEPOSITION. Shin-ichi Honda, Takashi Ikuno, Keita Tsuji, Takashi Kuzuoka, Takashi Miyake, Kuei-Yi Lee, Shigeharu Ohkura, Mitsuhiro Katayama and Kenjiro Oura, Dept. of Electronic Eng., Graduate School of Osaka Univ., Osaka, JAPAN; Takashi Hirao, Dept. of Electrical Eng., Graduate School of Osaka Univ., Osaka, JAPAN.

Carbon nanotubes (CNTs) are attractive for various applications due to their unique properties. For instance, CNTs are applicable for field electron emitters of field emission display (FED) for future generation of flat panel displays. For FED applications, CNTs need to be directly grown on soda-lime glass substrates. Since the glass has relatively low softening temperature (the softening temperature of the glass is 550°C), low temperature process is required to synthesize CNTs. Plasma enhanced chemical vapor deposition (PE-CVD) has been used to synthesize the CNTs. However control of the plasma has not fully made so that it is still difficult to control amount of the radicals or kinetic energy of the radicals in the plasma for CNT growth. In this study, we have developed a novel method for low temperature synthesis of CNTs using inductively coupled plasma combined with substrate biasing. The method enables to have independent control to produce plasma density and ion energy. The CVD was performed on the Ni catalyst thin films coating glass substrates introducing pure CH<sub>4</sub> gas without any dilution gases. The resultant CNTs grown on glass substrates were characterized by SEM and TEM. CNTs were not grown with no substrate bias. On the optimal conditions, CNTs found to be grown at a temperature as low as 500°C with high crystallinity. Moreover, emission properties of the CNT grown by ICP will be presented. This work was partly supported by a joint research program between Japan Fine Ceramics Center and Osaka University, under the Frontier Carbon Technology Project in New Energy and Industrial Technology Development Organization (NEDO), Japan.

#### Q11.4

IMPROVED CARBON NANOTUBE SCANNING PROBE. Cattien V. Nguyen, Ramsey M.D. Stevens, Chris So, ELORET Corporation/NASA Ames Research Center MS 229-1 Moffett Field, CA; Lance Delziet, M. Meyyappan, NASA Ames Research Center, Moffett Field, CA.

We have previously demonstrated that scanning probe with multi-walled carbon nanotube tip to be very robust, able to maintain resolution after more than ten hours of continuous scanning. In addition, our unique fabrication technique produces scanning probes composed of a single carbon nanotube which enable the imaging of deep and narrow features. Employing these multi-walled carbon nanotube probes in metrology applications, we demonstrate the imaging of high aspect ratio 193 nm lithographic features, with

critical dimension of 90 nm. We present results for high lateral resolution with our multi-walled carbon nanotube probes by sharpening the tip with an applied electric field. The radius of curvature of these sharpened multi-walled carbon nanotube tips approaches that of single-walled nanotube tips. Given the higher resolution, the advantage here is that these sharpened multi-walled nanotube probes are robust and suffer less from image-broadening due to the thermal vibration of the nanotube.

#### Q11.5

DESIGN AND CHARACTERIZATION OF NANOARCHITECTURES FROM MULTIFUNCTIONAL POLYPARAPHENYLENES. Renu Ravindranath, Suresh Valiyaveetil, Chinnapan Baskar, Department of Chemistry, National University of SINGAPORE; Ananda Putra, Fitri Fitrilawati, Wolfgang Knoll, Department of Materials Science, National University of Singapore, SINGAPORE.

Conducting polymers are interesting materials due to their wide range applications in electronics, sensing, photonics and display applications. Many polymers with interesting molecular architectures have been developed to establish the structure-property relationship of these materials. Our approach focuses on the design, synthesis and characterization of novel amphiphilic oligo- and poly(paraphenylenes) and to fine-tune the properties using an interplay of weak interactions (H-bonding, van der Waal's forces) and metal ion complexation. The talk will also focus on understanding the self-assembly of these materials on various substrates and the optical/morphological properties of thin films from these polymers.

#### Q11.6

Abstract Withdrawn.

#### Q11.7

PALLADIUM NANO-PILLAR STRUCTURES FOR ENHANCED KINETICS IN METAL HYDRIDE SWITCHABLE MIRRORS. M. Di Vece, J.J. Kelly, Debye Institute, Physics and Chemistry of Condensed Matter, Utrecht University, Utrecht, THE NETHERLANDS.

Rare-earth metal hydride mirrors[1] switch optically from opaque to transparent on intercalation of hydrogen. This reversible metal-insulator transition occurs on going from the dihydride to the trihydride phase and vice versa. The kinetics, i.e. optical switching times, are diffusion limited. Although thin films are employed (200 nm) a switching time decrease from about 10 s to 20 ms is desirable to open new fields of application, like displays and radar. The hydrogen diffusion coefficient of palladium is orders of magnitude lower than that of the rare-earth metals. In this work we describe how palladium pillars, 500 nm long and 30 nm thick, form a "bed of nails" on which a rare-earth metal is evaporated. Hydrogen diffusion could be enhanced by the palladium pillar "highways"; consequently, increased optical switching times are expected. [1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, and N.J. Koeman, Nature, 380, 231 (1996).

#### Q11.8

PHOTOLUMINESCENT PROPERTIES OF ZnO/ZnMgO QUANTUM STRUCTURE NANORODS. Won Il Park, Gyu-Chul Yi, Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, KOREA.

One-dimensional nanowire (nanorod) heterostructures with well-defined crystalline interfaces opens up many new device applications, as already proven in thin film semiconductor electronics and photonics. In particular, embedding quantum structures in a single nanorod would enable novel physical properties such as quantum confinement to be exploited, such as the continuous tuning of spectral wavelength by varying the well thickness. However, quantum confinement effects in heterostructure nanowires have not been clearly observed despite recent synthesis of compositionally modulated nanowire superlattices by the vaporliquid-solid (VLS) growth process. This may result from the relatively broad heterostructure interfaces caused by re-alloying of alternating reactants in the metal catalyst during the condensation-precipitation process. In contrast, nanoscale heterostructures with abrupt interfaces could be successfully fabricated using a non-catalytic growth technique by utilizing direct adsorption of atoms on the top surface of nanorods. In this presentation, we report photoluminescence (PL) properties of ZnO/ ZnMgO multiple quantum well (MQW) nanorods. The well layer thickness investigated in this study was as thin as 10 Å. From the PL spectra of the MQW nanorods, blueshifts of the excitonic emission were clearly observed, depending on the well layer thickness. Meanwhile, the blueshift decreases with increasing well width and is almost negligible for the MQW nanorods with a well layer thickness of 110 Å. The systematic increase in PL emission energy with reducing well width is consistent with the quantum

confinement effect as expected from theoretical calculation in 10 periods of one-dimensional square potential wells. We will also discuss the temperature-dependent PL properties of MQW nanorods.

#### Q11.9

ELECTRONIC TRANSPORT AND GAS SENSING PROPERTIES OF INDIVIDUAL INDIUM OXIDE NANOWIRES. Daihua Zhang, Chao Li, Song Han, Xiaolei Liu, Tao Tang, Wu Jin, Chongwu Zhou, Univ. of Southern California, Dept. of E.E.-Electrophysics, Los Angeles, CA.

Semiconducting nanowires have generated a lot interest due to their enormous potential for fundamental scientific studies and also practical applications. We present our investigations on the electronic transport and gas sensing properties of individual In<sub>2</sub>O<sub>3</sub> nanowires. Single crystalline In<sub>2</sub>O<sub>3</sub> nanowires were synthesized and then utilized to construct field effect transistors consisting of individual nanowires. These nanowire transistors exhibited nice n-type semiconductor characteristics with well-defined linear and saturation regimes, and on/off ratios as high as 10<sup>4</sup> were observed at room temperature. The temperature-dependence of the conductance revealed thermal emission as the dominating transport mechanism. Further more, chemical sensing measurements were also performed based on these In<sub>2</sub>O<sub>3</sub> nanowire transistors. Our devices exhibited far superior performance compared to previously reported results. For instance, our devices exhibited sensitivities of 10<sup>6</sup> for NO<sub>2</sub> and 10<sup>5</sup> for NH<sub>3</sub>, which are four or five orders of magnitude better than results obtained with thin-film-based sensors, and at least one hundred times better than the sensitivity of the carbon nanotube-based sensors. Response times (defined as time duration for resistance change by one order of magnitude) as short as 5 s for 100 ppm NO<sub>2</sub> and 10 s for 1% NH<sub>3</sub> have also been achieved. Our work clearly demonstrates the advantages of nanowire chemical sensors and may lead to single molecule detection in the near future.

#### Q11.10

CONTROL OF THE OPTICAL RESPONSE OF Cu:Al<sub>2</sub>O<sub>3</sub> NANOCOMPOSITE THIN FILMS. A. Suarez-Garcia, R. Serna, J. Gonzalo, C.N. Afonso, D. Babonneau<sup>a</sup>, D. Hole<sup>b</sup>, Instituto de Optica, CSIC, Madrid, SPAIN. <sup>a</sup>Laboratoire de Metallurgie, CNRS, Universite de Poitiers, Poitiers, FRANCE; <sup>b</sup>School of Engineering, University of Sussex, Brighton, UNITED KINGDOM.

Metal nanostructures show special catalytic, magnetic, electrical and optical properties. In particular, metal nanocrystals play an important role in surface enhanced Raman scattering or surface plasmon resonance microscopy. Dielectric thin films with embedded metal nanocrystals show an enhanced absorption at the surface plasmon resonance (SPR) wavelength that can be used for polarizers and solar absorbers. All these applications require the development of metal nanostructures with a well known and controlled spectral response. In the past we have successfully produced Cu:Al<sub>2</sub>O<sub>3</sub> nanocomposites formed by Cu nanocrystals (~3 to 6 nm) embedded in amorphous Al<sub>2</sub>O<sub>3</sub> by alternate pulsed laser deposition. The size and morphology of the nanocrystals have been controlled by varying the preparation conditions during the Cu deposit, giving negligible changes in the spectral response around the SPR. In this paper we will show an unconventional approach that arises as a new and alternative route to modify the morphology and control the optical response of the Cu:Al<sub>2</sub>O<sub>3</sub> nanocomposite around the SPR. In this work we show the effect induced by increasing the laser energy density on the Al<sub>2</sub>O<sub>3</sub> target, while keeping constant the Cu deposition conditions. As the laser energy density is increased in the interval 0.5-4.5 J/cm<sup>2</sup> the SPR band initially centered at ~630 nm shifts towards lower wavelengths, the intensity of the resonance decreases and finally disappears for the highest laser energy densities. No significant changes are observed on the average dimensions of the Cu nanocrystals, and a decrease of the metal content of 20% has only been observed in the films deposited with the highest energy density on the Al<sub>2</sub>O<sub>3</sub> target. The results are discussed as a consequence of the high kinetic energy of the species present in the laser induced plasma (10-100 eV), that is a unique characteristic of pulsed laser deposition. The kinetic energy of the ablated species from the Al<sub>2</sub>O<sub>3</sub> target increases as the laser energy density increases and thus, modifications of the morphology of the nanocrystals and/or chemical reactions at its surface are promoted. At the highest energy density, the arriving Al<sub>2</sub>O<sub>3</sub> species can even produce sputtering of the deposited Cu.

#### Q11.11

ELECTRIC FIELD INDUCED CARBON NANOSTRUCTURES FOR ELECTRONICS AND HIGH SURFACE AREA APPLICATIONS. Chao Hsun Lin<sup>a,b</sup>, Shu Hsing Lee<sup>a,b</sup>, Ming Her Tsai<sup>a</sup> and Cheng Tzu Kuo<sup>a</sup>; <sup>a</sup>Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, TAIWAN; <sup>b</sup>Photoetching Lab., Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, TAIWAN.



Strong influence of the applied or self-induced (i.e. self-biasing) electric field on the alignment, orientation and structures was found in the carbon nano-structure deposition process. This study applied microwave-plasma electron-cyclotron-resonance CVD (MP-ECR-CVD) technique for carbon nano-structure deposition. The deposited structure and its properties were characterized with SEM, TEM, Raman spectra and field emission I-V measurements. Especially, for the carbon nanotube (CNT) synthesis, the result shows that a negative dc bias applied on the substrate is a necessary condition. In this condition, all CNTs were well aligned and perpendicular to the substrate surfaces and independent to the plasma/gas flowing directions. The films with high density, uniform length and well perpendicularly aligned CNTs might be feasible for perpendicular magnetic recording media applications. However, it was always accompanied with screen effect which decreased the field emission current density. Interestingly, when applied an additional electric field near the substrate surface by a guiding metal plate, the CNT growth direction could be manipulated from perpendicular to nearly parallel to the substrate surface. This technique has high potential for nano-electronic device applications and could be used to eliminate the screen effect of field emission and obtain a higher field emission current density. Moreover, a rattan-like CNT would form when prolonging the deposition time or increasing the plasma carbon concentration. It is also found that the novel hybrid nanostructure has a lot of leaf-like carbon nanosheet attached on the CNT cylinder sidewall. It is believed that when the substrate surface electric field is shielded by the dense CNT films, by introducing the local electric fields among neighboring CNTs, the specific surface area of the CNTs with extra decorated carbon nanosheets will be greatly increased. These novel nanostructures are expected to have high potential in energy storage and gas sensing applications accordingly. Keywords: Carbon nanotube, Electron cyclotron resonance CVD, Field emission, High surface area.

#### Q11.12

MORPHOLOGY AND ELECTRO-OPTICAL PERFORMANCE OF H-PDLC GRATINGS FORMED BY THIOL-ENE PHOTOPOLYMERIZATION. Lalgudi V. Natarajan, Timothy J. Bunning, Vincent P. Tondiglia, Richard L. Sutherland and David Tomlin, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH.

Holographic polymer dispersed liquid crystal gratings (H-PDLC) were fabricated by photopolymerizing thiol-ene monomers using UV laser light. The reflection gratings formed with spacings of 0.15-0.20 micron consist of alternate layers of polymer and liquid crystal rich regions. Proper control of LC droplet size and positioning allow for electro-active yet transparent nano photonic films to be formed. Significant differences in morphology and electro-optical performance between acrylate and thiol-ene systems were observed. The morphology of the gratings was probed by TEM, SEM and STEM techniques. TEM showed that unlike the acrylate systems where very irregular surfaces were observed at the interface between the droplets and the polymer, the thiol-ene systems interface was very smooth. The droplets were more spherical and similar in shape. Electrical switching was observed at low fields (6-8 V/micron) and no evidence of post-polymerization effects were noticeable. The switching voltage and the notch wavelength were stable over a period of 8 months.

#### Q11.13

TIN OXIDE-BASED SINGLE NANOTUBE GAS SENSORS. Youxiang Zhang, Andrei Kolmakov, Martin Moskovits, University of California, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

Large scale, high aspect ratio metallic Sn nanotube arrays were fabricated by AC electrodeposition into the hexagonal ordered nanochannels of porous aluminum oxide (PAO). After released from the oxide matrix, the metal nanotube arrays were annealed in air to get semiconducting tin oxide nanotube arrays. Titanium and gold pads were deposited through TEM grid or by electron-beam lithography (EBL) technique to act as contacting electrodes after the tin oxide nanotube were separated and transferred onto silicon substrate. The tin oxide single nanotube sensors thus fabricated showed very good sensitivity to reducing gases such as CO.

#### Q11.14

MAGNETIC PROPERTIES OF  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  NANOCRYSTALS EMBEDDED IN A MESOPOROUS SILICATE. Shigemi Kohiki, Yoshihisa Ishida, Sinichiro Nogami, Hirokazu Shimooka, Kyusyu Inst Tech, Dept of Materials Sci., Kita-kyusyu, JAPAN; Takayuki Tajiri and Hiroyuki Deguchi, Kyusyu Inst Tech, Dept of Electric Eng., Kita-kyusyu, JAPAN; Masanori Mitome, NIMS, AML, Tsukuba, JAPAN; Masaoki Oku, Tohoku Univ, IMR, Sendai, JAPAN.

Nanocrystals of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x=0, 0.05, 0.15,$  and  $0.175$ ) embedded in a mesoporous silicate were prepared by calcination of the

MCM-41 molecular sieve soaked in precursor solution. Magnetization measurements using a SQUID magnetometer showed that at low temperatures the nanocrystals in both ferromagnetic ( $x=0.15$  and  $0.175$ ) and antiferromagnetic ( $x=0$  and  $0.05$ ) phases were in the superparamagnetic state. The field cooled and zero field cooled susceptibilities of the samples branched off at around 100K. For the ferromagnetic samples, the real part of the ac susceptibility decreased below  $\approx 100\text{K}$  and the imaginary part showed a hump at  $\approx 100\text{K}$ . The superparamagnetic moment of the antiferromagnetic sample corresponded to the uncompensated moments estimated for the single domain antiferromagnetic nanocrystal of diameter  $\approx 3\text{ nm}$ , while that of the ferromagnetic sample was smaller than that estimated for the ferromagnetic nanocrystal.

#### Q11.15

DIRECT SYNTHESIS OF NANOCONES ON SUBSTRATES FOR FIELD ELECTRON EMITTERS BY PLASMA CHEMICAL VAPOR DEPOSITION. Takashi Kuzuoka, Shin-ichi Honda, Yang-Gyu Baek, Shigeharu Ohkura, Mitsuhiro Katayama and Kenjiro Oura, Dept. of Electronic Eng., Graduate School of Osaka Univ., Osaka, JAPAN; Takashi Hirao, Dept. of Electrical Eng., Graduate School of Osaka Univ., Osaka, JAPAN.

Regarding field electron emitters applicable for vacuum microelectronics such as field emission display (FED), lamp and x-ray source, sharp tip of the emitters is effective due to electric field concentration. For instance, Spindt type electron emitters, which have a conical shape, was unique properties such as small radius of curvature at the tip and large contact area to substrates. When the cones are directly grown on the substrates, it is expected that the cone emitters are mechanically strengthen due to strong bonding to the substrates in contrast to carbon nanotube emitters. Conical shape emitters, have been fabricated using lithographic technique. However the technique requires much time and high cost. Therefore it is desirable to fabricate many emitters in the short time, and directly on substrates. In this study, we have developed a novel method for direct synthesis of conical shape emitters on substrates, based on plasma enhanced chemical vapor deposition (PE-CVD). In the apparatus, a hot-filament and permanent magnets were equipped to produce high density plasma ( $20\text{ mA/cm}^2$  at the sample). The CVD was performed on Ni thin films coating substrates introducing  $\text{C}_2\text{H}_4$  gas and Ne gas. From the SEM results, it was found that the density of the conical structures directly grown on the substrates can be varied from  $10^6$  to  $10^9/\text{cm}^2$  changing thicknesses of the metal films. From the field emission characterization of the resultant cones on the substrate, the low density samples showed the better properties ( $2.4\text{ V}/\mu\text{m}$  at  $1\text{ }\mu\text{A/cm}^2$ ). Screening effect can explain the relationship between the cone density and the field emission properties. This work was partly supported by a joint research program between Japan Fine Ceramics Center and Osaka University, under the Frontier Carbon Technology Project in New Energy and Industrial Technology Development Organization (NEDO), Japan.

#### Q11.16

THE INFLUENCE OF THE PREPARATIONS CONDITIONS ON THE GMI IN LOW MAGNETOSTRICTIVE AGCW. I. Murgulescu, H. Chiriac and N. Lupu, National Institute of Research and Development for Technical Physics, Iasi, ROMANIA.

Amorphous glass-covered wires (AGCW) are used widely in sensing applications due to their small dimensions and good magnetic response. One of the most appropriate effects for sensor applications is the giant magneto-impedance (GMI) effect. The strongest GMI effect was reported in Co-based amorphous wires with nearly zero magnetostriction [1]. GMI effect is strongly related to the basic magnetic properties of these materials as well as to the internal stresses induced by the glass cover during the preparation process. The aim of this paper is to study the influence of the metallic core diameter for a given glass cover thickness on the GMI signal. The GMI monotonously decreases with the metallic core diameter increase, regardless of the frequency value or external magnetic field. The two peaks of the magneto-impedance move towards higher values of the external magnetic field with the increase of the glass cover thickness for a given diameter of the metallic core. This displacement is due to the additional anisotropy induced by glass cover. The GMI signal increases with the frequency increase. At higher frequencies the rotational magnetization processes are dominant relative to the domain wall movements. Magnetostriction is other important parameter for the value of the GMI effect. The change of the magnetostriction constant from positive to negative values is investigated in  $(\text{Co}_{1-x}\text{Fe}_x)_{72.5}\text{Si}_{12.5}\text{B}_{15}$  AGCW for  $x = 5.5; 5.8; 5.9; 5.95; 6.0; 6.2$ . The influence of the alloy composition on the GMI is also presented. [1] L.V. Panina, K. Mohri, K. Bushida, and M. Noda, J. Appl. Phys. 76 (1994) 6198.

#### Q11.17

MAGNETIC FIELD AND HOPPING EFFECTS ON TUNNELING

IN GaAs-(Ga,Al)As DOUBLE BARRIER HETEROSTRUCTURE. H. Paredes Gutierrez and N. Porrás-Montenegro, Dept. de Física, Universidad del Valle, COLOMBIA; J.C. Arce, Dept. de Química, Universidad del Valle, COLOMBIA; A. Latge, Instituto de Física, Univ. Federal Fluminense, Niterói, BRAZIL.

Adopting a simple one-band tight-binding Hamiltonian and using the diagrammatic techniques for nonequilibrium processes proposed by Keldysh, we investigate the resonant tunneling transport properties through GaAs-(Ga,Al)As double-barrier heterostructures under the action of parallel and in-plane magnetic fields. The in-plane field configuration leads to a shift to higher bias and an intensity reduction of the resonant tunneling peak in the characteristic curves of current versus voltage, in good agreement with experimental results. Also, we have found that a diminishing of the hopping energy between nearest neighbors leads to the same effects on the current-voltage as those of an in-plane magnetic field. On the other hand, the intensity of the resonant peaks are found to increase when the magnetic field is applied parallel to the current direction, result that would be expected due to the increasing values of the magnitude of the hopping parameter with the magnetic field. Also, we have studied tunneling through shallow impurity states in GaAs-(Ga,Al)As double barrier heterostructure. We found that the bias voltage of the peak of the donor-assisted resonant tunneling is lifted to lower voltage values and the intensity of these peaks is clearly diminished with the magnetic field. Our results are in good agreement with experimental reports.

#### Q11.18

THEORETICAL STUDY ON TUNNEL MAGNETORESISTANCE OSCILLATION DUE TO COULOMB BLOCKADE IN NANOSCALE MAGNETIC TUNNEL JUNCTION. Yasushi Takemura, Yokohama National University, JAPAN; Jun-ichi Shirakashi, Akita Prefectural University, JAPAN.

It has been reported by both of experimentally and theoretically that the tunnel magnetoresistance (TMR) is enhanced by Coulomb blockade in nanoscale magnetic tunnel junctions (MTJ) whose charging energy is larger than thermal energy. We have calculated the current-voltage and TMR characteristics in nanoscale MTJ by Monte Carlo method. The enhancement of TMR is obtained at the temperature below 50K, 150K and 300K for the electrode size of 50nm, 10nm and 5nm, respectively. The charging energy of the device determined by total capacitance of the system should be 10 times larger than thermal energy for the critical temperature of Coulomb blockade. Therefore, the conventional multilayer-type MTJ may not exhibit Coulomb blockade at room temperature above 150K. Recently, Tohoku University fabricated nanoscale MTJ consisted of granular system and observed the enhancement of TMR in Coulomb blockade region and also the oscillation of TMR at the voltage range outside the Coulomb blockade region. As it is well known, the Coulomb staircase is observed in current-voltage characteristic of asymmetric multi-tunnel junction with different resistance and/or capacitance. From our calculation the TMR ratio is not oscillated as a function of applied voltage in asymmetric MTJ with the same TMR ratio for each junction, but is oscillated with different TMR ratio even though the spin accumulation is not considered. We also report the fabrication of planar-type MTJ, another candidate for the observation of Coulomb blockade, and theoretical analysis of ferromagnetic single electron transistor.

#### Q11.19

COMPUTATION WITH PHYSICAL SYSTEMS AND THE NANOTECHNOLOGY PROMISE. Thomas J. Bartolac, Tanner Research, Inc., Pasadena, CA.

Certain useful image processing functions are computationally expensive, making them impractical for real-time processing on a miniature sensor platform. These functions may have analogues in the natural behavior of certain physical systems. For example, an image can be spatially smoothed by applying it to a physical system that exhibits diffusive behavior, and then capturing the state of the diffusive response at a particular time later. But using diffusion for image smoothing is not an efficient computational approach, if performed on a digital computer. The diffusive behavior is described with a spatially discrete partial differential equation and then numerically solved, using the image as initial conditions. Most choose the more economical method, convolving the image with a smoothing kernel. However, if a 2-D spatial array of heat quanta is applied to a ceramic plate, where each quantum is proportional to its pixel in the image, then the heat would diffuse through the ceramic plate according to the laws of physics, and the "smoothed" image could be read later as a 2-D array of the temperature distribution throughout the plate. Computation with physical systems. Now a ceramic disk may not be convenient to work with, it may not offer the degree of thermal conductivity needed for a given application, and its conductivity is not easily varied. Fortunately, nanotechnology promises artificial materials that can exhibit desirable behavior of

physical systems (e.g., diffusion), but with properties in a more useful range, and that can be controlled. Plus, they may use physical quantities that are more convenient to work with (e.g., electrons) than those offered by nature (e.g., heat). This paper describes just such an image processing function, how its computation is mapped to the natural behavior of a physical system, and how that physical system could be realized in a useful form with nanotechnology.

#### Q11.20

MONTE CARLO SIMULATION OF ELECTRON TRANSPORT THROUGH NANOCRYSTALLINE TiO<sub>2</sub> IN DYE SENSITIZED SOLAR CELLS. Michael Cass, Alison Walker, Bath Univ, Dept of Physics, Bath, UNITED KINGDOM; Laurie Peter, Bath Univ, Dept of Physics, Bath, UNITED KINGDOM.

Dye sensitized nanocrystalline solar cells (Grätzel cells) have achieved solar-to-electrical energy conversion efficiencies  $\eta$  of 12% in diffuse daylight. The cell is based on a thin film of dye-sensitized nanocrystalline TiO<sub>2</sub> interpenetrated by a redox electrolyte. Photoexcitation of the dye is followed by fast (<100fs) electron injection into the conduction band of the TiO<sub>2</sub> nanoparticles. The injected electrons travel through the nanocrystalline TiO<sub>2</sub> to the anode. Transport is slowed by trapping in surface states. Detrapping from these surface states competes with the back reaction of electrons with I<sub>3</sub><sup>-</sup> ions in the electrolyte, this back reaction acts to reduce efficiency. The morphology of the film also acts to slow the electron transport, increasing the likelihood of back reaction occurring. The level of interconnection of the grains is varied through their coordination number and the size of the inter-grain neck. We employ a Monte Carlo simulation to investigate the effects of the morphology of the nanocrystalline film, trapping and back reaction on the electron transport. The passage of a large number of electrons through a network of interconnected spherical grains, 20nm in diameter, is simulated. We use a fine scale simulation, where the electrons move a few grains along the chain. By repeating such a walk many times, we have obtained probabilities for the number of grains moved and the likelihood of trapping. These can then be used in a coarse scale simulation, in which the position of each electron is recorded only in terms of which grain it occupies, and at each time interval the electron moves or is trapped according to these probabilities. This allows us to model the transient current in response to a pulse of optical illumination. We have quantified our results where possible in terms of an effective electron diffusion coefficient.

#### Q11.21

NOVEL GLUCOSE BIOSENSOR BASED ON THE MICROCANTILEVER. Jianhong Pei and Thomas Thundat, Life Science Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Recent advances in designing and fabricating microcantilever beams capable of detecting extremely small forces, mechanical stresses, and mass additions offer the promising prospects of chemical, physical, and biological sensing with unprecedented sensitivity and dynamic range. Molecular adsorption when confined to one surface of a cantilever resulting differential surface stress that leads to cantilever bending. Chemical selectivity is achieved by functionalizing cantilever beams with selective receptors. Here we report the development of a glucose sensor based on microcantilever platform. Glucose detection was achieved by immobilizing a layer of glucose oxidase enzyme (GOD) on the surface of cantilever and then detecting the mechanical bending as a function of physiologically relevant concentrations of glucose. Microcantilever glucose sensors exhibit high sensitivity and extreme high selectivity.

#### Q11.22

NANOSTRUCTURED MATERIALS FOR CHEMICAL SENSORS. Shabnam Virji, University of California Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA and The Aerospace Corporation, Materials Processing and Evaluation Department, Los Angeles, CA; Jiaxing Huang, University of California Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA; Richard B. Kaner, University of California Los Angeles, Dept of Chemistry and Biochemistry, Los Angeles, CA; Bruce H. Weiller, The Aerospace Corporation, Materials Processing and Evaluation Department, Los Angeles, CA.

Conducting polymers such as polyaniline are useful materials for chemical sensors. Conventional polyaniline, chemically synthesized by oxidative polymerization, exhibits strong, but relatively slow diffusion controlled, doping and dedoping characteristics when exposed to acid or base. These characteristics appear to be enhanced when polyaniline is produced with nanoscale features. The formation of polyaniline nanofibers, chemically synthesized in an immiscible organic-aqueous two-phase system, results in improved time response and sensitivity to acids and bases over conventional polyaniline thin films. Apparently, their small size allows the rapid diffusion of acids and bases into and out of the nanofibers and results in a faster and larger change in

electrical response upon doping and dedoping than conventional polyaniline. This unique property of polyaniline nanofibers makes them promising materials for chemical sensors. The response of nanofibers and conventional thin films to HCl and NH<sub>3</sub> is compared in order to develop chemical sensors for gas detection. Other materials that are useful for chemical sensors are metal nanoparticles. Palladium nanoparticles are synthesized by first reducing palladium metal and then capping the surface with either a thiol or surfactant so growth can be controlled. Results on the size specific synthesis of metal nanoparticles and their characterization as sensor materials will be presented.

#### Q11.23

A NOVEL ROUTE, A PtO<sub>x</sub>/SiO<sub>x</sub> ARTIFICIAL LATTICE APPROACH FOR THE SINGLE-ELECTRON-TRANSFER STRUCTURE. Jiun-Yi Tseng and Tai-Bor Wu, National Tsing Hua Univ, Dept of Materials Science and Engineering, Hsinchu, TAIWAN, R.O.C.; K.Y. Hsieh, Macronix International Co., Ltd., Science-Based Industrial Park, Hsinchu, TAIWAN, R. O. C.

The structure of insulator films with embedded metal nanoparticles can lead to quantized single-electron-transfer behavior due to the coulomb blockade effect. In this case, the nanoparticles are like nanoscaled electrodes, and the single-electron-transfer process between these nano-electrodes will take place with correlated tunneling. However, the function of the middle nano-electrodes in the matrix is like the floating gate of a MOS-transistor; the tunneling current is dependent on the applied voltage on the nano-electrodes. Therefore, the structure, like that of the single-electron transistor, can treat as a switch. In this research, we demonstrate a novel route, a PtO<sub>x</sub> / SiO<sub>x</sub> artificial lattice approach, for the single-electron-transfer structure. First, we prepare the amorphous PtO<sub>x</sub> / SiO<sub>x</sub> superlattices by a rf magnetron sputtering system with dual cathodes. Then, post annealing the films at 350 ~ 450°C in vacuum less than  $5 \times 10^{-8}$  torr for 10 ~ 60 mins results in phase separation of the ultrathin PtO<sub>x</sub> layers about 2 to 5 nm into nanometer-size Pt clusters surrounded by amorphous SiO<sub>x</sub>. According to transmission electron microscopy TEM investigations, the size and density of the Pt nanocrystals can be modified by changing the relative thickness of ultrathin PtO<sub>x</sub> layers and thick SiO<sub>x</sub> layers. The structure consisting of discontinuous and well-insulated Pt nanoparticles depends on the temperature and time of annealing in vacuum. Moreover, the recipe of the process, a PtO<sub>x</sub> / SiO<sub>x</sub> superlattice approach, is fully compatible with Si technology nowadays.

#### Q11.24

OPTICAL NONLINEAR PROPERTIES OF METAL Pt-Pd NANOCUSTER. Yinglin Song, Jianhong Zhou, Yuxiao Wang, Yachen Gao, Department of Physics, Harbin Institute of Technology, Harbin, P.R. CHINA; Yuliang Li, Hanfan Liu, Daoben Zhu, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P.R. CHINA.

The nanoparticle own special nonlinear optical behaviors that are absent in individual atoms as well as bulk materials. For instance, optical nonlinear properties and optical limiting effects of the nanocomposites with metal nanoparticles can be significantly enhanced by increasing the number density and the size of metal particles. In the present paper, the Pt-Pd cluster has been synthesized to investigate the nonlinear optical responses. The optical nonlinear properties of the metal cluster are investigated by using Z-scan technique with 8ns pulses at 532nm. The Z-scan experimental results showed that the sample under excitation shows strong nonlinear refraction and the nonlinear optical responses in the novel cluster are influenced by the interaction of metal elements Pt and Pd.

#### Q11.25

MAGNETISM AND MAGNETO-TRANSPORT IN AMORPHOUS CO<sub>100-x</sub>Pt<sub>x</sub> (0 ≤ x ≤ 50) FERROMAGNETIC NANO ALLOYS. Manju Lata Rao, S. Sundar Manoharan, Department of Chemistry, Indian Institute of Technology, Kanpur, INDIA.

Phase stabilized CO<sub>100-x</sub>Pt<sub>x</sub> (0 ≤ x ≤ 50) nano alloys have been prepared by sonochemical decomposition of solutions containing volatile organic precursors, CO<sub>2</sub>(CO)<sub>8</sub> and PtCl<sub>2</sub> in decalin in an argon gas flow. Magnetic and structural data show the existence of sustained ferromagnetism up to 50% Pt, while a delayed structural transformation is noted, an fcc phase being retained even up to temperatures of 900°C. Differential scanning calorimetry exhibits an endothermic transition at 150°C due to glass transition (T<sub>g</sub>) and an exothermic peak due to crystallization around 325°C. All compositions exhibit a negative magneto-resistance ratio of ~3% at room temperature with a maximum MR ratio for x = 20. Magnetization studies show that bulk magnetic properties are correlated with the structures on length scale compared to the fundamental length scales of magnetism. The sustained ferromagnetism is explained due to the strong exchange coupling effects between 4d and 5d transition metals. This is due to the similar

band structures and the magnetic up shift of spin down bands in the 3d metals, which result in a strong contrast in the spin dependent reflectivity at the 3d/4d interface.

#### Q11.26

COLLOIDAL CRYSTALS WITH REVERSIBLY TUNABLE STOP BANDS. Hiroshi Fudouzi, National Institute for Materials Science, Tsukuba, JAPAN; Younan Xia, University of Washington, Dept of Chemistry, Seattle, WA.

A new class of colloidal crystals has been fabricated whose stop bands could be reversibly shifted in position by changing the lattice constants. The crystals were composed of polystyrene (PS) microspheres embedded in an elastomer matrix. The center-to-center distance between the PS spheres, and thus the color displayed by this crystal could be tuned by swelling the matrix with an organic solvent. The tuning of stop band position can change a wide range on visible light wavelength (400 - 800 nm). For example, a composite film assembled with 175nm PS microspheres had a stop band at 440 nm (initial position), and this film exhibited a violet color. The stop band position shifted to 538 nm (green) for iso-propanol and to 717 nm (red) for hexane. In addition, the tuning the stop band is quickly reversible and reproducible. When the composite film was pulled out the solvent and dried in air, the stop band position returned to the initial position within a few minutes. The present work offers a new three-dimensional photonic crystal with tunable and reversible stop band on a wide range of visible light. The variable color film is potentially applicable to a simple and convenient optical sensor to detect solvents.

#### Q11.27

FUNCTIONAL BIMORPH COMPOSITE NANOTAPES. Rongrui He, Matthew Law, Rong Fan, Franklin Kim, Peidong Yang, University of California at Berkeley, Dept of Chemistry, Berkeley, CA.

Single-crystalline nanoribbons were used as substrates for the epitaxial growth of different functional thin films deposited by laser ablation techniques. This simple method yields highly crystalline bilayer nanotapes with sharp structural and compositional interfaces. As an example, Co<sub>0.05</sub>Ti<sub>0.95</sub>O<sub>2</sub>@SnO<sub>2</sub> nanotapes are shown to be ferromagnetic at room temperature. These composite nanotapes, with their various possible functionalities, represent an important new class of nanoscale building blocks for optoelectronic applications.

#### Q11.28

II-VI NANOCRYSTAL GAIN MEDIA: FROM AMPLIFIED SPONTANEOUS EMISSION TO LASING. Vikram C. Sundar, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; Hans-Juergen Eisler, Mouni G. Bawendi, Department of Chemistry, M.I.T., Cambridge, MA; Tao Deng, E.L. Thomas, Department of Material Science and Engineering, M.I.T, Cambridge, MA.

Recent observations of amplified spontaneous emission (ASE) from close-packed films of cadmium selenide nanocrystals (NCs) have hastened efforts to develop appropriate NC-microcavity feedback structures, which exploit the advantages of three-dimensional quantum confinement. This talk details our efforts in this regard. The synthesis of a new sol-gel NC/titania matrix is described, which provides a facile technique for spin-coating NC waveguides showing ASE with enhanced stability and processability. We use this flexibility to create and characterize more-complicated structures showing ASE simultaneously at different wavelengths. Next, we demonstrate the first optically pumped laser utilizing these NC-titania films as the gain media and distributed feedback (DFB) gratings as the optical feedback mechanism. Finally, recent results from coupling these gain media with soft-lithographically patterned substrates are presented.

#### Q11.29

NORMAL INCIDENT INFRARED INTERSUBBAND TRANSITIONS OF InGaAs/GaAs QUANTUM DOTS. Mohammad Hussein and Wenquan Ma, Univ of Arkansas, Microelectronics-Photonics, Fayetteville, AR; Omar Manasreh, University of New Mexico, Dept of Computer and Electrical Engineering, Albuquerque, NM; Greg Salamo, Univ of Arkansas, Dept of Physics, Fayetteville, AR.

Self-organized quantum dots (QDs) based on Stranski-Krastnov growth mode have attracted great interests for their unique optoelectronic device applications due to the three-dimensional quantum confinement. For photodetector devices utilizing intersubband transitions, normal incident intersubband transitions are forbidden for quantum well structures while, in principle, it can be realized for QDs. This gives QD photodetectors a great advantage compared to quantum well photodetectors. In addition, by controlling the size and shape of the QDs, the detection wavelength range can be tuned to the mid- and far-infrared. We have investigated IR absorption of self-organized InGaAs/GaAs QD structures and have

observed strong intersubband absorption at normal incidence. The structure consists of a 40-period InGaAs/GaAs QD multi-layer inserted between two heavily doped 1  $\mu\text{m}$ -thick GaAs layers with Si as the dopant. In order to generate carriers, the InGaAs layer was also doped by Si. Two typical samples with different InGaAs layer thickness were grown by molecular beam epitaxy (MBE). The samples were characterized by photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR) techniques. The comparison of the PL spectra show a different interband transition energy revealing a different QD size for the two samples. FTIR measurements were done at normal incidence geometry and a strong IR absorption was observed with the peak centered at 9.7 and 12  $\mu\text{m}$  at room temperature for the two samples respectively. In order to confirm the results measured at normal incidence geometry, the samples were polished 45° at the two edges. FTIR measurements were then performed using the waveguide geometry confirming the existence of the normal incident intersubband transition of the QDs. However, compared to the waveguide geometry, FTIR peak at the normal incidence geometry has a blue shift for the sample with thinner InGaAs layer while it has a red shift for the sample with thicker InGaAs layer. The PL and FTIR behavior and the observed difference between both sample structures will be discussed.

### Q11.30

**NANOPARTICLE BEAM PULSED LASER DEPOSITION OF NANOSTRUCTURED THIN FILMS FOR BIOMOLECULE SENSING APPLICATIONS.** Nicholas C. Cunningham, Mevlut Bulut, Thomas M. Nordlund, and Renato P. Camata, University of Alabama at Birmingham, Dept of Physics, Birmingham, AL.

The presence of metal surfaces 5-20 nm from weak fluorophores (e.g., DNA) can increase light absorption and radiative rate of the molecules by factors which can approach  $10^3$ . Recent studies show that consistent observation of this phenomenon requires nanoengineered metallic surfaces. Since actual adsorption of the biomolecules onto metal nanostructures quenches fluorescence, careful positioning of molecules at appropriate distances is crucial. To study this fluorescence enhancement as a potential route for biomolecule sensing, we created layers comprising metal nanoparticle ensembles of well-defined size and separation embedded in tetrahedral amorphous carbon (ta-C). Films were deposited using a novel technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD). Contrary to conventional PLD, this approach decouples gas-phase species and nanoparticles that often coexist in ablation plumes so that these constituents are manipulated independently. This is achieved by operating two independent PLD-based sources: One source exclusively generates nanoparticles while the other produces gas-phase dominated plumes. Furthermore, NBPLD allows the delivery of a focused or diffuse beam of size-selected nanoparticles to desired locations on a substrate with sub-50  $\mu\text{m}$  resolution. Different gas-phase species are simultaneously (or sequentially) deposited by PLD. In this work silver nanoparticles were deposited on silicon substrates by ablating a silver target at 300 Torr in the NBPLD source using a KrF excimer laser at 1-3 J/cm<sup>2</sup> fluences. This was followed by deposition of ta-C layers by ablation of pyrolytic graphite in high vacuum at fluences of 5-15 J/cm<sup>2</sup>. Nanoparticle diameter was tuned for different samples (2-15 nm) while ta-C thickness was varied from 5 to 200 nm. TEM and AFM on a typical sample yield nanoparticle diameter of (8.0 $\pm$ 0.6) nm and ta-C with thickness of  $\sim$ 20 nm. We will present total internal reflection fluorescence measurements of biomolecules dispersed on these nanoengineered substrates using photon-counting fluorescence and picosecond time-correlated single photon spectroscopies.

### Q11.31

**OPTICAL PROPERTIES OF A LIGHT-EMITTING POLYMER DIRECTLY PATTERNED BY SOFT LITHOGRAPHY.** Justin R. Lawrence, Organic Semiconductor Centre & Ultrafast Photonics Collaboration, School of Physics & Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM; Piers Andrew and William L. Barnes, Thin Film Photonics Group, School of Physics, University of Exeter, Exeter, UNITED KINGDOM; Manfred Buck, Organic Semiconductor Centre & School of Chemistry, University of St. Andrews, St. Andrews, UNITED KINGDOM; Graham A. Turnbull and Ifor D.W. Samuel, Organic Semiconductor Centre & Ultrafast Photonics Collaboration, School of Physics & Astronomy, University of St. Andrews, St. Andrews, UNITED KINGDOM.

Semiconducting polymers have attracted considerable attention for use in devices such as lasers and light-emitting diodes as they have scope for simple processing. Such devices can be improved by incorporating wavelength scale microstructure. We have previously demonstrated a LED with a photolithographically defined grating structure, which scatters out light trapped inside waveguide modes. Low threshold distributed feedback polymer lasers have also been fabricated in a similar fashion using a grating to provide feedback. We now show that these useful microstructures can be made in a very simple way using a technique known as hot embossing lithography. A

semiconducting polymer film is deposited onto a flexible substrate and brought into contact with an etched silica master, which has a surface profile consisting of 400 nm period crossed gratings. The polymer is heated above its glass transition temperature and then flows around the master structure. Upon cooling the desired pattern is "frozen" into the polymer film. Measurements of the angle dependent photoluminescence spectrum and photonic mode structure of the patterned film show the structure modifies the light emission from the film. This effect is due to Bragg scattering and can be modelled readily. This soft lithographic technique opens new directions for the simple fabrication of photonic devices.

### Q11.32

**FABRICATION OF ULTRA SHARP NANOTIPS AS A STABLE FIELD EMITTER.** H.C. Lo, J.S. Hwang, K.H. Chen, Academia Sinica, Institute of Atomic and Molecular Sciences, Taipei, TAIWAN; C.H. Hsu, C.F. Chen, National Chiao Tung University, Institute of Materials Science and Engineering, Hsinchu, TAIWAN; L.C. Chen, National Taiwan University, Center for Condensed Matter Sciences, Taipei, TAIWAN.

Silicon tips with 1-nm diameter and 5  $\mu\text{m}$  in height capped with silicon carbide have been successfully fabricated using SiH<sub>4</sub>-CH<sub>4</sub>-Ar-H<sub>2</sub> plasma etching technique in an electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) system. High-resolution transmission electron microscope (HR-TEM) and Auger electron spectroscopy (AES) analyses on the silicon carbide caps reveals a 3C-SiC structure of the caps with the Si/C compositional ratio of 1:1. A mechanism for the formation of the ultra sharp tips based on etching of a nanomask is proposed in this paper. Field emission (FE) from the silicon nanotips with a current density up to 3.0 mA/cm<sup>2</sup> at an applied field as low as 0.8 V/ $\mu\text{m}$  has been demonstrated. The field emission characteristic strongly correlates with the type of doping of the starting silicon substrate. The observed carrier-dependent and geometric factor-dependent field emission behavior will be discussed.

### Q11.33

Abstract Withdrawn.

### Q11.34

**OXIDATION OF Si<sub>1-x</sub>Ge<sub>x</sub>/Si HETEROSTRUCTURES FOR NON VOLATILE MEMORY APPLICATIONS.** M. Kanoun, A. Soufi, S. Decossas, C. Dubois, G. Bremond, Laboratoire de Physique de la Matière, UMR-CNRS 5511, INSA de Lyon, Villeurbanne, FRANCE; F. Bassani, Y. Lim, Antoine Ronda, I. Berbezier, CRMC2-CNRS Campus de Luminy, Case 913, Marseille, FRANCE.

The use of Si nanocrystals has been proposed by several groups in order to develop highly integrated few electron memories. After the first proposal of a memory transistor using silicon nanocrystals (nc-Si) as floating gates, other works have confirmed that non volatile memories (NVM) using PMOS or NMOS transistors can be achieved. In order to improve the data retention in NVM, it seems interesting to use Ge nanocrystals (nc-Ge) rather than nc-Si because of its smaller band gap. In spite of the fact that non volatile memories with implanted Ge-nanocrystals have been demonstrated by Tiwari et al., it is also important to obtain well ordered nc-Ge for future NanoFlash memories with a few number of nanocrystals. One way to fabricate an ordered array of nc-Ge for NVMs could be the oxidation of self-organized Ge nanostructures on silicon. In this work, we present an extensive study of the oxidation process of Si / nc-Ge / Si samples using SIMS, TEM, AFM and electrical characterization of MOS capacitors. Various samples with different oxidation times have been studied and it is demonstrated that dry oxidation kinetics is not influenced by the presence of Ge. As shown by SIMS measurements, a pure SiO<sub>2</sub> layer is formed on the top of the structure, while the Ge atoms are intermixed with the silicon substrate. The TEM and AFM analysis show that the nc-Ge height is drastically reduced during the oxidation process. The fabrication of MOS capacitors on the structures allowed to study electron and hole trapping in the Ge dots. From our analysis it is also demonstrated that the Ge nanostructures are covered by SiO<sub>2</sub> but are not isolated from the Si substrate.

### Q11.35

**FIELD EMISSION CHARACTERISTICS OF ZnO NANOSTRUCTURES.** Sang Hyun Lee, SeGi Yu, Taewon Jeong, Jungna Heo, Wonseok Kim, Changsoo Lee, Jeonghee Lee, J.M. Kim, Samsung Adv. Inst. Technol., NCRI Center for Electron Emission Sources, Suwon, KOREA; T.Y. Kim, K.S. Nahm, Chonbuk Nat'l Univ., School Chem. Engineering Technol., Chonju, KOREA; Whikun Yi, Hanyang Univ., Dept. Chem.; Ji-Beom Yoo, Sungkyunkwan Univ., Center for Nanotubes and Nanostructured Composites.

Field emission characteristics of ZnO nanostructures, which were grown on catalyzed Si (100) substrate by thermal chemical vapor deposition at 500 C, have been investigated. The as-grown

nanostructures are found to be needle shaped with diameters of 20-40 nm. The turn-on field was obtained to be 6 V/ $\mu\text{m}$  and the field enhancement factor became  $\sim 1100$ . Degradation was occurred during field emission measurements. From scanning electron microscopy, the tips of ZnO nanostructures were changed from sharp ones to dull ones after field emission measurements. The sharp end of nanostructure tips were removed during measurement. In addition, field emission energy distribution (FEED) was measured for as-grown ZnO nanowires. The two kinds of the FEED peaks were obtained one originated from the Fermi level and the other from the band banding.

#### Q11.36

##### DEVELOPMENT OF LOW-DIMENSIONAL SUPERLATTICES OF METAL NANOPARTICLES TO NANODEVICES.

Toshiharu Teranishi, Japan Adv Inst of Sci and Tech, School of Materials Science, and Japan Sci and Tech Co, PRESTO, Ishikawa, JAPAN; Akira Sugawara, Masafumi Nakaya, Y. Yamamoto, H. Hori, Japan Adv Inst of Sci and Tech, School of Materials Science, Ishikawa, JAPAN; Yuko Tsuchiya, Kenchi Ito, Hitachi Ltd, Tokyo, JAPAN.

Since the regularly ordered metal nanoparticles with well-defined 1D, 2D, or 3D spatial configuration, so-called superlattices, are expected to show the novel properties that are not present in the isolated nanoparticles, the current interests in colloid chemistry have been focused on the fabrication of superlattices of size- and shape-controlled metal nanoparticles. The fabrication of planar 1D chains and 2D superlattices of small metal nanoparticles would lead us to the development of nanoelectronic devices using the single electron tunneling effect, while 2D superlattices of magnetic nanoparticles would be applied to nanomagnetic devices like ultrahigh-density magnetic recording media [1]. Here we present the electron transport properties of 2D superlattices of Au nanoparticles [2,3] between nano-gap electrodes on GaAs, and then the fabrication of a planar array of Au nanowires via 1D chains [4] for nanowiring between nanoelectronic devices. Also an application of LB-type 2D superlattices of FePt alloy nanoparticles to ultrahigh-density magnetic recording media are discussed.

[1] T. Teranishi, "Metallic Colloids," In *Encyclopedia of Surface and Colloid Science*, ed. A. Hubbard, Marcel Dekker, New York, 2002, p. 3314.

[2] T. Teranishi, M. Haga, Y. Shiozawa, and M. Miyake, *J. Am. Chem. Soc.* **2000**, 122, 4237.

[3] T. Teranishi, S. Hasegawa, T. Shimizu, and M. Miyake, *Adv. Mater.* **2001**, 13, 1699.

[4] T. Teranishi, A. Sugawara, T. Shimizu, and M. Miyake, *J. Am. Chem. Soc.* **2002**, 124, 4210.

#### SESSION Q12: PROPERTIES AND APPLICATIONS I

Chair: Hongjie Dai

Friday Morning, April 25, 2003

Metropolitan II (Argent)

#### 8:30 AM Q12.1

SYNTHESIS AND TRANSPORT PROPERTY OF INDIUM NITRIDE NANOWIRES. Tao Tang, Song Han, Wu Jin, Xiaolei Liu, Chao Li, Daihua Zhang and Chongwu Zhou, Dept. of E.E.-Electrophysics, University of Southern California, Los Angeles, CA.

InN has a direct band gap in the visible range and large mobility at room temperature. These distinctive optical and transport properties have attracted significant research effort on InN nanowires because of their novel properties and potential applications in nanoscale electronics and photonics areas. Despite the utmost importance, all the synthesis methods reported previously lack precise control over the nanowire diameter, and no electronic devices based on the InN nanowires have been fabricated and studied. We will present an efficient route for the synthesis of single crystalline InN nanowires via a chemical vapor deposition method. Diameter control has been achieved by using monodispersed gold clusters with well-defined diameters as the catalyst. The synthesized nanowires have uniform diameters with the average as small as 10 nm, and the lengths are in the range of 5 to 10  $\mu\text{m}$ . Furthermore, InN nanowire field effect transistors (FET) have been fabricated for the first time and their electronic properties will be presented. Our work has paved the way for InN nanowires to be used as nanoscale electronic and photonic devices.

#### 8:45 AM Q12.2

ELECTRICAL TRANSPORT PROPERTIES OF TEMPLATE-DERIVED RuO<sub>2</sub> NANOWIRES. Y. Fan, R. Sordan, M. Burghard, K. Kern, Max-Planck-Institute for Solid State Research, Stuttgart, GERMANY.

Low-dimensional nanostructures like nanowires, nanotubes, or nanocrystals are attractive building blocks for nanoscale electronic devices. In this contribution, we present rutheniumdioxide (RuO<sub>2</sub>)

nanowires produced on vanadiumpentoxide (V<sub>2</sub>O<sub>5</sub>) nanofibers templates.

Rutheniumdioxide, a metallic conductor of excellent chemical stability, is of strong interest for applications in catalysis or sensors. For the template-based formation of RuO<sub>2</sub> nanowires, two different approaches have been used. In the first case, V<sub>2</sub>O<sub>5</sub> nanofibers (3-4 nm in height, 10 nm in width, and 5-10  $\mu\text{m}$  in length) were deposited on a chemically modified Si/SiO<sub>2</sub> substrate, and then exposed to RuO<sub>4</sub> vapour at room temperature. While this approach resulted in chain-like assemblies of isolated RuO<sub>2</sub> nanocrystals if unmodified V<sub>2</sub>O<sub>5</sub> were used, continuous (polycrystalline) RuO<sub>2</sub> wires could be obtained from chemically reduced V<sub>2</sub>O<sub>5</sub> wires. In the second approach, first a RuO<sub>2</sub> thin film was deposited on Si/SiO<sub>2</sub> substrate, and then modified V<sub>2</sub>O<sub>5</sub> nanofibers were deposited on top as etching mask during Argon ion beam etching. This procedure yielded continuous RuO<sub>2</sub> nanowires about 5~15 nm in height. The RuO<sub>2</sub> nanowires and nanoparticle assemblies were investigated by AFM and XPS. Moreover, electrical transport measurements in 4-probe configuration revealed the resistance of the wires obtained by the ion beam etching technique to be of the order of several hundreds of K $\Omega$ .

#### 9:00 AM \*Q12.3

ELECTRICAL TRANSPORT THROUGH INDIVIDUAL NANOWIRES AND NANOTUBES. David H. Cobden, Department of Physics, University of Washington, Seattle, WA.

We review recent developments in the study of electronic transport through individual carbon nanotubes and chemically formed linear nanostructures made of other materials, including semiconducting and metallic nanowires with dimensions similar to those of nanotubes. A wide range of phenomena is accessible in these systems.

#### 9:30 AM \*Q12.4

SYNTHESIS AND CHARACTERIZATION OF TRANSITION-METAL-OXIDE NANOSTRUCTURES. Hongkun Park, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA.

Single-crystalline barium titanate nanowires are synthesized using a solution-based method, and their ferroelectric properties are investigated by scanned probe microscopy. Pristine nanowires have diameters ranging from 5 to 60 nm and lengths exceeding 10  $\mu\text{m}$ , and they exhibit crystalline structure with the [001] direction aligned along the wire axis. Scanned probe microscopy investigations show that local non-volatile electric polarization can be reproducibly induced and manipulated on nanowires as small as 5 nm in diameter, demonstrating that these nanowires may serve as a basis for nanoscale non-volatile memory. The measurements of ferroelectric transition temperature (T<sub>c</sub>) as a function of nanowire diameter show that T<sub>c</sub> is depressed as the nanowire diameter becomes smaller.

#### 10:30 AM \*Q12.5

ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES OF SINGLE MOLECULES AND METAL NANOPARTICLES. J. G. Hou, Structure Research Laboratory, University of Science and Technology of China, Anhui, Hefei, CHINA.

The quest for novel quantum properties of devices has spurred a growing effort in pushing the materials' size down to nanometer scale or even use single molecules as functional components. Similar to single molecules, metal nanoparticles also have rich electronic structures because when their size reduced to a few nanometers, the quasi-continuous density of state is replaced by a discrete energy level structures. When single molecules or metal nanoparticles placed as the center electrode in a double barrier tunnel junction, rich tunneling spectrum were obtained because of the interplay between effects of Coulomb charging, excitation of discrete energy levels and resonant tunneling between localized states. Through controlled synthesis methods, we were able to get nano-structures (single molecules or metal particles) with different electronic structures. With a low temperature scanning tunneling microscope, we studied their electronic structures and transport properties in a double barrier tunneling junction. Novel transport effects associated to the electronic structure and charging energy of ultra small tunneling junction, and possible application of these nano-structures in devices of single electron tunneling, negative differential resistance (NDR) and rectifying diode are reported.

#### 11:00 AM \*Q12.6

CHEMICAL SENSING WITH METAL NANOWIRES. Reginald M. Penner, Ben Murray, Erich Walter, Erik Menke, Stacey Reogers, Dept. of Chemistry, Univ. of California, Irvine, CA; Gisela Kaltnepoth, Michael Grunze, Department of Physical Chemistry, Univ. of Heidelberg, GERMANY; Fred Favier, CNRS Montpellier, FRANCE.

Already well established is the notion that semiconductor nanowires can be used as transducers to detect the binding of charged analyte molecules. The physics of this transduction process are identical to those operating in a field-effect transistor. It is less clear what role, if any, metal nanowires have to play in chemical sensing. We address this issue in this presentation. In particular, the impedance of metal nanowires is probed - in the frequency range from DC to 1 MHz - as a function of the concentration of a chemisorbing gas phase species. The nanowires that form the basis for these investigations were prepared by Electrochemical Step Edge Decoration on graphite and silicon surfaces. These nanowires are polycrystalline, one grain in width, and have a diameter in the range from 20 nm to 400 nm. This paper will focus attention on nanowires composed of three metals: Palladium, silver, and copper.

**11:30 AM \*Q12.7**

**NANOTUBE SENSING AND SENSOR DEVICES.** Keith Bradley, John Cumings, Jean-Christophe P. Gabriel, George Gruner<sup>a</sup>, Joe Stetter, Nanomix Inc. Emeryville, CA. <sup>a</sup>On leave from UCLA Los Angeles, CA.

The characteristics of field effect transistors (FET's) incorporating single wall nanotubes have been variably described as due to the nanotube (NTFET) or due to the Schottky Barrier (SBFET) formed between the nanotube and metal contacts. Resolution of the issue is of paramount importance for electronic device and sensor applications. We have fabricated devices with various configurations which allow the role played by the nanotubes and by the contacts to be separated. The responses of devices to adsorbed and coating analytes give direct evidence that nanotubes are essential nonlinear elements that determine the FET response. Thus the devices can be used as sensitive transducers in a variety of sensor applications. A chemical sensor architecture, which includes a nanotube based transducer and recognition layers, leads to gas specific sensing. Examples based on the above sensor architecture - including metal, metal oxide and polymer recognition layers have been fabricated and tested for chemical sensing. The device performances, including sensitivity, specificity, response time etc. will be discussed and compared in some cases with other chemical sensors.

**SESSION Q13: PROPERTIES AND APPLICATIONS II**

Chair: J. G. Hou

Friday Afternoon, April 25, 2003

Metropolitan II (Argent)

**1:30 PM \*Q13.1**

**LIQUID CRYSTALLINE PHASES OF ANISOTROPIC INORGANIC NANOCRYSTALS.** Paul Alivisatos, University of California, Berkeley, CA.

In recent years there have been several advances that permit the preparation of anisotropic rod or disk shaped nanocrystals with tight control of the size distribution and the aspect ratio. These nanocrystals will spontaneously form lyotropic liquid crystalline phases at sufficiently high density in solution. These liquid crystalline phases are of considerable interest from both fundamental and practical point of view. Compared to conventional organic or macromolecular liquid crystals, the electric, optical, and magnetic properties can cover a much wider range. The nature of the forces between the nanocrystals can vary considerably depending upon the polarizability, dipole moment, and magnetization of the nanocrystals. This talk will describe recent work to determine the phase diagrams for CdSe nanorods, as well as for iron oxide and Co nanodisks. In addition, work to produce macroscopic alignment with external electric and magnetic fields of the inorganic nanocrystal liquid crystal phases will be described.

**2:00 PM \*Q13.2**

**INTEGRATED OPTOELECTRONICS ASSEMBLED FROM SEMICONDUCTOR NANOWIRE BUILDING BLOCKS.** Yu Huang, Xiangfeng Duan, Charles Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

Low-dimensional materials, such as nanocrystals and nanowires (NWs), have great potential for applications in optoelectronic circuits. Semiconductor nanowires are of particular interest because they are optically active and represent the smallest dimension for efficient transport of electrical carriers and optical excitons. In this talk, we will first present a general synthetic approach to a broad range semiconductor NW materials, which in turn enables us to assemble a series of nanoscale crossed NW light-emitting-diodes (LEDs) with nearly full color emission (from UV to near IR). Significantly, our assembly approach allows us to explore integrated multi-color LED

arrays and integration of LEDs with nanoscale electronics circuits (such as crossed NW field-effect transistors (FETs)), which serve as the driving circuit for the LEDs. Lastly, we've exploited the potential of incorporating NW optical functions into conventional silicon microelectronic circuits and the potential of fabricating nanoscale NW laser diodes.

**2:30 PM \*Q13.3**

**TOWARDS HIGH PERFORMANCE CARBON NANOTUBE ELECTRONICS** Hongjie Dai, Department of Chemistry, Stanford University, Stanford, CA.

This presentation will cover our latest results in the following areas and describe the potential of nanotubes in technological applications ranging from nanoelectronics to sensors and biosensors. (1) Controlled synthesis of nanotube structures on surfaces; patterned growth of nanotubes. (2) Nanoelectronics based on nanotube transistor arrays derived by chemical synthetic routes. It will be shown that the integration of high k zirconia dielectrics into nanotube transistors affords the highest performance nanotube transistor to date. Arrays of nanotube transistors for logic and ring oscillators will be presented. (3) The chemical functionalization and utilization of nanotubes as chemical sensors, and experimental results on interactions between nanotubes and small molecules, polymer chains and proteins will be presented.

**3:00 PM Q13.4**

**CHEMICAL ASSEMBLY OF ELECTRONICALLY FUNCTIONAL NANOWIRES AND NANOTUBES.** Nina Kovtyukhova, Jeremia Mbindyo, Thomas Mallouk, Penn State Univ, Dept of Chemistry, University Park, PA; Theresa Mayer, Penn State Univ, Dept of Electrical Engineering, University Park, PA.

We present template wet chemical self-assembly as a scalable technologically simple and inexpensive route to electronically functional nanotubes and nanowires. Free standing inorganic oxide and inorganic-oxide/polymer nanotubes have been layer-by-layer assembled as ultrathin multilayer films on the pore walls of an alumina membrane and released by dissolving the membrane. The method involves repeats of well-controlled adsorption or adsorption-reaction sequence on the pore surface and allows controlling nanotube wall thickness with sub-nanometer precision. While in membrane, the nanotubes can be electrochemically filled with metal to prepare metal nanowires coated with ultrathin uniform nanotube shell. A breakdown field of  $\sim 5$  MV/cm has been obtained for an insulating SiO<sub>2</sub>-nanotube coating on gold nanowires, which is comparable to that of the SiO<sub>2</sub> dielectric used in CMOS integrated circuits. The current-voltage characteristics of the nanowire structures containing semiconductor-nanotube coating have shown current rectifying and switching behavior. More complex p-n junctions have been synthesized by layer-by-layer assembling a p-conductive film on top of the semiconductor-nanotube coating. The incorporation of device elements into template-grown nanowires involves growing films of electroactive materials between metal segments. In-wire metal/semiconductor/metal junctions has been fabricated by using layer-by-layer assembly of a multilayer semiconductor/polymer film between two metal electroplating steps. SAMs of mercaptohexadecanoic acid (MHDA) and molecules containing a nitroaromatic redox center have been grown at the exposed tips of gold nanowires inside polycarbonate membranes. A top nanowire segment has been added by electroless deposition. Electron transport in the in-wire Au/MHDA/Au structure occurs by tunneling. The I-V characteristics of Au/nitroaromatic/Au device have exhibited negative differential resistance.

**3:15 PM Q13.5**

**CONTROLLED GROWTH OF ZnO NANOWIRES AND THEIR OPTICAL PROPERTIES.** Haoquan Yan and Peidong Yang, University of California at Berkeley, Department of Chemistry, Berkeley, CA.

This work surveys recent developments in rational synthesis of single crystalline zinc oxide nanowires and their unique optical properties. The growth of ZnO nanowires was carried out in a simple chemical vapor transport and condensation (CVTC) system. Based on our fundamental understanding of the vapor-liquid-solid (VLS) nanowire growth mechanism, different levels of growth controls including positional, orientational, diameter and density control have been achieved. Power dependent emission has been examined and lasing action was observed in these ZnO nanowires when the excitation intensity exceeds a threshold ( $\sim 40$  kW/cm<sup>2</sup>). These short-wavelength nanolasers operate at room temperature and the areal density of these nanolasers on substrate readily reaches  $1 \times 10^{10}$  cm<sup>-2</sup>. The observation of lasing action in these nanowire arrays without any fabricated mirrors indicates these single-crystalline, well-faceted nanowires can function as self-contained optical resonance cavities. This argument is

further supported by our recent near-field scanning optical microscopy (NSOM) studies on single nanowires.

**3:30 PM Q13.6**

**GAS SENSORS BASED ON METAL OXIDE NANOWIRES.**  
A. Kolmakov, Y. Zhang, G. Cheng, D. Jeong, and M. Moskovits,  
Chemistry Dept., University of California, Santa Barbara, CA.

The application of metal and semiconductor nanowires as solid state gas sensors has been an area of tremendous promise currently faced with challenges related to nanowire growth and device fabrication. We present an approach for fabricating both individual nanowires and arrays of aligned nanowires of a variety of metals and metal oxides relevant to gas sensing with tunable, uniform diameters and length in the range 10-100 nm and 5-200 micrometers. The materials successfully employed include Pd, Ag, Cu, Pb, PbO, CuO and SnO<sub>2</sub>. Arrays of nanowires were fabricated in hexagonal close-packed nanochannel alumina templates and configured for gas sensing application. Deposited porous electrodes on the surfaces of these nanostructured films provides electrical contacts and results in a device architecture which is compatible with the technological norms currently used in microelectronics. To complement these studies we explored the electronic and structural properties of nanowires using HRTEM, XRD, XPS and Auger spectroscopy. Chemical reactivity and gas sensitivity toward variety of gases of individual and assemblies comprised of a very large number of nanowires were assessed using conductivity measurements, micro-Raman and TPD analysis. We believe this approach constitutes a novel platform for micro- and nanosensor application.

**3:45 PM Q13.7**

**NANOWIRE ELECTROCHROMIC DEVICES.** Fu-Rong Chen and Ji-Jung Kai, Dept. of Engineering and System Science, National Tsing Hua University, Hsin Chu, TAIWAN.

Electrochromism is defined as a reversible color change of a device caused by the application of an electric current or potential. Basically, electrochromic devices consist of one or two closed cells which have fundamental structure of thin conducting glass-transparent metal-oxide film-electrolyte. In the past, the main limitation for electrochromic device in the application of flat panel display and smart window is the long switch time between transparent and color states. It has been suggested recently that the switching time can be greatly shorten to the order of milliseconds with a porous titanium dioxide film in the negative glass electrode and antimony-doped tin oxide nanocrystals in the positive glass electrode. In our talk, we will show an electrochromic device which is composed of MoO<sub>3</sub> nanowire. The MoO<sub>3</sub> nanowire was grown with thermal vapor transport technique. The atomic and electronic structure of MoO<sub>3</sub> nanowire was characterized using HRTEM and EELS. The MoO<sub>3</sub> nanowire is non-stoichiometric and it contains of crystallographic shear defects. The detail structure of the device and nanowire will be reported in the conference.