

SYMPOSIUM R

Three-Dimensional Nanoengineered Assemblies II

April 12 - 16, 2004

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* Invited paper

TUTORIAL

From Microfluidics to Nanofluidics: Stakes and Challenges

Monday April 12, 2004
1:30 PM - 5:00 PM
Room 2002 (Moscone West)

Microfluidics, which emerged in the 1990s as a branch of physics and biotechnology studying the behavior of fluids at the micro- and mesoscale, has enabled a wide range of technologies including gene chip, microthermal and micropulsion technologies. With the advent of nanotechnology, nanofluidics - where the underlying physics grows in great complexity - should make single-molecule studies more affordable. In this tutorial, the part on microfluidics will mainly focus on devices and their fabrication technologies; scientific challenges when reducing to the nanoscale, and specific routes to integrating various analytical nanodevices will be highlighted. The following series of projects will be described to illustrate both theoretical and experimental aspects of microfluidics: electrokinetic bioanalytical systems, micron-resolution particle image velocimetry, bleached-fluorescence imaging for electrokinetics, caged-fluorescence microscopy for electrokinetics, study of microchannels with non-uniform Zeta potentials, optimization of electroosmotic microchannel geometries, optimization of on-chip field amplified sample stacking, electrokinetic instability micromixing, electrokinetic instability in microflows, isoelectric focusing for multi-dimensional separations in microfluidic devices, electrokinetic band crossing, development of a planar electroosmotic micropump, and development of electroosmotic pumps for electronics cooling. As for nanofluidics, new devices will be described that allow single-molecule sequencing as a way to radically improve DNA sequencing. Devices and processes suitable for molecular separation using nanostructures will be highlighted, as these molecular separation techniques can be applied to sorting DNA fragments by length, and will potentially lead to rapid analysis of small amounts of material.

Instructors:

Juan G. Santiago, Stanford University
Stephen Turner, Nanofluidics, Inc.

SESSION R1: Photon, Electron & Ion Beam
Approaches to Nanofabrication
Chairs: John Pendry and David Taylor
Tuesday Morning, April 13, 2004
Room 3020 (Moscone West)

8:30 AM *R1.1

3D Nanofabrication by Optical Proximity Field

Photopatterning. John Rogers, Seokwoo Jeon, Jang-Ung Park and Joana Maria; University of Illinois at Urbana/Champaign, Urbana, Illinois.

Exposing a photopolymer to the distribution of intensity that develops when ultraviolet light passes through a phase mask provides a flexible and experimentally simple route to certain classes of complex 3D nanostructures. This talk describes the technique, as implemented with elastomeric phase masks. It describes in detail the full vector optics of this system and the requirements on the coherence and spectral properties of the exposure light. Key features of the technique are illustrated through examples of structures that we have produced. By using the patterned polymers as templates for growth or sedimentation of nanoparticles, it is possible to build 3D nanostructures out of materials that would be difficult to pattern directly. We provide some representative examples of devices that can be fabricated, including nanostructured mixers for microfluidics and tunable photonic bandgap elements.

9:00 AM *R1.2

Polariton-enhanced near field lithography and imaging with mid-IR light. Gennady Shvets, Department of Physics, University of Texas at Austin, Austin, Texas.

Despite the successes in making left-handed materials in the microwave frequency range, there has been little progress in achieving same for infrared frequencies. I will describe a novel approach to making a material with negative index of refraction using photonic dielectric components with a small (of order minus one) negative dielectric permittivity. Periodic structures with negative-epsilon dielectrics support surface waves which can have a negative group velocity. The nature of these surface waves depends on the dielectric components: they are surface plasmons for plasmonic materials (such as metals) or surface phonon polaritons for polar crystals (such as SiC, ZnSe, GaP) with the reststrahlen band. The advantages of using

phononic materials (long phonon lifetime, scientifically important frequency range) will be illustrated. I will also show that, depending on the photonic lattice (square or hexagonal), the resulting meta-material can be either isotropic, or strongly anisotropic. Supporting theory and simulations will be presented. Another application of the negative-epsilon materials is nano-lithography. As was suggested earlier, any material with epsilon = -1 can be used to significantly enhance near-field imaging. I will show results demonstrating that a thin slab of SiC is capable to focus the 10.55 micron radiation of a CO2 laser to several hundred nanometers, thus paving the way for a new nano-lithographic technique: Polariton Enhanced Near Field Lithography in Infrared (PENFIL). I will also discuss the possibility of enhancing mid-IR light transmission through nanoholes in SiC.

9:30 AM *R1.3

Nanopatterning of 3-D Structures Using Quantum Interference Effects in Electron Stimulated Desorption.

Thomas M. Orlando, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

T. M. Orlando, School of Chemistry and Biochemistry and School of Physics, Georgia Institute of Technology, Atlanta, GA. The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for electron-beam induced processes in materials growth, etching, and lithography. We have recently demonstrated experimentally and theoretically that total ESD yield of Cl⁺ from Cl-terminated Si(111) is a function of incident electron-beam direction [1]. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). The fine-structure in the desorption yields is due to quantum-mechanical scattering and interference of the incident electron to form a surface standing wave in the initial state of the desorption process. This electron standing wave exhibits spatially localized maxima and minima in the electron density. Whether a particular site or domain on a surface experiences a maximum or a minimum depends on i) the electron energy (wavelength), ii) the incident electron direction and iii) the arrangement of nearest-neighbor atoms. Since the probability of desorption is proportional to the incident electron density at the "absorber" sites, the total desorption yield depends upon the local atomic structure and the *k*-vector of the incident wave. We are exploring the utility of this low - energy electron beam technique as a prepatterning strategy for controlled growth of 3-D nanostructures. If viable, this nanolithography approach would be inexpensive and not rely upon serial processing. 1.) M. T. Sieger and T. M. Orlando, *Phys. Rev. Lett.* 82, 3348 (1999). thomas.orlando@chemistry.gatech.edu

10:30 AM *R1.4

Implanted 3D Micro/Nano-Structure Fabrication.

Meg H. Abraham, Center for Microtechnology, The Aerospace Corporation, El Segundo, California.

We have developed a novel method for making microstructures imbedded in silicon wafers. These structures can then be released using laser assisted chemical etches or conventional dry etch methods. This new process has the potential to revolutionize the way some types of microstructures are fabricated and will extend the lower limits of device size. Currently most microelectronics and MicroElectroMechanical Systems (MEMS) are constructed using modified versions of VLSI technology wherein layers of silicon nitride, silicon dioxide, and polysilicon are successively grown and patterned by conventional photolithography. This process is inherently time consuming and limited by the resolution of the lithography and wet or dry etch. We have developed a novel method of making structures using patterned implants and laser assisted chemical etching. The implantation of ion species or by the disordering of the Si material defines the etchable area and control of the "release" of the structure is achieved using laser direct-write chemical etching. The ability to construct devices that have micro and nano-scale dimensions has been demonstrated. Freestanding films with thickness on the order of hundreds of nanometers, defined by an ion beam implant, have been constructed. We have shown that these simple structures are inexpensive to prototype, and that the process can be scaled up for mass production using commercially available broad ion implantation services. The conventional layered growth processing of various oxides and nitrides on a Si substrate often introduces run-to-run variations. The new process produces films and structures that are remarkably uniform and can be extended to insulators and possibly conductors,

11:00 AM R1.5

Fabrication of Metal and Metal-Oxide Nanoparticle Arrays by Focused Ion-Beam Lithography and Vapor Deposition.

Richard F Haglund¹, Matthew D. McMahon¹, Rene Lopez¹, Leonard C. Feldman¹, Anthony B. Hmel¹, Robert H. Magruder^{2,1}, Kenneth E. Schriver¹, Jae Y. Suh¹ and Robert A. Weller^{3,1}; ¹Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ²Physics and

The development of working nanoscale photonic and electronic devices presupposes not only the ability to construct three-dimensional architectures, but also the capability to incorporate multiple materials families in the device in a manufacturable way. In this paper we demonstrate that nanoscale structures of moderate sophistication can be created in both metals and metal oxides, using a combination of focused ion-beam lithography, pulsed laser deposition and physical vapor deposition. The FIB is first used in pixel-by-pixel programming mode to pattern a poly(methyl methacrylate) resist approximately 70 nm thick. The patterns are generated as a two-dimensional lattice with an arbitrary basis set of nanoscale patterns at each lattice points. Typical basis patterns have included dimer, trimer and tetramer nanoparticle bases, with the separation of the nanoparticles essentially at arbitrary distances. Using appropriate deposition techniques (either pulsed laser deposition or physical vapor deposition), the desired metal or metal-oxide material is deposited following development of the photoresist. Standard lift-off techniques then leave behind an array of nanoparticles, typically in a pancake morphology 20 nm thick and with the shape programmed into the FIB. With this combination of techniques, device structures with three-dimensional architectures are possible by depositing a thin film over each two-dimensional nanopatterned layer and then repeating the lithographic step. We have used already this technique to create two-dimensional nanoparticle patterns in both vanadium dioxide and noble metals. The metal nanoparticles have plasmon responses in the visible portion of the spectrum, and can be used to generate harmonics of high-intensity laser pulses without requiring phase matching. When deposited by pulsed laser deposition, the metals appear to be granular, with a high surface area especially interesting for surface-enhanced Raman spectroscopy. The vanadium dioxide nanoparticles undergo a semiconductor-to-metal transition at 70°C; in the metallic state, they exhibit a broad plasmon band in the near-infrared (1.2 μm). The optical response comprises both Bragg diffraction from the long-range order imposed by the space lattice, and plasmonic and non-plasmonic response from individual basis nanoparticles. The optical characteristics of the particles have been studied using near-field scanning optical microscopy and nonlinear optical spectroscopy. This work is supported by the U. S. Department of Energy, the National Science Foundation, and the Vanderbilt Institute for Nanoscale Science and Engineering.

11:15 AM *R1.6

Nano-PROFIB: update of the Projection Focused Ion multi-Beam tool concept for 3D Nanoengineering.
Hans Loeschner and Elmar Platzgummer; IMS Nanofabrication GmbH, Vienna, Austria.

At the MRS 2002 fall meeting the PROFIB (Projection Focused Ion multi-Beam) tool concept has been presented (MRS Proc. Vol. 739, pp. 3-12). This talk provides an update of the tool concept together with ion beam sputter and deposition simulation results to predict the performance of PROFIB for 3D nanoengineering applications. This simulation program is in excellent agreement with FIB (single Focused Ion Beam) experimental results allowing PROFIB and FIB comparisons in the sub-100nm domain. PROFIB application fields will be discussed.

11:45 AM R1.7

Ion beam shaping of three-dimensional nano-assemblies. T. van Dillen¹, J.J. Penninkhof¹, C. Graf², K. Velikov², C.M. van Kats², M.J.A. de Dood¹, S. Roorda^{1,3}, A.M. Vredenberg², A. van Blaaderen² and A. Polman¹; ¹FOM-Institute AMOLF, Amsterdam, Netherlands; ²Debye Institute, Utrecht University, Utrecht, Netherlands; ³Universite de Montreal, Montreal, Quebec, Canada.

Ion irradiation of free-standing amorphous materials leads to anisotropic plastic deformation at constant volume at a well-defined rate. We have studied this process in detail for colloidal particles with diameters in the range 50-1000 nm using ion energies between 300 keV and 30 MeV. Spherical silica colloids expand perpendicular to the ion beam and contract parallel to the ion beam, changing their shape to oblate ellipsoidal, the final anisotropy determined by the ion fluence. The deformation is mainly driven by the energy lost in electronic excitations in the material and can be described by a visco-elastic free volume model that takes into account the shear stress relaxation in the cylindrically-shaped heated ion track. Size aspect ratios as large as 10 are achieved. We then fabricated three-dimensional photonic crystals by the self-assembly of spherical silica colloids and irradiated them with 4 MeV Xe ions. The collective deformation process leads to changes in both the unit cell symmetry and particle form factor, which in turn cause a significant shift in the Bragg reflection spectrum. Anisotropic photonic crystals can have larger photonic bandgaps than their symmetric counterparts. Next, we

address the ion beam deformation of core-shell particles, composed of a silica core and a 10-nm thick metal shell. Plastic deformation of the silica can impose an anisotropic shape change on the metal shell, leading to the formation of an oblate metallic shell. Interestingly, the reverse structure, with a metal core embedded in a silica shell, leads to the formation of a prolate metal core. The shape changes in these anisotropic metallo-dielectric colloidal nanomaterials are reflected in well-defined shifts in their surface plasmon resonance absorption spectrum. Finally, we show how ion irradiation of amorphous/crystalline silicon nanocomposites leads to a complex deformation process, where crystalline sections of the material do not deform, while amorphous sections do. This leads to the formation of unique microstructures that may find applications in e.g. optical microresonators.

SESSION R2: Fabrication, Self-Assembly and Characterization of 2-D and 3-D Nanostructures I
Chairs: David Mc Ilroy and Lhadi Merhari
Tuesday Afternoon, April 13, 2004
Room 3020 (Moscone West)

1:30 PM *R2.1

Semiconductor Nanocrystal Heterostructures. Delia Milliron¹, Steven Hughes¹, Yi Cui¹, Liberato Manna² and A. Paul Alivisatos¹; ¹Chemistry, UC Berkeley, Berkeley, California; ²National Nanotechnology laboratory, Lecce, Italy.

The "bottom-up" approach to fabricating nanodevices requires that nanoscale building blocks be assembled with control over their interactions. To reduce the variability and limited complexity of arranging discrete components, the recent trend is to incorporate more functionality into single nanostructures. Recent advances in growth of one-dimensional heterostructured nanowires, have enabled demonstrations of single nanowire light emitting diodes, single-electron transistors, and optical nanobarcodes. Colloidal nanocrystals offer precise size and shape control, and solution possibility, but heterostructure growth has been limited to core/shell structures that serve primarily to further isolate quantum dots from their environment. We have demonstrated the synthesis of colloidal heterostructures connecting quantum dots and rods at branched and linear junctions within single nanocrystals. We control branching and composition throughout nanocrystal growth to independently tune the properties of each component and the details of their interactions. Distinct dots and rods are coupled through potential barriers of tunable height and width, and arranged in space at well defined angles and distances. Such control opens the door to potential applications ranging from quantum information processing to artificial photosynthesis.

2:00 PM R2.2

Morphologically Well-defined Gold Nanoparticles Embedded in Thermo-Responsive Hydrogel Matrices. Chun Wang¹, Nolan T Flynn² and Robert Langer¹; ¹Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemistry, Wellesley College, Wellesley, Massachusetts.

An interesting group of polymeric matrices for controlled formation of colloidal nanoparticles is thermo-responsive hydrogels based on poly(*N*-isopropylacrylamide (PNIPAm)). It is well-known that a pure PNIPAm gel swollen in water displays a temperature-triggered reversible phase transition at 32°C, which is defined as the lower critical solution temperature (LCST). In recent years various composite materials consisting of colloidal nanoparticles, such as Pd or Au, embedded in PNIPAm gels were synthesized and used as novel catalysts, (bio)sensors, switchable electronics, and optically triggered drug delivery devices, which exploited the unique thermo-responsive behavior of PNIPAm gels. It has not been attempted, however, to use these gels for synthesizing nanoparticles with well-defined size and morphology. Furthermore, there has been no report on modulating the bulk properties, such as swelling and thermal phase transition, of the nanoparticle-PNIPAm composite gels. To this end, we synthesized PNIPAm hydrogels by free radical copolymerization of NIPAm and a chemical crosslinker, *N,N*-cystamine bis-acrylamide (CBAm), which is able to bind specifically with Au³⁺ and colloidal Au. Formation of Au nanoparticles inside CBAm-crosslinked PNIPAm hydrogels was achieved by chemical reduction of three-dimensionally immobilized Au³⁺ ions by NaBH₄. We found that the content of CBAm in the PNIPAm gels determines the size, morphology, and long-term stability of the Au nanoparticles. In the absence of CBAm, amorphous aggregates of Au formed which became large discrete particles with time. With increasing CBAm content, however, the aging process was inhibited, and the Au nanoparticles were much smaller and more uniform in size. The bulk properties of the Au-PNIPAm nanocomposite gels were also affected by the presence of Au nanoparticles. Immobilization of charged colloidal Au nanoparticles inside PNIPAm gels resulted in increased gel swelling in water. The

thermal phase transition of the nanocomposite gels was dramatically altered, with an apparent LCST at least 10 degrees higher than the 32°C of the pure PNIPAm gels. These findings illustrate the possibility of engineering thermo-responsive hydrogel-based nanocomposite materials with well-defined structure and novel properties that are likely to be useful in catalysis, photonics, electronics, optics, and biomedicine.

2:15 PM R2.3

Pseudomorphic Transformations of Nanostructured Silica to Titanium Oxides or Tungsten Carbides. Andreas Stein, Justin C. Lytle, Hongwei Yan and Ryan T. Turgeon; Department of Chemistry, University of Minnesota, Minneapolis, Minnesota.

In the last decade, many techniques have been developed to synthesize three-dimensional (3D) architectures on a nanometer scale including self-assembly and templating methods. While such architectural control has been applied to many compositions, the structural variety of silica on all length scales is rivaled by few, if any, other inorganic compositions. In particular on the micrometer and nanometer scales, the ability to structure other ceramic or metallic compositions with the complex architectures found in silica would benefit many materials and device applications. Pseudomorphic transformations are reactions capable of converting preforms of one composition to other compositions while maintaining the original shape. In the current study, the applicability of pseudomorphic transformations of 3D nanostructured silica to titania and tungsten carbide was examined. The preforms were prepared by colloidal crystal templating methods. They consist of smooth amorphous silica walls (ca. 60 nm in thickness) that surround periodically arranged, interconnected voids hundreds of nanometers in diameter. Multistep gas-solid reactions at relatively low temperature were employed to partially convert the amorphous silica skeleton to nanocrystalline TiO₂ and then to TiC. Within a limited temperature window, the periodic macroporous structure of the preform was maintained during these reactions. Pseudomorphism was also observed on the scale of the nanocrystals forming the inverse opal skeleton. A similar vapor phase reaction was applied to convert a silica preform to W_xC_y/W. The materials structures, as well as benefits and limitations of these reactions will be discussed.

2:30 PM *R2.4

Understanding Electronic Transport in 1D Arrays of Metal Nanoparticles. Christopher A. Berven, University of Idaho, Moscow, Idaho.

During the last thirty years, there has been a remarkable decrease in the size of electronic devices. Continued device evolution is facing serious fundamental challenges associated with quantum and other effects. To address these challenges a number of revolutionary departures from conventional semiconductor technology are being explored. Among these are nanostructures whose transport properties are governed by single-electron charging. For room-temperature operation, this generally implies that the islands have dimensions below about a nanometer. A possible building block for such devices is the ligand stabilized gold nanoparticle which when chemically attached to polymer scaffolds, allows organizing the nanoparticles into functional devices. In this talk, the novel electronic transport properties of 1-D chains of ligand stabilized gold nanoparticles decorating the biopolymer poly-L-lysine will be discussed. Some of the properties of the transport change with time, while others do not. Using theoretical arguments and modeling results, the time independent properties can be shown to originate in the nature of electronic transport in one-dimensional chains of nanoparticles in which the inherent self-capacitance is not negligible. These properties will be contrasted to those of traditional single-electron devices where the self-capacitance is negligible. Finally, modeling results of nanoparticle-based simple single-electron logic-gate circuits will be discussed.

3:30 PM *R2.5

Fabrication of 2-D and 3-D Photonic Bandgap Structures Using Laser-assisted Imprinting of Self-assembled Particles. Y.F. Lu¹, L.P. Li¹, K.K. Mendu¹, J. Shi¹, D.W. Doerr¹, D.R. Alexander¹ and X.Y. Chen²; ¹Dept of Electrical Engineering, University of Nebraska, Lincoln, Nebraska; ²Dept of Electrical and Computer Engineering, National University of Singapore, Singapore.

2-D and 3-D photonic bandgap (PBG) structures were fabricated on silicon substrates using laser-assisted nanoimprinting of silica particles will be discussed. Monolayers of silica particles, with different diameters ranging from 160 nm to 2 μm, were deposited on silicon substrates by self-assembly. A quartz plate, which is transparent to the laser wavelength of 248 nm, was tightly placed on the substrate surface. A KrF excimer laser beam with the wavelength of 248 nm was vertically irradiated on the quartz / nanoparticle / silicon structure. The silica particles were imprinted into silicon substrates by the quartz to form a 2-D PBG structure due to the transient Si

surface melting during the laser pulse. 3-D PBG structures were fabricated by repeating a process cycle of silica nanoparticles self-assembly, amorphous Si layer deposition, and simultaneous laser melting, imprinting and recrystallization.

4:00 PM R2.6

Rapid Fabrication of Patterned Arrays of Self-Assembled Hemi-Spherical Colloidal Aggregates Reflecting Multiple Colors. JooHo Moon¹, Hwa-Young Ko¹, Jungho Park¹ and Hyunjung Shin²; ¹Dept. of Ceramic Engineering, Yonsei University, Seoul, South Korea; ²School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

Self-assembled colloidal aggregates have been fabricated by placing an ink of submicron-sized colloidal particles on a hydrophobic substrate. The ink was prepared with well-dispersed aqueous suspension of monodisperse silica particles. The ink was selectively deposited on the substrate through a precision nozzle of orifice size 140 μm by micro-dispenser whose mechanical and pneumatic motions were controlled by computer interface. Monodisperse silica particle contained in the ink undergo self-assembly upon evaporation of the solvent. The shape and microstructure of the colloidal aggregates were strongly influenced by the physical and chemical properties of the ink such as solid loading, dispersion stability, and evaporation rate. Patterned array was rapidly fabricated using three different colloidal inks containing varying particle sizes of 300 nm, 500 nm, and 650 nm, respectively. Each hemispherical dot of 250 μm diameter in the patterned arrays was consisted of self-assembled colloidal aggregates in a closed packed ordered structure. It was observed that the colloidal aggregates reflect incident white light into three different colors (red, green, and blue) depending upon the size of the colloids. Microstructures of the colloidal aggregates were observed by optical microscopy, SEM, and AFM, and their optical properties were evaluated by transmission UV-vis-NIR spectra.

4:15 PM R2.7

Nanoscale Lithography on polystyrene particles. Dorjderem Nyamjav¹ and Albena Ivanisevic²; ¹Physics, Purdue University, West Lafayette, Indiana; ²Biomedical Engineering, Purdue University, West Lafayette, Indiana.

We couple Dip-Pen Nanolithography (DPN) with microcontact printing to fabricate polymer surface features on semiconductor substrates. The surfaces patterned with charged polymers by microcontact printing, were used as functional templates to guide the assembly of submicron sized, charged polystyrene particles. Subsequently, selected regions of the charged features on the surface were modified by DPN. As a result of the nanometer size patterning by DPN, an additional layer of particles can be directed to form pre-programmed 3D architectures. The fabrication strategy we report can be utilized in the construction of novel structures and materials.

4:30 PM R2.8

Fabrication of Ordered Nanotopographies on Large-Area Poly(Urethane Urea) by Two-stage Replication Molding. Keith Richard Milner^{1,2}, Mallory Balmer¹, Christopher A Siedlecki^{1,2} and Alan J Snyder^{1,2}; ¹Department of Bioengineering, Pennsylvania State University, Hershey, Pennsylvania; ²Department of Surgery, Pennsylvania State University, Hershey, Pennsylvania.

INTRODUCTION: A method is reported for producing ordered nanotopographies to 300 nm across a large area of biomedically relevant polymer. A master pattern is fabricated in soft photoresist across a 150 mm silicon wafer. A negative is formed by molding with poly(dimethylsiloxane) (PDMS). A biomedical poly(urethane urea) (PUU) is cast over the PDMS, resulting in a 150 mm PUU sample with ordered features of size down to 300 nm. As biomaterial surface topography is thought to affect cell behavior, this process is applicable in long-term implantable devices and tissue scaffolds. **METHODS:** A master pattern was fabricated in resist on a 150 mm silicon wafer. The wafer was spin-coated with a 700 nm layer of UV5 resist (Shipley). This was exposed with a 248 nm wavelength Stepper (Nikon) through a reticle patterned with arrays of squares with widths down to 200 nm in 50 nm increments. Development of the resist resulted in UV5 towers on the wafer surface. A negative was fabricated in Dow Corning Sylgard 184 PDMS, which was mixed at a ratio of 10:1 base:curing agent, degassed, cast over the master, degassed further to ensure conformation to the UV5 features, and cured under vacuum for 4 hr at 65 C. The PDMS was peeled from the master and rinsed in acetone to remove transferred UV5. The effect of a fluoro-terminated alkyltrichlorosilane-based self-assembled monolayer (SAM) on PDMS release from the master was investigated by depositing CF₃(CF₂)₇(CH₂)₂SiCl₃ prior to PDMS casting. The master pattern was replicated by casting Biospan MS.4 PUU, a commonly used blood-contacting material over the negative. The PUU was degassed, poured over the PDMS and spun at 500 rpm for 1 min to form a layer 10 μm thick. This was degassed further to ensure

conformation to the PDMS features, and cured under vacuum for 48 hr. The PUU was released from the PDMS mold while immersed in deionised water.

RESULTS: Samples of UV5 master, PDMS negative and PUU replica from SAM-treated and untreated masters were examined by SEM. The stepper lithography resolution limit with UV5 was found to be a reticle pattern size of 350 nm corresponding to $309 \text{ nm} \pm 7 \text{ nm}$ feature size in UV5. The efficiency of replicating UV5 resist towers in the MS.4 PUU was found to exceed 90 % for all feature sizes to 309 nm for untreated masters. In comparison, the replication efficiency from masters with SAM was greatly reduced for feature sizes below 500 nm.

CONCLUSIONS: This study demonstrates that ordered nanoscale features may be fabricated in a biomedically relevant PUU to dimensions of 309 nm, the resolution limit of the Stepper that produced the master pattern. Optimum replication is obtained without SAM. The nanotopographies are readily produced on PUU sheets at full wafer size and may be readily integrated in biomedical devices. **ACKNOWLEDGEMENTS Funding:** Commonwealth of Pennsylvania Tobacco Settlement Grant; NIH; NSF Assistance: Prof G Hess (Messiah College, PA); Mr T Rusnack (PSU); PSU Nanofabrication Facility

4:45 PM **R2.9**

Synthesis and Self-Assembly of Metal-Coated Dielectric Spheres for 3D Photonic Crystal Structures. Wounghang Park and Tomoko Borsari; Department of Electrical & Computer Engineering, University of Colorado, Boulder, Colorado.

Recently, dielectric spheres with thin metal coating have received much attention as they produce metallic structures with feature sizes of the order of 100nm as needed for photonic applications and also the metal thickness can be tuned to minimize the absorption loss in the visible wavelengths while maintaining wide and robust photonic bandgap (PBG). We have performed FDTD simulations and found that the metal-dielectric fcc structure can exhibit PBG width up to 3 times larger than the popular Si inverted opal structure. The wide PBG not only provides wide bandwidth of operation but also is more resistant to disorders. For fabrication, we developed a well-controlled gold nanoparticle synthesis process that can produce particles sizes between 1-50nm. The nanoparticle sizes were confirmed by TEM and also by optical spectra showing surface plasmon resonances. The optical spectra were in excellent agreement with the theoretical spectra by the Mie theory. These nanoparticles were then used to coat highly monodispersed silica particles (270nm) synthesized by a refined Stober method. Extremely small gold nanoparticles were first affixed on chemically modified silica sphere surfaces. Subsequent reduction of gold was then used to grow thin gold shells. TEM micrographs showed that uniform gold shells were formed and the original monodispersity of silica spheres was maintained. The shell thickness could be varied between 2-20nm. Optical extinction spectra showed distinct features in the near IR region, consistent with the predictions by the Mie theory. However, this process generated a large concentration of free gold nanoparticles remaining in the colloidal solution which caused severe agglomeration of coated spheres. To limit the agglomeration, both the silica sphere and gold nanoparticle concentrations had to be kept very small, which substantially reduced the yield of gold-coated spheres. To circumvent this problem, we devised a new approach in which gold nanoparticles were embedded inside the silica core spheres. This method was found to limit gold precipitation almost exclusively to the silica surface and the SEM micrographs showed that the uniformity of metal coating was about the same as the previous method and that the original monodispersity was also maintained. This process allows at least 10 times higher concentration of spheres, which is critical for the subsequent self-assembly process. We also performed the self-assembly of the metal-coated spheres. The sphere concentration and temperature gradient must be controlled to adjust to the much heavier weight of the metal coated spheres. Also, in order to insulate metal shells from one another and also to maintain similar surface properties to the case of conventional silica self-assembly, we performed silica overcoating with uniform thickness of 40nm. The details of structural and optical characterization results on the self-assembled structures will be reported at the conference.

SESSION R3: Plasmonic and Optical Nanoengineered Devices

Chairs: John Pendry and David Taylor
Wednesday Morning, April 14, 2004
Room 3020 (Moscone West)

8:30 AM ***R3.1**

Transmission of light through subwavelength apertures. Francisco J. Garcia-Vidal¹ and Luis Martin-Moreno²; ¹Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Spain; ²Departamento de Fisica de la Materia Condensada, Universidad de Zaragoza, Zaragoza, Spain.

Dielectric response of a metal is completely governed by its free electron plasma. Associated to the negative character of the dielectric constant of a metal is the appearance of surface electromagnetic modes decorating its surface. In this talk we address from a theoretical point of view two physical phenomena that are related to the excitation of these resonances: i) extraordinary optical transmission through single and periodically structured subwavelength apertures [1] and ii) beaming of light through single apertures surrounded by periodic corrugations [2]. We will present the theoretical foundation for these phenomena and discuss the various dependences of the transmission [3] and emission profiles [4] on the different geometrical parameters defining the system, providing guidelines for the optimisation of these profiles for different possible applications, like lensing [5] and demultiplexing [6] among others. Finally, we will explore how these results found for metal surfaces can be exported to dielectric photonic crystals (PCs). We will show that, through appropriate corrugation of the PC surface, it is possible to obtain both enhanced transmission through slits in PC slabs, and strong beaming of light coming out of a PC waveguide. [1] T.W. Ebbesen, H.J. Lezec, H.F. Ghaemi, T. Thio, and P.A. Wolff, Nature 391, 667 (1998). [2] H.J. Lezec, A. Degiron, E. Devaux, R.A. Linke, L. Martin-Moreno, F.J. Garcia-Vidal and T.W. Ebbesen, Science 297, 820 (2002). [3] F.J. Garcia-Vidal, H.J. Lezec, T.W. Ebbesen and L. Martin-Moreno, Phys. Rev. Lett. 90, 213901 (2003). [4] L. Martin-Moreno, F.J. Garcia-Vidal, H.J. Lezec, A. Degiron and T.W. Ebbesen, Phys. Rev. Lett. 90, 167401 (2003). [5] F.J. Garcia-Vidal, L. Martin-Moreno, H.J. Lezec and T.W. Ebbesen, Appl. Phys. Lett. (in press). [6] J. Bravo-Abad, F.J. Garcia-Vidal and L. Martin-Moreno, Photonics and Nanostructures (in press).

9:00 AM ***R3.2**

Giant Light Transmission Through Nanometer-Scale Apertures. Tineke Thio, Arinna LLC, Princeton, New Jersey.

The transmission of light through a sub-wavelength aperture in a metal film is extremely small, since the aperture acts as a waveguide beyond cutoff and the transmitted power drops exponentially with the thickness of the metal. However, when the metal surface in the vicinity of the aperture has a periodic corrugation, grating coupling allows the interaction of the incident light to surface plasmon polaritons and other evanescent modes on the metal surface which are inaccessible on a smooth metal surface. If the incident light is resonant with these modes, the effective intensity at the entrance of the central aperture can be far larger than the average intensity in the incident beam. The resulting enhanced transmission can be larger than the geometric limit (for which the light intensity at the aperture exit equals that at the aperture entrance), despite the fact that the aperture is well beyond cutoff. The transmission enhancement also occurs for periodic arrays of subwavelength apertures, where the apertures themselves provide the surface corrugation. In this talk I will discuss the physics of the transmission enhancement, and the ideal surface corrugation which yields the highest transmission enhancement. I will review potential applications of this phenomenon in near-field optical microscopy, data display devices, and sensor technology. More information at www.arinnaresearch.com

9:30 AM ***R3.3**

Polarization properties of metallic nanohole arrays. Han Woerdman, Erwin Altewischer, Martin van Exter and Cyriaque Genet; Huygens Laboratory, Leiden University, Leiden, Netherlands.

Subwavelength metal hole arrays in metal films have generated a lot of interest lately since they show anomalously large transmission of light at surface plasmon (SP) frequencies [1,2]. The SP's "live" on the two surfaces of the metal film, coupled to each other by tunneling via the holes and coupled to incoming and outgoing light beams via the momenta supplied by the array. We report here on the polarization properties of these arrays, both in a classical and a quantum context. Our classical experiments show surprising polarization behavior; in particular, we observe that the state of polarization of the outgoing light is no longer a pure state. This depolarization occurs if two conditions are fulfilled: (i) The transmission-facilitating SP's must propagate along the surfaces of the perforated metal film and (ii) The incoming light beam must have a spread of wave vectors (e.g. it must be a Gaussian beam instead of a plane wave). Using a tensorial description we find theoretically that the degree of depolarization depends on the point group symmetry of the hole array; this is confirmed by our experiments on square and hexagonal arrays. In our quantum experiments we use polarization-entangled twin photons as incoming light [2]. SP propagation along the surfaces of the perforated metal film leads then to degradation of the entanglement. This decoherence can be seen as a quantum consequence of the coupling of spatial and polarization degrees of freedom ("which way" information). We find, experimentally and theoretically, that the quantum decoherence and the classical depolarization, when expressed in "natural" units, are numerically equal. REFERENCES 1. T.

Ebbesen et al., Nature, vol. 391, pp. 667-668 (1998). 2. E. Altewischer et al., Nature, vol. 418, pp. 304-306 (2002).

10:30 AM *R3.4

Coupling from Wavelength Scale to Subwavelength Scale Photonic Structures: The Engineering Tradeoffs of Loss and Localization. Harry A. Atwater, Luke A Sweatlock, Jennifer A. Dionne and Albert Polman; Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California.

It is now apparent that excitation of localized surface plasmons on metal surfaces, in thin films and in metal nanoparticles can form the basis for optical waveguides operating either 1) below the diffraction limit, at nanoscale dimensions, with quite large attendant loss/length or 2) in smooth planar films with very low (db/cm) loss. A challenge for plasmonics is to define the engineering of waveguide circuit architectures that allow in-coupling of light into surface plasmon modes from optical sources with low coupling and propagation loss, but which also enable light localization in volumes of a few cubic nanometers, where the high (eV/nm) local electric fields may enable nonlinear phenomena to be exploited for optical switching and molecular detection. Thus a methodology is required to enable coupling from surface plasmon polariton modes in planar thin films into localized dipole surface plasmons of small particles and the dielectric gaps between metal structures. We describe recent work along these lines to define the thickness-dependent plasmon polariton dispersion relations for thin films that enable estimation of wavelength- and wavevector-dependent propagation loss and critical coupling angles from radiative free space modes. Coupling from planar thin film waveguides into nanostructure waveguides and resonators via subwavelength apertures is compared to results for tapered metal structures. Recent experimental observation of eV/nm fields in nanoparticle chain arrays, and constraints to three-dimensional plasmon waveguide circuit construction are also discussed.

11:00 AM *R3.5

Rational Design of Plasmonic Nanoarchitectures. Naomi Halas, Electrical and Computer Engineering, Rice University, Houston, Texas.

The interesting observation that some nanoscale geometries support plasmon resonances that are highly tunable, such as nanoshells or nanorods, provides a starting point for a plasmon hybridization model for predicting the plasmon response of complex geometries (Prodan et al., Science 302,419(2003)). This simple and intuitive picture shows that as geometries are made more complex, we can interpret their plasmon response as the mixing and "hybridization" of plasmons of simpler geometries, in rigorous analogy with the hybridization of electronic orbitals in molecular orbital theory. Plasmon hybridization provides a nanoscale "design rule" that guides the development of more complex plasmonic materials, either as nanostructures or in extended assemblies, with a predictable plasmon response.

11:30 AM *R3.6

The Optics of Negative Refraction. David Richard Smith and David Schurig; Physics, 0319, University of California, San Diego, La Jolla, California.

Metamaterials are artificially structured materials that rely on macroscopic scattering elements to provide tailored electric and magnetic response to electromagnetic materials. Because those materials and compounds that occur in nature do not display the full range of theoretically allowed electromagnetic response, metamaterials offer a path to developing materials with previously unrealized properties. As an example, materials with simultaneously negative permittivity and permeability-or negative index-of-refraction materials-do not occur in nature; however, by tailoring the properties of conducting scattering elements, we can produce metamaterials that possess this intriguing property. The possibility of negative refraction, first proposed by V. G. Veselago in 1968, has brought about a reconsideration of many fundamental optical and electromagnetic phenomena. Many interesting and potentially important effects not possible in positive refracting materials, such as near-field refocusing and sub-diffraction limited imaging, have been predicted to occur when the refractive index changes sign. The first experimental realization of a negative metamaterial in 2000 has prompted a remarkable effort by the physics, optics and engineering communities to explore the consequences of negative index to both fundamental wave propagation phenomena as well as devices. The negative index of refraction suggests the potential for novel compact lenses, based on geometrical arguments. The standard methods for deriving the imaging properties of a lens can be applied in the usual manner, resulting in the standard formula relating the lens radius of curvature (R) to focal length (f), $f=R/-(n-1)$. The thin lens formula, valid for lenses composed of either positive or negative index material, shows an important asymmetry: a lens with index of $n=-1$ has the same focal length as a lens with index $n=+3$, for the same radius of

curvature. This simple example shows that materials with negative refractive indices of modest magnitudes possess remarkable refractive power that can be leveraged to produce novel optics. The property of negative refraction is not restricted to isotropic media. Certain classes of anisotropic media can be found, for which not all of the permittivity or permeability tensor elements have the same sign, that can also exhibit negative refraction. While these materials are inherently reflective, compensated bilayers can be formed from positively and negative refracting anisotropic materials that will be perfectly matched to free space. Such bilayers can also be contoured into lenses, and have identical properties as lenses formed from isotropic negative index materials. Given the reduced burden of fabrication, anisotropic materials may be advantageous for lensing applications, and have the additional feature that spatial filtering functionality can be simultaneously introduced.

SESSION R4: Photonics and 3D Optical Assemblies

Chairs: John Pendry and David Taylor

Wednesday Afternoon, April 14, 2004

Room 3020 (Moscone West)

1:30 PM *R4.1

Plasmonics; Optical Frequencies, X-ray Wavelengths.

Eli Yablonovitch, Dept of Electrical Engineering, University of California-Los Angeles, Los Angeles, California.

Optical frequency electromagnetic waves, running in close proximity to a metal surface, can have surprisingly short wave-lengths, as short as 1nm. This opens the door to 1nm imaging, including plasmon lenses, and other in-plane optical components. In effect plasmon waves experience a high effective refractive index, $n > 100$, and can form a type of "immersion objective" to a conventional optical system. This is only the beginning of new science & technology that is manifested in the "plasmon regime". There are many other examples that represent major new nano-meter opportunities, new circuits, and new opto-electronic components.

2:00 PM *R4.2

Plasmonic Nanophotonics. Vladimir M. Shalav, School of E&CE, Purdue University, West Lafayette, Indiana.

Metal nanostructured materials can open new avenues for manipulating light on the nanoscale and sensing molecules. We study specially designed plasmonic structures that act as smart optical nano-antennas focusing light on nanometer scale areas, with high spatial and spectral control of the energy concentration. These nano-antennas are capable of strong enhancing a number of optical phenomena, such as the extraordinary optical transmittance, Raman scattering, nonlinear photoluminescence, Kerr optical nonlinearity, and many other important optical effects. We show that plasmonic nanoantennas open up the feasibility to detect molecules with unsurpassed sensitivity and perform lithography with nanometer spatial resolution. Plasmonic nanostructures can be employed for developing photonic nano-circuits where photons are controlled in a similar manner as electrons in conventional electronic circuits. They can also be employed for developing novel left-handed materials with negative refraction index in the optical spectral range that can revolutionize the current optics.

2:30 PM *R4.3

Concentration of Light with Photonic Crystals and Surface Plasmons. Axel Scherer¹, M. Loncar¹, B. Maune¹, T. Yoshie¹, K.

Okamoto¹, M. Adams¹ and J. Vuckovic^{1,2}; ¹Applied Physics and Physics, Caltech, Pasadena, California; ²Stanford University, Stanford, California.

Photonic crystal and surface plasmon nanocavities enable the interaction of nonlinear optical material with very high optical field intensities. For example, we have we have recently developed photonic crystal lasers, with mode volumes of one tenth of a cubic half-wavelength, that permit the introduction of analyte into the peak of the optical field of a lasing mode. Such nanocavity lasers can be used to perform spectroscopic tests on femtoliter volumes of analyte - enabling the optical trapping and interrogation of small particles - and are expected to ultimately lead to single molecule spectroscopy. Metal nanostructures enable the construction of even smaller optical cavities with even higher optical fields. By careful design and fabrication, high quality optical resonators with ultra-small mode volumes have been constructed and optimized to achieve the highest possible optical fields. Here we describe the design, fabrication and characterization of a new class of opto-fluidic devices in which light is concentrated to high fields to efficiently interact with small volumes of material. When combined with nonlinear optical polymers, such photonic crystal and plasmon nanocavities will lead to very compact optical modulators or tunable filters with high efficiencies and modulation frequencies.

3:30 PM *R4.4

Self-Assembled 3-Dimensional Photonic Crystal Waveguides.

Kang-Hyun Baek and Anand Gopinath; Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Photonic crystals with photonic bandgaps are expected to be used in the variety of applications including optical filters and very low threshold lasers, and have been investigated widely. Of special interest are three-dimensional photonic crystals, which may have lower loss than two-dimensional photonic crystals of the slab type. In general, the fabrication processes of photonic crystals require the use of semiconductor nanofabrication techniques. An alternative fabrication method for photonic crystals takes the form of self-assembled crystalline structures using colloidal spheres. The crystalline structure, opal, which has a hexagonal closed-packed or face centered cubic lattice, may be removed after infiltration with high refractive index material to obtain the inverse opal, which has a complete three-dimensional photonic bandgap. In this paper, we discuss a self-assembled three-dimensional photonic crystal waveguide with a Si₃N₄ layer as the guide layer and a three-dimensional photonic crystal as a cladding. The colloidal crystal cladding has a pseudo-stop band at 1550 nm wavelength, and is formed by self-assembled silica spheres of 710 nm diameters. Subsequent experiments will convert this opal cladding into an inverse opal. To obtain silica spheres with required diameters and narrow size distributions, the seeding technique based on the modified Stober method was used in the chemical synthesis of silica spheres. Also, to reduce aggregations and adhesions between the spheres which result in structural defects and dislocations in the photonic crystal, we have developed an effective method for the synthesis of silica spheres using slow stirring and sphere collection with a centrifuge, using the relative difference of sedimentation velocity between singles and undesired sphere aggregates. The high quality silica spheres colloidal suspension of 0.5 % by volume was prepared in the ethanol to initially coat a silicon substrate. The coating method using capillary force at a meniscus and convection of the colloidal suspension by heating to avoid the sedimentation of silica spheres was used in inducing uniform crystallization of silica spheres. Under optimized coating conditions, including the evaporation temperature and declined substrate angle in the colloidal suspension, we obtained very uniform crystals with 18 silica sphere layers on 1 cm by 3 cm silicon substrate. After coating the optical waveguides under the same conditions, we determined that the crystalline opal structure had few defects. This paper will discuss the results of this fabrication technique, and measurements of the losses in these photonic crystal waveguides. Time permitting, we will also discuss the inverse opal waveguides.

4:00 PM R4.5

Three-dimensional photonic structures with nano-order resolution of titanium dioxide. Koichi Awazu¹, Akihhide Sai², Yoshimichi Ohki², Mokoto Fujimaki², Hiroaki Imai³ and Xiaomin Wang¹; ¹CAN-FOR, AIST, Tsukuba, Ibaraki, Japan; ²Electrical Engineering and Bioscience, Waseda University, Tokyo, Tokyo, Japan; ³Chemistry, Keio University, Tokyo, Kanagawa, Japan.

We report on fabrication of three-dimensional photonic structures in PMMA resist and their use as porous templates for transferring three-dimensional patterns to titanium dioxide. Following the original gthree drilling holes approach first proposed by Yablonovitch. The technology employs X-ray lithography methods based on synchrotron radiation to deeply and precisely form a submicron-order mask. A submicron patterning with hole diameter 400nm was thus obtained in 5micron thick PMMA layer. Titanyl sulfate (TiOSO₄·xH₂O, x=4.6) was used for preparation of supersaturated solutions for poly-crystalline TiO₂. An aqueous solution at 0.01M TiOSO₄ prepared by adding TiOSO₄ into a hydrochloric solution at pH 0.50 for growth of rutile TiO₂ crystal. Anatase TiO₂ was deposited in the TiOSO₄ precursor solution containing 2.0M urea. PMMA templates were immersed in the precursor solutions. After immersion for appropriate reaction time at 60C, TiO₂-loaded PMMA templates were rinsed with purified water and dried at room temperature. TiO₂ micro-array was obtained by dissolving PMMA with ethyl acetate. Photonic band gap was also examined by optical characterization. Titanium dioxide, the material used to form these photonic crystal structures, transmits light in the waveband of optical communication better than silicon and other semiconductors. Furthermore, the refractive index of the compound is near that of fiber optics, making it compatible with the latter. This feature translates into a much lower loss during device I/O, making titanium dioxide essential in the development of photonic devices for next-generation photonic networks. Finally, titanium dioxide has a lower coefficient of thermal expansion than semiconductors; regulating the temperature of TiO₂ devices is simple. The research involved with this project was made possible through funds from the Atomic Study Research Funding of the Ministry of Education, Culture, Sports, Science, and Technology based on an assessment of the Japanese Atomic Energy Commission.

4:15 PM R4.6

Fabricate Photonic Crystals Based on ZnS/opal System via Solvothermal Method.

Jieming Cao, Xin Chang, Lijia Pan, Hongmei Ji, Jinsong Liu, Jie Feng, Fang Zhang, Haiyan Wang, Jie Tao and Guoyue Xu; Nanjing University of Aeronautics and Astronautics, Nanjing, China.

In the past decade, a new optical materials called photonic crystals (PCs), which can offer many interesting applications in photonics and electronics[1], have attracted considerable attention since the original idea was kicked off by Yablonovitch[2] and John[3] independently. Self-assembly of colloidal crystals has emerged as a cost-effective route to fabricating 3D photonic bandgap (PBG) materials[4]. ZnS can be used as an appropriate candidate for forming PCs due to its high refractive index. In this paper, the artificial FCC crystal named as opal, which was formed by natural sedimentation of monodisperse silica spheres synthesized following the Stober method[5], was used as a 3D scaffold template for ZnS semiconductor nanocrystals embedded in the template with a novel and efficient solvothermal technique. We show here that the solvothermal method has several advantages over previous techniques and is a workable method to fill the opal interstices with ZnS in an attempt to modify the photonic properties. The samples were characterized by means of XRD, Raman spectroscopy, SEM and optical transmission spectra. We found the as-synthesized ZnS nanocrystals reveal a cubic phase and a small diameter of about 4nm from XRD pattern. Therefore, in the ZnS/opal system the size of nanocrystals is very small in comparison of the void dimensions to have the uniform periodicity required for PCs. Raman spectrum indicates that the semiconductor crystalline quality is fairly good. The SEM images show that the opals with diameters of 200nm and 350nm exhibit a well-ordered and close-packed arrangement and the ZnS nanocrystals are more homogeneously distributed inside the matrix via solvothermal synthetic route. Consequently, we supposed the 3D periodicity of opal host can be replicated by the guest material ZnS under the solvothermal condition. Moreover, the photonic properties of the pure and different ZnS filling ratio infiltrated opals were studied by transmission spectroscopy. It can be seen clearly that the PCs composed of ZnS and opal in our experiment exhibit a near IR PBG in the Γ -L direction of the Brillouin zone. As expected, after more infiltration the Bragg peak shifts to longer wavelengths due to an increase in the average refractive index. Such 3D structure of ZnS/opal system synthesized by solvothermal method is reported for the first time. The composite materials system is believed to control the emission properties of phosphors in the PCs and have potential applications in optoelectronic devices and host-guest chemistry. References 1. P. RUSSELL, Science 299 (2003) 358. 2. E. YABLONOVITCH, Phys. Rev. Lett. 58 (1987) 2059. 3. S. JOHN, Phys. Rev. Lett. 58 (1987) 2486. 4. Y. XIA, B. GATES, Z. LI, Adv. Mater. 13 (2001) 409. 5. W. STOBER, A. FINK and E. BOHN, J. Colloid Interface Sci. 26 (1968) 62.

4:30 PM *R4.7

Photonic Crystals in Wide Band Gap Semiconductors.

Armand Rosenberg, Naval Research Laboratory, Washington, District of Columbia.

An important advantage of photonic crystals is the scalability of their optical properties to any portion of the spectrum. This concept enables the design of opto-electronic devices, based on photonic crystal concepts, whose functionality is independent of the intended operational wavelength. Thus, the wavelength can be chosen after the design is essentially complete. Although this is conceptually achieved through an appropriate scaling of the physical dimensions, in practice one must overcome materials issues to realistically achieve such scaling. In particular, if the optical properties of the materials involved change significantly over the scaling range, the scaling is invalidated and a new design is required. This can happen whenever the optical properties are modified through the presence of such phenomena as band gaps, other electronic levels, strong dispersion, etc. In order to avoid these effects and to allow us to take full advantage of the inherent scaling properties, we must fabricate photonic crystals from materials that have relatively constant optical properties over broad spectral regions. An important class of such materials is the wide band gap semiconductors, including diamond, gallium nitride, silicon carbide, et al. However, each of these materials presents specific opportunities and challenges in terms of photonic crystal fabrication and applications. This talk will describe some of our efforts to demonstrate photonic crystals, as precursors to opto-electronic devices, in wide band gap semiconductors.

[Acknowledgment: This work is being done in collaboration with Vasgen A. Shamamian, Charles R. Eddy, James E. Butler, Jae Y. Choe, and Dennis W. Prather.]

R5.1

Electrochemical Fabrication of Porous Magnetic Nanostructures. Li Sun¹, Peter C Season² and Chia-Ling Chien³; ¹Department of Mechanical Engineering, University of Houston, Houston, Texas; ²Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ³Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland.

Using Ni-Cu as a model system, we demonstrate that three dimensional nanoporous magnetic structures can be fabricated by electrodepositing NiCu alloys and subsequently leaching out the Cu in the same aqueous solution electrochemically. By adjusting the deposition condition, alloys with controllable Ni concentration have been fabricated. Structural and magnetic characterizations confirm the homogeneity of the alloys. Composition, lattice parameters, spontaneous magnetization and Curie temperature of the alloys can be precisely controlled by varying electrodeposition conditions. Due to the surface passivation of Ni, chemically more stable Cu can be removed by anodic polarized current and results in nanoporous Ni sponge. Our study shows the dealloyed material exhibits structurally related enhanced coercivity and modified magnetization anisotropy compare to uniform alloys. The electrochemical co-deposition and selective etching process provides new approach to nanomaterial fabrication to alter material properties.

R5.2

Patterning and Reactive ion etching of Diamond Films using Light Coupling Masks. Patrick William Leech¹, Geoff K Reeves² and Anthony S Holland²; ¹CMIT, CSIRO, Clayton, Victoria, Australia; ²School of Computer Systems and Electrical Engineering, RMIT University, Melbourne, Victoria, Australia.

The ability to pattern and selectively etch diamond on a very fine scale has become essential in producing new types of sensors and electronic devices. This work examines the novel application of light coupling masks (LCMs) in the patterning of fine structures in diamond films. The soft lithography technique of near-field contact-mode lithography was used with a PDMS mask to form complex patterns of gratings in AZP 1205 resist on Al/diamond. The profiles of these grating patterns were then modified on a localised scale by a process of reflow of the resist. We report on the etching transfer of the patterns formed by the LCMs into the diamond film using a sputtered Al layer as a mask. Various parameters of etching were studied in order to achieve the highest selectivity of the mask in relation to diamond. In a first series of experiments, the etch rates were measured in SiCl₄/Cl₂ gases to enable the initial patterning of the Al from the resist. The comparative etch rates of the diamond, resist and Al were also measured in CF₄/O₂ and CHF₃/O₂ gases. The etch rate of diamond was linearly dependent on the square root of bias voltage in both gas mixtures. The selectivity of etch rates for Al/diamond was increased with O₂ concentration (0-12 sccm); this effect was greater in CF₄/O₂ than in CHF₃/O₂ gases. The grating structures (with pitch 0.7-1.3 microns) fabricated using the LCMs were characterised by scanning probe microscope. The application of these results using LCMs to finer scale patterning in diamond will be discussed in the paper.

R5.3

Anatase Inverse Opal: Preparation and Electrochemical Properties. Marketa Zukałova, Martin Kalbac and Ladislav Kavan; J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic.

Anatase inverse opal is a solid with highly ordered macroporous structure over a large area, which has attracted considerable interest recently(1-4). High refractive index of the wall material together with a pore size of hundreds of nanometers (comparable to the wavelengths of visible light) are responsible for photonic crystal properties. Owing to its ability to inhibit the range of wavelengths from propagation through the material over all directions, this unique structure offers many applications in the field of sensors, optoelectronics, chromatography, and photocatalysis. This paper aims at preparation, characterization, and electrochemical investigation of anatase inverse opal, either in form of powder or in thin layer. The material was characterized by SEM, TEM, XRD, nitrogen adsorption, UV-Vis spectroscopy, and lithium insertion electrochemistry.

Acknowledgement: This work was supported by Grant Agency of the Czech Republic, contract No. 203/03/0824. 1. Schroden, R. C.; Al-Daous, M.; Blanford, C. F.; Stein, A. Chem.Mater. 2002, 14

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R5.4

Investigation of Layer-by-Layer Assembly of Colloid Crystals on a Template Pattern. Sonia Grego, Thomas Jarvis, Brian R Stoner and Jay S Lewis; MCNC - Research & Development Institute, Research Triangle Park, North Carolina.

One of the major limitations of self-assembled colloid crystal structures is the difficulty of inserting a defect layer or defect structure within the crystalline arrangement. We have investigated the fabrication of a 3D colloid crystal assembled in layer-by-layer fashion on a template substrate. Such method of assembling an ordered structure offers flexibility in the choice of crystal orientation, because of the template, and in the insertion of "defect" layers, because of the layer-by-layer deposition. A defect layer is capable of introducing defect modes in the band gaps of the crystal and could be used for sensing application. We used template substrates fabricated on silicon by photolithography and DRIE etching with square symmetry [i.e. with (100) planes parallel to the substrate] for beads with diameter 1 μm and 4.4 μm . We studied the assembly of layers of polystyrene microspheres on the micropatterned substrates using a combination of evaporation and chemical binding and we observed that the ordering process depends on parameters of the physical pattern such as hole size and depth. In order to achieve a robust multilayer structure we investigated the effects of different chemical coating of the substrate and of the functionalization of the beads. We found a convenient method of patterning polyelectrolytes from aqueous solution to achieve a strong bond between the first ordered layer of beads and the substrate. We observed that efficient binding is an obstacle in achieving crystalline 2-D arrays above the first layer and investigated the tunability of the bond strength. This work was partially supported by DARPA through SPAWARSYSCEN Grant Number N66001-03-1-8900.

R5.5

Construction of low-dimensional surface patterns using nanoscale objects. Siu-Tung Yau, Physics, Hunter College of City University of New York, New York, New York.

We describe two simple and versatile techniques for constructing nanoscale patterns on a solid surface using nanoscale objects such nanoparticles and protein molecules. Each technique is based on a two-step process. These techniques can be used to generate architectural structures on a solid surface on various length scales. The first technique depends on physical processes between a colloid of nanoparticles and a hydrophobic surface that contains relief patterns. The effects of sedimentation of particles and of dewetting of the surface result in deposition of nanoparticles only within the patterns. This method has been used to generate spatially confined monolayers of nanoparticles, to assemble a small number of particles to each point of a 2D array and to construct 1D chains of interconnected particles on a surface. The second technique is essentially inlaying a solid surface using nanoscale objects. This mechanical approach provides anchorage for nanoscale objects so that they are secured firmly on a surface while forming patterns. To demonstrate this approach, we used inorganic nanoparticles and protein molecules to inlay silicon surfaces. We have characterized the interfacial electron transfer between the protein molecules confined in a pattern and the silicon wafer that contains the pattern using cyclic voltammetry.

R5.6

Ab-initio Structural Properties and Stress-Deformation Analysis by Rheological Modeling of Diamonds-containing Nanocomposites. Maksim V Kireitseu, ¹Department of Mechanics and Composites, Institute of mechanics and machine reliability, Minsk, Belarus; ²Composite materials research LAB, University of New Orleans, New Orleans, Louisiana.

The principal goal of the paper is to study fundamentally pure interfaces diamond-like C / metal or polymer structure (matrix). Diamonds nanoclusters with effective sizes between 2 nm and 50 nm were used. The present work describes study of stable atomic structure of diamond-like nanoclusters embedded into metal or polymer matrix. Diamond nanoparticles have spherical, fullerene or pyramidal-type shapes and diamonds fibers as well. Local structure deformation (rearrangement) of diamonds/metal interfaces was principal object of researches. Energy or band structure and density of electronic states analysis was investigated. Possible defect or surface states were described. Ab initio LCAO (HF or DFT) schemes, LASTO (Linear augmented Slater-type orbital method), MLASTO (Modified linear Slater-type orbital method), ab initio DFT LDA (FLAPW, LASTO, pseudopotential) super cell schemes and semi

empirical LCAO (AM1, PM3, PM5, etc.) methods were used for diamonds nanoclusters with effective size less than 2 nm. It was found that embedded diamonds might be reconstructed in a fullerene-like manner. Fundamental parameters for tight-binding and molecular dynamics calculation schemes were further based on computer simulation at each direction can be easily developed for better understanding and faster calculations. Study of size dependent mechanical and structural properties revealed at what scale principal fundamentals may give reliable explanations at examining fracture mechanics of nanostructured composites. The core of principal Newtons fundamentals was combined with developed rheological modeling technique for describing correlation between stress and deformation of nanostructured coatings. Analysis of the models and experimental results revealed better understanding of nanocomposites failure and degradation mechanics. Stresses and deformations depend upon the state of the surfaces, its roughness and the fundamental mechanical properties of the two solids that are both indenter and substrate. Mechanical behavior between the coatings and another solid nanoindenter are discussed from a theoretical consideration of the mechanical constants (elasticity, plasticity and viscosity) of the coatings and experimentally by relating loading forces and stresses to the interface resulting from the contact.

R5.7
Effects of Rapid Thermal Annealing on the Microstructural and Optical Properties of Self-Assembled InAs/GaAs Quantum Dots. Kyu Hyung Lee¹, Ho Seong Lee¹, Jeong Yong Lee¹ and Tae Whan Kim²; ¹Dep. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea; ²Division of Electrical and Computer Engineering, Hanyang University, Seoul, South Korea.

Self-assembled quantum dots (QDs) fabricated by the Stranski-Krastanov (SK) method have attracted much attention due to potential applications of this material in optoelectrics devices, such as QD lasers and infrared photodetectors. The tuning of the QD interband transition energy is important in device applications. Usually, this can be achieved by adjusting the shape or the size of QDs, by changing the material of the QD or barrier, by changing barrier thickness, and by high-temperature annealing of QDs. In our works, high-temperature annealing was used to tune the interband transition energy. This method is usually performed in rapid thermal annealing (RTA) system with SiO₂ capping or proximity capping. The structure investigated in this study was grown by molecular beam epitaxy (MBE). After growth of the GaAs buffer layer at 580°C on (001) GaAs s.i. substrate, the temperature was lowered to 460°C and self-assembled InAs QDs were grown in Stranski-Krastanov mode. Then, the temperature was increased to 500°C while growing 50nm of the GaAs capping layer. Samples were proximity capped and RTA treated in nitrogen ambient for 60s at 650, 700, 750, 800, and 850°C. The effects of rapid thermal annealing (RTA) on self-assembled InAs/GaAs quantum dots (QDs) has been investigated by using transmission electron microscopy (TEM) and photoluminescence (PL) measurements. The TEM images show that the lateral size of the InAs/GaAs QDs increases with increasing annealing temperature. When the InAs/GaAs QDs are annealed, the peak, which is related to interband transitions from the ground electronic subband to the ground heavy-hole subband, shifts to higher energy resulting from thermally induced strain relaxation due to RTA treatment. The strain relaxation in the InAs QDs due to thermal treatment leads to enhancement of the In/Ga interdiffusion in InAs/GaAs QDs, which significantly affects the microstructural and optical properties of the InAs/GaAs QDs. These results can help improve the understanding of the thermal annealing effect on the microstructural and optical properties of InAs/GaAs QDs

R5.8
Nanoparticle-Mediated Epitaxial Assembly of 3-D Photonic Crystals on Patterned Substrates. Wendy W. Chan, Wonmok Lee, Angel Chan, Summer K. Rhodes, Jennifer A. Lewis and Paul V. Braun; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We have studied the assembly of 3-D colloidal crystals from binary microsphere-nanoparticle mixtures on flat and epitaxially patterned substrates created by focused ion beam milling. 1.18 μm, 750 nm, and 520 nm colloidal microspheres were settled on these substrates from dilute binary mixtures that also contained 3 nm zirconia nanoparticles. Upon settling, the nanoparticle solution surrounding the colloidal crystal was gelled in situ by introducing ammonia vapor, which increased pH and enabled drying with minimal structural rearrangement. Laser scanning confocal microscopy was used to directly observe the structural evolution of the colloidal crystals during sedimentation, gelation, and subsequent drying. UV-Vis-NIR spectroscopy was additionally used to study the evolution of optical properties over these three stages. By infilling the dried colloidal crystals with an index-matched fluorescent dye solution, we generated

full 3-D reconstructions of their structure including both vacancies and line defects as a function of initial suspension composition and pitch of the patterned features. Through proper control over these important parameters, 3-D colloidal crystals were created with low defect densities suitable for use as templates for photonic crystals and photonic band gap materials. Preliminary results on the infilling of these colloidal crystals with silicon through CVD, and other routes to increase the refractive index contrast as required for photonic band gap applications will also be presented.

R5.9
Three-stage Nucleation and Growth of Ge Self-Assembled Quantum Dots (SAQDs) Grown on Partially Relaxed SiGe Buffer Layers. Hyung-jun Kim, Zuoming Zhao and Ya-Hong Xie; Materials Science and Engineering, University of California Los Angeles, Los Angeles, California.

Three-stage nucleation and growth of Ge self-assembled quantum dots (SAQDs) on a partially relaxed SiGe buffer layer has been investigated. Plastic relaxation of the SiGe buffer layer is associated with a network of buried 60 degree dislocations leading to an undulating strain field. As a result, the surface possesses three different types of sites for the nucleation and growth of Ge SAQDs: over the intersection of two perpendicular buried dislocations, over a single dislocation line, and in the region beyond one diffusion length away from any dislocation. Ge SAQDs are observed to nucleate exclusively over the dislocation intersections first, followed by over single dislocation lines, and finally in the region far away from dislocations. By increasing the Ge coverage at a slow rate, the pre-nucleation stage at the various sites is observed. It appears that the varying strain field has a significant effect on both the diffusion of Ge adatoms before SAQD nucleation, as well as the shape evolution of the SAQDs after they form. Moreover, two distinctly different self-assembly mechanisms are observed at different sites. There exist denuded zones free of Ge SAQDs adjacent to dislocation lines. The width of the denuded zone can be used to make direct determination of the Ge adatom diffusion lengths. The partially relaxed substrate provides a useful experimental vehicle for the in-depth understanding of the formation mechanism of SAQDs grown epitaxially in Stranski-Krastanov (SK) growth mode.

R5.10
Optical Reflectivity Measurements on Opal-Based Metallo-Dielectric Photonic Crystals. Vladimir Kamaev¹, Alexandre Pokrovsky¹, Valy Z Vardeny¹, Alexei Efros¹, Dmitry Kurdyukov² and Valery Golubev²; ¹physics, University of Utah, Salt Lake City, Utah; ²Ioffe Institute, St. Petersburg, Russian Federation.

Theoretical calculations show that metallo-dielectric photonic crystals have relatively broad frequency bands of forbidden EM modes and narrow frequency bands of allowed modes, provided that the metallic absorption is small in these spectral regions. Theory also predicts that below a certain cut-off frequency, ω_c , EM waves cannot penetrate into the metallo-dielectric photonic crystal. We have successfully fabricated opal photonic crystals infiltrated with metals such as Ag, Cu, In and Pb and measured their reflectivity spectra in a broad spectral range from 0.3 μm to 25 μm. The opals were grown by sedimentation of monodispersed silica balls with 0.245 μm, 0.285 μm and 0.550 μm diameters, respectively. In and Pb infiltrated opals were fabricated by placing the opal templates into the melted metals, while applying high pressure and subsequent crystallization. The metal filling factor, f , of the voids in the opal templates for these two samples were estimated to be about 100%. Ag and Cu were deposited into opals by means of electrolysis with f of about 60%. The reflectivity spectra in the UV, visible and NIR spectral ranges were measured using a conventional monochromator set up, whereas the reflectivity in the MIR spectral range was obtained using a FTIR spectrometer. We found that the reflectivity, R , of all samples is low at high frequencies; at frequencies lower than ω_c , which is about 1 eV, R increases rapidly to reach a sample dependent saturation value, which scales with f . ω_c itself depends on the photonic crystal periodicity, f , and the particular metal used. In addition, at frequencies higher than ω_c (visible spectral range) we found several stop band structures with low R due to the metal absorption in the visible range.

R5.11
Abstract Withdrawn

SESSION R6: 3D Nanomaterials and Structures in
 Biotechnology and Biomimetics
 Chairs: Lhadi Merhari and David Taylor
 Thursday Morning, April 15, 2004
 Room 3020 (Moscone West)

8:30 AM *R6.1
Hybrid Protein-based Frameworks for the Creation of

Inorganic Structures. Rajesh R. Naik¹, Ryan M. Kramer¹, Dan Carter², Chester Li², Lawrence L. Brott¹, Sophie M. Rozenzhak¹, Laura A. Sowards¹, Francisco Rodriguez¹ and Morley O. Stone¹;

¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio; ²New Century Pharmaceuticals, Huntsville, Alabama.

Biological systems have mastered the ability to sum numerous intra-inter-molecular interactions to promote self-assembly, usually following very specific pathways and rules. Additionally, this self-assembly is often hierarchical in nature with organized length scales spanning several orders of magnitude. In this work, we have chosen to exploit biology's ability to self-assemble by incorporating additional functionality, in the form of metal and semiconductor nucleating peptides, within the final structure. In previous work, we have demonstrated how peptides can be selected from a combinatorial phage display 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. On-going work will be presented that examines hybrid structures based on viral and metal-transport protein architectures and the controlled deposition of these structures.

9:00 AM *R6.2

Biologically-derived Three-Dimensional Nanostructured Silica from Diatoms. Mark Hildebrand, Marine Biology Research Division, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California.

The unicellular algae known as diatoms make three-dimensional nanoscaled silica structures as part of their cell walls. Each of the tens of thousands of diatom species has unique silica morphology; hence diatoms have a tremendous ability to make complex three-dimensional silica structures, and do so under ambient conditions. The mechanism of silica structure formation in diatoms is fundamentally different from current manufacturing techniques, and is largely controlled by expansion and molding of an internal cellular compartment known as the silica deposition vesicle. We are investigating the process of cell wall silicification in diatoms, currently focusing on the species *Thalassiosira pseudonana*. We have developed methods to grow cells synchronously, enabling us to follow the step-by-step progression of cell wall synthesis, and to enrich for cells in the process of wall formation. Intermediate structures in cell wall formation have been identified by scanning electron microscopy, which, when coupled with similar studies in other species, are enabling us to reconstruct the process of cell wall formation. In addition, we are examining the process at the molecular level. *T. pseudonana* is the first diatom species to have its genome sequenced, and the genome information is being used to apply high throughput proteomic and genomic approaches to isolate proteins and genes involved in silicification. Identifying silicification genes and proteins is the first step toward understanding the underlying mechanisms of silica structure formation, and could lead to genetically modifying silica structure to suit specific materials or device applications. Diatom silica can be converted, with maintenance of detailed structure, into other materials, extending possible materials or device applications.

9:30 AM *R6.3

A Hybrid (Biogenic/Synthetic) Route to 3-D Nanoparticle Assemblies with Tailored Chemistries: The Bioclastic and Shape-Preserving Inorganic Conversion (Basic) Process.

Ken H. Sandhage¹, C. Gaddis¹, M. Dickerson¹, S. Allan¹, P. Graham¹, S. Shian¹, M. Weatherspoon¹, Y. Cai², R. R. Naik² and M. O. Stone²; ¹School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Biotechnology Group, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

Nature provides elegant examples of organisms that generate three-dimensional (3-D) structures with complex patterns from the macroscale to the nanoscale. For example, diatoms are single-celled aquatic microorganisms that possess intricate microshells (called frustules) comprised of 3-D assemblies of amorphous silica nanoparticles. Each diatom species assembles a frustule with a unique shape and/or a unique pattern of fine, meso-to-nanoscale features (pores, channels, protuberances, etc.). Given that the number of extant diatom species is 10^4 - 10^5 , a dazzling variety of frustule morphologies can be found in nature. Diatom reproduction under ambient conditions can yield enormous numbers of offspring with similar frustules (e.g., 80 sustained reproductions of a single parent diatom would yield $2^{80} = 1.2$ trillion trillion, or more than Avogadro's number, of descendent diatoms). Such genetically-precise, massively-parallel, and direct generation of 3-D nanoparticle structures has yet to be equaled with man-made processes. However, although diatom frustules may possess shapes and fine features

appropriate for micro/nanodevices, the use of such natural frustules is limited by the properties of amorphous silica. To expand the range of applications, a novel method has been invented to change the frustule chemistry while preserving the frustule morphology: the BaSIC (Bioclastic and Shape Preserving Inorganic Conversion) process. Such shape-preserving conversion has been accomplished with the use of gas/solid displacement reactions (e.g., oxidation-reduction and metathetic reactions) and coating methods. Reaction sequences and nanostructural evolution associated with chemical conversion will be discussed in this talk. The micro/nanostructures of such converted frustules have been examined by electron microscopy (SEM, TEM). Focused ion-beam milling has also been used to provide 3-D views of internal structures of starting and converted frustules. By coupling the attractive characteristics of biology (precise, massively-parallel, and direct generation of 3-D nanoparticle structures) with those of synthetic processing (low-temperature syntheses of a wide range of compositions), the BaSIC process can yield micro/nanostructures with 3-D tailored shapes and chemistries for a host of applications.

10:30 AM *R6.4

Atomic Force Microscopy Applications to Neuroscience.

Helen A. McNally, Center for Paralysis Research, Purdue University, West Lafayette, Indiana.

In this research, Atomic Force Microscopy (AFM) is used for the investigation of living neurons. Three-dimensional images of developing and dying neurons have been obtained, providing neuroscientists their first detailed views of these dynamic structures. The unparalleled resolution provided by AFM reveals dorsal root ganglion (DRG) cells to be more complex and variable than anticipated. AFM is also used to physically contact/manipulate the cell, perturbing its development or to measure physiologically important parameters such as surface pressure. Neural cell damage is induced by the AFM tip which is subsequently used to image the morphological response of the cell. A 3-D view of the collapse of a neural cell due to this insult suggests alternative ideas concerning acute neuronal (cellular) sealing and repair. Repair of the injured neuron using electric fields and biomolecules is also investigated, supporting clinical trials for paralysis research. AFM force measurements are used to monitor cellular activity and membrane interactions during these various stages of the neural cell life cycle. The full versatility of AFM will be applied to further the understanding of neurogenesis and neurotrauma.

11:00 AM R6.5

Tailoring Nanoparticles for Biomolecular Detection.

Molly M Miller and Anne A Lazarides; Mechanical Engineering Materials Science, Duke University, Durham, North Carolina.

The effect of a dielectric medium or layer on the optical properties of an SPR-supporting planar interface has been well studied and quantified. More recently, corresponding environmental sensitivity has been observed in the optical properties of nanoparticles, making them important candidates for nanoscale molecular sensing applications. However, the levels of sensitivity and the sensing volumes of nanoparticles vary widely as a function of particle shape, size, and composition. Here, we report on the particle size and composition dependence of the sensitivities of plasmon bands of single component nanospheres and of core/shell particles to dielectric surface layers. Sensitivities are explained in terms of the intensities and geometric extent of the enhanced local electromagnetic fields. We then demonstrate how systematic studies of the relationships between particle properties and surface layer sensitivities can lead to rules for tailoring nanoparticle design to specific target molecule sensing applications.

11:15 AM *R6.6

Microfluidics and Beyond - Devices for Applications in

Biotechnology - . Martina Daub, Rolf M Kaack, Oliver Gutmann, Chris P Steinert, Remigius Niekrawietz, Bas de Heij, Peter Koltay and Roland Zengerle; IMTEK - Institute of Microsystem Technology, University of Freiburg, Freiburg, Germany.

For the performance of certain analytical and diagnostic tasks in modern life science applications high throughput screening (HTS) methods are essential. Miniaturization, automation and parallelization allow to decrease costs of expensive materials and lead to faster analyzing times. The miniaturization of total assay volumes by the use of microtiter plates as well as the microarray technology have revolutionized the field of biotechnology and life sciences. Neither printing of microarrays with droplet volumes of several picoliters, nor handling of precious enzymes in the upper nanoliter range can be accomplished with traditional liquid handling devices like air displacement pipettes. The development of novel low volume liquid handling devices, which are subject to current research, addresses the diverse requirements shifting steadily to lower volumes. Various novel non-contact dispensing methods in the nanoliter and picoliter range

are presented and classified according to their working principles like air displacement and direct displacement methods (TopSpotTM, NanojetTM, Dispensing Well PlateTM). Properties of the various methods are compared in terms of flexibility, integration density, speed of operation, precision, addressable volume range and amenability to multi-parallel operation. By integrating processing steps of biological assays within these novel non-contact dispensing dispensers multifunctional Lab-on-a-chip (LOAC) devices can be developed. A prototype of such a flexible and modular application platform (nanoMAP) was developed. This platform enables to perform various processing steps (e.g. PCR, purification) in one chip with subsequent probe transfer into another chip with a different functionality (e.g. detection). This basically points into the direction to reach new functionalities by combining advantages of novel low volume liquid handling devices with LOAC applications. The LOAC work was supported by grants from the German Ministry of Science and Technology (BMBF) in the field of Nanobiotechnology (nanoMAP 0312001D).

11:45 AM R6.7

Effects of the presence of nanotubes on heat transfer in microfluidics. Nishitha Thummalu and Dimitrios V Papavassiliou; Chemical Engineering and Materials Science, The University of Oklahoma, Norman, Oklahoma.

The drive for technical advancements in the micro/nano world, emerging from the desire to manipulate flow fields at smaller and smaller scales, is indeed challenging. Heat transfer in microscales involves absorption of heat from a confined space by a conducting medium and subsequent convection by the flowing fluid. This type of mechanism has potential applications in a variety of technologies like space, microelectronics, micro channels, heat exchangers and bioreactors to name, but a few. An effective and reliable numerical tool for the analysis of transport properties in microfluidics is the Lattice Boltzmann Method (LBM). It can efficiently link the microscopic and macroscopic phenomena. Our group is using LBM to simulate single phase flow in different configurations (e.g., channel flow, flow through porous media). The paper will focus on the simulation of heat transport from surfaces that are covered by nanotubes. The high thermal conductivity of these nanosources makes them a good choice for a conducting medium. They can be vertically aligned as line sources of heat or placed on the surface of the channel as point sources. Lagrangian Scalar Tracking (LST) methods are used to track the trajectories of heat particles released in the flow field, and to synthesize the behavior of the mean temperature profile from the behavior of the instantaneous sources of heat. The effect of the presence of nanotubes on the heat transfer characteristics will be discussed.

SESSION R7: Fabrication and Applications of
Nanotubes, Nanowires and Nanosprings
Chair: David Mc Ilroy
Thursday Afternoon, April 15, 2004
Room 3020 (Moscone West)

1:30 PM *R7.1

Synthesis, Physical Properties, and Applications of Aligned Carbon Nanotubes. Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts.

Periodically aligned carbon nanotubes have many potential applications in electronics, optics, etc. In this talk, I will first discuss the growth of aligned carbon nanotubes by plasma enhanced chemical vapor deposition on Ni films by magnetron sputtering, periodic Ni dots by e-beam lithography, random Ni dots by electrochemical deposition, and large-area periodical Ni dots array by nanosphere self-assembly. Then I will discuss a variety of applications as field emitters, biosensors, photonic band gap crystals, etc. And finally I will talk the recent study on nanoantenna phenomenon observed on these arrays.

2:00 PM R7.2

Nano-scale surface patterning Using Interfacial Surface Grooves. Moneesh Upmanyu^{1,2} and Paul Martin³; ¹Engineering Division, Colorado School of Mines, Golden, Colorado; ²Materials Science Program, Colorado School of Mines, Golden, Colorado; ³Mathematical and Computer Sciences, Colorado School of Mines, Golden, Colorado.

Theory of surface grooves formed when an interface intersects a free surface has been well known. Surface profile evolution can occur due to surface diffusion and/or evaporation-condensation. In this talk, we present a theoretical analysis of surface profile evolution due to a periodic array of interfacial grooves. We solve the surface profile evolution due to both surface diffusion, as well as evaporation-condensation. Theoretical analysis of a triple junction

groove profile is also presented. The thermal stability of such a methodology for surface patterning using interfacial surface microstructures and its potential for surface assembly is discussed.

2:15 PM R7.3

Macroscopic Neat SWNT Fibers from Liquid Crystalline Dispersions. Virginia Angelica Davis^{1,2}, Hua Fan², Nicholas Parra-Vasquez^{1,2}, Lars Ericson², Valentin Prieto¹, Sivarajan Ramesh², Carter Kittrell², Joey Sulpizio², Karen Winey³, Jack Fischer³, Robert Hauge², Matteo Pasquali^{1,2} and Richard Smalley²; ¹Chemical Engineering, Rice University, Houston, Texas; ²Center for Nanoscale Science and Technology, Rice University, Houston, Texas; ³Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Macroscopic Single Walled Carbon Nanotube (SWNT) fibers have been produced by spinning liquid crystalline dispersions of SWNTs in superacids. The direct protonation of the SWNT sidewalls overcomes van der Waals interactions, promoting the dispersion of high concentrations of SWNTs. At very low concentrations, the SWNTs dissolve as individuals which behave as Brownian rods. At intermediate concentrations, the dispersion consists of an isotropic phase in equilibrium with an unusual nematic phase, termed SWNT spaghetti, consisting of self-assembled supermolecular strands of mobile solvated tubes. At high concentrations (> 4% vol.), the SWNT spaghetti form a polydomain nematic liquid crystal. Under anhydrous conditions this liquid crystalline phase can be solution spun into continuous, highly aligned SWNT fibers with diameters between 50 and 100 microns. Fiber morphology and properties (electrical, thermal, mechanical) are influenced by SWNT concentration, mixing conditions, coagulation, and post processing.

2:30 PM R7.4

Self Assembly of Carbon Nanotubes and Quantum Dots for Nanoscale Device Applications. Cengiz Sinan Ozkan, Mechanical Engineering, University of California at Riverside, Riverside, California.

Successful development of carbon nanotube devices is largely dependent on the ability to preserve the electrical properties of the tube in a device configuration. Current devices rely on the overlapping or the bending of the carbon nanotubes, which could result in a decrease in their conductivity, due to bond distortion resulting in a barrier for electron transfer. In order to avoid this bending, heterojunctions of carbon nanotubes with nanoparticles can be envisioned. Here, we present results from recent experiments where semiconducting nano particles are integrated with the ends of multiwalled carbon nanotubes for potential electronic device applications. Quantum dots have received great attention due to their size-dependent electronic, optical, and electrochemical properties. The size dependent property tuning of the quantum dots enables the designing of a network of nanocrystals with built-in properties suited to specific applications. A novel method has been developed to synthesize multiwalled carbon nanotube-quantum dot (MWCNT-QD) heterojunctions comprising artificial solids of quantum dots conjugated to carbon nanotube ends. The apparent ordering of the quantum dots visualized by high resolution transmission electron microscopy suggests that individual nanoparticles are held together in two-dimensional pseudo hexagonal close packing forming a mesoscale structure, but there is no mutual orientation of the atomic planes between adjacent quantum dots. This means that the regular order of Cd and Se atoms does not extend beyond the boundaries of each individual quantum dot. The lack of ordering between adjacent quantum dots is probably due to the fact that each quantum dot is coated with a very thin amorphous layer. The long-range mesoscale ordering of the quantum dots in the cluster is induced most probably by the need to obtain a minimal energy configuration and due to the presence of a possible amorphous coating. This allows the quantum dots to be arranged in a pattern governed by the requirement for minimum volume rather than the direction of possible strong bonding which would cause specific orientation between adjacent quantum dots, the lack of which as confirmed by the polycrystalline nature of the electron diffraction patterns. Previous work has shown that the quantum-mechanical coupling between adjacent quantum dots is weak and excitations are largely confined to individual quantum dots, and that the long range Coulombic interactions between charge carriers are expected to play a significant role in the carrier transport properties. The optical and electrical properties of the quantum dot arrays can be tuned by selection of the composition and the size of the individual quantum dots and through their packing. The novel heterojunctions presented here are potential structures for nanoelectronic and nanophotonic devices and biosensors.

2:45 PM R7.5

Electron transport and magnetic properties of carbon nanowalls. Yihong Wu^{1,2}, Bingjun Yang^{2,3} and Zexiang Shen³;

¹Electrical and Computer Engineering, National University of

Singapore, Singapore, Singapore; ²Data Storage Institute, Singapore, Singapore, Singapore; ³Department of Physics, National University of Singapore, Singapore, Singapore.

Shape and dimensionality are two important parameters that affect the properties of materials at nanometer scale. Depending on the relative size of the material in three spatial directions with respect to the length scale of physics objects/quantities/phenomena that are concerned, materials can be divided into four categories of different dimensionality, i.e., 0D, 1D, 2D and 3D. Being able to be made into 0D, 1D and 2D nanostructures, carbon provides unique opportunities that other materials lack. Although a huge amount of efforts has been devoted to the study of the fullerenes and carbon nanotubes, the scope of work on 2D nanocarbons is still limited to a few theoretical studies. The latter have suggested that paramagnetic, ferromagnetic, antiferromagnetic, and superconducting phases may appear along or coexist with one another in nanometer sized graphite ribbons [1] or graphene sheets [2], depending on the nature of electron-electron interactions and atomic configurations at some boundaries or defects. Of particular interest is the theoretical prediction of Fermi surface instability in nanographite ribbons due to edge states [1] and superconducting instability at high temperature in graphene sheets due to topological disorders [2]. Despite the theoretical efforts, to our best knowledge, there has been no report on the experimental study of the transport and magnetic properties of two-dimensional (2D) nanographite sheets, probably due to the unavailability of such kind of materials. Recently we have succeeded in the growth of network-like 2D carbon nanostructures (dubbed carbon nanowalls) using the microwave plasma enhanced chemical vapour deposition [3]. Here we report transport and magnetic measurements on two-dimensional nanocarbon networks which provide the evidence of superconducting instability in nanographite sheets below 7 K. Due to the unique network-like morphology of the sample, the phenomenon manifests itself not only in the decrease of resistance and appearance of the Meissner effect at low temperature but also as a cause of strong oscillatory magnetoresistance and fluctuating magnetization. The behaviour of the carbon networks at low temperature resembles well disordered Josephson junction arrays. [1] K. Wakabayashi et al., Phys. Rev. B 59, 8271 (1998); [2] J. Gonzalez, et al., Phys. Rev. B 63, 134421 (2001); [3] Y. H. Wu et al., Adv. Mater. 14, 64 (2002).

3:30 PM *R7.6

Fabrication and Characterization of Organized Arrays of Quantum Dot and Wire Heterostructures. Harry Ruda, Department of Materials Science and Department of Electrical & Computer Engineering, University of Toronto, Toronto, Ontario, Canada.

Anodic alumina templates are used for the direct fabrication of heterostructured quantum dot and wire arrays. Such structures can offer exceptional optical and electronic properties suitable for developing photonic devices such as lasers, and electronic devices such as those based on Coulomb blockade at room temperature, for example. In our approach, the templates are used as masks for molecular beam epitaxial growth of GaInAlAs based structures - that is using both direct growth in the pores, leading to quantum dot arrays, and using indirect growth by the so-called vapor-liquid-solid mechanism to fabricate quantum wire arrays. These structures are shown to have a strong anisotropic optical response. Both steady-state luminescence, photovoltage and photoreflectance data are presented, as well as ultrafast optical characteristics.

4:00 PM R7.7

Carbon-nanotube based nano-electro-mechanical devices. Stergios J. Papadakis, A. R. Hall, D. V. Spivak, M. R. Falvo, R. Superfine and S. Washburn; Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

We report on the fabrication and performance of nanometer-scale electromechanical devices which use multi-walled carbon nanotubes as torsional springs. Carbon nanotube devices may offer high quality factors due to the inert surface of the torsional member, and high sensitivity due to their nanoscale dimensions. They also provide a means to study the effects of torsion on nanotube transport. The devices have a paddle-oscillator geometry and are driven electrostatically. In previous work we manipulated these devices in our combination AFM/SEM to directly measure the torsional properties of the nanotube, its shear modulus, and its subsequent stiffening under repeated strain. Here we use both optical and electron-beam techniques to measure the response of the devices to applied voltages. We demonstrate both quasi-static and on-resonance performance characteristics. 1: P. A. Williams, S. J. Papadakis, A. M. Patel, M. R. Falvo, S. Washburn, and R. Superfine, Phys. Rev. Lett. 89, 255502 (2002).

4:15 PM R7.8

SIMOX 3-D Sculpting for the Fabrication of Nano-Optical

Integrated Circuits. Prakash Vijayan Koonath, Koichiro Kishima, Tejaswi Indukuri and Bahram Jalali; Electrical Engineering, University of California, Los Angeles, Los Angeles, California.

Vertically integrated optical devices offer the possibility of dense three-dimensional(3-D) integration. In addition, the control over the critical dimension is more precise than laterally patterned structures, where the limits are set by the photolithography process. Silicon-on-Insulator (SOI) structure provides an excellent platform for the fabrication of a variety of integrated optical structures with the prospect of full integration of electronic and optical devices on the same substrate. Tight confinement of the optical mode in these high index contrast structures allows for the fabrication of low loss nano-optical structures, facilitating the goal of miniaturization. Fabrication of 3-D integrated nano-optical structures in SOI substrates using the process of Separation by Implantation of Oxygen (SIMOX) is reported in this paper. Buried waveguides with lowest ever loss with the SIMOX process are reported, with the fabrication of vertically integrated structures that demonstrate the capability to sculpt 3-D integrated optical devices. SIMOX process involves the implantation of Oxygen ions into a Silicon substrate, followed by a high temperature(around 1300C) anneal of the substrate in order to cure the implantation damage. A novel method, utilizing the implantation of Oxygen ions into a masked SOI substrate, is proposed to realize buried rib waveguides of submicron dimensions. Implantation of Oxygen ions is performed on a SOI substrate that has been patterned with thermally grown oxide of suitable thickness to decelerate the Oxygen ions that penetrate into the area underneath the oxide. After the implantation and subsequent high temperature anneal, rib waveguides may be defined on the top layer using conventional lithography and etching process. This process may be utilized in fabricating laterally patterned resonator rings with accurate vertical spacing. The inherent sidewall smoothing that takes place during the SIMOX process offers the possibility of synthesizing resonators with high quality factors. A SOI wafer with 0.5 microns of Silicon on top of 3 microns of buried oxide layer, was oxidized and patterned using reactive ion etching to form oxide stripes of thickness 0.15 microns, with widths varying from 2 microns to 12 microns. The patterned wafer was implanted with oxygen with a dose of 1e18 ions/cm2 and annealed afterwards at 1300C. This results in the formation of rib waveguides in a single implantation step, of thickness 286 nm, with excellent uniformity observed for the buried oxide formed by the implantation. The propagation losses for the waveguides that have been fabricated are in the range of 3-4 dB/cm. The feasibility of 3-D integration is demonstrated by defining a rib waveguide on the top silicon layer using conventional lithography. This demonstrates the suitability of the SIMOX process to sculpt 3-D nano-optical structures in Silicon

4:30 PM R7.9

Field emission and gas sensing properties of carbon nanowalls. Bingjun Yang^{1,3}, Yihong Wu^{1,2} and Zexiang Shen³;

¹Data Storage Institute of Singapore, Singapore, Singapore; ²Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore; ³Department of Physics, National University of Singapore, Singapore, Singapore.

Carbon can be grown into different forms of nanostructures. So far, most of the works have been concentrated on zero-dimensional (0D) fullerene and one-dimensional (1D) carbon nanotubes. Recently, we have succeeded in the growth of two-dimensional carbon nanostructures (dubbed carbon nanowalls) [1]. The carbon nanowalls exhibit several salient features which may make them more suitable for field emission applications; these include catalyst-free growth, metallic-type electrical transport, large effective emission areas, and sharp edges. A series of experiments have been carried out to study the field emission characteristics of this novel type of carbon nanostructure under different conditions including cathode-anode distance, electrode size, temperature and background gases. A low turn-on field of 1.00 V/ μ m was obtained with a vacuum gap of 200 μ m and it decreases monotonically with increasing the vacuum gap. This value is comparable to some of the best results ever reported for carbon nanotubes. For some nanowall samples, we have even obtained a turn-on field as low as 0.16 V/ μ m. In addition to field emission, the carbon nanowalls have also been investigated as resistive gas sensors for O₂, N₂, CH₄ and H₂ at different temperatures. The samples studied include both bare carbon nanowalls and those coated with oxides like ZnO, TiO₂, SnO₂ and SiO₂ [2]. [1] Y.H. Wu et al. Adv. Mater. 14, 64 (2002); [2] Y. H. Wu et al, Adv. Funct. Mater.12 (8), 489 (2002).

4:45 PM R7.10

Influence of H₂ Preconditioning on the Nucleation and Growth of Self-assembled Germanium Islands on Silicon (001). Gabriela Delia Dilliwai¹, Nicholas E.B. Cowern², Chris

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Southampton, Southampton, Hampshire, United Kingdom; ²Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom; ³Research Institute for & Communications Engineering, School of Electronic Engineering, Dublin City University, Dublin, Ireland.

Self-organization of Ge nanostructures on Si with controlled size distribution is a key requirement for their practical applications. In this study we investigate the effect of preconditioning with a high-temperature hydrogenation step on the nucleation and subsequent temporal evolution of Ge self-assembled islands on Si. Two sets of structures with and without H₂ preconditioning, for comparison, were grown by low pressure chemical vapor deposition (LPCVD) at 650°C. Their structural and compositional evolution was characterized by atomic force microscopy, transmission electron microscopy, Rutherford backscattering spectrometry and micro-Raman spectroscopy. In the absence of preconditioning, we observe the known evolution of a bimodal size distribution, with a steady increase in surface coverage and island size as a function of deposition time. On the H₂ preconditioned surface, however, both surface coverage and nucleation rates are dramatically increased at the beginning of the self-assembly process. For the shortest growth duration, the density of nanostructures self-assembled on the preconditioned surface is almost double that on the unconditioned surface. A completely different type of bimodal size distribution is observed for the shortest growth duration on the preconditioned surface. A small fraction of islands (about 6%) that grow extremely rapidly to large sizes (50-60 nm in height and 250-350 nm in width) coexist with a population of smaller islands. For longer deposition times, the large islands shrink whilst the small ones grow steadily (similarly to the ones on the unconditioned surface). Ultimately all islands converge toward similar sizes. We propose that this transient behaviour arises from the nonequilibrium topography of the H₂ preconditioned Si surface. Close attention to standard processes used during growth, like H₂ preconditioning, could yield dramatic changes in the uniformity and distribution of Ge nanostructures self-assembled on Si.

SESSION R8: Fabrication, Self-Assembly and Characterization of 2-D and 3-D Nanostructures II
Chairs: David Mc Ilroy and Lhadi Merhari
Friday Morning, April 16, 2004
Room 2007 (Moscone West)

8:15 AM R8.1
Syntheses of Mesostructured/Mesoporous Materials with Controlled Morphologies. Jianfang Wang¹ and Galen D. Stucky^{1,2};
¹Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California; ²Materials Department, University of California, Santa Barbara, Santa Barbara, California.

Mesostructured/mesoporous silica spheres, rods, and fibers have been synthesized using cationic ammonium surfactants with varying carbon chain lengths in a quiescent aqueous solution under strong acidic conditions. With dodecyltrimethylammonium bromide (C12TMABr) as surfactants, only micrometer-sized spheres are obtained. With C14TMABr as surfactants, micrometer-sized spheres, rods, and curve-shaped particles are obtained, depending on the synthesis temperature. The syntheses using C16TMABr give nanofibers that are suspended in the growth solution and curve-shaped particles that are precipitated at the bottom. The nanofibers have diameters ranging from 50 to 300 nm and lengths up to millimeters. Transmission electron microscopy studies show that the nanofibers exhibit either a circular pore architecture with pore channels running in a circular direction around the fiber axis or a longitudinal pore architecture with pore channels running parallel to the fiber axis. The pore channels in both architectures are hexagonally packed. The circular or longitudinal architecture can be selectively obtained during synthesis by varying reaction temperature or using inorganic salts as additives. With C18TMABr as surfactants, only nanofibers are obtained. The pore channels of these nanofibers are hexagonally organized and they are aligned parallel to the fiber axis. This structure-selective synthesis by varying surfactants and growth conditions could offer opportunities for further understanding the fundamental mechanism governing the cooperative organization of organic and inorganic molecular species into three dimensionally structured arrays. In addition, the nanofibers with their pores aligned parallel to the fiber axis might find applications in nanofluidics and nanoscale pore-based chemical/biochemical sensing.

8:30 AM R8.2
Novel Mesostructures in Anodized Alumina Nanopores and Applications in Large-area Mesoporous Functional Membrane. Yiyang Wu¹, Guosheng Cheng¹, Martin Moskovits¹ and Galen Stucky^{1,2}; ¹Chemistry and Biochemistry, University of

California, Santa Barbara, Santa Barbara, California; ²Materials Department, University of California, Santa Barbara, Santa Barbara, California.

The surfactant-templated synthesis of highly ordered mesoporous materials is a cooperative inorganic-organic self-assembly process. In this presentation, we are going to show our recent study about mesostructures inside nanoscale alumina pores. New phenomenon occurs when the diameter of alumina pores is reduced to a size comparable to the periodicity of the mesostructures, because the extensive interface significantly influences the self-assembly process. We observed the transition of mesostructures from 3-dimensional ordering, to concentric ring stacking, to one-dimensional inverse "peapod" structure when the diameter of alumina pores is systematic reduced. This study is also important for mesoporous materials in membrane-based applications. Sol-gel chemistry with dip-coating method is one of the most appropriate methods for the preparation of mesoporous layer on top of a porous support. Sol precursor solution will penetrate into porous support under capillary force. It's therefore important to understand the mesostructures formed inside nanoscale space and their permeation.

8:45 AM R8.3
Formation of three dimensional Ni nanostructures at low temperatures. David Carey, Patrick Poa, Richard Smith, Christina Giusca, Simon Henley, Damitha Adikaari and Ravi Silva; University of Surrey, Guildford, United Kingdom.

The formation of nanometer-sized Ni nanostructures on both oxide and conducting substrates, under non-UHV conditions, is reported. It is shown that the size and distribution of Ni islands is strongly dependent on the temperature of annealing on the Ni layer. By annealing in the temperature range 300 - 500 oC we observe an increase in the mean diameter of the islands, accompanied by a reduction in the mean island density. We attribute this effect to mass transport of weakly bound individual Ni atoms and/or small clusters across the surface to form larger isolated islands, in a process similar to Oswald ripening. The effect of the initial Ni layer thickness, annealing temperature and annealing time is also reported. Low annealing temperatures were chosen to employ the resultant nanostructured films as catalyst sites for carbon nanotube growth. In addition, alternative ways using rf plasma processing or single and multiple pulse excimer laser annealing to produce Ni nanostructures, at low processing temperatures, are also discussed.

9:00 AM *R8.4
3d Assembly with Nanorobotics: New Methods and Results. Rodney S Ruoff, Mechanical Engineering, Northwestern University, Evanston, Illinois.

Nanorobotics is a nascent field. We employ a scanning electron microscope as a testbed, and insert multi degree-of-freedom (DOF) nanomanipulator tools into the SEM. The actuators employed are PZT-based piezoactuators, such as picomotors, theta stages, piezo tubes/plates/bimorphs; we use a modular platform that allows for relatively easy and rapid configuration of a variety of experiments, such as tensile loading of nanostructures, driving nanostructures into mechanical resonance, and others [1]. In this talk, I will outline how robotics concepts can be usefully employed, to develop a 3-dimensional representation of the workspace, and of the SEM nanomanipulator tool set. With such a simulacrum as an end goal, and when it is fully realized, then nanorobotics will be powerful for rapid prototyping and possibly for nanomanufacturing at high speed. Several examples of devices we have made with this approach will be given, including a nanopipette, and some of the barriers facing nanorobotics 3d assembly, and some of the methods to overcome those barriers, will be developed in this talk. 1. Three-dimensional nanomanipulator with complementary tools and capabilities, Dmitry A. Dikin, Zebin Huang, and Rodney S. Ruoff, submitted to Rev. Sci. Instr. We gratefully acknowledge the Office of Naval Research Mechanics of Nanostructures grant (award No. N000140210870), and the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02037. This work was also supported by the NASA Langley Computational Materials Nanotechnology Program. Scanning electron microscopy was done at the Electron Probe Instrumentation Center at Northwestern University.

9:30 AM R8.5
Chemical Synthesis: New Bottom Up Approach for 3D Nanostructures. Z. Ryan Tian¹, Louise J. Criscenti², Randall T. Cygan², James A. Voigt¹ and Jun Liu¹; ¹Chemical Syntheses and Nanomaterials, Sandia National Lab, Albuquerque, New Mexico; ²Department of Geochemistry, Sandia National Labs, Albuquerque, New Mexico.

As nature has shown, solution-based synthesis is a powerful method

for creating a wide variety of nano-structured 3D materials. Recent work in biomimetic-based processing has shown that, although many interesting materials and structures have been prepared, much work remains before we are able to efficiently imitate nature's complex processes to produce technologically interesting products. Here we describe a simple bio-inspired approach to producing a range of complex, crystalline 3D structures. Through the use of growth modifiers and control of system supersaturation, modulated, extended films structures have been prepared for material systems ranging from mesoporous silicates where the growth units are micelles to the formation of ZnO where growth is by hydrolysis and precipitation. For the silicate system, surfactant mediated self-assembly of hierarchical mesoporous octahedra structures will be discussed in terms of solution growth conditions. Manipulation of ZnO morphology will be described using results of molecular modeling studies in which the relative adsorption energies of simple growth modifiers (citrate, hexamethylene tetramine, etc.) on specific ZnO growth surfaces have been determined. Through use of crystallographically specific modifiers and controlled growth conditions, a wide range complex ZnO structures have been prepared. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:15 AM **R8.6**

Morphology Control of Continuous Metallic 3-D Nanomesh and Nanowire Films. Rong Kou, David T Johnson, Donghai Wang and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Properties of metal and semiconductor change from the bulk properties toward quantum-derived properties as their critical dimensions are decreased toward the nanoscale. One focus of current nanotechnology research is to utilize these unique properties and to convert the nanoscale materials into useful devices. We have demonstrated the formation of nanostructured films composed of metal 3-D nanomeshes or nanowires via electrodeposition using cubic or hexagonal structured mesoporous silica film as templates. As-synthesized nanostructured thin films usually possess pores with 2-8 nm in diameter. Many applications require large pores to allow the access for larger molecules. This research addresses this challenge through fabricating continuous metallic 3-D nanomesh/wire thin film with hierarchical pore structures. We have successfully prepared silica templates with hierarchical 3-D pore structures and use them as the templates to synthesize such nanowire or nanomesh thin films. These nanostructured thin films have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), cyclic voltogram, and other techniques. For example, morphology and structures of the nanowire or nanomesh thin films can be tuned through doping different sizes of silica spherical particles or nanorods. This approach provides a ready and efficient route to fabricate continuous hierarchical 3-D nanomesh or nanowire thin films for biosensor, photovoltaic and other applications. *Adv. Mat.*, 2003, 15, 130-133.

10:30 AM **R8.7**

3D-Templating of hierarchical ceramics. Helga C. Lichtenegger¹, Christina Fritscher¹, Juergen Stampfl¹, Nicola Huesing², Robert Liska³ and Sabine Seidler¹; ¹Institute for Materials Science & Testing, Vienna University of Technology, Wien, Austria; ²Institute for Materials Chemistry, Vienna University of Technology, Wien, Austria; ³Institute of Applied Synthetic Chemistry, Vienna University of Technology, Wien, Austria.

Hierarchically structured cellular ceramics are a common motif in Nature - bones and teeth are constructed according to this very principle: many of them are cellular, in order to save weight, and they exhibit a sophisticated hierarchical architecture starting from the millimeter down to the nanometer range. Here, hierarchically structured ceramics were produced in a combined bottom-up and top-down procedure. Rapid prototyping (RP) with stereo-lithography is a suitable method to produce 3-D structures of arbitrary shape and was used here to build cellular molds from resins soluble in alkali (sacrificial molds). Mesostructured silica was synthesized directly in the molds via sol-gel processing. After polycondensation of silica, the molds were dissolved and a hierarchical ceramic-polymer composite material was obtained. Position resolved small-angle x-ray scattering (scanning SAXS) was used to investigate the nanostructure in a non-destructive way. Mechanical properties of the cellular nanocomposite ceramics were tested and compared to those of cellular ceramics with different or no additional structure on the nanometer scale.

10:45 AM **R8.8**

Ag nanoparticle arrays synthesized in the void network of a porous semiconductor. Kaan Kalkan and Stephen J. Fonash; Nanofabrication Facility, Penn State University, University Park,

Pennsylvania.

Ag nanoparticles were synthesized in the void network of void-column Si films simply by film immersion into pure metal salt solutions. Nanoparticle formation is found to occur without the need for an external reducing agent, complexing agent, or electric bias. 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, in addition to functioning as a reducer, the Si nanocolumns further enable monodispersion and narrow size distribution of Ag particles by immobilizing the nanoparticles and sterically constraining their growth. The Ag nanoparticle / Si nanocolumn array films obtained, function as active substrates for surface-enhanced spectroscopy. Detection of single dye molecules has been demonstrated. Furthermore, direct-write of metal lines is possible on the films with a laser beam.

11:00 AM **R8.9**

The formation of nanoporous noble metal thin films on Si by electrochemical dealloying of PtxSi1-x. J. C. Thorp¹, K. Sieradzki¹, T. Michael¹, P. Crozier¹, S. T. Picraux¹, D. Mitlin², A. Misra² and M. Nastasi²; ¹Arizona State University, Tempe, Arizona; ²Los Alamos National Laboratory, Los Alamos, New Mexico.

Electrochemical dealloying of bi-metallic alloy mixtures provides a novel way to form nanoporous structures. In the present study we demonstrate the extension of this concept to metal-silicon alloys on silicon platforms for PtxSi1-x. The PtxSi1-x (x = 50, 33, and 25%) alloys are formed by co-deposition and by thermal reaction of Pt films for PtSi silicide layers. The films (50 to 400 nm thick) are then dealloyed in concentrated HF by an electrochemical process that leaches out the silicon resulting in a local self assembly of Pt into a nanoporous structure. Anodic polarization curves are used to establish the critical concentration and optimum potential for dealloying, for example near + 400 mV (SCE) for Pt.25Si.75. Rutherford Backscattering Spectrometry (RBS) depth profiling demonstrates the formation of a pure Pt nanoporous layer on the metal silicide layer as dealloying process progresses and thus provides a direct observation of the dealloying kinetics. The resulting morphology of the nanoporous noble metal structures is determined by field emission scanning electron microscopy and the microstructure by Z contrast and high resolution electron microscopy. Results are presented for various Pt silicon alloys and dealloying conditions. Thermal annealing of the nanoporous films results in a ripening of the pore size with increasing temperature due to surface diffusion, with mean pore diameter growing from 10 nm as dealloyed to 40 nm after annealing to 900C. These nanoporous metal thin film structures provide high surface area electrodes on Si. This new approach to forming ultra-high surface area noble metal films has the advantage of being compatible with integrated circuit processing. Such nanostructures are expected to have to be useful in emerging applications such as micro-fuel cells, biosensors, and micro-batteries.

11:15 AM **R8.10**

New Approach to Chemistry for the 3-D fabrication and Novel Synthesis of Nanoparticles via Soft Lithography, Template Transfer, and Microfluidic Droplet Reactor. Kyung M. Choi¹ and John A Rogers²; ¹Bell Labs, Lucent Technologies, Murray Hill, New Jersey; ²Materials Science and Engineering, University of Illinois at UC, Urbana, Illinois.

In microfabrication, the soft lithography technique has been widely used in stamping and printing processes because it is a low cost alternative to photolithography for fabricating small features from masters and transferring to a variety of substrates such as plastics by using polydimethylsiloxane (PDMS) stamp materials. However, conventional PDMS stamp materials have shown limitations, especially in the submicron range, due to their low physical toughness and high thermal expansion coefficients. To achieve high performance in stamping and printing, we employed a chemical approach by designing a new version of stiffer, photocured PDMS silicon elastomer that is developed specifically for nano-scale resolution soft lithography. We demonstrate its excellent performance for nano-features (300 nm wide) with narrow and tall heights (600 nm) of photoresist, which is one of the most challenging '3D-nanopatterning' task in submicron scale soft lithography. We also developed molecularly imprinted polymers (MIP) to fabricate patterns based on functional polymers with specific tasks -for instance, molecular recognition function-through template patterning technique for fabricating novel bio-devices or drug delivery purpose. Nanoparticles are also synthesized through a novel approach by developing microfluidic droplet reactor, which was fabricated using new PDMS material.

11:30 AM **RS.11**

Fabrication and characterization of three dimensional ordered quantum dot lattices using self assembled epitaxy.

Rainer T. Lechner¹, Tobias U. Schuelli^{1,2}, Vaclav Holy³, Gunther Springholz¹, Julian Stangl¹, Anneliese Raab¹, Till H. Metzger² and Guenther Bauer¹; ¹Institut fuer Halbleiterphysik, Johannes Kepler Universitaet, Linz, Austria; ²European Synchrotron Radiation Facility, Grenoble, France; ³Department of Solif State Physics, Masaryk University, Brno, Czech Republic.

Three dimensional (3D) quantum dot structures can be obtained, e.g., by the growth of self-assembled quantum dot multi-layers in which vertically and laterally ordered dot superstructures are formed as a result of the elastic interlayer dot interactions between the dots. This not only results in a significant narrowing of the size distribution, but also provides an effective means for tuning the size and spacing of the dots by changes in the superlattice period. For different material systems, different ordered dot arrangements have been observed, which is due to the strong dependence of the dot interactions on the growth orientation as well as on the anisotropy of the elastic material properties. Even more, different interlayer correlations can be obtained by changes in the spacer thickness, dot size or growth temperature, as has been demonstrated for the PbSe/PbEuTe quantum dot material system. In particular a vertical dot alignment is obtained when the spacer thickness spacing between the dot layers the PbEuTe spacer thickness is below about 35 nm, resulting in a 3D hexagonal dot lattice, whereas an fcc-like ABCABC.. stacking is formed for thicker spacer layers. Apart from microscopic techniques, X-ray diffraction is a very powerful tool to characterize the ordering in such 3D assembled quantum dot structures. However, the analysis of the diffraction spectra is usually complicated by the weak scattering contrast between the self-assembled quantum dots and the surrounding matrix material. In the present work, we therefore employ anomalous x-ray diffraction with synchrotron radiation to drastically enhance the chemical contrast in such multilayers by tuning the wavelength close to an inner shell absorption resonance. This technique is applied to determine the ordering of differently stacked self-assembled PbSe quantum dot lattices fabricated by molecular beam epitaxy. In this case, the x-ray wavelength is tuned to the Pb M-shell a to suppress the scattering of the (111) reflection of the matrix material. For the analysis of the measured diffraction spectra, a combination of a short-range order model with a finite domain size is employed to deduce the order parameters for the differently correlated 3D PbSe dot lattices. As a result, it is shown that the lateral ordering is significantly better for fcc-stacked PbSe dot superlattices with 3D trigonal dot structure as compared to those with 3D hexagonal dot arrangement. This is due to the more efficient ordering mechanism based on the elastic interlayer dot interactions. In contrast nearly perfect vertical dot alignment is shown for the 3D hexagonal dot lattice samples.

11:45 AM **RS.12**

Multiscale Modeling of Size-dependent Materials Properties in NEMS Resonators. Robert Rudd, Lawrence Livermore National Laboratory, Livermore, California.

The design of nanoscale mechanical systems poses a novel set of challenges for modeling and simulation. We consider one set of these problems associated with modeling and predicting the behavior of nanoscale flexural resonators. We have used atomistic and concurrent multiscale simulation to investigate the size dependence of the elastic and dissipative properties of the nanoscale beams that form the mechanically active flexural resonator components in Nano-Electro-Mechanical Systems (NEMS) under development. [1] We have simulated a several different types of materials, semiconductors, oxides and metals, in order to understand the origin of the size effects. It has been recognized for some time that the size dependence of the Young's modulus is due to surface stress [2,3], but the atomistic origin of this effect has not been described previously. We have also studied the mechanisms of dissipation in silicon flexural resonators, and find that the dissipation is proportional to the surface-area-to-volume ratio at the nanoscale, in agreement with many experiments. [1] R.E. Rudd, "Coarse-Grained Molecular Dynamics for Computer Modeling of Nanomechanical Systems," submitted to Int. J. Multiscale Comput. Eng., 2003 [2] J.Q. Broughton, et al, Phys. Rev. B 56, 611 (1997). [3] R.E. Rudd and J.Q. Broughton, J. Model. of Microsys. 1, 26 (1999). Acknowledgment: This work was performed under the auspices of the US Dept. of Energy at the University of California/Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.