SYMPOSIUM R
Three-Dimensional Nanoengineered Assemblies II
April 12 - 16, 2004

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* Invited paper
Microfluidics, which emerged in the 1990s as a branch of physics and biotechnology, studies the behavior of fluids at the micro- and mesoscale, has enabled a wide range of technologies including gene-chip, microthermophoric and propulsion technologies. With the advent of nanotechnology, microfluidics—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 devices 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, study of microchannels with non-uniform Zeta potentials, optimization of electrocromic microchannel geometries, optimization of on-chip field amplified sample stacking, electrokinetic instability microscopy, 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. These molecular-sequence 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, Nanofluids, Inc.

SESSION R1: Photon, Electron & Ion Beam Approaches to Nanofabrication
Chair: John Pendry, Seeckooe Jon, Jing-Ung Park and Joana Maria; University of Illinois at Urbana/Champaign, Urbana, Illinois.

8:30 AM *R1.1
3D Nanofabrication by Optical Proximity Field Photopatterning. John Rogers, Seeckooe Jon, Jing-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 Illinois at Urbana, Urbana, Illinois.

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 of focusing the 10.55 micron radiation of a CO2 laser to several hundred nanometers, thus pushing the way for a new lithography technique: Polariton-Enhanced Near Field Lithography (PENFL). 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 C1 from C1-terminated Si(111) is a function of incident electron-beam direction [1]. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DES). The final structure in the desorption yields are 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 a combination of 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 feasibility of this low-energy electron beam technique as a prepatteming strategy for controlled growth of 3-D nanostructures. If viable, this nanolithography approach will be inexpensive and not rely upon serial processing. 1) J. T. Sieger and T. M. Orlando, Phys. Rev. Lett. 82, 3308 (1999). thomas.orlando@chemistry.gatech.edu

10:30 AM **R1.4

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 control devices that have material and nano-scale dimension 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
The development of working nanoscale photonic and electronic devices presupposes not only the ability to construct three-dimensional architectures, but also the capability of 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 (FIB)-based technology, pulsed laser deposition, and vacuum deposition. The FIB is 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 nanoscale path at each lattice point. Based on this technique, 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 this technique to create nanostructures in silicon and gallium arsenide of various areas and aspect ratios.

The deformation is mainly driven by the energy lost in the cylindrically-shaped heated ion track. Size effects and stress relaxation in the nanoscale domain have been studied by Prof. S. Roorda using multi-beam tools for 3D nanoengineering. This work is supported by the U.S. Department of Energy, the National Science Foundation, and the Vanderbilt Nanoscience and Nanotechnology Institute. The collaboration with the NIST on nanotechnology will be discussed.

The bottom-up approach to fabricating nanodevices requires that these nanoscale building blocks be controlled with coverage over their interactions. To reduce the variability and limited complexity of using discrete components, the recent trend is to develop more functionality into a single nanodevice. Recent advances in the growth of nanostructures have enabled demonstrations of single nanowire light emitting diodes, single-electron transistors, and optical nanocarriers. 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 each other. We have demonstrated the synthesis of colloidal heterostructures using quantum dots and rods at branched and linear junctions within single nanocrystals. We control branching and composition to synthesize nanocrystals of well-defined size 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.

A small 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 the temperature-induced 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 Au or embedded in PNIPAm gels were synthesized and used as novel catalysts, biosensors, switchable electronics, and optically controlled 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 nanoparticles–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 these 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.

In this paper we present an update of the Projection Focused Ion Beam (PROFIB) multi-beam tool concept for 3D Nanoeengineering. Hans Loscheiner and Elmar Pintschinger; IMS Nanofabrication GmbH, Vienna, Austria.

At the MRS 2002 fall meeting the PROFIB (Projection Focused Ion 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 nanoeengineering applications. This simulation program is in excellent agreement with the experimentally obtained results allowing ion beam shaping of three-dimensional nano-assemblies.

Halogenation is a traditional method for the functionalization of silica colloids and irradiated them with 4 MeV Xe ions. The collective electronic excitations in the material and can be described by a high-order susceptibility. The deformation is mainly driven by the energy lost in the cylindrically-shaped heated ion track. Size effects and stress relaxation in the nanoscale domain have been studied by Prof. S. Roorda using multi-beam tools for 3D nanoengineering. This work is supported by the U.S. Department of Energy, the National Science Foundation, and the Vanderbilt Nanoscience and Nanotechnology Institute. The collaboration with the NIST on nanotechnology will be discussed.

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thermal phase transition of the nanocomposite gels was dramatically altered, with an apparent LCST at least 10 degrees higher than the 35°C of the original PMMA 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 R2.5
Pseudomorphic Transformations of Nanostructured Silica to Titania or Titrogen Carbides, Andreas Stein, Justin C. Lytle, Hongwei Yan and Rynn T. Turgeson; 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 rivalled few if any, of any 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 precursors 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 precursors were prepared by colloidal crystal templating methods. They consist of smooth amorphous silica walls (ca. 60 nm in thickness) that support nanorod-like 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 TiO2F and then to TiO2. Within a limited temperature window, the periodic macroporous structure of the nanocomposites was preserved. Pseudomorphism was also observed on the scale of the nanocrystalline structures forming the inverse opal skeleton. A similar vapor phase reaction was applied to convert a silica precursor to W2O5. 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 nanowires 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 a series of ligand stabilized gold nanosheets, 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 are extractable in the nature of electronic transport in one-dimensional chains of nanoparticles in which the inherent self-capacitance is negligible. Finally, modeling results of nanoparticle-based simple single-electron logic-gate circuits will be discussed.

3:00 PM R2.5
Fabrication of 2-D and 3-D Photonic Bandgap Structures Using Laser-assisted Imprinting of Self-assembled Particles, Y. F. Li1, L. P. Li1, K. K. Mendoz1, J. Shi1, D. W. Doerr2, 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 imprinting of self-assembled colloids. Surface plasmon resonance (SPR) of a silver nanoparticle, 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/silica/nanoparticle/silicon structure. The nanoparticles were incorporated 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 Hemispherical Colloidal Aggregates Reflecting Multiple Colors, Jeono Moon1, Hwa-Young Ko1, Junglo 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 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 Albina Ivanisevic1; 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 Polydimethylsiloxane (PDMS) (Duchan Urea) by Thermal Processing, Keith Richard Minner1,2, Mallory Balmer1, Christopher A Siedlecki1,2 and Alan J Snyder1,2; 1Dept of Bioengineering, Pennsylvania State University, University Park, 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. The wafer was exposed under vacuum for 4 hr at 65 °C. The PUU was made by mixing 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 PUU 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 C18(CH3)3SiCl 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
for all feature sizes to 309 nm. The resolution limit of the Stepper that produced the masters with SAM was greatly reduced for feature sizes below 500 nm.

RESULTS: Samples of UV5 master, PDMS negative and PUU replica masters with SAM was greatly reduced for feature sizes below 500 nm. The PUU was found to exceed 90\% and the replication efficiency from 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. Lott. 90, 167410 (2002). [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 Nanofluidic Devices. AKNOWLEDGEMENTS Funding: Commonwealth of Puerto Rico. The transmission of light through a subwavelength 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 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.ariniresearch.com

9:00 AM *R3.2 Giant Light Transmission Through Nanometer-Scale Apertures, Linde, Thio, Aria, LLC, Princeton, New Jersey.

The transmission of light through a subwavelength 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 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.ariniresearch.com

9:30 AM *R3.3 Polarization properties of metallic nanohole arrays, Han Woedman, Erwin Altschwer, Martin van Exter and Cyrille 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 moments 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 phenomena in near-field optical microscopy, data display devices, and sensor technology. More information at www.ariniresearch.com

SESSION R3: Plasmonic and Optical Nanoeengineered Devices

Chair: John Pendry and David Taylor

Room 3020 (Moscone West)

8:30 AM *R3.1 Transmission of light through subwavelength apertures, Franchini, J. Garcia-Vidal and Luis Martin-Moreno, 1 Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Spain; 2 Departamento de Fisica de la Materia Condensada, Universidad de Zaragoza, Zaragoza, Spain.

The transmission of light through a subwavelength 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 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.ariniresearch.com

REFERENCES 1. T. T.

10:30 AM *R3.4

Coupling from Wavelength Scale to Subwavelength Scale Photonic Structures: The Engineering Tradeoffs of Loss and Localization. David Schurig, Purdue University, West Lafayette, Indiana; 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 thin planar films with reduced loss. The 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 allow efficient localization in volumes of a few million nanometers, where the high (eV/nnm) local field effects 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 polarization 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 gaps has been compared for tapered metal nanostructures. Recent experimental observation of eV/nnm 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 nanohole arrays, 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 components 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 refrocusing 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 and 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, however, using the usual formula, 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 culprit in a lens with index n = ±1, having a focal length as a lens with index n = ±1, for the same radius of curvature. This simple example shows that materials with negative refractive indices of modest magnitudes possess remarkable refractive properties that can be leveraged to produce novel optical components. The possibility 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 cantored 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

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 wavelengths, as short as 1nm. This opens the door to Inm imaging, including plasmon lenses, and other in-plane optical components. In effect plasmonic materials 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. Shalaev, School of ECE, 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 nanoscale 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 nanonantennas open up the feasibility to detect molecules with unsurpassed sensitivity and perform lithography with nanometer spatial resolution. Plasmonic nanostuctures can be employed for developing photonic nano-circuits where photonic components 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 Schure1, M. Lonca1, B. Moun1, T. Yoshie1, K. Okamoto1, M. Adams1 and J. Vuckovic2,1, Applied 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 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. 360
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 [1], have attracted much attention. In particular, 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, we developed 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, we used a method based on the modified Stober method, and 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 spheres of 710 nm diameters. Subsequent experiments will convert silica sphere layers on 1 cm x 3 cm silicon substrate. After coating the silicon substrate with a colloidal suspension, we obtained very uniform crystals with 18 silica sphere layers on 1 cm x 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 waveguide technique.

4:00 PM R4.6
Three-dimensional photonic structures with nano-order resolution of titanium dioxide. Keiichi Awaizumi1, Akhile Kail3, Yoshihico 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 use as porous templates for transferring three-dimensional photonic structures to titanium dioxide by three-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 a hole diameter 500 nm was then obtained in 5 micron thick PMMA layer. Titanium sulfate (TiOSO4·H2O, x=4.6) was used for preparation of supersaturated solutions for poly-crystalline TiO2. An aqueous solution at pH 0.1 M TiOSO4 prepared by adding TiOSO4 into a hydrochloric solution at pH 0.50 for growth of rutile TiO2 crystal. An aqueous solution at pH 0.1 M TiOSO4 was deposited in the TiOSO4 precursor solution containing 2.0M HCl. PMMA templates were immersed in the precursor solution for 24 hours. After immersion, the appropriate reaction time at 60°C 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 bandgap properties of the composite were measured by an optical fiber spectrometer. The crystal of 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 this compound is lower than that of silicon, 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. Furthermore, using titanium dioxide has the advantage of thermal expansion higher 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 Fund of the Ministry of Education, Culture, Sports, Science, and Technology based on an assessment of the Japanese Atomic Energy Commission.
R5.1 Electrochemical Fabrication of Porous Magnetic Nanostructures. Li Sun 1; Peter C. Serenson 1 and Chin-Ling Chien 2; 1Department of Mechanical Engineering, University of Houston, Houston, Texas; 2Department of Materials Science and Engineering, 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 Ni-Cu alloys and subsequently leaching out the Cu in the same aqueous solution electrolytically. 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 also shows the dealloyed Ni 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 Coupled Optical Masks. Jeffrey M. Silver 1; Siu-Tung Yau 2; Geoff W. Reeves 3; and Anthony S Holland 2; 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 lithographic 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 localized 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 SiC/O2 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 C4F8 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 eccm); this effect was greater than 2 times 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. Rizwan Zakezak, Madihah 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 fields of sensors, optoelectronics, chromatography, photocatalysis, etc. This work 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 spectrophotometry, and in situ FTIR spectroscopy. Energy 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), and DFT LDA (FLAPW, LUSTO, 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 potentials might be correctly fitted in a full 3-D 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 Newtonian fundamentals was combined with the molecular 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 mechanisms. Stress and deformation 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 two contacting solids into a 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 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-Krastanow(SK) method have attracted much attention due to potential of this material in optoelectronics, 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-Krastanow 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 full 3-D reconstructions of their structure including both vacancies and fullerenes were obtained using transmission electron microscopy (TEM) and photoluminescence (PL) measurements. Two 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 dislocation line. Ge SAQDs are observed to nucleate exclusively over the dislocation intersections, first, followed by 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 critical strain field has a significantly effect on both the diffusion of Ge adatoms before SAQD nucleation, as well as the shape evolution of the SAQD 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 mechanisms of SAQDs grown epitaxially in Stranski-Krastanow (SK) growth mode.

R5.10 Optical Reflectivity Measurements on Opal-Based Metallo-Dielectric Photonic Crystals. Vladimir Kupsyn1, Alexandre Pokrovsky1, Valy Z Vardeny2, Alexei Efros1, Dmitry Kurdyyakov3 and Valery Golubev3, 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, \( \omega_c \), EM waves cannot penetrate into the metallo-dielectric photonic crystal. We have successfully fabricated opal photonic crystals infiltrated with metals such as Ag, In, Cu and Pb and measured their reflectivity spectra in a broadband spectral range from 0.3 \( \mu m \) to 25 \( \mu m \). The opals were grown by sedimentation of monodispersed silica balls with 2.345 \( \mu m \), 2.265 \( \mu m \) and 0.550 \( \mu m \) diameters, respectively. After RTA treatment, 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 90%. 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 \( \omega_c \), which is about 1 eV, \( R \) increases rapidly to reach a sample dependent saturation value, which itself depends on the photonic crystal periodicity, \( f \), and the particular metal used. In addition, at frequencies higher than \( \omega_c \) (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: Lhdhi Merhari and David Taylor
Thursday Morning, April 18, 2004
Room 3020 (Moscone West)

S8:30 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. Brotz1, Sophie M. Rozenzhak1, Laura A. Nekoda3, Francisco Rodriguez4,5,6,7,8,9,10,11,12,13
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 multiple 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 molecules to ultrahigh density, 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 an intended nanoscale conversion. The full versatility of AFM will be applied to further understand the cellular environment of developing and dying neurons and to probe the surface layer sensitivities of nanoparticles, making them important candidates for nanoscale molecular sensing applications.

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 species has a unique cell wall shape. In addition, 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 silicaification. Identifying silification genes and proteins is the first step toward understanding the chemical mechanism 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 (Biotic/Synthetic) Route to 3-D Nanoparticle Assemblies with Tailored Chemo- and Shape-Preserving Inorganic Conversion (Basic) Process. Ken H. Sandhage1, Christine Hall2, David R. Brill3, John M. Cudney4, Mark A. Petersen5, 6, 7, 8, 9, 10, 11, 12, 13
1School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2Biotechnology Group, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

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 volume of a microarray 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 dispensing requirements shifting steadily to lower volumes. Various novel non-contact dispensing methods in the nanoliter and picoliter range 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 control the structure of inorganic nanostructures while preserving the frustule morphology: the BaSIC (Biotic and Shape Preserving Inorganic Conversion) process. Such shape-preserving conversion has been accomplished with the use of gas-liquid 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 physiologically to contact/manipulate the cell, perturbing its development or to measure physiologically important parameters such as surface pressure. Neuronal cell damage is induced by the AFM tip which is subsequently used to image the morphological response of the neuron to the AFM tip. The 3-D view of the neuronal cell due to this insult suggests alternative ideas concerning acute neuronal (cellular) scaling 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 neuronal cell lifecycle. 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 nanoparticles and of core/shell nanoparticles to dielectric surfaces. 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 nanoparticle 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 Kaucz, Oliver Guttmann, Christian Wehner, Reinhard Niesert, Bernd Heij, Peter Koltay and Roland Zengerle, IMTEK - Institute of Microsystems 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 volume of a microarray 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 dispensing requirements shifting steadily to lower volumes. Various novel non-contact dispensing methods in the nanoliter and picoliter range
Effects of the presence of nanotubes on heat transfer in microfluidics. N. Thummala and D. 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 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 nanomaterials 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. Lattice Stochastic Temperature Tracking (LSTT) may be used to track the trajectories of heat particles released in the flow field, and to visualize the behavior of the mean temperature profile from the presence of nanotubes on the heat transfer characteristics will be discussed.

SESSION R7: Fabrication and Applications of Nanotubes, Nanowires and Nanoringgs
Chair: David McIlroy
Thursday, April 15, 2004
Room 3029 (Moscone West)

1:30 PM *R7.1 Synthesis, Physical Properties, and Applications of Aligned Carbon Nanotubes. S. R. Ebbesen, The Rockefeller University, New York, New York; and Thomas J. Marks, Stanford University, Stanford, California.

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 electron 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. M. E. Toney, AND, Department of Physics, Boston College, Chestnut Hill, Massachusetts.

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 Nanotube Fibers from Liquid Crystalline Dispersions. Virginia Angela Davis,1,2,3, Nina Fan,4,5, Nicholas Parra-Vasquez1,2,3, Lars Ericsson2, Valentin Prieto1, Sivarajan Ramesh,2 Carter Kittrell,4,5, Joey Sulpio2, Karen Winey,4, Jack Fischer,6 Robert Hauge,7 Matteo Pasquali,1,2,7 and Richard Smalley1,7.

Chemical Engineering, Rice University, Houston, Texas; Center for Nanoscale Science and Technology, Rice University, Houston, Texas; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Macroscopic Single Walled Carbon Nanotube (SWNT) fibers have been produced by directly spinning liquid-crystalline dispersions of SWNTs in supercritical CO2. The direct protonation of the SWNT sidewalls overcomes van der Waals interactions, promoting the dispersion of high concentrations of SWNTs. At 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 spin 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. Congnan Cao, Mechanical Engineering, University of California at Riverside, Riverside, California.

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 the conductivity of the quantum dots. Therefore, a barrier for electron transfer is needed to avoid this. Heterostructures presented here are potential structures for nanoelectronic and nanophotonic devices, and excitations are largely confined to individual quantum dots, and heterostructures presented here are potential structures for nanoelectronic and nanophotonic devices and biosensors. The novel approach 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 mesoscopic 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 mesoscopic 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 within them. This could cause specific orientation between adjacent quantum dots, the lack of which has been 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 an important 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 size of the individual quantum dots and through their packaging. The novel heterostructures 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 Yang2,3 Zexiang Shen3,4

1Electrical and Computer Engineering, National University of
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 fullerene 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, and anti-ferromagnetic phases may 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 subsequent 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 vapor deposition [3]. Here we report on the transport and magnetic measurements on two-dimensional carbon nanostructures 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 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 temperatures resembles well-disordered Josephson junction arrays. [1] K. Watanabe et al., Phys. Rev. B 59, 8271 (1999); [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 as nanotransistors as well as masks for the molecular beam epitaxial growth of GaInNAs 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.


We report on the fabrication and performance of nanometer-scale, electromechanical devices which use multi-walled carbon nanotubes as torsional springs. The 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 torsional motion on nanoscale 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 structural modulus, and its subsequent stiffness as well as the response of the devices to applied voltages. We demonstrate both quasi-static and on-resonance performance characteristics.

**14:15 PM** R7.8 SIMOX 3-D Sculpting for the Fabrication of Nano-Optical Integrated Circuits. Prakash Vijayan Koonath, Koichiro Kishima, Tejsawi Indukuri and Balrman 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 possibility of electronic and optical functionalities 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 opto-electronic 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 very well 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 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. The rib waveguides 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 suppressing resonators with high Q 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 strips of thickness 0.15 microns, with widths varying from 2 microns to 15 microns. The patterned wafer was implanted with oxygen with a dose of 1e18 ions/cm2 and annealed afterwards at 1300°C. This results in the formation of rib waveguides in a single implantation step, of thickness 286 nm, with excellent uniformity obtained on the buried oxide layer 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 feasibility of the SIMOX process to sculpt 3-D nano-optical structures in Silicon.

**4:30 PM** R7.9 Field-effect and gas sensing properties of carbon nanowalls. Bingjun Yang1, 2, Yihong Wu1, 2 and Zeixiang Shen1, 2.

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Carbon can be grown into different forms of nanostructures. So far, many of the works have been concentrated on the growth of two-dimensional (2D) 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/μm was obtained with a vacuum gap of 200 μm, which decreases markedly with increasing pressure. 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/μm. In addition to field emission, the carbon nanowalls have also been investigated as reactive 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 SO2 [2].


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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 preconditions with a high-temperature hydrogenation step on the nucleation and subsequent temporal evolution of Ge self-assembled islands on Si. Two sets of structures were grown with and without H$_2$ pre-conditioning, 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 pre-conditioning, we observe the known formation of a bimodal distribution, with a steady increase in surface coverage and island size as a function of deposition time. On the H$_2$ pre-conditioned 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 pre-conditioned 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 pre-conditioned 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 larger islands shrink whilst the smaller ones grow steadily (similarly to the ones on the unconditioned surface). Ultimately, all islands converge toward similar sizes. We propose that this transient behavior arises from the nonequilibrium topography of the H$_2$ pre-conditioned surface. Close attention to standard processes used during growth, like H$_2$ pre-conditioning, could yield dramatic changes in the uniformity and distribution of Ge nanostructures self-assembled on Si.

SESSION R8: Fabrication, Self-Assembly and Chemical Synthesis of 2-D and 3-D Nanostructures II

8:15 AM R8.1 Syntheses of Mesostructured/Mesoporous Materials with Controlled Morphologies. Jianfeng Wang1,2; and Galen D. Stucky1,2; 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 quasi-aqueous solution under strong acidic conditions. With dodecyltrimethylammonium bromide (C12TMABr) as surfactants, only micrometer-sized spheres are obtained. With C14TMABr as surfactants, nanosized spheres, nanorods, and curve-shaped particles are obtained, depending on the synthesis temperature. The syntheses using C16TMABr give nanostructures 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 self-assembly process inside nanoscale alumina pores. New phenomena occur 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 con-centric ring stacking, to one-dimensional inverse "peapod" structure when the diameter of alumina pores is systematically reduced. This study is significant for the preparation of mesoporous layers 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 Giuca, Simon Henley, Damitha Adisham 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 of 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 piezoelectronics, such as piconanotubes/micromotors, and silicon micromotors that allow for relatively easy and rapid configuration of a wide 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 developed for 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 Nanoscale Interfaces Grant (award No. N000140210870), and the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02047. This work was also supported by the NASA Internal 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. Crisciti, Randall T. Cygan2, James A. Voigt1 and Jianfeng Wang1,2; 1Chemical Syntheses and Nanomaterials, Sandia National Labs, 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 nano-structured materials 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 nanostructures. Through the use of growth modifiers and control of system supersaturation, modulated, extended films have been prepared for material systems ranging from mesoporous silicates where the growth units are micelles to the formation of 3D nanowire or nanorod structures. For the silicate system, surfactant mediated self-assembly of hierarchical mesoporous octahedral 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, hexamethyloctatetramine, etc.) on specific ZnO growth surfaces have been determined. Based on the interpretation 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 Kong, 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-derivated 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 them into functional materials into new technologies. We have successfully 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 by fabricating continuous metallic 3-D nanomesh/wire thin films with hierarchical pore structures. We have successfully developed silica templates with hierarchical 3-D pore structures and used 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 voltamgram, 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 bioanor, photovoltaic and other applications. Adv. Mat., 2003, 15, 130-133.

10:30 AM R8.7

3D-templating of hierarchical ceramics, Helga C. Lichtenegger1, Christina Pitscher3, Juergen Stumpf3, Nicola Huesing2, Robert Liska3 and Sabine Seifert3; 1Institute for Materials Science & Testing, Vienna University of Technology, Vienna, Austria; 2Institute for Applied Synthetic Chemistry, Vienna University of Technology, Wien, Austria; 3Institute of Applied Synthetic Chemistry, Vienna University of Technology, Wien, Austria.

Hierarchically structured ceramic materials 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 process and prototyping of such hierarchical ceramic nanostructures is a suitable method to produce 3-D structures of arbitrary shape and was used here to build cellular molds from resins soluble in alcohols (sacrificial molds). Mesostructured silica was synthesized directly in these sacrificial molds. After removal of the sacrificial templates, 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. The morphological properties of the cellular hierarchical 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, Kwan Kukwon and Stephen J. Fonash; Nano fabrication Facility, Penn State University, University Park, Pennsylvania.

Ag nanoparticle arrays 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 in the thickness of the Si film results in an increase 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 strongly constraining their growth. The Ag nanoparticle 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 de-alloying of PtSi1-x: J. C. Thorp1, K. Sieradzki1, T. Michael3, P. Crozier3, S. T. Picraux2, D. Mitlin2, A. Misra2 and M. Nastasi1; 1Arizona State University, Tempe, Arizona; 2Los Alamos National Laboratory, Los Alamos, New Mexico.

Electrochemical de-alloying 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 (100) platforms for PtSi1-x (x = 20, 30, 40 and 50%) alloys which 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 de-alloyed in concentrated HF by an electrochemical process that leaches out the silicon component of the alloy. X-ray reflectivity and transmission electron microscopy performed on PtSi1-x/Si nanocomposite films obtained, function as active substrates for the formation of nanoporous structures. Anodic polarization curves are used to establish the critical concentration and optimum potential for de-alloying, for example when x = 400 mV (SCE) for Pt:Si 75. Rutheford Backscattering Spectrometry (RBS) depth profiling demonstrates the formation of a pure Pt nanoporous layer on the metal silicide layer as de-alloying process progresses and thus provides a direct observation of the de-alloying kinetics. The resulting morphology of the nanoporous monometallic metal thin film 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 de-alloying 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 de-alloyed to 40 nm after annealing to 900°C. These nanoporous metal thin films 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 fabrication. Such nanoporous materials are expected to be useful in emerging applications such as micro-fuel cells, biosensors, and micro-batteries.

11:15 AM R8.10


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)/stamped materials. However, conventional PDMS stamp materials have shown limitations, especially in the submicron and nanometer 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 than was developed specifically for low-pressure soft lithography. We demonstrate its excellent performance for nano-features (300 nm wide) with narrow and tall heights (1000 nm) of photoreist, 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-device or drug delivery platforms. Nanoparticles were synthesized through a novel approach by developing microfluidic droplet reactor, which was fabricated using new PDMS material.
Fabrication and characterization of three dimensional ordered quantum dot lattices using self assembled epitaxy.

Rainer T. Lechner¹, Tobias U. Schuelli¹,², Vaclav Holy³, Gunther Springholz¹, Julian Stangl¹, Anneliese Raab¹, Till H. Metzger² and Guenther Bauer¹; ¹Institut fuer Halbleiterphysik, Johannes Kepler Universität, Linz, Austria; ²European Synchrotron Radiation Facility, Grenoble, France; ³Department of Solid 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.

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. and Sim. 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.