

SYMPOSIUM G

Nonlithographic Approaches to Micro- and Nanoscale Organization

November 29 – December 3, 1999

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* Invited paper

8:30 AM *G1.1

ORDERING OF ORGANIC/INORGANIC HYBRID STRUCTURES AT MULTIPLE LENGTH SCALES. Ihan A. Aksay, Princeton University, Department of Chemical Engineering and Princeton Materials Institute, Princeton, NJ.

This presentation will focus on the simultaneous synthesis and processing of organic/inorganic composites on two distinct length scales: (i) Self-assembly of organic surfactants is used to generate patterns at the 10 Å to 1 μm length scale; and (ii) field-assisted alignment is used to generate patterns at length scales larger than 1 μm. In our recent work, we illustrated the potential of this method through orientational epitaxy of adsorbed micelles on templates. The organic surfactants self-assemble to form micellar nanodomains which are then used to pattern an inorganic phase with nanoscale modulations. The ability to process inorganic/organic nanocomposites by these methods provides new technological opportunities for creating unusual composites. The utilization of such nanostructured "building blocks" for the construction of larger, viable composite materials can be accomplished through lamination of thin films and patterning through microcontact printing and electrohydrodynamic (EHD) manipulation of fluids/suspensions.

9:00 AM *G1.2

PATTERNED MAGNETIC MEDIA FOR HIGH DENSITY DATA STORAGE. B.D. Terris, IBM Almaden Research Center, San Jose, CA.

The growth in density of magnetic disk drives (6 Gb/sq. in. at present with 60% increase/year) has traditionally been accompanied by a reduction of the grain size of the magnetic media to maintain sufficient signal to noise levels by keeping a constant number of grains per written bit. However, at some density below 100 Gb/in², this scaling process will lead to grains which are susceptible to thermally excited reversals of the magnetization direction; they become superparamagnetic. One approach to avoid this is to create single domain magnetic bits in a patterned magnetic film. We are exploring a number of routes to producing such patterned magnetic islands, with the goal of producing sub-100 nm magnetic islands covering a 1-2 inch diameter disk. In addition to meeting the stringent pattern requirements, the successful method must also leave the disk surface extremely clean so that the magnetic head can fly at a sub-10 nm height and must also be economically viable. In one process, for example, 100 nm magnetic features are created, without the use of any resist, by ion irradiating a magnetic multilayer film through a silicon stencil mask. The ion irradiation rotates the direction of the magnetic easy axis and creates regions of magnetic contrast when imaged using MFM. A second approach we are pursuing to patterning magnetic films involves the uses of stamped polymer films. By stamping a thin uv curable polymer film, we are able to transfer sub-100 nm features. We are exploring using this stamped film as a mask to use in patterning a magnetic film.

9:30 AM G1.3

NANOCHANNEL TEMPLATES AND METAL WIRES BY ION-BEAM IRRADIATION. J.H. Barkyoumb, J.L. Price, N.A. Guardala, N. Lindsey, D.L. Demske, J. Sharma, Carderock Division, Naval Surface Warfare Center, West Bethesda, MD; H.H. Kang and L. Salamanca-Riba, Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD.

Cylindrical nano-scale channels (hollow nanotubules) and semiconductor or metal filled nanochannels have been studied for some time to attempt to engineer their physical, electronic, and material properties. We have used a positive ion beam from a tandem Pelletron accelerator to produce ion tracks in thin mica samples. The resultant nanochannels are then filled electrochemically with bismuth from an acid solution to create nanowires with potentially enhanced thermoelectric properties. The radiation damage tracks are etched with hydrofluoric acid to produce nanochannels. The nanochannel transverse and longitudinal etching growth rates are monitored through a laser polarization technique that allows for controlled growth of smaller channels than has been achieved previously. AFM, SEM, and TEM analyses are used to verify and calibrate the laser monitoring system and show that channels as small as 50 Å are produced with this technique. The etching rates, channel size and taper, and channel production efficiency are then studied as a function of beam fluence and energy for H⁺, He²⁺, Li³⁺, B³⁺, and C⁴⁺ beams. The thickness of the template is governed by the range of the ions in the material. Characterization of the initial radiation track damage and of the etched channels will be presented. Optical

measurements of the quality of the nanochannel template and the Bi filled channels will be presented.

9:45 AM G1.4

IMPRINTED ELECTRICALLY CONDUCTIVE 3D-PATTERNS FROM POLYANILINE BLENDS. Tapio Makela, Jouni Ahopelto, Heikki Isotalo, Technical Research Center of Finland, VTT Electronics, Microelectronics, Espoo, FINLAND.

Imprinting electrically conductive patterns using electrically conductive polymer blends was investigated. Glass substrates were spin- and solution coated by polyaniline/ polymethylmethacrylate (PANI/PMMA) blends in m-cresol. The amount of polyaniline was 10 - 20wt% in the blend and the resulting conductivity of the films about 10-2S/cm. The structures were imprinted using a silicon stamp having a 500 nm deep grating with 5 μm wide lines and spaces. The imprinting temperature was typically 150°C and duration 10 minutes. The blend remained conductive in the process. The anisotropy of the conductivity after imprinting depended on the original thickness of blend film. The film could be removed from the grooves by Ar-ion etching. AFM showed that the resulted patterns were uniform. Anisotropy in conductivity perpendicular and parallel to the polymer ridges was several orders of magnitude. The advantage of this technique is that 3D-structures can be realised without reducing the electrical conductivity of the film.

10:30 AM *G1.5

PRINTED MICRO-ELECTRO-MECHANICAL SYSTEMS AND LOGIC. Joseph Jacobson, Brent Ridley, Brian Hubert, Colin Bulthaupt, Saul Griffith, Sawyer Fuller, MIT, Media Laboratory, Cambridge, MA.

Techniques for directly printing and patterning, without an etch resist, of high performance semiconducting and conducting materials onto a surface in the micro and nanoscale regimes will be discussed. We employ these techniques to fabricate printed micro-electro-mechanical systems (PEMS) as well as logic. Device characteristics and performance will be described.

11:00 AM *G1.6

LITHOGRAPHICALLY-INDUCED SELF-ASSEMBLY OF PERIODIC SUPRAMOLECULAR POLYMER PILLAR ARRAY. Stephen Y. Chou, Lei Zhuang, Xiao-yun Sun, and Paru Deshpande, NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ.

We report of a recent discovery of self-formation of periodic, supramolecular (micrometer scale) pillar arrays in a thin, single-homopolymer film melt, which was originally flat on a plate [1]. The self-formation was induced by placing a second plate (called mask) a distance above the polymer film. The pillars, formed by raising against the gravitational force and surface tension, bridge the two plates, having a height equal to the plate separation, which is 2-7 times of the film's initial thickness. If the surface of the mask has a protruding pattern (e.g. a triangle or rectangle), the pillar array can be formed only under the protruding pattern with the edge of the array aligned to the boundary of the mask pattern. LISA cannot be explained with the existing self-assembly models. A model for LISA will be discussed. Finally, a number of novel applications of LISA will be presented.

[1] S.Y. Chou and L. Zhuang, (a) unpublished 1997, and (b) March Meeting of American Physical Society, March 1999.

11:30 AM G1.7

FORMATION OF SELF-ORDERED POROUS ANODIZED ALUMINUM ON SEMICONDUCTOR SUBSTRATES AND SUBSEQUENT PATTERN TRANSFER. David Crouse, Y.H. Lo, Cornell University, Dept of Electrical Engineering, Ithaca, NY; A.E. Miller, M. Crouse, University of Notre Dame, Notre Dame, IN.

A highly ordered hexagonal array of pores is fabricated in a thin film of alumina on silicon by anodization of an evaporated film of aluminum on silicon. Several anodizing conditions were chosen to produce pore diameters of 15-150 nm, and pore spacings of 55-250 nm. The self-ordered alumina structure, alumina-silicon interface, and alumina barrier layer have been studied and characterized. The effect of the substrate on the barrier layer and other properties of the alumina film is studied resulting in some cases in barrier layers that are distinctly different than in the bulk porous alumina material. Various applications are discussed for such a structure including the use as an etch mask to transfer the pattern into the silicon substrate. For this application the barrier layer is removed by a pore widening chemical procedure, the alumina mask is thinned to 300 nm by ion milling, and the resulting alumina structure is then directly used as an etch mask to transfer the hexagonal pore pattern into the silicon substrate using reactive ion etching. The porous alumina structure is an ideal etch mask showing very little degradation during the RIE

process but can be easily removed by several chemical procedures. These results are then extended to other substrates besides silicon including III-V semiconductor structures.

11:45 AM **G1.8**

MICROSCALE RAPID PROTOTYPING USING UV CURING POLYMERS. Seth Mann, Ioannis Miaoulis, Peter Wong, Thermal Analysis of Materials Processing Laboratory, Tufts University, Medford, MA.

This investigation involves the development of microscopic coatings and patterns that can be used for a number of applications including optical filters and biological material simulation. Ultraviolet (UV) curing polymers are used with a modified optical microscope to create the microscopic prototypes. UV light can be focused through the microscope onto a UV curing polymer target. The target can then be moved on a XYZ stage to create a pattern of the cured substance. Current technology is available for rapid prototyping of objects on the order of millimeters. The polymer curing of microscopic patterns offers potential for many new applications to be developed. The setup includes the incorporation of a high powered mercury vapor lamp to the microscope setup and integration of a feed back control system for monitoring the polymer curing process. The feed back control system can be implemented using image processing techniques. A precise dispensing system of the polymer layers is used for accurate control of heights. Three dimensional structures with feature sizes on the order of 20 μm can be made using this technique.

SESSION G2: NANOPARTICLE ARRAYS

Chair: Vinay Gupta

Monday Afternoon, November 29, 1999

Salon E (M)

1:30 PM **G2.1**

ASSEMBLY OF MICROSTRUCTURED POROUS PARTICLES IN SUSPENDED DROPLETS. Orlin D. Velev, Abraham M. Lenhoff and Eric W. Kaler, Dept of Chemical Engineering, University of Delaware, Newark, DE.

The unique properties of colloidal crystals can only be realized when the structures obtained are self-supported and of well defined sizes and shapes. We report a novel method to form spherical or globular crystalline structures (microballs) by crystallization of colloidal particles in template aqueous droplets suspended on the surface of a heavier liquid immiscible with water. The colloidal particles in the suspended droplets are gradually concentrated by drying to the point of transition to an ordered state. After complete evaporation of the water, highly ordered and symmetric composite particles with smooth surfaces are obtained. Experiments with latex suspensions have yielded crystalline millimeter-sized assemblies with interesting optical properties and remarkable structural stability in air and water. The shape of the microballs is controlled by gravitational deformation of the drying microsuspended droplets. By varying the droplet size, latex concentration and the rate of water evaporation, we obtained assemblies with shapes ranging from spherical through ellipsoidal and even to toroidal. When the droplets contain mixtures of two types of particles of widely different sizes, these two kinds of particles are segregated into different regions of the microstructured assembly. The method can be applied to the controlled assembly of a variety of composite nano- and microstructured particles with extraordinary optical, electro-optical and structural properties.

1:45 PM **G2.2**

SELF-ASSEMBLY OF COLLOIDAL PARTICLES INTO 3D CRYSTALLINE ARRAYS OVER LARGE AREAS AND THEIR APPLICATIONS. Byron Gates, Younan Xia, University of Washington, Department of Chemistry, Seattle, WA.

We have developed a convenient method for self-assembling colloidal particles (50 nm to 5 μm in size) into highly ordered 3D arrays over areas as large as several square centimeters. This method offers a number of attractive features: it is relatively fast; it has a tight control over the surface morphology and the number of layers of the crystalline assemblies; and it works for colloidal systems of a wide variety of materials. Using this method, we have demonstrated the fabrication of a photonic band gap (PBG) crystal that exhibits a strongly attenuated (~ 25 dB), large (510 - 690 nm) photonic gap in the visible region whose spectral position and width were found to be insensitive to the direction of light propagation. We have also fabricated 3D porous membranes of various materials that are potentially useful as PBG structures.

2:00 PM **G2.3**

MICROSTRUCTURE OF Au NANOCUSTER SUPERLATTICES. P.P. Provencio, J.G. Odinek, J.E. Martin, J.P. Wilcoxon, Sandia

National Laboratories, Albuquerque, NM.

We have synthesized superlattices of Au nanoclusters grown by inverse micelle techniques. The monodisperse nanosize metal clusters used in this study were synthesized as surfactant aggregates surrounded by an oil-like environment (inverse micelle). Reaction byproducts, such as excess surfactant and inorganic ion salts, were fractionated and separated using a liquid-liquid technique. The nanoclusters were capped with various length ligands. Two- and three-dimensional hexagonal arrays formed readily on surfaces from evaporation of solution. Both the cluster size and the size of the capping ligand can be controlled to form superlattices having a range of lattice parameters. We have found that the capping agent exerts a marked influence on the tendency of these clusters to order. We have characterized the long-range order in these superlattices using a JEOL 1200 TEM for imaging and electron diffraction with a cooled slow scan CCD camera. A small objective aperture for is used for TEM imaging in order to obtain first order lattice fringes of the superlattices. Using low energy electron diffraction with digital imaging, diffraction rings of large areas of nanoclusters were resolved. The images display nanocluster size, distribution, and lattice fringes from superlattices. These images were further processed using pair correlation functions to determine single domain size and character. This work is performed at Sandia National Laboratories, Albuquerque, NM. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy under Contract DE-AC04-94AL85000.

2:15 PM **G2.4**

ANISOTROPIC SHAPE DEFORMATION OF COLLOIDAL PARTICLES AND STRUCTURES BY ION IRRADIATION. A. van Blaaderen^{a,b}, E. Snoeks^b, T. van Dillen^b, C.M. van Kats^a, M.L. Brongersma^b, A. Polman^b; ^aVan 't Hoff Laboratory, Debye Institute, Utrecht Univ, THE NETHERLANDS; ^bFOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

From measurements on thin films it is known that ion irradiation at high energies (> 2 MeV) can result in an anisotropic plastic deformation. Irradiation experiments (4 MeV, Xe ions) on layers of colloidal spheres of amorphous SiO_2 , and microcrystalline spheres of ZnS , TiO_2 and Fe_2O_3 with sizes between 100-2000 nm indeed demonstrate a dramatic anisotropic plastic deformation of the spheres. Unconstrained particles show a deformation in which the diameter increases in the direction of the ion beam and decrease in the direction of the beam in a reproducible manner. By using irradiations at multiple incident angles, oblate and prolate shaped particles with adjustable aspect ratio can be made. By redispersing the monodisperse colloidal particles anisotropic model systems are obtained with high control over the particle shape. Initial experiments on oblate silica ellipsoids displayed nematic ordering at high particle concentrations. Ion irradiation can also be used to deform two dimensional and thin three-dimensional colloidal crystals. Here interactions between the deforming particles results in a stress build-up that causes the deformation to depend on the relative orientation between the crystal and the beam. We will show how the deformation can provide additional control over the properties of self-assembled lithographic masks and photonic crystals.

2:30 PM **G2.5**

Abstract Withdrawn.

2:45 PM **G2.6**

AEROSOL/COLLOIDAL PROCESS FOR THE SYNTHESIS OF OXIDE-PASSIVATED SILICON NANOPARTICLE ARRAYS. Michele L. Ostraat, Harry A. Atwater, Richard C. Flagan, California Institute of Technology, Pasadena, CA.

Silicon nanoparticle-based floating gate MOS field effect devices are attractive candidates for terabit per square centimeter density nonvolatile memory applications. However, variability in the size, location, and interface quality of the nanoparticles in an ensemble limits nonvolatile memory access speed and retention time. We have designed an aerosol/colloidal process to achieve better control of the properties of oxide-passivated silicon nanoparticles. In the first stage, silicon nanoparticle synthesis is performed by thermal decomposition of silane gas in an aerosol reactor optimized to produce nonagglomerated nanoparticles at rates sufficiently high for layer deposition. Nanoparticles are size-classified by differential mobility analysis (DMA) to produce narrow size distributions ($< 10\%$ diameter at 5 nm). In the second stage, oxide passivation of monodisperse silicon particles is achieved either by thermal oxidation or tetraethylorthosilicate (TEOS) deposition. Depending upon the TEOS partial pressure and reactor temperature, uniform thickness silicon dioxide layers in the nanometer size range can be deposited on the nanoparticles. At temperatures of 800-1000 K, TEOS reacts on the nanoparticles, producing a final uniform 1 nm oxide layer on the particle. At temperatures greater than 1050 K, TEOS vapor undergoes

homogeneous nucleation to form silica nanoparticles, producing large-scale agglomerates with fractal dimension of many tens to hundreds of nanometers. Passivated silicon nanoparticles can be collected as stable colloidal solutions in a variety of solvents. Synthesis of highly organized planar arrays and wires of oxide-passivated silicon nanoparticles from these colloidal solutions will also be discussed.

3:00 PM **G2.7**

SYNTHESIS AND CHARACTERIZATION OF INORGANIC/ORGANIC HYBRID MATERIALS. Michael Breulmann, Sean Davis, Steve Mann, Univ of Bristol, School of Chemistry, Bristol, UK; Hans-Peter Hentze, Markus Antonietti, Max Planck Inst for Colloids and Interfaces, Golm, GERMANY.

There is considerable interest in the preparation of hierarchical inorganic and organic/inorganic composite materials. We are currently developing strategies for the production of such structures based on the assembly (self-, directed-, and templated) of pre-formed inorganic nanoparticle 'building blocks' into higher order structures. The templated deposition of colloidal particles within various biological and synthetic structures with micron scale organization has proved a particularly successful strategy. Recently we have investigated the production of fibrous composite materials containing an inorganic phase loaded onto a bacterial thread backbone. Using certain colloidal particles such as silica, a continuous microarchitecture was formed around the bacterial template. Removal of the bacteria by controlled heating produced highly porous inorganic replicas. Similar experiments using an MCM-41 synthesis mixture resulted in the formation of a meso- and macroporous silica framework. Our current studies are concentrating on using a similar strategy with monolithic, synthetic polymer gel templates. The gels are prepared by polymerization within a microemulsion, producing macroporous materials with a bicontinuous structure. A common property of these gels is that they display pH dependent reversible swelling. It is this property that is exploited to allow incorporation of inorganic filler particles with specific properties such as magnetic behavior, porosity, etc.

3:30 PM ***G2.8**

GUEST-HOST COMPOSITE AEROGELS AS THREE-DIMENSIONAL ARCHITECTURES FOR HIERARCHICAL ELECTROCATALYSIS. Michele L. Anderson, Debra R. Rolison, Karen E. Swider, Rhonda M. Stroud and Celia I. Merzbacher, Surface Chemistry, Surface Modification, and Optical Techniques Branches, Naval Research Laboratory, Washington, DC.

Silica sol, just before it gels into a nanoscale mesoporous network, acts as a nanogel to incorporate a solid-phase guest into the gel network. Composite aerogels can then be formed upon extraction of the pore fluid so as to retain the bulk of the wet gel's free volume as a continuous mesoporous network that serves as a molecular autobahn. Composite guest-host aerogels combine the high surface area and porosity of aerogels with the optical, electrical and physicochemical properties of the guest. Electronic conductivity may be tuned into the structure with a sufficient volume fraction of the guest, for example, Vulcan carbon black. Vulcan carbon, in turn, assembles metal colloids onto its outer surface through adsorption of the metal by its innate thiophene-like sulfur. Colloid-modified Vulcan carbon guests in composite aerogels now permit metal colloids ranging in size from ca. 2 nm - 100 nm to be electrochemically addressed within the three-dimensional mesoporous silica aerogel network. These carbon-supported, pre-formed (and pre-characterized) nanoscale metal particles may also be functionalized for specific sensing, reactive, or catalytic applications via direct adsorption of molecules onto the surface of the colloid. An architecture with all the appropriate reaction or catalytic requirements, including high surface areas readily accessed by molecular reactants, may now be nonlithographically assembled. The electrocatalytic properties of colloidal Pt/C-silica composite aerogels will be discussed as a function of the Pt particle size and chemical state. Such studies can be used to design electrode structures for fuel cell catalysts in which the noble metal catalyst is optimized for both reactivity and facile molecular access.

4:00 PM **G2.9**

SELF-ORGANIZATION OF COLLOIDAL SiO₂ ON UNPATTERNED AND PATTERNED POLYELECTROLYTES. K.M. Chen, M.F. Rubner, and L.C. Kimerling, Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA; X.-P. Jiang and P.T. Hammond, Dept of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

In this work, self-organization of microspheres was accomplished on unpatterned and patterned polyelectrolyte multilayer thin films. The unpatterned films consisted of alternately adsorbed poly(acrylic acid) (PAA) and poly(allylamine) hydrochloride (PAH) on glass or Si substrates. The patterned films consisted of alternately adsorbed PAA and linear poly(ethylene imine) (LPEI) adsorbed onto microcontact

printed Au-coated Si surfaces resulting in electrostatic selectivity. For all multilayers, the surfaces were terminated by the polycationic species. Monodisperse colloidal SiO₂ spheres 0.5-1.6 μm in diameter were deposited from a slurry onto both types of surfaces. For the unpatterned PAA/PAH surfaces, deposition could be controlled to occur in random and ordered fashion. Optical characterization was done to measure the degree of local packing perfection in the ordered arrays. For the patterned PAA/LPEI surfaces, deposition of the colloidal particles was achieved with excellent selectivity between areas with and without the polyelectrolyte. In both the PAA/PAH and PAA/LPEI materials systems, modulation of multilayer surface charge density by pH adjustment of the colloidal slurry leads to regimes of strong and weak colloidal adhesion. The self-organization of microspheres onto charged polymer platforms could lead to methods for fabricating 2- and 3-D photonic bandgap materials.

4:15 PM **G2.10**

DIRECTED SELF-ASSEMBLY OF MICRO-PATTERNED MONOLAYER AND BILAYER RIBBONS OF CLOSE-PACKED NANO-SCALE METAL CLUSTERS. Jia Liu and Ronald P. Andres, Purdue Univ, School of Chemical Engineering, West Lafayette, IN.

Directed chemical self-assembly is of potential interest as a way of achieving high density structures for electronic and optoelectronic applications. One such scheme that has been proposed is the self-assembly of a close-packed monolayer film of uniform size metal clusters on a flat substrate followed by introduction of an organic "linking" molecule that both mechanically and electronically joins the clusters to each other without destroying the cluster superlattice [1]. What has been lacking up to now is a scheme for self-assembling micron-scale electrical interconnects and active devices from such a nano-scale ordered film. We have developed such a scheme. The key steps in the process are: 1) microcontact printing of a defined pattern on the surface of a flat substrate using an organic "tether" molecule, 2) self-assembly of a uniform monolayer of clusters on a water surface 3) transfer of the intact cluster film from the water surface by touching the surface of the film with the patterned substrate, and 4) rinsing with a solvent to remove those portions of the film not attached to the substrate by the tether molecules. This scheme can be used to fabricate complex micro-patterned networks composed of close-packed monolayer and bilayer ribbons of clusters.

[1] Andres, et al., Science 273, 1690 (1996)

4:30 PM **G2.11**

SILVER PHOTONIC CRYSTALS VIA SELF-ASSEMBLY OF QUANTUM DOTS. Yu. A. Vlasov, M. Deutsch, T. Thio, E. Dujardin, NEC Research Institute, Princeton, NJ; N. Yao, Princeton Material Institute, Princeton, NJ; A.A. Sirenko, I.A. Akimov, Penn State University, University Park, PA; and D.J. Norris, NEC Research Institute, Princeton, NJ.

We show how to utilize self-assembly to make silver solids that are three-dimensionally patterned on an optical length scale. Colloidal Ag nanocrystals are induced to self-assemble inside a silica template. The template consists of monodisperse silica spheres (diameter 200-600nm) that are self-organized on a face-centered cubic lattice. Once inside the template, the nanocrystals can be sintered to form a periodic bulk silver structure that has potential as a metallo-dielectric photonic-bandgap material. Furthermore, if desired, the template may be removed by selective etching to yield a macroporous silver solid. The optical and transport properties of the material, as characterized by reflection, transmission, Raman scattering, and magnetoresistance measurements, will be discussed.

4:45 PM **G2.12**

SUB-MICRON METALLIC STRUCTURES WITH 2D AND 3D PERIODICITIES. Mikhail E. Kozlov, New Jersey Institute of Technology, Newark, NJ; Igor A. Udod, Lo-Min Liu, Sanjeeva N. Murthy, AlliedSignal Inc., Morristown, NJ; Ilyas I. Khayrullin, New Jersey Institute of Technology, Newark, NJ; Changxing Cui, Anvar A. Zakhidov, Ray. H. Baughman, AlliedSignal Inc., Morristown, NJ; Brian L. Justus, Elizabeth A. Bolden, Naval Research Laboratory, Washington, DC.

We report two-dimensionally and three-dimensionally periodic sub-micron structures that are obtained by templating carbon, silica sphere, and two-dimensionally periodic glass matrices with various metals. Prepared two-component composites consist of arrays of hundred-nanometer-size metallic spheres, octahedral/tetrahedral voids joined with nanoscale necks, or oriented cylinders packed into artificial crystals. Since the lattice periodicities range from hundred nanometers to microns, these materials are metallic mesoscopic crystals for comparable frequency range. The structures were prepared by melt-infiltration under an applied pressure. The materials used for templating include indium, bismuth, lead, tellurium, antimony and their alloys. The employed matrices had the structure of SiO₂ opal, carbon inverse opal, and channeled glass. We were able to exploit the

influence of magnetic admixtures, gradient doping, and variation of composition on properties of the structures. The degree of anisotropy of the three-dimensional composites was found to depend on fabrication conditions, and could be engineered to desired values by varying the solidification procedure. The structures were characterized by SEM, TEM, EDS, differential scanning calorimetry, and by small- and wide-angle X-ray diffraction, which indicate highly ordered structures. The described methods provide generally applicable approaches for varying materials properties by creating either two- or three-dimensionally periodic mesoscopic systems. Research is supported by DARPA grant DAAB07-97-C-036

SESSION G3: PRINTING, MOLDING, TRANSFER AND OTHER TECHNIQUES II

Chair: James M. Tour
Tuesday Morning, November 30, 1999
Salon E (M)

8:30 AM G3.1

A SOFT LITHOGRAPHIC APPROACH TO 2D ARRAYS OF MAGNETIC NANOPARTICLES SUPPORTED ON SILICON SUBSTRATES. Ziyi Zhong, Byron Gates, Younan Xia, University of Washington, Department of Chemistry, Seattle, WA.

We have demonstrated a simple procedure for generating 2D arrays of magnetic nanoparticles (for example, Fe, Co, Ni, and $ZnFe_2O_4$) supported on Si substrates. In this procedure, a combination of microcontact printing of self-assembled monolayers and selective dewetting was used to generate an ordered array of femtoliter reactors (i.e., water droplets) on the surface of a Si substrate. Subsequent chemical reactions and crystallization in the reactors yielded spatially ordered arrays of nanocrystallites, whose sizes can be easily tuned over a wide range. These ordered arrays of magnetic nanoparticles have been characterized by SEM, SPM and TEM.

8:45 AM G3.2

DIRECT WRITING OF ELECTRONIC AND SENSOR MATERIALS USING A NOVEL LASER TRANSFER TECHNIQUE. A. Pique, R.C.Y. Auyeung¹, J. Fitz-Gerald, H.D. Wu¹, S. Lakeou², R. Chung³, D.B. Chrisey, R.A. McGill, and M. Duignan⁴; Naval Research Laboratory, Washington DC; ¹SFA, Inc., Largo, MD; ²Univ. of the District of Columbia, Washington, DC; ³Geo-Centers, Inc., Ft. Washington, MD; ⁴Potomac Photonics, Inc., Lanham, MD.

MAPLE direct write (MAPLE DW) is a new laser-based nonlithographic direct write technique which combines the basic approach employed in laser induced forward transfer (LIFT) with the unique advantages of matrix assisted pulsed laser evaporation (MAPLE). The technique utilizes a laser transparent substrate with one side coated with a dilute matrix consisting of the material to be transferred mixed with an organic binder or precursor. As with LIFT, the laser is focused through the transparent substrate onto the matrix coating. When a laser pulse strikes the coating, the matrix decomposes and aids in transferring the material of interest to an acceptor substrate placed parallel to the matrix surface. MAPLE DW is a maskless deposition process designed to operate in air and at room temperature, that allows for the generation of complex patterns with micron scale linewidths. With MAPLE DW, diverse materials including metals, dielectrics, ferroelectrics, ferrites, polymers as well as polymer-conductor composites have been successfully transferred onto various types of acceptor substrates. The capability for laser-modifying the surface of the acceptor substrate as well as post-processing the transferred material has been demonstrated as well. This simple, yet powerful technique has been used to fabricate passive thin film electronic components such as resistors, capacitors, cross-over lines, inductors, antennas, as well as chemical sensor devices. The various structures produced by MAPLE DW were characterized using 3-D surface profilometry, scanning electron microscopy and x-ray diffraction. The electrical resistivity of the metal layers and the dielectric constant and loss tangent of the dielectric layers were measured using an impedance analyzer and compared to their bulk counterparts. An overview of the key elements of the MAPLE DW process including our current understanding of the material transfer mechanism as well as its capabilities and current limitations as a rapid prototyping technique will be presented. This work was supported by DARPA, through the DARPA-MICE program and the Office of Naval Research.

9:00 AM *G3.3

NONLITHOGRAPHIC APPROACHES TO MICRO & NANOSCALE PATTERNING. George M. Whitesides, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

This talk will describe exploratory approaches to the formation of microstructures. Techniques included in the talk will be meso-scale

self-assembly, laminar flow patterning, and spontaneous buckling of elastomers to give ordered structures.

9:30 AM *G3.4

PROGRESS IN THE FABRICATION OF PERIODIC STRUCTURES WITH CHANNEL GLASS. Brian L. Justus, Optical Sciences Division, Naval Research Laboratory, Washington, DC.

Recent advances in channel glass fabrication technology will be discussed. A new generation of channel glass is now being fabricated having micron- and submicron-scale channel diameters but with overall diameter up to 30 times greater than that previously possible. This is accomplished using traditional channel glass fabrication methods to make composite glass fibers that are then bundled and fused within a glass cladding to yield channel glass having an increased outer diameter that is independent of channel diameter. These large-area channel glasses are well-suited for patterning applications via methods such as replica mask transfer, imprinting and stamping. The fabrication of arrays of submicron-scale gold rings on a silicon substrate, using replica mask transfer methods, will be described. A metal replica mask is used first as a shadow mask for sputtering an array of gold posts. The channels in the mask are then partially closed by sputtering at a glancing angle. Rings are formed by ion milling at normal incidence to remove the center portion of the gold posts. Removal of the mask exposes the array of rings. This method permits parallel patterning of dense arrays of complex structures without removal or realignment of the mask between fabrication steps. The use of channel glass in the fabrication of two-dimensional photonic band gap structures will be discussed. Photonic band gap materials are composite materials having a spatially modulated index of refraction, with the modulation on the order of the wavelength of light. Thus, in order for photonic band gap effects to be observed at visible and near infrared wavelengths the scale of the spatial modulation is necessarily submicron. Channel glass and replica masks are well-suited for the fabrication of such structures and two-dimensional photonic band effects at these wavelengths have been observed in our laboratory.

10:30 AM *G3.5

PRINTING, MOLDING, AND NEAR-FIELD PHOTO-LITHOGRAPHIC METHODS FOR ORGANIC ELECTRONICS AND INTEGRATED OPTICS. John A. Rogers, Zhenan Bao, Martin Meier and Ananth Dodabalapur, Lucent Technologies, Bell Laboratories, Murray Hill, NJ; Olivier J.A. Schueller and George M. Whitesides, Harvard University, Department of Chemistry, Cambridge, MA.

This talk describes applications and extensions of several 'soft lithographic' techniques that use rubber stamps, molds, and conformable photomasks for micro and nanofabrication. It summarizes some of our recent work in (i) roller printing of organic transistors and related circuitry for organic 'smart pixels' and complementary inverters that have critical dimensions as small as 1 micron and are supported by lightweight flexible plastic substrates, (ii) nanomolding of first and third order distributed feedback, distributed Bragg reflector and photonic crystal resonators for lasers that have narrow emission profiles in the visible range, (iii) fabrication of low voltage organic transistors and inverter circuits with 0.1 micron channels formed using simple near-field photolithographic methods, and (iv) full-wafer nanolithography with ultrathin spin cast photocurable resists and mechanically flexible, optically transparent composite molds.

11:00 AM G3.6

HOLOGRAPHIC RECORDING USING TWO-PHOTON INDUCED PHOTOPOLYMERIZATION. Sean Kirkpatrick, Jeff Baur, Casey Clark, Lisa Denny, David Tomlin, Bruce Reinhardt, Ramamurthi Kannan, Morley Stone, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, OH.

Molecular excitation via the simultaneous absorption of two photons can lead to improved three-dimensional control of photochemical or photophysical processes due to the quadratic dependence of the absorption probability on the incident radiation intensity. This has led to the development of improved three-dimensional fluorescence imaging, optical data storage, and microfabrication. The latter of these involves the fabrication of three-dimensional structures using a spatial variation in the incident intensity within a photopolymerizable resin. In the past, the translation of the focal plane of a tightly focused laser beam was used to induce localized photopolymerization and fabrication of three-dimensional structures. Here we report the first successful demonstration of large area patterning via ultrafast holography-based two-photon polymerization of a commercially available optical resin and a large two-photon cross-section dye (AF380). This opens tremendous possibilities for the wide spread use of two-photon absorption for the three-dimensional control of photoinduced processes. Our eventual goal is to use this holographic

process to duplicate biological structures that have been implicated as being important in infrared reception.

11:15 AM *G3.7

A SIMPLE APPROACH FOR PREPARING PATTERNED, MICRON-SCALE CORRALS FOR CONTROLLING CELL GROWTH: APPLICATIONS TO BIOSENSING. Mary Lee Amirpour, Richard M. Crooks, Pradyut Ghosh, William M. Lackowski, Michael V. Pishko, Texas A&M University, Departments of Chemistry and Chemical Engineering, College Station, TX.

In this talk we describe a new method for patterning thousands of cells into individual corrals on surfaces, and then describe how such bioarrays can be used for biosensing applications. Micron-scale patterns of thick, covalently grafted films of hyperbranched poly(acrylic acid) (PAA), poly(tert-butylacrylate) (PTBA), and nanocomposite poly(acrylic acid)/poly(ethylene glycol) (PAA/PEG) organic thin films are prepared by micro-contact printing (μ -CP) and subsequent polymer-grafting steps. Importantly, PAA polymer growth only occurs in regions of the gold substrate originally modified with monolayers having reactive terminal groups (mercaptoundecanoic acid, MUA). The 3-PAA films (the 3 indicates the number of activation, grafting, and hydrolysis iterations used to prepare the film) contain a high density of derivatizable -COOH groups, and we have taken advantage of these to covalently graft PEG onto the surface of the 3-PAA films. Ellipsometry, reflectance FTIR, tapping-mode atomic force microscopy, and optical profilometry confirm that it is possible to pattern 250 Å-thick 3-PAA films and ~500 Å-thick PEG-grafted 3-PAA films (3-PAA/PEG) having critical lateral dimensions as small as 2 μ m. Patterns of similar quality can be prepared on plastic substrates. Our studies indicate that many different cell lines adhere to and grow on n-alkylthiol monolayer surfaces. Cell viability and spreading studies were performed using fluorescent assays, and they demonstrate that spreading and growth completely cease when cells reach the PAA/PEG corral walls. Picoliter volumes of chemicals can be delivered to individual corrals by micropipetting, which allows us to control and monitor individual cell behavior. Libraries of cells containing genetically engineered enzymes can be immobilized as individual pixels on the patterned surfaces. The pixels can be screened for activity in parallel using optical methods to reveal the presence of highly efficient mutants.

SESSION G4: BIOMOLECULAR AND BIOMIMETIC ASSEMBLY

Chairs: Linda G. Griffith and Buddy D. Ratner
Tuesday Afternoon, November 30, 1999
Salon E (M)

1:30 PM *G4.1

BIOMOLECULAR TEMPLATES FOR CONTROL OF MICRO- AND NANOSCALE ORGANIZATION. Jeffrey Linhardt, Kevin Thigpen, Michael Yu, Hanna Rapaport, David Tirrell, California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA.

Biological amphiphiles and biological macromolecules mediate the complex assembly processes that generate the striking architectural diversity of cells, tissues and organisms. This lecture will examine recent progress in the use of amphiphilic and macromolecular templates to create much simpler molecular and supramolecular systems with organizational control at the micron and nanometer length scales. Phospholipid nanotubes, liquid crystalline arrays of helical polymers, and two-dimensional peptide crystals will be discussed.

2:00 PM *G4.2

TEMPLATE SYNTHESIS OF NANOMATERIALS: APPLICATIONS TO LITHIUM-ION BATTERIES. Charles J. Patrissi and Charles R. Martin, Colorado State University, Department of Chemistry, Fort Collins, CO.

We are exploring a nonlithographic approach for the preparation of nanomaterials which we call "template synthesis". Briefly, template synthesis entails deposition of the material of interest, or a precursor for that material, into the pores of a microporous template membrane. The diameter and aspect ratio of the deposited nanomaterial is controlled by selection of the template membrane pore diameter and thickness. Using this approach we have prepared nanostructured metals, polymers, semiconductors and carbon. Our research focuses on the effects of particle size and shape on the physical and chemical properties of a material or class of materials. For example, the performance of lithium-ion batteries critically depends on the particle size and shape of the Li-insertion material in the electrodes. In order to study the relationship between particle size and rate performance, we combined sol-gel chemistry and template

synthesis in order to prepare nanofibrous Li-insertion cathodes of polycrystalline V_2O_5 . The electrodes consist of nanofibrils of V_2O_5 which protrude, like the bristles of a brush, from a Pt foil current collector. The preparation method involves the deposition of an anhydrous sol-gel precursor into the pores of a polycarbonate template membrane. Slow hydrolysis of the precursor occurs initially at low water partial pressure. Subsequent processing of the membrane / hydrolyzed precursor / Pt foil composite includes further hydrolysis of the precursor, removal of the membrane with an oxygen plasma and, finally, heating at 400°C in oxygen. The result is a nanoengineered V_2O_5 electrode.

Galvanostatic results show that the nanostructured electrode delivers higher capacity, at high discharge current, than thin-film control electrodes with the same mass and geometric area of V_2O_5 . This is because the high surface area of the nanostructure decreases the lithium insertion-rate density at high discharge current. Lower insertion-rate density reduces the effects of concentration polarization and increases rate performance.

2:30 PM G4.3

PROGRESS TOWARDS DNA TEMPLATING OF NANO-ELECTRONIC STRUCTURES. Scott M. Reed, Marvin G. Warner, Leif O. Brown, James E. Hutchison, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR; Margaret E. Saks, Department of Biology, University of Oregon, Eugene, OR.

Fabrication of functional ultra-small electronic devices will require the development of new methodologies for assembly. Our approach to creating nanoelectronic structures or devices utilizes biological molecules with well understood self-assembly as construction templates for the design of nanoelectronic devices. There are three basic elements to this approach; 1) the synthesis of stable, water soluble gold nanoparticles, 2) the synthesis and selective incorporation of ligands that can provide a linkage to the biomolecules, and 3) the preparation of an appropriate biomolecule that will anchor the nanoparticles and bridge electrodes of a specific gap size. Here we will describe progress towards achieving those goals using DNA as the bridge between electrodes. We have synthesized a number of water soluble gold nanoparticles by exchanging thiols onto small ($d = 1.4$ nm) phosphine-stabilized nanoparticles and have characterized them by NMR, TEM and XPS. We have also developed a method for introducing a small amount of a functionalized thiol into a gold nanoparticles ligand shell that serves the purpose of creating a bridge between the nanoparticle and the biomolecule. This method creates a dual ligand sphere in which one ligand functions to provide high solubility while the other functions to create the bridge between the nanoparticles and the biomolecule. We have also synthesized thiol ligands that will bind to double stranded DNA by reversible non-covalent interactions. Such an approach allows using the same functionalized nanoparticle with any DNA length, sequence and architecture. Currently, we are synthesizing DNA fragments to bridge the gap between two gold electrodes separated by 340nm. Use of these to bridge the electrode gap and to assay the binding ability of various nanoparticles to DNA will be presented.

2:45 PM G4.4

LATEX MICROSPHERES FOR PATTERNING OF BIOMOLECULES AT SURFACES. Darrell J. Irvine, Pallab Banerjee, Anne M. Mayes, Massachusetts Inst. of Tech., Dept. of Materials Science and Engineering, Cambridge, MA; Linda G. Griffith, Massachusetts Inst. of Tech., Dept. of Chemical Engineering, Cambridge, MA.

We have examined the use of novel latex microspheres in the design of substrates presenting patterned biomolecules with the objective of eliciting controlled cell responses to biomaterials surfaces. The microspheres have been prepared by dispersion polymerization of methacrylate and acrylate monomers from water/ethanol solutions in the presence of an amphiphilic comb copolymer having hydrophilic poly(ethylene glycol) side chains. The comb stabilizes growth of nearly monodisperse polymer particles with sizes ranging from approximately 0.2 microns to 5.0 microns, and provides a hydrophilic coating to the microspheres formed. The PEG side chains of the comb extend from the surface of the beads into solution, providing a protein- and cell-resistant surface layer to the particles. The chain ends of the comb at the surface of the beads can be used to covalently tether biomolecules to the microspheres. Films formed by coalescing the beads on a suitable support are resistant to cell adhesion, while films prepared from beads bearing tethered adhesion peptides support strong specific cell attachment and spreading. We have pursued the design of surfaces presenting peptide ligands in domains determined by the microsphere diameter by preparing films from mixtures of adhesion peptide-modified and unmodified beads. Surface distributions of the peptide have been characterized using atomic force microscopy. The adhesion and spreading response of cells to these surfaces had been quantified, and the resulting cell cytoskeletal

organization in response to the surfaces has been studied by fluorescence microscopy.

3:00 PM G4.5

NANOSCALE ORGANIZATION OF FUNCTIONAL MATERIALS VIA BIOMIMETIC COMPOSITE ASSEMBLIES. Y. Lu, J. Dodd, D.Y. Sasaki, A.R. Burns and C.J. Brinker, Sandia National Laboratories, Albuquerque, NM.

There is considerable interest in functional materials, such as conjugated polymers and chromophore-containing lipid bilayers, that optically report chemical recognition processes. To be useful as sensors in optical platforms, they must be supported in a fashion that both is stable and robust, but does not restrict molecular motion. We have been successful in this endeavor by organizing functional organic materials into mesoporous inorganic host matrices using a novel biomimetic self-assembly process [1]. Specifically, we begin with a solution of silica, organic monomer, and surfactant (if necessary), and induce micelle formation by evaporative dip-coating. Subsequent self-assembly of the silica-organic micelles into lyotropic mesophases simultaneously organizes the organic and inorganic precursors into nanolaminates. Coatings were deposited on glass slides. We will discuss results using diacetylene (10,12-pentacosadiynoic acid (PCA)) monomers modified with oligoethylene glycol headgroups to achieve the proper amphiphilic character and molecular geometry to form stable micellar or lamellar structures. We have formed highly ordered lamellar structures, with a 47 Å spacing as determined by X-ray diffraction measurement. In situ UV polymerization of the diacetylene monomers into the intense blue form of polydiacetylene was observed. Thermochromic and lyochromic (solvent dependent) behavior of the polydiacetylene/inorganic matrices will be discussed, as well as the formation of the fluorescent red form. Polarized fluorescence microscopy has revealed significant ordering of the conjugated backbones in the matrix. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000 [1]. Sellinger et al., Continuous self-assembly of organic-inorganic nanocomposite coatings that mimic nacre Nature v.394 (1998) p.256.

3:30 PM *G4.6

TEMPERATURE DEPENDENT BEHAVIOR OF DNA-LINKED QUANTUM DOTS. Chad A. Mirkin, Gregory P. Mitchell, Robert L. Letsinger, Northwestern University, Department of Chemistry, Evanston, IL.

Methodology for immobilizing oligonucleotides on the surfaces of semiconductor quantum dot materials will be described. This methodology involves the development of a novel pH trigger, which allows one to adjust the water solubility of TOPO-stabilized CdSe particles so that they are compatible with DNA. The hybridization properties of these materials and their temperature-dependent optical properties will be discussed.

4:00 PM G4.7

DIRECTED SELF-ASSEMBLY OF NANOPARTICLES INTO MACROSCOPIC MATERIALS USING ANTIBODY-ANTIGEN RECOGNITION. Wayne Shenton, Sean Davis, Stephen Mann, The University of Bristol, Department of Chemistry, Bristol, ENGLAND.

The organization and patterning of inorganic nanoparticles into two- and three-dimensional functional structures is a potential route to chemical, optical, magnetic and electronic devices with useful properties. A range of non-lithographic protocols, including solvent evaporation of hydrophobic colloids, molecular cross-linking in colloidal aggregates and template-directed synthesis using porous protein crystals or bacterial superstructures have been reported. Here we describe a method for self-assembling nanoparticles using the recognition properties of surface-attached antibodies. We attach IgE or IgG antibodies with specificities to dinitrophenyl (DNP) and biotin, respectively, to individual Au nanoparticles, and add antigens with appropriate double-headed functionalities to induce the formation of metallic or bimetallic macroscopic filaments and aggregates comprising covalently-linked Au, or Au and Ag nanoparticles. Antigen connectors with homo- (DNP-DNP) or hetero- (DNP-biotin) Janus structures connected by at least an eight-atom spacer have been synthesized for this purpose. The versatility of our directed self-assembly approach, and the ability to exploit antigen engineering in general, should make it possible to produce a wide range of poly-metallic nanoparticle aggregates with specific cross-linked structures, compositions and macroscopic architectures.

4:15 PM *G4.8

THE FABRICATION OF DNA ARRAYS ON GOLD SURFACES AND SPR IMAGING MEASUREMENTS OF SEQUENCE-SPECIFIC PROTEIN-DNA BINDING. Robert M. Corn, Department of Chemistry, University of Wisconsin, Madison, WI.

A multi-step surface modification procedure for the creation of DNA arrays on chemically modified gold surfaces that can be used in surface plasmon resonance (SPR) imaging studies of protein-DNA interactions is demonstrated. The multi-step procedure is required to create an array of spots that are surrounded first by a hydrophobic background which allows for the pinning of aqueous DNA solutions onto individual array elements and then to replace that hydrophobic background with one that resists the non-specific adsorption of proteins during in situ SPR imaging measurements. An amine-terminated alkanethiol monolayer is employed as the base layer, and Fmoc and PEG modifiers are used to create the sequentially hydrophobic and protein adsorption-resistant surfaces, respectively. A combination of polarization-modulation FTIR spectroscopy, contact angle and scanning angle SPR measurements are used to characterize the surface modification procedure. SPR imaging measurements of the sequence specific adsorption of the proteins single-stranded DNA binding protein (SSB) and single base mismatch protein MutS onto oligonucleotide arrays created by this procedure are used to demonstrate the utility of these surfaces.

4:45 PM G4.9

TEMPLATE-IMPRINT NANOSTRUCTURED SURFACES FOR BIORECOGNITION. Huaiqiu Shi, Buddy D. Ratner, University of Washington Engineered Biomaterials, Seattle, WA.

Specificity and recognition are perhaps the primary lessons we can take from nature and bring to synthetic materials. How can we create synthetic materials that demonstrate biorecognizability? In this study, surfaces with tailored protein-binding cavities are prepared by an imprinting technique based on RF-plasma deposition of organic thin films. A polysaccharide-like surface with protein-imprinted nanopits allows only the template protein to fill the pits, and to bind strongly, because the nanopits are complementary to the template protein in shape and in the distribution of functional groups. The bound protein in its pit is prevented from exchange with protein in the solution due to a strong binding and steric hindrance, while non-template protein that is weakly adsorbed on the surface is displaceable. A number of techniques including ESCA, ToF-SIMS, AFM and radio-labeled protein studies are used to explore these nanopitted recognition surfaces.

SESSION G5: NANOSCALE ORDERING AND LITHOGRAPHY VIA POLYMER SELF ASSEMBLY

Chairs: Paula T. Hammond and Paul F. Nealey
Wednesday Morning, December 1, 1999
Salon E (M)

8:30 AM *G5.1

SURFACE NANOPATTERNING VIA BLOCK COPOLYMER THIN FILMS. Christopher K. Harrison, Miri Park, Matthew L. Trawick, Douglas H. Adamson, Paul M. Chaikin, and Richard A. Register, Princeton University, Princeton Materials Institute, Princeton, NJ.

Block copolymers spontaneously self-assemble into microdomain structures, which are simple repeating patterns with a size scale (typically 1-100 nm) controlled by the polymer molecular weight. Similar patterns are obtained when these block copolymers are deposited as single-microdomain layers on substrates. Using these thin films as templates, we have developed techniques based on reactive ion etching to uniformly and completely pattern the underlying substrate with a dense periodic pattern of dots or holes (typically 20 nm diameter), as well as metal dots prepared by backfilling these holes. To image the structure of the block copolymer films, we have developed a technique employing nonselective reactive ion etching followed by examination with a low-voltage, high-resolution SEM. Recently, we have also been able to image the microdomain structures using AFM, without staining or etching; the nondestructive nature of AFM offers the promise of sequentially imaging a particular region of the material as the grain structure evolves in time. The orientational order of the pattern has a very limited range, as block copolymers typically show a grain structure. In the pursuit of structures with better long-range order (larger grains), we have investigated the process of grain growth. At short times, the growth rate is essentially diffusive, but at longer times, the average grain size appears to saturate, or at best to grow only very slowly, far more slowly than the square root of time. This slowing down is found both for polymers with both cylindrical and spherical microdomain structures, and we attribute it to the barrier to defect motion imposed by the regular microdomain structure. Finally, we have begun to explore how other nanofabricated surface structures can be used to control the orientation of these grains.

9:00 AM *G5.2

NANOPATTERNING BY ABC TRIBLOCK COPOLYMERS. Georg Krausch, Robert Magerle, Kenji Fukunaga, Hubert Elbs,

We discuss the thin film morphology of ABC triblock copolymers with preferentially adsorbing middle block B. Thin films of the materials are studied both on homogeneous and pre-patterned surfaces. We discuss the use of selective solvent vapors for creation of materials contrast between neighboring blocks using AFM imaging. Furthermore, the influence of the preparation conditions on the resulting structures are discussed. We demonstrate that suitable macroscopic sample geometries combined with treatment in solvent vapors can be used to create large lateral monodomains.

9:30 AM G5.3

SELF-CONSISTENT FIELD STUDY OF SUBSTRATE CHEMICAL PATTERN RECOGNITION BY COPOLYMER CHAINS. Jan Genzer and James Semler.

The one-dimensional self-consistent field (SCF) scheme of Scheutjens-Fleer has been extended to three dimensions. Such 3D SCF model was used to investigate the adsorption of A-B copolymers from A homopolymer matrices onto planar substrates composed of two chemically distinct sites (C and D), one of which has a preferential affinity for the B segments of the copolymer. To address the role of the substrate chemical heterogeneities on copolymer adsorption, we keep the number of the C and D sites constant and vary their spatial distribution on the substrate. The interplay between the surface chemical heterogeneity and the chain microstructure is examined for A-b-B diblock and A-alt-B alternating copolymers. Our results indicate that regardless of the type of the surface chemical heterogeneity the A-b-B copolymer adopts a brush-like structure while the A-alt-B chains is zipped to the substrate. For a fixed chemical potential of the copolymer in the A-B/A mixture, the amount of the adsorbed copolymer depends on i) the number of the B segments, ii) the copolymer microstructure, iii) the surface adsorption energy of B, and iv) the distribution of the C and D regions on the substrate. 3D maps of the spatial density of copolymer segments provide insight into copolymer conformation at the mixture/substrate interface.

9:45 AM G5.4

SELF-ASSEMBLY OF 3D MESOSTRUCTURES, AND DISCRETE OBJECTS FROM SYNTHETIC POLYMERS. Samson A. Jenekhe and X. Linda Chen, UNIVERSITY OF ROCHESTER, Department of Chemical Engineering, Rochester, NY.

Macromolecular architecture and non-covalent forces play central roles in the hierarchical self-assembly of proteins and other natural polymers into complex mesoscopic structures in living systems. Although flexible-coil block copolymers can self-organize into segregated nanostructures and mesophases, they lack rigid sequences and well-defined intermolecular interactions essential to controlling three-dimensional shape of assemblies. We are exploring new structural motifs for designing synthetic polymer systems capable of hierarchical self-assembly into complex, well-ordered, functional mesostructures. Our synthesis and investigation of amphiphilic rod-coil block copolymers have resulted in the controlled self-assembly of various 3D mesostructures such as hollow spheres, microtubules, vesicles, lamellae, and doughnuts. These supramolecular assemblies with size scales in the 50 nm to 200 micrometer range and electroactive/photoactive functions are comparable in size to self-assembled objects in cellular biology. The discrete macromolecular assemblies can sequester large molecules in the cavity of each spherical aggregate. Hierarchical self-assembly of periodic mesoporous materials from the same rod-coil block copolymers has also been demonstrated. These results demonstrate the potential of synthetic self-assembling polymers for engineering complex two- and three-dimensional periodic mesostructures or discrete objects. Besides their promise as model systems for fundamental studies in the new field of supramolecular polymer chemistry, these self-assembling polymer mesostructures have many potential technological applications.

10:30 AM *G5.5

FORMING PATTERNED INTERFACES WITH NANOSCALE PARTICLES AND BLOCK COPOLYMERS. Valeriy Ginzburg, Feng Qiu, Gongwen Peng and Anna C. Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA.

Using a coarse-grained computer model, we determine the influence of nanoparticles on the phase separation and the morphology of diblock copolymer films. The particles modify the microphase separation patterns and create new "steady-state" morphologies. We calculate the dependence of the characteristic domain size on the density of particles and develop a mean-field rate-equation model to describe this dependence. Our results are particularly important for optimizing the design and fabrication of novel nanoscale devices.

11:00 AM *G5.6

NONLITHOGRAPHIC PATTERNING: COPIES OF LIQUID CRYSTALS AND SURFACE MIGRATION OF MOLECULES. Samuel I. Stupp, Departments of Materials Science and Engineering and Chemistry, Northwestern University, Evanston, IL.

Spontaneous patterning of materials based on thermodynamic structures is a potential source of novel functionality without complex processing. One such process of interest in our laboratory is the mineralization of metal doped liquid crystals to produce hard copies of their characteristic order. We have demonstrated that great fidelity in nanoscale dimensions and symmetry can be achieved using these soft templates for inorganic semiconductors such as cadmium telluride, cadmium sulfide, and zinc sulfide. We are also interested in patterns formed by molecules with thermodynamic tendencies to migrate to surfaces of materials. Here our interest focuses on functionalized molecules with dendron rodcoil architecture which migrate to surfaces when combined with polymers.

11:30 AM *G5.7

SELF-ASSEMBLED COPOLYMER TEMPLATES FOR QUANTUM TRANSPORT DEVICES. Heinrich M. Jaeger, Ward Lopes, Terry L. Morkved, James Franck Institute and Dept. of Physics, The University of Chicago, Chicago, IL.

Diblock copolymers consist of two polymer species, A and B, covalently bonded together. They spontaneously phase separate into alternating domains of A and B, resulting in ordered structures with repeat spacings in the range 10-100 nm. This talk discusses experiments on ultrathin films of diblock polymers with thicknesses between 1/2 to 3/2 the repeat spacing. In this ultrathin limit, differences between the surface free energies for the two blocks can be used to stabilize new morphologies that have no counterpart in the bulk. In particular, it is possible to create morphologies in which A and B domains alternate along the film surface [1]. Such nanometer-scale lateral modulation of the film surface is difficult to achieve with conventional fabrication methods; the different chemical and physical properties of A and B domains make such structures highly suited as templates for device applications. To this end, we have used electric fields to align copolymer domains between planar electrodes [2], and differential wetting to selectively load one of the blocks with metal nanoparticles. For ultrathin lamellar- or cylindrical-phase diblock films this approach produces a single layer of parallel chains of nanoparticles extending over microns between the electrodes. Electronic transport through these chains occurs by tunneling in the presence of strong single electron charging effects. We find highly nonlinear current-voltage characteristics with threshold voltages of several volts. 1. T.L. Morkved and H.M. Jaeger, Europhys. Lett. 40, 643-648 (1997). 2. T.L. Morkved et al., Science 273, 931-933 (1996).

SESSION G6/H11: JOINT SESSION:
NANO TO MOLECULAR SCALE ELECTRONICS OF
ORGANIZED STRUCTURES

Chairs: Samson A. Jenekhe and Jane Shaw
Wednesday Afternoon, December 1, 1999
Salon E (M)

CONCURRENT WITH G7/CC6

1:30 PM G6.1/H11.1

NANOSCALE PATTERNS OF METAL NANOPARTICLES CHEMICALLY-ASSEMBLED ON BIOMOLECULAR SCAFFOLDS: ASSEMBLY STRUCTURE, STABILITY AND ELECTRON TRANSPORT PROPERTIES. James E. Hutchison, Leif O. Brown, Jana Mooster, Scott M. Reed, Mary E. Schmidt, Dept of Chemistry and Materials Science Inst, Univ of Oregon, Eugene, OR; Laura I. Clarke, Martin N. Wybourne, Dept of Physics and Astronomy, Dartmouth College, Hanover, NH.

The novel electronic properties (e.g., Coulomb blockade) of nanometer scale assemblies of metal nanoparticles make them potentially useful in nanoelectronic devices and extremely sensitive chemosensors. To date, no straightforward and reproducible methods are available for the fabrication of low-dimensional nanoparticle assemblies. The fabrication of nanoscale lines is a particularly challenging, yet important goal. Our method for nanofabrication of linear nanoparticle arrays involves the assembly of functionalized metal nanoparticles onto rigid biomolecular scaffolds cast upon an insulating substrate and bridged between narrowly spaced electrodes. Our previous investigations of unpatterned nanoparticle thin films provided clear evidence of Coulomb blockade at room temperature, but the response was unstable over time. In this paper we present a wet chemical approach to preparing one- and two-dimensional arrays of gold nanoparticles assembled onto a polypeptide (poly-L-lysine) scaffold

layer. The assembly process provides a simple, chemical method to immobilize the particles and is found to stabilize the electrical response (Coulomb blockade) of the array compared with unpatterned samples. A striking feature of the electrical properties is that the electron transport properties are dominated by transport through one-dimensional chains within the sample. Structural studies by AFM and XPS will be presented that support the transport findings and provide evidence for the formation of one-dimensional assemblies within the arrays.

1:45 PM G6.2/H11.2

CHARGE TRANSPORT IN SEMICONDUCTOR QUANTUM DOT SOLIDS. C.A. Leatherdale, N.Y. Morgan, I. Prasad, M.G. Bawendi, and M.A. Kastner, Departments of Chemistry and Physics, Massachusetts Institute of Technology, Cambridge, MA.

Close-packed arrays of semiconductor quantum dots represent a model system in which to study the evolution of electronic structure in an artificial solid. We study photoconductivity in close-packed solids of nearly monodisperse CdSe semiconductor nanocrystals. We observe quantum dot size and surface passivation dependent photoconductivity that can be qualitatively understood by considering the energy required to overcome the Coulomb energy of the initial electron-hole pair. The temperature dependence of the photocurrent indicates that tunneling processes dominate both charge separation and charge transport. We model the initial charge separation step using simple tunneling calculations. Simultaneous fluorescence quenching and photoconductivity measurements suggest that many more charge separated pairs are created than reach the electrodes. Measurements of the fluorescence intensity as a function of charge in the film, reveal that excess charge causes reversible photodarkening of the quantum dot solid accounting for some of the discrepancy. Hysteretic behaviour and long time transients, observed in both the photoconductivity and conductivity measurements, suggest that charge is easily trapped in the solid. Strong electron-electron interactions between charges on different sites in the lattice may be limiting the carrier mobility.

2:00 PM G6.3/H11.3

OPTICAL PROPERTIES OF SEMICONDUCTOR QUANTUM-DOT PHOTONIC CRYSTALS. Yu. A. Vlasov, M. Deutsch and D.J. Norris, NEC Research Institute, Princeton, NJ.

We explore the optical properties of semiconductor quantum-dot photonic crystals. These materials are made by combining colloidal chemistry with two steps of hierarchical self-assembly. First, monodisperse sub-micron silica spheres slowly settle onto a flat substrate and self-organize as a face-centered cubic lattice that is periodic on an optical length scale. Second, this template serves as a three-dimensional scaffolding for the self-assembly of colloidal CdSe nanocrystals into densely packed arrays, referred to as quantum-dot solids. Subsequently, the silica template can be removed by selective etching and a three-dimensionally patterned material consisting solely of semiconductor quantum dots is obtained. The resulting material is particularly interesting as a photonic crystal since we control several key parameters that determine its final behavior. First, we control the unique optical properties of individual semiconductor quantum dots. They have discrete optical transitions, efficient luminescence, high gain and optical nonlinearities, which are tunable with the size of the nanocrystal. Second, we control the structure of the silica template. By adjusting the size, spacing, and arrangement of the silica spheres, we determine how the quantum-dot solid is patterned on an optical-length scale. This structure modifies the internal electro-magnetic environment and influences the propagation of photons through the material. Here we study the optical properties of such semiconductor quantum-dot photonic crystals by transmission, reflection and diffraction. We present results that show the strong influence of the periodic structure of the photonic crystal on the photoluminescence of the semiconductor quantum-dot solid.

2:15 PM G6.4/H11.4

SYNTHESIS OF LUMINESCENT ULTRA-SMALL Si NANO PARTICLE COLLOIDS AND THIN FILMS. Munir H. Nayfeh, J. Therrien, O. Akcikir, G. Belomoin, Z. Yamani, N. Barry, E. Gratton, University of Illinois at Urbana-Champaign, Department of Physics, Urbana, IL.

We describe a procedure for conversion of solid porous silicon into a dispersed colloid of ultra-small (~1 nm) silicon nano particles. When the colloid is excited at 355 nm, blue emission is observable with the naked eye, in room light. The luminescence is dominated by an extremely strong deep blue band at 390 nm, with a structureless weak orange/red tail, and a weak infrared band at 760 nm. We recorded, using two-photon infrared femto second excitation, the auto-correlation of the blue luminescence of a few particles in the laser interaction volume (of one pico cubic centimeter) including single particles. The measurements yield a particle's diffusion, size, and

excitation efficiency comparable to those of fluorescein dye molecules, one of the top efficient dyes in the blue. Thin films of particles are formed on device quality silicon substrates by gentle evaporation from a volatile (acetone) particle colloid, without compromising the blue emission. Two-terminal I-V spectra of the deposited film, taken using a scanning tunneling microscope, will be presented.

2:30 PM G6.5/H11.5

HIGHER-ORDER SYNTHESIS OF MOLECULAR MAGNETS. Sebastien Vaucher and Stephen Mann, School of Chemistry, University of Bristol, Bristol, UNITED KINGDOM.

A major goal in contemporary materials science is the synthesis of molecular based materials that exhibit spontaneous magnetisation. Previously, research approaches have been focused on the synthesis of new types of compounds, essentially by engineering at the unit cell level. A wide range of synthetic pathways to molecular magnets with appealing properties (high T_c, photoinduced magnetisation, etc.) are now available. Whereas it has been shown that inorganic materials, such as silica or titania, can be synthesised across a range of length scales by constructional, morphological and hierarchical coding of precipitation reactions, the analogous control of the higher-order structural features of molecular magnets has to our knowledge not been investigated. In this presentation, we illustrate how it is possible to use similar approaches to control the growth and organization of molecular magnets at the nano- and mesoscale. Several synthetic methods have been investigated and the products characterised by SEM and TEM. The general application of higher-order synthesis of functional molecular systems will be discussed.

2:45 PM G6.6/H11.6

ELECTROCHEMICAL METAL DEPOSITION CONTROLLED BY SELF-ASSEMBLED MONOLAYERS AND POLYMERS.

Andrea D. Wells, John T. McDevitt, William R. Murray, University of Texas at Austin, Chemistry & Biochemistry Dept, Austin, TX.

To more effectively process materials, new procedures were developed to anchor molecular reagents atop samples using self-assembled monolayers (SAM's) and polymers. Just as end group functionality allows specific ligands to interact with charged metal centers, appropriate choice of terminal functional group allows certain organics to interact strongly with metallic ions in the electrolyte solution. Through this interaction, organic layers can exert control over the electrochemical deposition of metal layers on high-T_c superconductors. Nucleation and growth of metal deposits on the surface are monitored by various electrochemical techniques. Electron microscopy, scanning probe and surface science methods are used to characterize the metal/superconductor assemblies.

3:30 PM *G6.7/H11.7

NANOSCALE PROCESSING OF ELECTROACTIVE MATERIALS. Michael Rubner, Department of Materials Science and Engineering, MIT, Cambridge, MA.

Nanoscale processing techniques have been utilized to manipulate a variety of electroactive materials such as light emitting Ru(II) complexes, inorganic nanoparticles and conjugated polymers into thin film devices. Control at the nanoscale level has made it possible to dramatically improve the performance of these thin films. Details concerning the processing and electrical/optical properties of these new nano-composites will be discussed.

4:00 PM G6.8/H11.8

LAYER-BY-LAYER ASSEMBLY OF NANOPARTICLES. Arif Mamedov, John Ostrander, Oklahoma State University, Chemistry Department, Stillwater, OK; Farkhad Aliev, Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, SPAIN; Miguel Correa-Duarte, Luis Liz-Marzan, Departamento de Quimica Fisica, Universidade de Vigo, Vigo, SPAIN; Nicholas Kotov, Oklahoma State University, Chemistry Department, Stillwater, OK.

The layer-by-layer assembly (LBL), i. e. the cyclic deposition of monolayers of oppositely charged materials, has been applied to the preparation of hybrid polyelectrolyte/nanoparticle thin films. This technique affords combining mechanical properties of polymers and unique physical characteristics of size-quantized clusters. Other advantages of the LBL processing of nanoparticulate films include simplicity, universality, tolerance to the substrate's shape, accurate control over the size, size distribution and structure of nanoparticles being assembled. Selection of nanoparticles defines the properties and the area of application of the produced assemblies. LBL films of CdS, CdSe, magnetite, yttrium iron garnet (YIG), cobalt nanoparticles, and aluminosilicate sheets yielded coatings with interesting light-emitting, electrical, magnetic, magnetoresistive, and magneto-optical properties. Importantly, the LBL technique opens a possibility to design sophisticated stratified structures. In particular, the layer sequence was demonstrated to affect the coercivity, ion-sieving effect,

magneto-optical properties of magnetite/alumosilicate/polyelectrolyte, CdSe/alumosilicate/polyelectrolyte, and YIG/polyelectrolyte assemblies respectively. The LBL deposition was also applied to the preparation of films from naked and silica-coated nanoparticles of magnetite. The insulating SiO₂ coating affords isolation of individual magnetic grains and prevention of the exchange coupling between the nanoparticles. It was shown that the assembly of coated particles has a potential to reduce the noise of magnetic storage media and increase its storage capacity.

4:15 PM G6.9/H11.9

PHOTOVOLTAIC RESPONSES IN POLYMER-FULLERENE IONICALLY SELF-ASSEMBLED NANOSTRUCTURES.

P.J. Neyman, W. Graupner, J.R. Heflin, Virginia Tech, Dept of Physics, Blacksburg, VA; D. Marciu, M. Miller, A. Drake, Luna Innovations, Inc., Blacksburg, VA; H. Wang, H.W. Gibson, H.C. Dorn, Virginia Tech, Dept of Chemistry, Blacksburg, VA; R.M. Davis, Virginia Tech, Dept of Chemical Engineering, Blacksburg, VA.

The ultrafast photoinduced electron transfer from conjugated polymers to fullerenes has allowed the production of efficient organic photovoltaic devices. Since the exciton diffusion distance is on the order of 10 nm, however, the charge transfer cannot occur unless the fullerene acceptor is within this distance of any given optically-excited electron-hole pair. We have recently fabricated polymeric photovoltaic devices from ionically self-assembled monolayers (ISAMs) and variations thereon. The ISAM nanostructure fabrication method simply involves the alternate dipping of a charged substrate into aqueous cationic and anionic solutions at room temperature. Each monolayer is fully formed within a couple minutes of immersion, and the bilayer thickness can be controlled from 0.3 to greater than 5.0 nm by variation of the solution parameters. Large-area, conformal, flexible, optoelectronic thin films can thus be fabricated with detailed structural and thickness control at the sub-nanometer level combined with ease of fabrication and low cost. We have employed several approaches to combine the tetrahydrothiophenium precursor of poly(para-phenylene vinylene) (PPV) with fullerenes. As two examples, hydroxylated C₆₀ forms direct ionic bonds with the cationic PPV precursor while pristine C₆₀ forms covalent bonds with the amine groups of a second polycation incorporated into the ISAM films. Comparison of the short-circuit currents, open-circuit voltages, and energy conversion efficiencies are presented for photovoltaic devices made from these and other novel polymer-fullerene self-assembled nanostructures.

4:30 PM G6.10/H11.10

CHARGE TRANSPORT AND ELECTROLUMINESCENCE IN NOVEL HETEROCYCLIC LIQUID CRYSTALS. Rong Fan, George G. Malliaras, Cornell University, Dept. of Materials Science and Engineering, Ithaca, NY; L. Sukhomlinova, S. Gu, R.J. Twieg, Kent State University, Chemistry Dept., Kent, OH.

We have investigated charge transport in a family of novel liquid crystals containing five member ring heterocycles (oxadiazoles, thiadiazoles, etc.). Efficient electron transport was observed in the smectic phase. The electric field and temperature dependence of the electron mobility was studied. Apart from being able to simultaneously function as liquid crystals and charge transport agents, these materials are highly fluorescent, allowing the fabrication of organic light emitting diodes. Their electroluminescent properties in devices with various electrode materials were studied.

4:45 PM G6.11/H11.11

SOL-GEL SYNTHESIS AND NONLINEAR OPTICAL PROPERTY OF SILICA THIN FILMS DOPED WITH CYANINE DYE J AGGREGATES. Takashi Watanabe, Keisuke Asai, Kenkichi Ishigure, The University of Tokyo, Dept of Quantum Engineering and Systems Science, Tokyo, JAPAN; Hao-Shen Zhou, Itaru Honma, Electrotechnical Laboratory, Tsukuba, JAPAN; Akihiro Mito, National Research Laboratory of Metrology, Tsukuba, JAPAN; Makoto Furuki, Osamu Wada, FESTA Laboratory, Tsukuba, JAPAN; Satoshi Tatsuura, Corporate Research Laboratories, Fuji Xerox Co. Ltd., JAPAN.

It is widely known that J aggregates formed by cyanine dyes show strong nonlinear optical properties. In order to apply them to practical devices such as an optical switching device, many J aggregate material morphologies have been suggested. However, since the J aggregates are unstable in many matrices, it has been difficult to realize such applications. We tried to embed cyanine dyes such a 1,1'-diethyl-2,2'-cyanine bromide into thin silica films by simple sol-gel processing and succeeded in making the dye molecules to form stable J aggregates in the films. The films were prepared in the following way; tetraethylorthosilicate was mixed with ethanol and stirred. The solution was added with dilute HCl solution and stirred. And then, the dye was added to it and the sol-solution was stirred.

Finally, the sol-solution was used for film deposition on glass substrates by spin casting. In spite of containing plenty of the J aggregates, these films are transparent, homogeneous in thickness and stable at room temperature. The J aggregation depends on both of the dye concentration in the sol-solutions and the spinning speed during spin casting. The third order susceptibility $|\chi^{(3)}|$ of the films was measured by Z-scan method with sub-ps pulse laser. The films were irradiated with the beam at 77 K in vacuum environment ($< 10^{-5}$ Torr). The $|\chi^{(3)}|$ of the film doped with dye till saturated concentration is 5×10^{-7} esu at on-resonant wavelength of 577 nm, which is larger than that of other organic materials. In addition, according to measurement of the response time τ of the optical nonlinearity by pump-probe method with fs pulse laser at 577nm, it was found that the τ is sub-ps. Thus, stability of the J aggregates, large $\chi^{(3)}$ and fast τ can be expected on the silica film doped with the J aggregates, simultaneously.

SESSION G7/CC6: JOINT SESSION:
NONLITHOGRAPHIC APPROACHES
Chairs: Richard A. Register and Thomas P. Russell
Wednesday Afternoon, December 1, 1999
Salon J/K (M)

CONCURRENT WITH G6/H11

1:30 PM *G7.1/CC6.1

NANOSCALE ASSEMBLY OF RECHARGEABLE BATTERY COMPONENTS. A.M. Mayes, P.P. Soo, B. Huang, P.E. Trapa, D.R. Sadoway, M.I.T., Dept. of Materials Science and Engineering, Cambridge, MA.

Rechargeable lithium polymer batteries, with the highest energy density of all rechargeable technologies now under development, are of interest in applications ranging from microbatteries to wireless communications to automotive traction. We have developed a class of self-organizing block copolymer electrolytes (BCEs) that exhibit nanoscale periodic domains formed from mutually immiscible, covalently joined polymer chains. The nanoscale morphology confers mechanical properties similar to a crosslinked rubber and creates continuous Li ion-conducting pathways through the material. The BCEs are also being exploited as ion-conducting binders for electrodes that incorporate nanoscale active components, e.g., metal nanoclusters or carbon nanotubes. The high specific interface inherent in these nanocomposite materials facilitates ion/electron transport, translating into increased battery current and capacity.

2:00 PM G7.2/CC6.2

SURFACE MORPHOLOGIES OF SMECTIC LIQUID CRYSTALLINE DIBLOCK COPOLYMER ULTRATHIN FILMS. Jung-Sheng Wu, Michael J. Fasolka and Paula. T. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

New terraced surface morphologies of side chain liquid crystalline (LC)-amorphous PS diblock copolymers are examined. Ultrathin films exhibit terracing on two length scales corresponding to the block copolymer lamellar period, L_0 , and the smectic LC layer period, so . We use AFM, TEM, XPS, and ellipsometry data to construct the complicated morphologies and explain in a proposed model. The vertical profile is also proved by the cross-section TEM. A complex surface morphology is observed within the holes and upon the islands of these films, which present a free surface composed of LC columnar perforations in a continuous PS top layer. Unlike earlier reports of LC block copolymers, the homeotropic LC layer in the air surface may be parallel to the block copolymer interface. Thin films with different bulk morphologies, like lamellae (41% LC content), predominately lamellae (50%), and cylinder (79%, 80%) are also investigated by varying the LC contents of this series of diblock copolymers. These self-oriented LC ultrathin films can be used to approach nano-patterning and potential advantages in electrical and optical applications.

2:15 PM G7.3/CC6.3

ORGANIZATION OF TWO- AND THREE-DIMENSIONAL ELECTRICALLY SWITCHABLE LC NANOCOMPOSITES. T.J. Bunning, Air Force Research Laboratory, Materials and Manufacturing Directorate/MLPJ, WPAFB, OH; V.P. Tondiglia, L.V. Natarajan, R.L. Sutherland, Science Applications International Corp., Dayton, OH.

Holography is a standard tool to impart information in thick and thin polymeric films. The information is typically induced via anisotropic polymerization and diffusion processes. Conventional holographic information, once written, remains indefinitely. The use of holography

to induce periodic phase separation of nanosized domains of liquid crystal molecules is described here. The use of liquid crystalline media as one of the components allows for structured elements with switchable optical properties to be generated. The ability to fabricate two- and three-dimensional arrays (periodicities of 100 nm to microns) of switchable nanocomposites will be demonstrated. We report here on the real-time monitoring of the optical properties as a function of Bragg spacing, LC concentration, and light intensity for films in a reflective geometry. These studies are being used to shed insight into the kinetics of the phase separation process.

2:30 PM G7.4/CC6.4

POLYELECTROLYTE-SURFACTANT COMPLEXES AS TEMPLATES FOR NANOPOROUS BIOPOLYMER MATERIALS. Helmut H. Strey, Michael Leonard, Univ. of Massachusetts Amherst, Polymer Science and Eng., Amherst, MA.

When polyelectrolytes are mixed with oppositely charged surfactant at 1:1 charge ratio, they form water-insoluble complexes possessing long-range order. The surfactant molecules assemble into micelles, cylinders or membranes, with the polyelectrolyte filling the intervening space. Little is known about the polyelectrolyte-mediated attraction between surfactant moieties. We present the phase diagram of polyelectrolyte-surfactant complexes as a function of polyelectrolyte charge density, osmotic pressure, salt concentration and type, and surfactant chain length. We utilize ordered polyelectrolyte-surfactant complexes as templates for preparing materials with uniform pore sizes in the nanometer range. By crosslinking the polyelectrolyte matrix by either chemical or physical means, and then washing out the surfactant, we are preparing materials ideally suited for applications, such as filtration, electrophoresis, or controlled drug release.

2:45 PM G7.5/CC6.5

COLLOIDAL CORE-SHELL PARTICLES FOR PHOTONIC APPLICATIONS. K.P. Velikov^a, A. van Blaaderen^{a,b}, ^aVan 't Hoff Laboratory, Debye Institute, Utrecht Univ, THE NETHERLANDS, ^bFOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

A new kind of composite particles with a ZnS core and a SiO₂ shell has been developed. ZnS cores up to a micron in size are coated by a silica layer of well-defined thickness in a seeded growth procedure to produce a core-shell particle. Due to the high refractive index of ZnS (~2.35) these particles strongly interact with light. In addition they can be made with low polydispersity which makes these particles ideal building blocks for photonic applications; either on a single particle level (e.g. as optical resonator) or in self-organised 2D and 3D photonic crystals. Both the optical properties and interaction potential between the particles can be tuned by changing shell thickness with respect to the core. Moreover, the ZnS can be doped with manganese to induce fluorescence or a fluorescent dye can be incorporated into the silica layer at a well-defined radial position. In this way the local density of photonic states can be probed. The location of the dye inside the particle is guided by theoretical calculation of local radiation rate enhancement. The structure and optical properties of a single particle are studied by means of static light scattering and absorption measurements and compared to Mie scattering theory. Transmission measurements on 2D and thin 3D colloid crystals on a glass substrate will be discussed.

3:30 PM *G7.6/CC6.6

NANOARRAYS: THE EASY WAY USING BLOCK COPOLYMERS. Lee Rockford, Thomas Thurn-Albrecht, Jason DeRouchey, Mark Tuominen and Thomas Russell, Univ of Mass, Depts of Polymer Science and Engineering and Physics and Astronomy, Amherst, MA.

Using controlled interfacial interactions and electric fields, thin films having high ordered and aligned arrays of block copolymers were prepared. Standard lithographic processes were used to generate well-ordered arrays of cylindrical pores and channels having dimensions of several nanometers with aspect ratios ranging from unity to in excess of one hundred. Reactive ion etching with CF₄ was found to be an effective means by which the nanoscopic pattern could be transferred to a silicon substrate. Applications of these porous films and patterns transferred into the silicon will be discussed.

4:00 PM G7.7/CC6.7

SELF-ORGANIZING POLYMER MEMBRANES FOR WATER FILTRATION. J.F. Hester, P. Banerjee, A. Akthakul, A.M. Mayes, M.I.T., Department of Materials Science and Engineering, Cambridge, MA.

Filtration of oil- and protein-containing solutions using polymer membranes is strongly limited by fouling of the membrane surface and pores, which results in decreased permeate flux over time. In this work, self-organizing blends of amphiphilic comb polymers and

poly(vinylidene fluoride) are investigated as a means to impart fouling resistance to PVDF filtration membranes. Surface segregation of the comb component is shown by XPS analysis to occur during the coagulation step of phase inversion casting. Ultrafiltration studies indicate substantial reduction of protein adsorption on the surface-modified membranes. The development of self-healing membrane surfaces is described, as well as strategies to impart pH-tunable pore sizes.

4:15 PM G7.8/CC6.8

THIN FILM PHASE SEPARATION ON A NANOSCOPICALLY PATTERNED SUBSTRATE. Kenji Fukunaga, Hubert Elbs, Robert Magerle, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, Bayreuth, GERMANY.

We investigate phase separation in a thin film of a binary polymer blend A/C in the presence of a solid substrate covered with immobilized nanoscopic domains of the respective polymers. The patterned substrate is realized by physisorbing a microphase separated brush of an ABC triblock copolymer. We observe a marked suppression of phase separation in the blend on the pattern as compared to a laterally homogenous substrate. The effect is studied as a function of blend film thickness. The results are compared to a simple estimate of the interfacial energies.

4:30 PM G7.9/CC6.9

MICRODOMAIN STRUCTURE OF ULTRATHIN SBS AND SBM COPOLYMER FILMS. Robert Magerle, Matthias Konrad, Armin Knoll, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, Bayreuth, GERMANY.

Block copolymers composed of two or more blocks of immiscible polymers tend to phase separate into regular structures with translational symmetry resembling crystalline materials with characteristic lengths given by the size of the blocks. The particular morphology characteristic of a given block copolymer is determined by both volume filling arguments and by the degree of incompatibility between the blocks. In thin films the interfacial energies at the film boundaries constitute an additional factor for the resulting film structure. In the present contribution we study the morphology of ultrathin films of SBS and SBM tri-block copolymer films with scanning force and optical microscopy. The samples have been spin cast and subsequently exposed to the vapours of different solvents. Details of the microdomain structure (observed on the micron and nanometer scale) resemble phenomena like island formation, surface reconstruction, and dislocations, which are generally observed in crystalline material on the atomic scale. We present a new method for 3D imaging of block copolymer microdomain structures with nanometer resolution.

4:45 PM G7.10/CC6.10

PERM-SELECTIVE ELASTOMERIC MEMBRANES FROM SELF-ASSEMBLED BLOCK COPOLYMER IONOMERS. N. Beck Tan, D. Crawford, E. Napadensky, Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Grounds, MD; K. Laverdure, S. Gido, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA; D. Reuschle, D. Mountz, K. Mauritz, Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS; W. Liu and B. Hsiao, Department of Chemistry, State University of New York, Stony Brook, NY.

Current technology in protective clothing materials utilizes high barrier elastomers to prohibit the penetration of toxins. This method, though effective, imposes a tremendous physiological heat stress on the wearer. New technologies being explored for protective materials include perm-selective membranes. These membranes are designed to allow the passage of water vapor thereby providing for heat transfer without sacrificing the resistance to toxin penetration. Ideally, these materials should have fast water vapor transport, flexibility, ready processability, and low cost. One potential candidate material for perm-selective clothing is based on a self-assembled triblock copolymer. The copolymer, Poly(styrene-*b*-isobutylene-*b*-styrene) has a morphology composed of a high barrier elastomer matrix (isobutylene) with glassy, cylindrical polystyrene channels. The styrenic component is sulfonated to encourage water vapor transport. Initial studies, reported here, show that the sulfonation does not change the morphological pattern in the system (cylinders), but greatly disrupts the long range order. Mechanical properties are also significantly modified by sulfonation. Sorption and permeation studies indicate that water transport is greatly enhanced by sulfonation. Effects of processing conditions, choice of sulfonic acid counter-ion and sulfonation level in the styrene block are presented.

G8.1
DENSE ARRAY OF ORDERED GaAs NANOSTRUCTURES BY SELECTIVE AREA GROWTH IN SELF-ORGANIZED NANO-SCALE FEATURES BY BLOCK COPOLYMER NANOLITHOGRAPHY. R.R. Li, P.D. Dapkus, W. Jeong, Univ. of Southern California, Dept of EE-Electrophysics, Los Angeles, CA; M.E. Thompson, Univ. of Southern California, Dept of Chemistry, Los Angeles, CA; C.K. Harrison, Paul M. Chaikin, Princeton Univ, Dept of Physics, Princeton, NJ; Richard A. Register, Princeton Univ, Dept of Chemical Engineering, Princeton, NJ; D.H. Adamson, Princeton Univ, Princeton Materials Institute, Princeton, NJ.

GaAs has been selectively grown into hexagonally ordered nanometer-scaled hole patterns with density as high as $\sim 10^{11}/\text{cm}^2$. The hole patterns are created in 150Å thick SiN_x films on GaAs wafers by block copolymer nanolithography [ref.1]. Selective Area Growth (SAG) of GaAs nanoscale features on the patterned wafers is performed by metalorganic chemical vapor deposition at 76 Torr. The experimental results shown that the growth temperature, V/III ratio and growth rate affect the nucleation and selectivity of the growth. The selectively grown GaAs dots have been characterized by tapping mode AFM and field-emission SEM. The SAG features are characterized by average lateral and vertical dimensions of $\sim 20\text{nm}$ and 7nm, respectively. The narrow size distribution and the uniform spatial position of the nano-scale dots observed in our studies offer potential advantages over self-assembled dots grown by Stranski-Krastanow mode. Furthermore, we demonstrated for the first time the copolymer nanoscale pattern transfer technique to a variety of MOCVD grown semiconductor structures, including doped and undoped layers, lattice matched and mismatched layers, and materials, including GaAs, GaAs/AlGaAs and GaN. These observations open enormous opportunities for growth of various quantum structures. [1] Miri Park, C.K. Harrison, P. Chaikin, R.A. Register, D.H. Adamson, Science 276, 1401(1997)

G8.2
SUPRAMOLECULAR SELF-ORGANIZED STRUCTURES: ROD-LIKE CONJUGATED POLYMERS HYDROGEN BONDED TO AMPHIPHILIC MOLECULES. Matti Knaapila, Janne Ruokolainen, Olli Ikkala, Helsinki Univ of Technology, Materials Physics Lab, Espoo, FINLAND; Mika Torkkeli, Kaija Jokela, Ritva Serimaa, Helsinki Univ, Dept of Physics, Helsinki, FINLAND; Gerrit ten Brinke, Univ of Groningen, Materials Science Centre, Groningen, THE NETHERLANDS; Lockhart Horsburgh, Andrew P. Monkman, Univ of Durham, Dept of Physics, Durham, UNITED KINGDOM.

We show that a conjugated electroactive rod-like polymer poly(2,5-pyridine diyl), i.e. polypyridine, poly(p-pyridine), which is stoichiometrically protonated by methane sulphonic acid to form a polymeric salt poly(2,5-pyridine diyl) methane sulphate, forms self-organized nanoscale structures upon hydrogen bonding with octyl gallate (1-octyl-3,4,5-trihydroxybenzoate). A polymeric supramolecular structure is formed which resembles hairy rod polymers showing an isotropic solution at high temperatures based on optical microscopy, self-organized liquid phase at intermediate temperatures and co-crystallized phase near room temperature. Such structures show temperature dependent conductivity, thus allowing switching.

G8.3
SELF ARRANGEMENT OF PORES IN ANODICALLY-ETCHED GaP UNDER IN-SITU ILLUMINATION. I.M. Tiginyanu, I.M. Tiginyanu, Technical Univ, Chisinau, Moldova; H.L. Hartnagel, Technical Univ, Darmstadt, GERMANY; J. Monecke, Technical Univ, Freiberg, Germany; I. Kravetsky, G. Marowsky, Laser-Laboratorium Goettingen e.V., Goettingen, GERMANY.

Over the last years, increasing attention has been paid to porous III-V materials due to their strongly enhanced photoresponse, birefringence at the wavelength of optical communication systems and ability to support Froehlich-type surface vibrations. Nevertheless, the porous layers and free-standing membranes fabricated by anodic etching of as-grown substrates are optically inhomogeneous, resulting in multiple scattering of the visible light in the porous network. Obviously, the porous medium will become optically homogeneous providing that the dimensions of both the pores and skeleton are much lower than the wavelength of the electromagnetic radiation. To fulfil this requirement, one has to introduce in the semiconductor materials uniformly or quasi-uniformly distributed pores at sufficiently high densities. In this work, we present experimental evidence of self arrangement of pores with dimensions within 20 to 50 nm in

anodically etched GaP under proper conditions of in-situ illumination. Optically-transparent free-standing porous membranes with the thickness up to tens of micrometers were developed for different schemes of optoelectronic applications. Results of a systematic study of non-linear optical properties of the membranes involved are presented. In particular, optical second harmonic generation in porous membranes was found to be enhanced in comparison with that inherent to as-grown crystals (a Q-switched Nd-YAG laser was used as a pump beam source). The physical and electrochemical processes leading to the observed uniformity in pore distribution are discussed.

G8.4
SELECTIVE AREA EPITAXY ON A NANOSCALE: RESISTLESS MASK FABRICATION AND EPITAXIAL GROWTH. Y.Y. Wei and G. Eres, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Resistless scanning electron beam lithography was used for generating ultra-high resolution templates for selective area epitaxy of group-IV semiconductors on the sub-100 nm feature scale. A focused electron beam with energy in the range from 10 to 40 keV induces local desorption of hydrogen from a hydrogen passivated silicon surface. Subsequent oxidation of the bare silicon in the residual background of the specimen chamber results in formation of an ultrathin silicon oxide pattern of 1-10 nm thickness with a minimum linewidth of 50 nm. A supersonic molecular jet was employed for delivering the growth species in a line-of-site mode to constrain the film growth process to surface limited reactions. Both, the nascent oxide patterns and the films, were characterized using atomic force microscopy and scanning electron microscopy. Several different test patterns were designed to investigate the effects of such parameters as the line width, the line height, and the line density on the film process. The film growth parameters including the growth temperature and the flux of the growth species were varied to evaluate the integrity of the templates under different growth conditions, and to investigate the effects of the template on the properties of the films.

G8.5
LASER DIRECT WRITING OF HIGH RESOLUTION PHOSPHOR SCREENS. J.M. Fitzgerald, Naval Research Laboratory, Washington DC; P.D. Rack, Rochester Institute of Technology, Department of Microelectronic Engineering, Rochester, NY; R.C.Y. Auyeung, SFA, Inc., Largo, MD; A. Pique, D.B. Chrisey, Naval Research Laboratory, Washington DC.

A novel rapid prototyping technique developed at the Naval Research Laboratory (NRL) was used to deposit phosphor powder screens for high-resolution display applications. With this technique, called matrix assisted pulsed laser evaporation direct write (MAPLE DW), dense phosphor oxide phosphor powders of Y₂O₃:Eu (red) and Zn₂SiO₄:Mn (green) were successfully deposited onto ROGERS and polymer substrates. All processing was performed at room temperature and at atmospheric pressure. Cathodoluminescence measurements showed that the luminous efficiency of the phosphor powders were not degraded by the deposition process. A 6x6 red and green matrix with pixel sizes of 100µm (250 lines per inch) is demonstrated, however this technique is easily scalable to pixel sizes <10µm (> 2500 lines per inch). In this presentation, the MAPLE DW technique will be reviewed and its transfer mechanisms will be discussed. Detailed results from writing high-resolution powder phosphor screens will be shown.

G8.6
SOLID-STATE NMR AND MOLECULAR MODELING INVESTIGATION OF THE MOLECULAR CONFORMATIONS OF LONG-CHAIN ALKANOIC ACIDS SELF-ASSEMBLED ON OXIDE SURFACES. Li-Qiong Wang, Kim F. Ferris, and Jun Liu Materials Sciences Department, Pacific Northwest National Laboratory, Richland, WA.

Molecular conformations of stearic acid and oleic acid self-assembled on Al₂O₃ and ZrO₂ are investigated using solid-state NMR and electronic structure calculations. This study clearly shows that the molecular conformation of long-chain molecules at the interface is influenced by interfacial interactions and the shape of the molecules. Two conformations are resolved in NMR for stearic acid on Al₂O₃, but only all-trans conformation is observed for stearic acid on ZrO₂, indicating that the molecular conformation of surfactant is greatly influenced by the interfacial interactions. Stearic acid shows more ordered conformation than oleic acid due to the perturbation to the chain packing from the double bond in oleic acid. Theoretical calculations have been used to examine the interactions of these acids with ZrO₂ and Al₂O₃ surfaces, and interpret the NMR results, showing that alkanolic acid has a stronger interaction with ZrO₂ than Al₂O₃.

G8.7
NANOMETER PATTERNING OF ULTRA-THIN COBALT DISILICIDE BY LOCAL APPLICATION OF STRESS. Q.T. Zhao, P. Kluth, J. Xu, L. Kappius, Steffi Mesters, S. Mantl, Institute for Thin Film and Ion Technology, Forschungszentrum Juelich, GERMANY.

A novel self-assembly nanometer patterning method, which uses local stress effects, was investigated to pattern ultra thin cobalt disilicide layers. Epitaxial CoSi₂ layers, which were grown on Si(100) by molecular beam epitaxy, were patterned by local oxidation. The patterning process involves two key steps. First, a conventional oxidation mask of a SiO₂ layer (~20nm) and a Si₃N₄ layer (200-400nm) was deposited by plasma enhanced chemical vapor deposition on CoSi₂/Si(100) and patterned by optical lithography and dry etching. The masking technique used is similar to the well-known local oxidation of silicon technology. The patterned nitride layer causes the highest stress below the edges. Second, rapid thermal oxidation (RTO) was performed in dry oxygen. During RTO, near the nitride edges the diffusion of the Co atoms through the silicide layer is affected by the stress field. The diffusion becomes anisotropic and leads to a well defined separation of the silicide layer at the line of maximum stress. Oxide formed on top of the gap and on the surface of the uncovered CoSi₂. Highly uniform gaps as narrow as 50nm between the masked and the unprotected regions of the silicide layer have been fabricated for 20nm thick CoSi₂ layers. The silicide is vertically displaced by less than 10nm. It was shown that the separation gap is not only dependent on the oxidation parameters, but also on the thickness and the width of the nitride mask due to the stress effects. Patterning of poly-CoSi₂ layers was also achieved by local application of the stress during solid-state reaction of deposited Co layer with Si substrate. The patterning process of epitaxial CoSi₂ has been used to fabricate nanometer transistors.

G8.8
NANO-DOMAIN FORMATION IN BINARY SAMs OF ALKYL-SILOXANES ON SILICON. L. Breuil, D. Vuillaume, Institut d'Electronique et de Micro-electronique du Nord, CNRS, Villeneuve d'Ascq, FRANCE.

We have studied the formation of nano-sized domains (phase separated) in binary self-assembled monolayers (SAM) of alkylsiloxanes on silicon. Binary SAMs of short [S] (12 carbons) and long [L] (18 carbons) alkyltrichlorosilanes were fabricated for various molar ratio [L]/[S] in solution and at various temperatures (-3°C - RT) and durations. They were studied by AFM, FTIR, ellipsometry and contact angle measurements. Nano-sized domains (10-300 nm) of L were observed to form only for [L]/[S]>1, in contrast with previous works on mixed SAM of thiols on Au ([L]/[S] about 1/20-1/40) [1]. Size distributions were analyzed as function of [L]/[S], temperature and duration. Even at large [L]/[S] ratios, the surface coverage by the nano-domains of L does not reflect the respective molecule concentrations in solution. A careful comparison of ellipsometry and AFM shows that the dominant phase around the nano-domains is probably made of a homogeneously mixture of both molecules. The nano-domains of L show dendritic geometries as observed during the growth of single constituent SAMs of similar molecules. These results are discussed regarding previous results on mixed SAMs (mainly thiols on Au) and available models. These results have important implications for non-lithographic patterning of nanostructures. [1] K. Tamada et al., Langmuir 13, 1558 (1997)

G8.9
COHERENT ARRAY OF SUBMICRON SIZE PARTICULATE ON A SINGLE CRYSTAL SURFACE OF TUNGSTEN BY Nd:YAG LASER IRRADIATION. Yuji Kawakami, Eiichi Ozawa, Vacuum Metallurgical Co., Ltd., Nano Particle Division, Chiba, JAPAN.

We found self-assembled micro-scale organization structure: two types of coherent arrays of hemisphere particles with 500-800 nm around a laser irradiated mark on a single crystal surface of tungsten. The tungsten specimens were irradiated by a short-pulse Nd:YAG laser under low pressure in an inert gas atmosphere. Two types of coherent arrays, were two-dimensional cubic and hexagonal systems. The distance between the particles was about 1 μm. Some researchers observed a kind of grating or ripple patterns on the irradiated material surfaces. They discussed about the patterns focusing on the relationship between the optical characteristics of the laser beam and periodic configuration of ripples with spacing and direction. The ripples run only one direction, however our patterns were coherently arranged on two or three directions. It seems difficult to consider that this coherent array of particles is related to the ripple patterns which are concluded to depend on the laser characteristics. In this study, we tried to clarify whether the angle of incident and the polarization were related to the formation of the coherent array and also examined the number of shots to form the coherent array. We think that the formations of coherent array might depend on the kind of the crystal surface structure and crystal growth rather than the

optical characteristics of laser. The rapid solidification of molten tungsten induced by the laser beam also should be considered to understand the coherent array formation

G8.10
InP AND CuInSe NANOCCLUSERS IN 3D ORDERED CRYSTALLINE STATE - SYNTHESIS AND MOLECULAR STRUCTURES. Andreas Eichhoefer, Dieter Fenske, Carsten von Haenisch, Forschungszentrum Karlsruhe, Institut fuer Nanotechnologie, Eggenstein-Leopoldsh, GERMANY.

The synthesis of perfectly ordered nanoclusters in the crystal is a needed requirement for the investigation and interpretation of the molecular structure and the properties of such compounds. In this context single crystal X-ray diffraction has been used to determine the structures of CuInSe, InP and GaAs molecules and clusters. In previous work we were able to crystallize a huge variety of copperchalcogenide nanoclusters from reactions of copperhalides with silylated chalcogens by using tertiary phosphines as shielding ligands. In order to extend this successful reaction principle we start now to synthesize and crystallize ternary phase clusters of copper indium chalcogenides CuInE₂ (E = S, Se and Te). In the poster we will present first results of crystal structures from these reactions. Optical absorption spectra of these molecules will be compared to investigations on nanoparticles synthesized by the same method. We want also to focus on thermal properties of these nanoclusters in order to cleave the volatile ligand shell to synthesize nanostructured powders of these materials. In the second part we present III/V-molecules and clusters such as [In₉(PPh)₁₀(PEt₃)₃Cl₇]. These compounds are prepared by cyclocondensation reaction of MCl₃ (M = Ga, In) with E(SiMe₃)₃ or RE(SiMe₃)₂ in the presence of tertiary phosphines under liberation of Me₃SiCl. Crystal structures and theoretical studies of these molecules are described.

G8.11
SYNTHESIS AND SELF-ASSEMBLY OF NANOPARTICLE CHAINS, SUPERLATTICES AND FILAMENTS IN COMPLEX FLUIDS. Mei Li, School of Chemistry, University of Bristol, Bristol, UK; Heimo Schnablegger, Max-Planck-Institut of Colloids and Interfaces, GERMANY; Stephen Mann, School of Chemistry, University of Bristol, Bristol, UK.

Barium chromate nanoparticles have been synthesized in AOT water-in-oil reverse micelles and microemulsions. The shape, size and interfacial properties of BaCrO₄ crystallites can be controlled to form three unusual nanostructures: C chains, superlattices and filaments. The linear chains and rectangular superlattices form specifically at [Ba²⁺]:[CrO₄²⁻] molar ratios of ca 1, whereas molar ratio excesses of Ba²⁺ or CrO₄²⁻ produce single crystal nanofilaments or non-interacting spherical nanoparticles, respectively. Both the chains and superlattices consist of ordered arrays of prismatic nanoparticles that are held together by the interdigitation of surfactant molecules on specific crystal faces. Particles were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), small angle X-ray scattering (SAXS), and selected area electron diffraction (SAED). The linear chains were 50 to 500 nm in length and consisted of rectangular-shaped particles (16 nm × 6 nm). The superlattices constructed from a pseudo-rectangular array of uniform nanoparticles (6.8 nm × 5.9 nm). The filaments were 50 μm in length and 20 to 500 nm wide. The structures were formed by spontaneously self-assembling in solution through surfactant-induced aggregation.

G8.12
FABRICATION OF Ge/Si HETERO-NANOCRYSTALS ON SiO₂ LAYER. J. Wu, Y. Shi, S.L. Gu, W. Bu, H.M. Bu, X.L. Yuan, L.Q. Hu, Y.D. Zheng, X.B. Yin, M. Wang, and N.B. Min, Department of Physics & National Laboratory of Solid State Microstructures, Nanjing University, Nanjing, P.R.CHINA.

Hetero-nanostructures have recently become the focus of extensive research because of their novel physical phenomena and great potential applications. Ge/Si hetero-structure would play an important role in future VLSI, and also be very attractive to be applied in fabricating hetero-nanostructures and related devices due to its excellent properties such as flexible growth, selective etching and oxidation. In this paper, we report firstly on the fabrication of Ge/Si hetero-nanocrystals by combining Ge/Si hetero-epitaxy and selective chemical wet etching. In fabrication, a poly-Si film was first grown at 600C using SiH₄ gas on a thermally oxidized SiO₂ layer, and Ge nanocrystals were subsequently self-organized using diluted GeH₄ gas in a low-pressure chemical vapor deposition system. Before exposing to air the sample was heated up to a higher temperature to improve the quality of as-grown film as well as to form SiGe alloy at the interface. Finally, the selective chemical etchant consisting of NH₄OH solution was used to remove the poly-Si layer and to form expected Ge/Si hetero-nanocrystals on SiO₂ layer. Basing on the observation of Scanning Electron Microscopy and Atomic Force

Microscopy, the characteristics of the growth and selective etching were evaluated. Self-organized process of Ge nanocrystals on ploy-Si film is different from that on SiO₂ layer, the average size from 20 to 80nm are controlled by changing the growth temperature in the range of 500 ~ 550C. The NH₄OH solution is a high-performance etchant, the selectivity for Si to Ge and SiGe is better than 100.

G8.13

BIOMOLECULAR RECOGNITION AND NUCLEATION OF SEMICONDUCTOR AND MAGNETIC MATERIALS. Angela Belcher, Sandra Whaley, University of Texas at Austin, Dept of Chemistry and Biochemistry, Austin, TX.

A peptide combinatorial approach is being used to select proteins that bind to non-traditional inorganic substrates, such as III-V semiconductors and magnetic materials, for the purpose of nucleating these materials on the nanoscale and producing semiconductor-magnetic heterostructures. Peptides that select specific inorganic substrates were amplified and sequenced. Putative consensus sequences and binding epitopes have been mapped, allowing for analysis of the chemical driving forces of these interactions. Positive binding peptides were characterized for substrate recognition, discrimination, and binding using X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fluorescence Microscopy, and Atomic Force Microscopy (AFM).

G8.14

A NEW ELECTROCHEMICAL SYSTEM FOR PICK AND PLACE OF DEVICES AND BIOLOGICAL CELLS ON A SILICON SUBSTRATE. Mihrimah Ozkan, Daniel Hartmann, Cengiz S. Ozkan and Sadik Esener, University of California at San Diego, Electrical and Computer Engineering Department, San Diego, CA; Eugene Tu and Michael Heller, Nanogen Incorporated, San Diego, CA.

We have developed a novel electrochemical system for nonlithographic pick and place assembly of devices on a silicon substrate by means of electrical and optical addressing. We present results of experiments where charged polystyrene beads of various sizes (0.8 - 20 μ m in diameter) have been utilized for the initial pick and place assembly on blank substrates. In addition, 50 μ m diameter light emitting diodes and 100 μ m diameter SiO₂ pucks were utilized in pick and place assembly on patterned substrates. We finally present results of experiments where 20 - 30 μ m diameter biological cells are placed on a regular array on which the growth process of the cells is observed.

G8.15

LIGAND ACCESSIBILITY AS A MEANS TO CONTROL CELL RESPONSE TO BIOACTIVE BILAYER MEMBRANES. Y. Dori¹, S. Ochsenhirt¹, H. Bianco-Peled¹, J.B. McCarthy², M. Tirrell¹; ¹Department of Chemical Engineering and Materials University of Minnesota, Minneapolis, MN, ²Department of Laboratory Medicine and Pathology, University of Minnesota, Minneapolis, MN.

We report a new method to create a biofunctional surfaces in which the accessibility of ligands is used as a means to control the cell behavior. We have created supported bioactive bilayer membranes by Langmuir-Blodgett deposition of binary mixtures of a PEG-lipid and novel peptide amphiphiles on a hydrophobic surface. The peptide amphiphiles contain either a peptide sequence from the triple helical domain of type IV collagen, known as peptide IVH1, or the well-known GRGDSP peptide sequence. Bilayer membranes were characterized using atomic force microscopy and neutron reflectivity. Cell adhesion and spreading assays were done on supported membranes containing binary mixtures of the peptide amphiphile and a PEG-lipid. Cells adhere and spread on mixtures of the IVH1 peptide amphiphile with the PEG-lipids having 120 and 750 MW PEG chains. Because these PEG chains are much shorter than the IVH1 peptide head group, the PEG chains do not interfere with the interaction of the peptide ligand and the cell surface receptors. In contrast, cells adhere but do not spread on the mixture containing the 2000 MW PEG, in which the peptide and PEG are about the same length. Cells did not adhere on mixtures containing the 5000 MW PEG because the IVH1 is completely masked by the longer PEG chains. Another approach to manipulating accessibility has been to manipulate the secondary structure of the peptide-ligand. We synthesized two GRGDSP peptide amphiphiles. Dialkyl tails (HC) are attached to the N terminus, presenting a linear peptide, or to the N and C termini, presenting a looped peptide. Endothelial cells are plated on these surfaces for one hour incubations. The cells respond in a dose dependent manner to the surfaces of linear and looped. The average cell area on looped GRGDSP is significantly larger than the cell area on linear GRGDSP, suggesting the accessibility and conformation of the looped peptide has increased.

G8.16

A BIOMOLECULAR CONSTRUCTION KIT BASED ON S-LAYER

TECHNOLOGY. Dietmar Pum, Angela Neubauer, Erika Gyoervary, Sabine Dieluweit, Uwe B. Sleytr, Center for Ultrastructure Research and Ludwig Boltzmann Institute for Molecular Nanotechnology, Universitat fur Bodenkultur Wien, Vienna, AUSTRIA.

Self-assembly is a basic building principle in nature for generating large arrays of biomolecules with well defined geometrical and physicochemical surface properties. In the development of nanoscale functional devices, the application of self-assembly for achieving perfect positional control at the molecular level appears feasible, both theoretically and experimentally, and offers striking advantages for a manufacturing process. Crystalline bacterial cell Surface layer (S-layer) proteins seem to be perfectly suited for this purpose since (i) they have the intrinsic property to reassemble into two-dimensional arrays at various interfaces including silicon surfaces, (ii) functional groups are repeated (with the periodicity of the S-layer lattice) at a distance of approximately 10nm, leading to (iii) regular arrays (superlattices) of bound functional molecules. Many species of bacteria and most archaea possess a crystalline S-layer as the outermost component of their cell envelopes. These crystalline arrays are composed of a single (glyco)protein species with molecular mass ranging from 40 to 200.000. S-layers exhibit either oblique, square or hexagonal lattice symmetry with unit cell dimensions in the range of 3 to 30nm. S-layers are generally 5 to 10 nm thick and show pores of identical size (diameter, 2 to 8nm) and morphology. This contribution will summarize the characteristic properties of S-layer proteins as building blocks in a biomolecular construction kit. Particular attention will be paid towards the reassembly of S-layer proteins into monolayers, the well ordered binding of functional molecules, and their application as templates in the formation of monodisperse nanoparticle arrays.

G8.17

SYNTHESIS OF STRUCTURED MESOPOROUS INORGANIC MATERIALS WITH FUNCTIONALIZED WALLS.

Deepa Khushalani, Stephen Mann, University of Bristol, School of Chemistry, Bristol, UNITED KINGDOM.

Templating of mesoporous structures with nonionic block copolymers has offered a novel and versatile route to the synthesis of composite materials. The porosity of the resulting structures is found to be ordered, tunable and in the range of 80 - 100 Å with a wall thickness in excess of 20 Å. In this presentation, studies performed with triblock copolymers (the Pluronic range) as the templating moiety will be discussed. Emphasis will be placed upon formation of composite materials not only in terms of organic-inorganic mixtures, but predominantly on formation of mixed silica-metal oxide frameworks. Introduction of non-silica based units in the wall allow for formation of catalytically active centres along with providing several novel characteristics to mesoporous materials. Although this area has been actively pursued in materials research over the last few years, the process, however, has been found not to be trivial. In the talk, novel strategies for incorporation of specific units in the walls of silica based mesoporous structures synthesized with Pluronic surfactants will be discussed.

G8.18

LONG-SCALE ORDERED NANOPATTERNS FORMED BY ELECTROCHEMICAL POLISHING AND ANODIZATION OF POLYCRYSTALLINE AND SINGLE-CRYSTAL ALUMINUM. Valery V. Konovalov, Robert M. Metzger, Giovanni Zangari, Center for Materials for Information Technology (NSF MRSEC), and Departments of Chemistry, Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL.

Nanometer-scale (10-200 nm) self-ordered structures may become hosts for magnetic, electronic and optical devices. Electrochemical anodization (pore growth) and electropolishing can produce perfectly ordered surface patterns on polycrystalline Al with micrometer domain sizes. Using voltamperometry, electrochemical impedance spectroscopy, AFM, TEM, and SEM, we are studying self-ordering in anodized and electropolished Al, and the factors that control the formation of larger domains. Electropolishing Al single crystals by a series of voltage pulses produced different nanometer-scale topographies on different crystalline faces. For Al(110) highly ordered periodic stripes (wavelength 40-65 nm, height 2-7 nm) covered the whole sample (area of 1 square cm), aligned along the [-1,1,0] direction. On Al(100) and Al(111) surfaces ordered topographies with hexagonal symmetry were obtained over only 1-2 square micrometer domains. The interatomic distance are 2 orders of magnitude smaller than the observed topographic periodicities, and thus cannot explain them. Anodization of Al with ordered pore growth, following Masuda and Fukuda, Science 268: 1466 (1995), produces hexagonally ordered pores with domains 1 to 4 micrometers squared. A new and improved procedure extends this to 100 square micrometers. Optimal conditions were found for (100), (110), and (111) Al faces. Mechanisms for ordering will be discussed.

G8.19

BLOCK COPOLYMER TEMPLATED MESOPOROUS SILICATE THIN FILM BY SPIN COATING. Takeo Yamada, Keisuke Asai, Kenkichi Ishigure, The Univ of Tokyo, Dept of Quantum Engineering and Systems Science, Tokyo, JAPAN; Akira Endo, National Institute of Materials and Chemical Research, Tsukuba, JAPAN; Hao-Shen Zhou, Itaru Honma, Electrotechnical Laboratory, Tsukuba, JAPAN.

Mesoporous materials have attracted considerable interest because of applications in molecular sieve, catalyst, and adsorbent. Efforts to create sensor, electronic, and photonic devices, based on ordered molecules, have been inspired by these self-assembled mesoporous materials. However, for these applications, it is very important to change the material's state from powder to thin film with large pore size. We succeed in synthesizing mesoporous silicate thin films by commercially available poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) triblock copolymers. The thin film was prepared as follows: The source solution for coating was mixed by two solutions. One is the ethanol solution containing a required amount of triblock copolymer, and the other is the silica sol-gel solution mixed by tetraethoxysilane, ethanol, water, and diluted HCl on a required ratio. Mesoporous silicate thin film was synthesized by spin coating method on glass substrate and calcined at 450°C. The film is transparent and homogeneous. The characteristic of the film also is investigated by XRD measurement and nitrogen adsorption-desorption isotherm measurement. The XRD and the nitrogen adsorption-desorption isotherm results show that the thin film exhibits ordered and oriented large periodic mesostructure. The d-spacing, phase state, pore size, and surface area could be controlled by synthesis condition and triblock copolymers.

G8.20

MESOSCOPIC GALLIUM NITRIDE POWDERS CONFINED IN POROUS ALUMINA. Holger Winkler, Oliver Stark, Roland A. Fischer, Ruhr-Universitaet Bochum, Bochum, GERMANY; Marcus Geerkens, Guenter Schmid, Universitaet Essen, Essen, GERMANY.

Because of its unique properties like the direct bandgap of 3.45 eV, the high thermal conductivity and chemical/physical inertness Gallium Nitride is in the focus of interest of developing new optoelectronic devices which is supported by bright blue LEDs and laserdiodes based on Gallium Nitride already commercial available. Because of the limited resolution of lithographic or etching techniques which are connected with excitonic quenching at etched boundaries we present our idea of producing functional structures by filling the pores (tunable 10 - 250 nm in diameter) of a transparent porous alumina membrane with Gallium Nitride resulting in a light-emitting device. The alumina membrane was synthesized by anodic oxidation of aluminium in polyprotic acids. For porefilling with Gallium Nitride we impregnated the alumina membrane with a solution of the precursor triazido(trimethylamin)-gallium followed by thermal treatment in ammonia. The resulting composite was characterized with the help of photoluminescence spectroscopy, excitation spectroscopy, UV, TEM among other techniques.

G8.21

COLLOIDAL EPITAXY STUDIED WITH FLUORESCENCE CONFOCAL SCANNING LASER MICROSCOPY. J.P. Hoogenboom^a, A. van Blaaderen^{a,b}, ^aFOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS, ^bVan 't Hoff Laboratory, Debye Institute, Utrecht Univ, THE NETHERLANDS.

Colloidal epitaxy provides a means to grow large, well-oriented 3D-crystals with characteristic spacings in the photonic range. Using fluorescent core - silica shell particles makes it possible to study both the 3D-structure of these crystals and the crystallization dynamics. We present results on growing a hard-sphere hexagonal-close-packed crystal, which has a slightly lower free energy than the face-centered-cubic structure. Furthermore, we have used the templates to manipulate the growth of thin colloidal crystals in a layer-by-layer drying process and the growth of colloidal crystals in a confined geometry. A good understanding of the mechanisms behind colloidal epitaxy might lead to a better understanding of the possibilities and limitations of the template directed growth of colloidal crystals. As a first step we investigated the crystallization transition and subsequent crystal growth on a patterned substrate under the influence of gravity and increasing particle concentration.

G8.22

PHASE SEPARATION OF POLYMER BLEND THIN FILMS ON A PATTERNED SUBSTRATE. Bi-min Zhang, Newby, Russell J. Composto, University of Pennsylvania, Department of Materials Science and Engineering and Laboratory for Research on the Structure of Matter, Philadelphia, PA.

Thin films of polymer blends were patterned into micron-sized strips on a silicon-wafer using two soft-lithography techniques, micro-contact printing and micromolding. The strips with respective width and thickness ranged from 2 microns and 150 nm to 20 microns and 1.5 microns were used in our study. We have investigated confinement effects on the phase separation of poly(methyl methacrylate) (PMMA) and poly(styrene-ran-acrylonitrile) (SAN), which exhibits a lower critical solution temperature. Scanning force microscopy was employed to examine surface roughness and combined with selective etching to determine phase morphology. During the early stage, the PMMA layer wets both the air/polymer and the polymer/substrate interfaces and, at the surface, grows by hydrodynamic flow. This behavior is similar to the homogeneous substrate case. In contrast to the homogeneous case, PMMA channels grow from the surface to the substrate during the intermediate stage. Relative to the early stage, phase coarsening slows down during intermediate stage; eventually, the channels begin to shrink during late stage, indicating the flow of PMMA out of the channels and into the wetting layers. Because of the semi-cylindrical shape of the film, the wetting layer varies from about 200 nm over the SAN rich phase located along the strip center to about 600nm near the edges of the film. Similar wetting and phase behavior were observed for stripes down to 2 micron with the same aspect ratio of thickness to width.

SESSION G9: SURFACE-INDUCED ORGANIZATION

Chair: Orlin D. Velev

Thursday Morning, December 2, 1999

Salon E (M)

8:30 AM *G9.1

SYMMETRY BREAKING IN SELF-ASSEMBLING POLYMERIC FILMS ON SAM PATTERNED SURFACES. Alamgir Karim, Brett Ermi, Giovanni Nisato, Jack Douglas, Polymers Division, NIST, Gaithersburg, MD.

Symmetry-breaking effects of a chemically patterned self-assembled monolayer (SAM) substrate on the self-organizing process of phase separation and dewetting of thin polymer films is investigated. Several parameters are determined to be important controlling factors in determining the evolutionary and final state morphology of the polymeric film structures. Preferential polymer-surface interaction results in chemically selective wetting of a polymer or a polymeric phase on the SAM pattern. In order for the self-assembly process to interactively recognize the underlying substrate pattern, the natural length scale of the self-assembly process and the modulation scale of the surface patterns must be commensurate. The final degree of alignment of the polymeric pattern with the underlying SAM pattern increases with decreasing film thickness, but only down to a limiting scale. Further decrease of thickness apparently results in a capillary wave break-up of the ultrathin film. These results are interpreted in light of recent simulations.

9:00 AM *G9.2

SELF-ASSEMBLY OF POLYMER THIN FILMS ON CHEMICALLY HETEROGENEOUS SURFACES. P.F. Nealey, X.M. Yang, R.D. Peters, T.K. Kim, Department of Chemical Engineering and Center for NanoTechnology, University of Wisconsin-Madison, WI.

The size of features of the most advanced electronic devices is approaching the scale of 10 nm. According to the National Technology Roadmap for Semiconductors, the minimum feature size of microprocessors (isolated lines) and DRAMs (dense lines) will shrink to 50 nm and 70 nm respectively by 2010. The development of nanofabrication techniques based on block copolymers has attracted a lot of attention because these materials self-assemble at the scale of 10 nm, and the size and shape of microphase-separated domains can easily be manipulated by controlling the molecular weight and composition of the polymer. The strategy to direct the self-assembly block copolymers has great potential for fabrication at the molecular scale because it leads to equilibrium structures that are at (or close to) thermodynamic minimum. In previous studies using block copolymers for applications in nanofabrication, thin films of block copolymers have been deposited on substrates, and microphase-separated domains serve as templates for pattern transfer into the substrate. The periodic structures created with this technique are defect free over length scales of 1 micron. Our research focuses on the inducing macroscopic order (regions of 1 cm²) in the morphology of thin films of block copolymers using substrates patterned with regions of different chemical functionality. Polymer surface interactions are well known to control the morphology of thin films of block copolymers. To induce macroscopic orientation of the block copolymer structure perpendicular to the surface, the substrate must be patterned with regions with dimensions commensurate with the size of the polymer molecules, and with adjacent regions that are wet by different blocks of the polymer. We use self-assembled monolayers as imaging layers

with x-ray and extreme ultra violet lithography to create chemically patterned surfaces, and we investigate the behavior of thin films of poly(styrene-b-methylmethacrylate) on these substrates.

9:30 AM **G9.3**

SELF-ASSEMBLY OF PATTERNED POLYMER SURFACES BY ANISOTROPIC SPINODAL DEWETTING. Anthony Higgins, Richard Jones, Sheffield Univ, Dept of Physics and Astronomy, Sheffield, UNITED KINGDOM; Robert Cubitt, ILL, Grenoble, FRANCE; John Webster, David Bucknall, Rutherford Appleton Lab, ISIS, Didcot, UNITED KINGDOM; Michele Sferazza, Cambridge Univ, Cavendish Lab, Cambridge, UNITED KINGDOM.

A thin film of poly(methyl methacrylate) on a polystyrene substrate dewets by the dispersive force driven amplification of capillary waves at the polymer/polymer interface - spinodal dewetting. Under normal circumstances there is a strong wavelength selection mechanism, and the dewetted pattern thus has a characteristic length scale, but the dewetted domains have random orientation and phase. In some circumstances the orientation of the dewetting process can be controlled by rubbing the substrate on which the PMMA film is cast; this produces a dewetted pattern with a strong anisotropy in the form of well-defined stripes of PMMA with periodicities of around a micron. We have demonstrated spinodal dewetting in this system using off-specular neutron reflection experiments, which show the growth of the unstable capillary wave which is the precursor to dewetting, and microscopy of the final dewetted patterns.

9:45 AM ***G9.4**

CRITICAL DEPENDENCY OF THE CONDUCTIVITY OF POLYPYRROLE AND POLYANILINE FILMS ON THE HYDROPHOBICITY/HYDROPHILICITY OF THE SUBSTRATE SURFACE. P.-C. Wang, Z. Huang and A.G. MacDiarmid, Dept of Chemistry, Univ of Pennsylvania, Philadelphia, PA.

High quality thin films of doped polypyrrole and doped polyaniline can be conveniently deposited during a few minutes at room temperature on glass and plastic substrates from dilute aqueous solutions of the respective monomers as they undergo oxidative polymerization by an in-situ deposition process.[1] The deposition rate, electronic spectroscopic properties and morphologies of the films are greatly dependent on the nature of the substrate surface, e.g. whether hydrophilic or hydrophobic. For each polymer the conductivity of the film deposited on a hydrophobic substrate is $\sim 10^4$ greater than that of the film of approximately the same thickness deposited on a hydrophilic surface. Films exhibit a memory effect characteristic of the nature of the original substrate surface. This effect decreases as the thickness of the film increases.

Acknowledgements:

This work was supported by the US Office of Naval Research under contract number N00014-92-J-1369. It also made use of MRSEC shared facilities at the University of Pennsylvania supported by the National Science Foundation under award number DMR-96-32598.

Reference:

[1] Z. Huang, P.-C. Wang, J. Feng, A.G. MacDiarmid, Y. Xia and G.M. Whitesides, *Synth. Met.*, 85 (1997) 1375 and references therein.

10:30 AM **G9.5**

FORMATION OF MICRO-PATTERNED POLYANILINE FILM VIA SELECTIVE DEPOSITION DURING CHEMICAL OXIDATION OF ANILINE. Yu-Tai Tao, Wen-Chung Lee, Institute of Chemistry, Academia Sinica, Taipei, TAIWAN ROC.

Chemical polymerization of aniline was carried out on a surface patterned with monolayers of a dimer aniline derivative and a saturated alkyl molecule using micro-contact printing technique. Selective growth of polyaniline proceeded on the dimer aniline-derivatized area. Non-selective deposition of solution-grown polymer on alkyl-derivatized area occur at a later stage of the reaction. Difference in adhesion between the polymer and the underlying surface allowed selective removal of the polymer deposited on alkyl-derivatized area by adhesive tape to leave behind a smooth, micro-patterned polyaniline film. The approach was demonstrated on the surface of gold by using thiol derivatives and on the surface of silicon wafer by using silane derivatives. Spectroscopic and morphological characterizations are presented.

10:45 AM **G9.6**

SURFACE-INITIATED RING OPENING METATHESIS POLYMERIZATION. Namyong Y. Kim, Paul E. Laibinis, Massachusetts Institute of Technology, Depts of Chemistry and Chemical Engineering, Cambridge, MA.

Polymerization processes originating from a surface could provide a way to generate covalently tethered thin films from surfaces with a high degree of flexibility in designing the films. To this end, we have developed a simple and straightforward surface-initiated ring opening

metathesis polymerization (ROMP). The procedure includes the formation of a norbornene-containing monolayer on silicon (bearing native oxide), immobilization of a ruthenium-based ROMP catalyst through norbornenyl units, and growth of polymer films upon exposure to various norbornenyl monomers. The thickness of the resulting polymer films can be controlled by variations in the monomer concentration or the reaction time, where grafted polymer films with thicknesses up to a micron have been formed by this method. The omission of any step in the procedure results in no polymer formation, suggesting that the polymerization proceeds by the ruthenium-based catalyst immobilized via the norbornenyl group at the surface. The ability to grow these ROMP-based films from directed nucleation sites has allowed us to generate patterned polymeric films on silicon by employing these methods in combination with the technique of microcontact printing. Upon exposure of silicon substrates patterned with a norbornene-containing monolayer to the ROMP process, polymeric films grow selectively from the patterned regions, with the same levels of control over composition and thickness mentioned above. These resulting films can serve as resist patterns under etchings of silicon such as reactive ion etching (RIE) and generate lithographed structures in the underlying silicon.

11:00 AM **G9.7**

SURFACE-INITIATED POLYMERIZATION FROM SELF-ASSEMBLED MONOLAYERS OF ORGANOMETALLIC CATALYSTS ON GaAs AND ZnS SURFACES. Hanrong Gao, Thomas A.P. Seery, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Monolayers of tethered organometallic complexes were formed on GaAs and ZnS plate surfaces by adsorbing thiols containing a terminal functional group on these surfaces and then coordinating the organometallic species to selected terminal groups. The terminal moieties were chosen to be initiators for the polymerizations of hexyl isocyanate, norbornene and cyclooctadiene. The organometallic species have previously been shown to be active catalysts for chain growth polymerizations. This approach was designed to give polymer layers on GaAs and ZnS surfaces. The initiator surfaces and the resulting polymer layers were characterized by IR, XPS, ellipsometry, XRD and TEM. The results show that the polymer layers were formed on the surfaces.

11:15 AM **G9.8**

CHEMICALLY TEMPLATED THREE DIMENSIONAL PATTERNING TECHNIQUES IN ELECTROSTATIC ASSEMBLY. Xueping Jiang, Paula T. Hammond, MIT, Dept. of Chemical Engineering, Cambridge, MA.

Patterned multilayer thin films with 3-D complex structures have been prepared. One structure is a vertical composite thin film, consisting of two or more levels of patterned multilayer microstructures. This multi-level pattern is achieved by combining polyelectrolyte layer-by-layer assembly and a patterning method which involves the micro-contact printing of functional polymers to create patterns atop polyelectrolyte layered assemblies. A second type of complex structure under investigation in our group is a lateral composite structure comprised of regions of alternating composition within a single level pattern. First, chemically templated ionic multilayer assembly was used to obtain a set of patterned thin films. Then a second layer-by-layer film can be introduced into the gaps of the original patterns by changing the original adsorption resist regions to adsorption promoting sites and switching the original adsorption sites to resist regions. Such lateral composite structures have been demonstrated with ruthenium dye multilayers, which can be alternated with polyelectrolyte multilayers. The concept behind these composite structures is the ability to change surface functionality by stamping or adsorbing difunctional molecules on the existing surfaces. This concept and the resulting complex structures hold promise for making functional polymer devices such as displays, sensors and optical circuits etc.

11:30 AM **G9.9**

SELF-PATTERNING MONOLAYERS: LANGMUIR-PHASE ASSISTED ASSEMBLY OF LONG-CHAIN SILANE MONOLAYERS AT OXIDE SUBSTRATES. Atul N. Parikh, Rong Wang, Jaime D. Beers, Andrew P. Shreve, Basil I. Swanson, Chemical Science & Technology Division, Los Alamos National Laboratory, Los Alamos, NM.

Pre-polymerized n-octadecyltrichlorosilane (OTS) monolayers were transferred onto oxidized silicon substrates from precursor Langmuir monolayers (at an air-water interface) in two-dimensional liquid (LE), solid (LC) or mixed (LE/LC co-existence phase) states at four different pulling rates. Morphologies of the transferred monolayers have been investigated using atomic force microscopy (AFM). The OTS monolayers formed from the LE phase precursor reveal an incipient condensation transition exhibiting a novel ring-in-a-ring

morphology, wherein uniformly distributed circular domains consisting of two concentric walls of ordered OTS molecules in a high density phase, sandwich and encapsulate disordered OTS molecules in a reduced density phase. On the other hand, the monolayers formed from the LC/LE phase precursor implicates a complete condensation transition, evidenced in the AFM images showing a uniform tiling of near-circular domains composed of ordered OTS molecules in a dense monolayer phase. The monolayers derived from the 2D solid or LC precursor state reveal near-complete surface coverages and uniform film structures, comparable to those obtained by adsorption from dilute organic solution of OTS molecules (conventional self-assembly process). These structural reconstructions at the substrate surface, namely lateral redistribution into 2D domains, condensation transitions and film coverages, are discussed in terms of the competition between short-range and long-range interactions. The most dominant effect of increasing pulling rates is the appearance of coalesced domain structures, presumably due to drainage of the water layer at the substrate surface as well as occasional substrate pinning. These results substantiate the idea that templating surface self-assembly of monolayers by using their Langmuir phase precursors provides a useful alternative to classical solution-phase self-assembly approaches and affords a wide range of control over film structures and surface morphologies.

11:45 AM G9.10

CONTROL OF SURFACE REACTIONS ON SILICON : SPATIAL SELECTIVITY AND PATTERN FORMATION. Kuniyil

Prabhakaran, Toshio Ogino, NTT Basic Research Laboratories, Atsugi, JAPAN.

The field of fabrication of semiconductor nanostructures has been rapidly growing, with the advent of novel methods and approaches. In order to realize nanodevices, introduction of functional elements into these structures and their wafer scale integration are two essential factors. We have been focussing our attention on control of surface structure and reactions, self-organization and manipulation of surface chemical bonds to address the above demands. In the case of surface reactions, occurrence of selective reaction on specific areas of the wafer is a highly desirable feature. In this paper, we describe two different aspects of surface reactions. The first one being, reactions on a patterned substrate and the second one is, generation of patterns through surface reactions on a planar substrate. We performed oxidation, nitridation and oxynitridation reactions under UHV conditions, on patterned (mesa pattern) Si(111) wafer, by employing NO, NH₃ and O₂ gases (individually as well as mixture). Reaction with NO at high temperatures (>800C) results in oxygen free nitride, formed entirely around the mesa edges, as clearly observed by scanning Auger mapping. When the reaction was carried out in the absence of oxygen (for example, NH₃ only) we do not observe this phenomenon and therefore we believe that oxygen etching generates reactive centers where the reaction nucleates and propagates in a highly selective manner. Exposure of a planar Si(111) surface, to a mixture of NO & O₂ or NH₃ & O₂ at high temperatures (>800C) results in the formation of faceted patterns with needle like structures located in the center of the pattern. These appear to be self-organized and we obtain a single needle like structure per each faceted unit. The faceted units are surrounded by trenches formed due to the etching reaction.

SESSION G10: FIELD-INDUCED ORDER IN STRUCTURES AND ARRAYS

Chairs: Timothy J. Bunning and Alamgir Karim
Thursday Afternoon, December 2, 1999
Salon E (M)

1:30 PM *G10.1

ALL OPTICAL FABRICATION OF SURFACE RELIEF STRUCTURES ON AZO POLYMER FILMS. Sukant K. Tripathy, Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA.

Unique photoinduced properties of azobenzene functionalized polymer film makes it an ideal candidate for all optical fabrication of intricate surface relief structures and novel device applications. Diffraction properties, near field and far field optical features of the surface relief gratings fabricated under appropriate writing conditions will be presented. Mechanistic aspects of this phenomenon and the importance of the photoanisotropic characteristics of the azopolymer will be discussed.

2:00 PM *G10.2

SURFACE RELIEF GRATINGS PHOTOINSCRIBED ON AZOBENZENE-BASED POLYMERS: NOVEL POLYIMIDE MATERIALS, DECREASING THE SPACING BETWEEN GRATINGS AND APPLICATIONS IN LIQUID CRYSTAL CELL ORIENTATION. Almeria Natansohn, Department of Chemistry,

Queen's University, Kingston, Ontario, CANADA; Paul Rochon, Department of Physics, Royal Military College, Kingston, Ontario, CANADA.

Interfering light can create a stable grating by surface modification of azobenzene based polymer films. Images can be stored along more than one direction, since the first grating is not erased by the light used to inscribe subsequent gratings.

First, we report here a novel material used for such holographic gratings inscription: an azocarbazole-based polyimide. The polyimide itself is extremely thermally stable, but its absorbance is relatively low. Doping the polyimide with an azocarbazole-based diamine produces an optimized material. Gratings inscribed on the doped films are stable even after one hour baking at 240°C.

The spacing between the gratings can be easily varied upwards of 350 nm by changing the geometry of the inscription set-up. However, due to the required wavelength of the inscription light, it is more difficult to obtain gratings with shorter spacings. A procedure to produce gratings with spacings below 200 nm, useful for optical couplers and filters, will be described in this presentation.

Finally, such gratings can be photoinscribed on the interior surface of a prefabricated empty liquid crystal cell. Subsequent filling of the cell with a liquid crystal produces a uniform alignment. The azimuthal surface anchoring energy is calculated to be 1.1×10^{-4} J/m², a value comparable to the anchoring obtained in cells with rubber polyimide film surfaces.

2:30 PM G10.3

BIPERIODIC SURFACE RELIEF GRATINGS ON PHOTO-ANISOTROPIC AZOPOLYMER FILMS. Nirmal K. Viswanathan, Srinivasan Balasubramanian, Jayant Kumar and Sukant K. Tripathy, Department of Physics, Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA.

Biperiodic surface relief gratings (SRG) are formed when photoanisotropic azobenzene functionalized polymer thin films are exposed to an interference pattern due to orthogonal linear polarized light beams (s- p-). Spatially varying electric field orientation due to the interference of coherent light beams, despite constant intensity inscribes this unique grating structure. Periodic modulation of the state of polarization induces spatial variations in the orientation of the induced azo chromophore axis. This along with the force due to a component of electric field gradient, parallel to the grating vector direction, acting on the azo chromophore attached polymer chains is responsible for the formation of biperiodic SRGs. The biperiodic SRGs formed under appropriate writing conditions can be observed in an Atomic Force Microscope (AFM) scan. A systematic experimental study is carried out to understand the underlying mechanism. Influence of the writing beam intensity, grating period and polarization impurity on the formation of biperiodic SRGs will be discussed. The results are explained using a theoretical formalism developed based on the spatially varying induced susceptibility change and electric field gradient in the sample plane. Diffraction properties of these polarization gratings along with possible applications will be discussed at the meeting.

2:45 PM G10.4

PINPOINT ARRANGEMENT OF MICRO SPHERES BY CHARGED BEAM ELECTRIFICATION. Hiroshi Fudouzi, Mikihiko Kobayashi and Norio Shinya, National Research Institute for Metals, Tsukuba, JAPAN.

Assembly of particles is one of the built-up methods to fabricate an organized structure in the scale of from micro to nano meter. We proposed a new technique to assemble micro scale particles for the fabrication of two- or three- dimensionally controlled microstructure. The technique is based on positioning individual particles on a dielectric substrate by electrostatic force. An electrified spot formed on a substrate acts as a potential well on which a particle is attracted. If the size of the well is smaller than that of a particle, the particle would deposit on the spot. Therefore we can deposit each particle on each predetermined pinpoint position on the substrate. By repeating the process for other particles, different kinds of particles can be arrayed on the substrate. In this paper the detail of the technique and results of experiments, using polymer spheres (5µm in diameter) covered with gold as a model particle, are presented. An array of the positively electrified spots were formed with a spacing of 25µm on a CaTiO₃ substrate by drawing a focused Ga⁺ ion beam. The substrate was dipped in a suspension in which the spheres were dispersed. The spheres were attracted to the spots and deposited on the spots. The deposited spheres formed a two-dimensional array with a spacing of 25µm. These results show that the technique enables to deposit a lot of particles on predetermined pinpoint positions on the substrate. It is thought that the arrayed microspheres can be applied to micro-devices in optical, biochemical and medical fields. This technique is expected to be applied to the fabrication of the micro-devices.

3:30 PM *G10.5

FIELD INDUCED POLYMER ARCHITECTURES. John L. West, O.D. Lavrentovich, Kent State University, Liquid Crystal Institute, Kent, OH.

We recently reported formation of self-assembled polymer walls in liquid crystal displays induced by a patterned electric field. The patterned field is produced by the row and column electrodes that form the pixels in liquid crystal displays. A patterned electric field induces phase separation and segregation of a solution of a photo-polymerized monomer and liquid crystal. The monomer moves to the low field, interpixel regions. The segregated monomer forms polymer walls around the liquid crystal rich pixels upon blanket UV irradiation. The polymer walls provide mechanical strength without interfering with the optical performance of the liquid crystal. More recently we used the periodic, structure of a cholesteric liquid crystal to form periodic, micron sized polymer structures in a solution of photo-polymerized monomer and liquid crystal.

4:00 PM G10.6

SELF-ASSEMBLY OF FLOATING MAGNETIC PARTICLES INTO PERIODIC TWO- AND THREE-DIMENSIONAL LATTICES- A PROMISING ROUTE FOR THE FABRICATION OF TUNABLE PHOTONIC BANDGAP MATERIALS. Michael Golosovsky, Yuval Saado, Dan Davidov, Hebrew University of Jerusalem, Racah Institute of Physics, Jerusalem, ISRAEL.

We report stable planar arrays of millimetre- size magnetic particles encapsulated into a styrofoam and floating on the liquid surface with their magnetic moments perpendicular to it. Self-assembly results from the magnetic interaction between the particles. The symmetry and lattice spacing of the resulting lattice may be easily tuned by the external magnetic field. The symmetry of the array is designed by using varying particle shapes, magnets, and magnet position inside the particle, so that complex symmetries may be achieved. At high particle concentration they acquire tilt (similar to smectic-C liquid crystals) due to the tendency of magnetic moments to form chains. The tilt is strongly affected by the external magnetic field. We report also three-dimensional structures obtained in a stack of troughs with magnetic layers oriented either in ferromagnetic or antiferromagnetic order. We perform simulations of electromagnetic wave propagation in such systems and conclude that they may be used as a tunable photonic bandgap material for microwaves. We discuss possibility of scaling the particle dimensions down to microns in order to achieve tunable photonic bandgap material for optical wavelengths.

4:15 PM G10.7

SELF-ALIGNMENT AND ORIENTATIONAL TRANSFORMATIONS IN Al-Fe HYDROXIDE (AlUreaka) NANOPARTICLES. L.J. Martinez-Miranda, O.C. Wilson, I. Aninye, D. Young, University of Maryland, Dept. of Materials and Nuclear Eng., College Park, MD; P. Vakil, University of Maryland, Baltimore County, MD.

Aluminum and Iron Hydroxide (AlUreaka) particles prepared using an aqueous solution method form elongated, tubular nanostructures. Typical dimensions for the long and short axes are 150 nm and 30 nm respectively, as confirmed by AFM, TEM and SAXS. The self-alignment processes of these particles are studied as models for biological systems such as collagen. Similar particles have potential in magnetic-driven devices, and can serve as templates for the alignment of other nanostructured materials. We have studied the self-alignment and orientational transformations of these particles as a function of solution density using optical microscopy. We find these transformations are isomorphic to liquid crystal alignment transformations at solid interfaces. In the presence of a magnetic field, the final arrangement of the particles is the result of a competition between the surface aligning forces and the field reorientation forces. This work is supported in part by a NSF Career Advancement Award grant No. ECS-9710789, the UMCP ESTEEM program and the UMCP-MRSEC Research Experiences for Undergraduates Program, under NSF grant. No. DMR-9632521.

4:30 PM G10.8

MAGNETOSENSITIVE SELF-ORGANIZING FERROFLUID ARRAYS FOR LABORATORY-ON-CHIP APPLICATIONS. Jean-Louis Viovy, Patrick Doyle, Institut Curie, FRANCE; Jerome Bibette, CRPP, Bordeaux, FRANCE.

Separation sciences are at the dawn of a deep mutation, associated with the development of highly automated, integrated and miniaturized microfluidic devices called laboratory-on-chip. The principle of this approach is to integrate into an array of channels (generally prepared by microlithographic techniques) several sample preparation and analysis processes. This approach implies a deep reconsideration of separation mechanisms an matrices, because the media used in conventional methods (e.g. gels or packed beds) are poorly adapted. We developed new matrices based on self-organizing

ferrofluids, that can be reversibly switched from a liquid state (for easy and automated regeneration) to a self-organized maze with good sieving properties, by proper tuning of an external magnetic field. Examples of applications to the separation of DNA will be presented. Separation in the range of hundreds of kb is achieved in less than one hour. The mechanism responsible for separation, as observed in direct videomicroscopy, is consistent with the "collision and stretching" mechanism previously proposed by Duke and Austin, Sevick and Williams and André, Long and Ajdari, for microlithographic arrays. Future directions for research will be discussed.

4:45 PM G10.9

PERIODIC MICROSTRUCTURES FORMATION BASED ON INTRACAVITY LASER PROCESSING. Vladimir P. Osipov, Vasily V. Valyavko, Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, BELARUS.

At the MRS 1996 Fall Meeting we reported about the original laser intracavity method of periodic microstructures formation on the high-reflecting solid-state surface. The main feature of this method was the possibility to create structures with characteristic sizes, which were about 30 times less than the used laser radiation wavelength. In case of carbon dioxide laser application with 10.6-micrometer wavelength, the width of the formed parallel microgrooves was about 0.3 micrometer. This unexpected result was explained on the base of multibeam interference of the radiation in the laser cavity. The subject of this work is the further development of the intracavity method of laser formation of periodic microstructures. The usage of laser sources emitting in the visible spectral range and the application of original construction of laser cavity scheme allows to form the regular systems of microstructures (with characteristic sizes up to 0.15 micrometer), looking as parallel grooves, periodically disposed microhollows (dot-structures), microgrids. It should be marked, that the whole pattern is formed during the single laser shot and the periods of microstructures may be tuned from 0.5 to 100 micrometers. The intracavity laser treatment approach may be useful at the submicrometer organization of solid-state surface, thin films and membrans.

SESSION G11: 2D AND 3D PHOTONIC STRUCTURES

Chairs: Michael F. Rubner and Ned Thomas
Friday Morning, December 3, 1999
Salon E (M)

8:30 AM *G11.1

MACROPOROUS POLYMERS, OXIDES AND METALS FROM SINGLE CRYSTAL COLLOIDAL TEMPLATES. Peng Jiang, Jane F. Bertone, Joel Cizeron, Kevin S. Hwang, Kristen Kulinowski, Mary Turner, Kim Firestone, Daniel M. Mittelman, Yicki L. Colvin, Rice University, Department of Chemistry, Houston, TX.

We report the use of single crystal colloidal arrays as templates for the formation of macroporous polymer, ceramic oxides and metals. These films contain interconnected and monodisperse spherical voids with diameters between 200 and 400 nanometers. Samples have been characterized by SEM, TEM, BET surface area analysis, PXRD and UV-vis spectrometer. All of these techniques provide evidence that these monolithic samples are fully porous and contain a highly crystalline network of air spheres. Highly ordered ceramic oxides hollow shells with controlled thickness can be made by a double-template method using different polymer templates. We will also discuss the unusual optical properties and their dependence on the material and order of the sample.

9:00 AM G11.2

TEMPLATE DIRECTED SELF ASSEMBLY OF COLLOIDAL CRYSTALS FOR PHOTONIC BAND GAP APPLICATIONS. Robert W. Zehner, Paul V. Braun, Pierre Wiltzius, Christopher A. White, Marcus Weldon, Sanjay S. Patel, Bell Labs, Lucent Technologies, Murray Hill, NJ.

Large, defect-free colloidal crystals have the potential to serve as scaffolds for the creation of photonic band gap (PBG) materials. Although sedimentation of micron-scale colloids from solution ordinarily yields disordered assemblies, face centered cubic (fcc) crystals can be grown by settling the particles onto a patterned template that induces the formation of a square lattice. The size of the resulting crystal is limited only by the size of the template, and the defect density is ~1%. In contrast with previous reports in which templated colloidal crystals were observed under liquid, these crystals have been successfully dried and further processed to yield periodic materials with high dielectric contrast. The synthesis and characterization of the resulting photonic crystals will also be discussed.

9:15 AM G11.3

ORDERED POROUS STRUCTURES FOR PHOTONICS USING SELF-ASSEMBLY OF COLLOIDS. G. Subramania, Ames Laboratory-USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA; K. Constant, Ames Laboratory-USDOE and Department of Materials Science and Engineering, Iowa State University, Ames, IA; R. Biswas, M.M. Sigalas, K-M. Ho, Ames Laboratory-USDOE, Microelectronics Research Center and Department of Physics and Astronomy, Iowa State University, Ames, IA.

We have developed a simple and novel ceramic technique to form ordered porous structures in ceramic materials with uniform pore size distribution. This material shows photonic gaps at visible/near-IR wavelengths. The template for uniformed ordered pores is obtained making use of the self-assembly property of the monodisperse polystyrene spheres. A suspension is formed from commercially available polystyrene microspheres and nano-crystalline titanium dioxide. This suspensions is then spread on insulating substrates and allowed to slowly dry. A film with large regions of close-packed ordered spheres interspersed in a background of titania were spontaneously formed. Ordered air pores are left behind when the template polystyrene spheres are calcined by heating the formed material above 300C. Ordered regions were few mm across with grain sizes of 50 – 70 μ . Optical reflectivity measurements indicate peaks at the stop band wavelengths that scale with the pore size. Visual inspection and optical microscopy reveals uniform colored regions for sufficiently small pore sizes. We will describe further structural characterization of this material using scanning electron microscopy(SEM) and optical diffraction. In addition position of the reflection peak as function of incident angle will be discussed. Comparison with theoretical calculations will be presented.

9:30 AM G11.4

NANOSTRUCTURED POROUS MATERIALS TEMPLATED BY COLLOIDAL CRYSTALS: FROM INORGANIC OXIDES TO METALS. Orlin D. Velev, Peter M. Tessier, Raul F. Lobo, Abraham M. Lenhoff and Eric W. Kaler, Dept. of Chemical Engineering, University of Delaware, Newark, DE.

We have introduced a novel approach for forming nanostructured materials by using colloidal crystals as templates (Velev et al., Nature, 389: 447, 1997; Chem. Mater., 10:3597, 1998). The templates comprise 3D close-packed crystals of submicrometer latex microspheres assembled on a membrane surface. In the first application, the colloidal crystals are functionalized with surfactant and infused with silica solution, which polymerizes in the cavities. Silica with highly uniform and ordered pores that represents a negative replica of the original colloidal crystal is obtained after calcination. The pore size can be precisely controlled in a wide region (100 to 1000 nm) that had previously been unattainable. Lately we have modified our method to obtain a unique new material - nanostructured porous gold. The metallic structure is assembled from nanometer size gold particles that are templated by the colloidal crystal to yield a metallic nanostructure with 3D ordered pores. Two alternative pathways for the formation of the porous gold were developed, one of which leads to a structure that is simply macroporous, while the other results in a hierarchical macroporous-mesoporous structure. The material has unique optical and photonic properties. It represents a replica of the 3D metallic mesh photonic crystals described earlier by the Yablonovitch group, but scaled down by a factor of 20000 to the sub-micrometer region. This novel photonic metal holds promise for advanced applications in electro-optics, microelectronics, catalysis, or self-lubricating or reflective coatings. Our presentation will also discuss the potential and limitations of the colloidal crystals as templates for novel materials.

9:45 AM G11.5

TWO DIMENSIONAL PHOTONIC BANDGAP HOSTS FOR RARE EARTH DOPED LOW PHONON LASER CRYSTALS.

Casey M. Clark, University of Dayton, Dayton, OH; Sean M. Kirkpatrick, Science Applications International Corporation, Dayton, OH; Ron J. Tonucci, Naval Research Laboratory, Washington DC.

Provided there is limited multiphonon quenching, rare earth ions have the potential to act as mid infrared sources of radiation due to their ground state splitting. High multiphonon quenching in conventional oxide and fluoride host materials deactivates these radiative transitions. Doping rare earth ions into a low phonon host, i.e. materials with a low phonon density of states, eliminates multiphonon quenching and enhances radiative emission. These rare earth low phonon crystals have been shown to emit, at room temperature, in the mid-IR region. It is believed that some of the IR emission and absorption transitions of the rare earth low phonon crystals will be affected by growing these materials inside a two-dimensional photonic crystal. Two-dimensional photonic crystals consist of a regular matrix of parallel channels, which serve to halt the transmission of certain frequency bands, thus forming a band gap. In this work we report on

the growth of single crystal rare earth low phonon materials in combination with a two dimensional photonic crystal and the spectroscopic behavior of these materials. Absorption spectra, fluorescence spectra, and lifetime measurements are reported on bulk crystals and crystals grown within a photonic bandgap host. In the analysis, changes in the energy transfer mechanisms and the fluorescence lifetimes between the bulk crystals and those grown within the photonic bandgap will be examined.

10:30 AM *G11.6

SELF ASSEMBLED BLOCK COPOLYMER STRUCTURES AS PHOTONIC BAND GAP MATERIALS. Yoel Fink, Augustine Urbas, Edwin L. Thomas, MIT, Dept. of Materials Science.

Periodic dielectric structures effect properties of photons much like periodic atomic potentials effect the properties of electrons in matter. Understanding the similarities and appreciating the differences between the photonic and electronic interactions allows one to design and optimize structures and fabrication methods for producing novel photonic band gap materials. By creating complex periodic dielectric structures one can achieve plurally directional photonic band gaps which can be utilized to localize and guide light. In order to fulfill the promise that these concepts hold, challenging issues associated with the processing and formation of such structures at optical length scales need to be addressed. Most of the current research and fabrication efforts into creating two and three-dimensional photonic crystals has relied on conventional semiconductor processing techniques or colloidal assemblies of spheres. These tend to be costly and structurally restrictive. An alternative methodology for creating photonic crystals out of self-assembling block copolymers has been formulated. By enhancing the dielectric contrast between the block copolymer domains one can create overlapping photonic band gaps which will inhibit the propagation of certain electromagnetic frequencies in the material. These in turn can be used as frequency selective reflectors that can be deposited on arbitrarily shaped surfaces for confining or reflecting light. Recent experimental results on the interaction of self assembled layered styrene-isoprene diblock copolymers with visible light will be presented. The usefulness of these materials would be greatly enhanced if one could control the locality and the dimensionality of imperfections in the structures. Defects in a photonic band structure could lead to localized electromagnetic states, such that a point defect could act as a microcavity, a line defect like a waveguide. Depending on the block copolymer microdomain geometry, various point, line and surface defects can occur during the transformation from the homogeneous disordered state to the microphase-separated state. Understanding how to control the defects in block copolymer based photonic structures is critical for creating a new class of self-assembling optical materials.

11:00 AM G11.7

MESOSTRUCTURED SILICA OPTICAL DEVICES. Peidong Yang, Steven Cordero, Frank Marlow, Howard Huang, Brian Scott, Gernot Wirmsberger, Bradley F. Chmelka, Steven K. Buratto, Galen D. Stucky, Chemistry Department, University of California, Santa Barbara, CA; Tao Deng, George M. Whitesides, Chemistry Department, Harvard University, Cambridge, MA.

Patterned mesostructured silica optical arrays were fabricated using micromolding techniques. The mesostructured silica was templated in an acidic sol-gel process using either low molecular-weight surfactants or block copolymers as structure-directing agents. Waveguiding is successfully demonstrated using these arrays. In addition, efficient gain narrowing in optically pumped composites of dye molecules in mesoporous microfibers was achieved. The gain-narrowed emission occurs from the end of the fiber parallel to the fiber axis. These results indicate that the mesostructured composites have a large cross section for stimulated emission, that population inversion can be achieved, and that emitted photons are guided over distances considerably longer than the gain length within the gain medium. The mesostructured host medium offers various ways for the incorporation of luminescent species and for the controlled assembly of laser materials and other optical devices. The implication of fabricating mesostructured silica into optical circuits will be discussed.

11:15 AM G11.8

CHEMICAL ROUTES TO THREE-Dimensionally MICROPERIODIC HIGH REFRACTIVE INDEX STRUCTURES.

Paul V. Braun, Robert W. Zehner, Pierre Wiltzius, Christian Kloc, Marcus K. Weldon, Christopher A. White, Sanjay S. Patel, Bell Labs, Lucent Technologies, Murray Hill, NJ.

The creation of low refractive index three-dimensionally microperiodic structures through colloidal templating is relatively straightforward, but high refractive index structures as would be required for photonic band gap applications remains quite challenging. Lithographic approaches to high refractive index structures have been proposed, but practically, are limited low dimensional structures. Materials

chemistry may provide several routes to create essentially infinite high refractive index structures. Two of the routes we have explored are the imbibing of nanocrystalline titania, and the electrodeposition of II-VI semiconductors around highly regular colloidal assemblies. Several other routes to even higher refractive index materials are currently under exploration. Following deposition of the high refractive index phase, the colloidal template is either dissolved or burnt out. Both the electrodeposition and colloidal routes may circumvent the current difficulty in fully mineralizing the interstitial space of a colloidal assembly. Optical and physical characterization of the resulting photonic crystals will be discussed.

11:30 AM G11.9

OPTICAL PROPERTIES OF THREE-Dimensionally MICROPERIODIC DIELECTRIC STRUCTURES. Pierre Wiltzius, Paul V. Braun, Marcus K. Weldon, Christopher A. White, Robert W. Zehner, Sanjay S. Patel, Bell Labs, Lucent Technologies, Murray Hill, NJ.

Reflection and transmission spectra were obtained from high dielectric structures containing long range three-dimensional microperiodicity. The structures were formed through a templating approach using a face centered cubic (fcc) colloidal crystal as the template. The optical properties along specific crystallographic axes were determined, and the effect of refractive index contrast and structural defects was identified. Very strong, nearly complete band gaps were observed for the inverse fcc structures when the refractive index contrast approached 2.5. The results compared favorably with spectra calculated from theoretical band structures.

11:45 AM G11.10

THREE-DIMENSIONAL COLLOIDAL PHOTONIC CRYSTALS MADE FROM SUBMICRON-SIZED POLYSTERENE LATEX GLOBULES WITH LUMINESCENT POLYELECTROLYTE/NANOCRYSTAL SHELLS. Andrey L. Rogach, Andrei S. Susha, Physico-Chemical Research Institute, Belarusian State University, Minsk, BELARUS; Frank Caruso, Gleb B. Sukhorukov, Helmuth Moehwald, Max-Planck- Institute of Colloids and Interfaces, Golm, GERMANY; Steve V. Kershaw, Mike Burt, BT Laboratories, Martlesham Heath, Ipswich, Suffolk, UK; Andreas Kornowski, Alexander Eychmueller, Horst Weller, Institute of Physical Chemistry, University of Hamburg, Hamburg, GERMANY.

We present a method combining three consecutive steps of nano/microengineering. Wet-chemical synthesis of semiconductor nanocrystals with desirable sizes and surface chemistry provide controllable light emission and surface charge of the nanoparticles. Charged luminescent nanocrystals have been included by the layer-by-layer self-assembly technique into polyelectrolyte shells on submicron-sized monodisperse polystyrene latex globules. Latex globules with luminescent composite polyelectrolyte/nanocrystal shells have been used as building blocks to fabricate 3 D colloidal photonic crystals.