

SYMPOSIUM AA
Self-Assembly Processes in Materials

November 26 – 30, 2001

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* Invited paper

This “virtual” symposium addresses the burgeoning interest in materials self-assembly processes by offering related presentations from nominally disparate fields.

Nine symposia (K, M, N, V, W, Y, BB, DD, HH) have incorporated entire sessions concerning self assembly into their overall programs, and scheduling was coordinated to enable convenient viewing of any or all of these sessions. The topic of self assembly is also evident in 23 other symposia.

SESSION AA1/K1: JOINT SESSION
COLLOIDAL SELF ASSEMBLY AND PHOTONIC
CRYSTALS

Chair: Pierre Wiltzius
Monday Morning, November 26, 2001
Room 201 (Hynes)

8:30 AM *AA1.1/K1.1

TOWARDS MICROPHOTONIC CHIPS. Geoffrey A. Ozin, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA.

The physical dimensions of contemporary optical circuits may profoundly shrink in size if microphotonic chips are reduced to practice. Such a development is envisioned to disrupt contemporary photonic technologies and revolutionize optical circuit miniaturization in a way analogous to the displacement of traditional electrical circuits by integrated silicon microelectronic chips. This is an on-going research goal of our photonics materials chemistry group using as platform materials silicon inverse opals (Ozin and co-workers, Nature 2000, 405, 437-440) and opal-patterned silicon chips (Ozin and Yang, ChemComm 2000, 2507-2508, Adv Funct Mat 2001, 11, 1-10).

9:00 AM AA1.2/K1.2

INVERSE OPALS SYNTHESIZED THROUGH A HIERARCHICAL SELF-ASSEMBLY APPROACH. Byron Gates, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated a hierarchical self-assembly approach to the fabrication of inverse opals. In a typical process, building blocks with dimensions on two different scales – monodispersed spherical colloids with diameters in the range of 0.2 to 1.0 μm and nanoparticles with sizes below 15 nm – were mixed with appropriate ratios and crystallized into opaline lattices that exhibit long-range order in all three dimensions of space. Subsequent removal of the template resulted in the formation of inverse opals made of various functional materials such as magnetite and titania. The optical properties of these inverse opals will also be discussed in this presentation.

9:15 AM AA1.3/K1.3

LIGHT PROPAGATION IN 3D PHOTONIC CRYSTAL. H. Kitano, F. Minami, Dept of Physics, Tokyo Institute of Technology, Tokyo, JAPAN; T. Sawada, National Institute for Material Science, Tsukuba, Ibaraki, JAPAN; S. Yamaguchi, K. Ohtaka, Center for Frontier Science, Chiba University, Chiba, JAPAN.

By using femtosecond optical pulses, we have studied light propagation near the stop band of a 3D photonic crystal. This crystal was fabricated from a colloidal suspension of polystyrene microspheres, having a diameter of 0.194 μm and monodisperse to within 3.4%. From Kossel line patterns, the crystal was found to have a fcc structure. The phase and amplitude of the transmitted optical pulses have been measured in the energy- and temporal domain with the Spectrally Resolved Cross-correlation technique. The transmission spectrum of the fcc crystal along the [111] direction showed a stop band centered around 800nm with a spectral width of 10 nm. The phase of the optical pulses changes drastically at the band edges, thus reflecting the enhanced variation of group velocity according to its frequency. The obtained dependence of group delay on frequency is in good agreement with that predicted by the dispersion (E versus k) curve along the [111] direction calculated from the photonic band calculation.

9:30 AM AA1.4/K1.4

FABRICATION OF COMPLEX STRUCTURES THROUGH SELF-ASSEMBLY WITH SPHERICAL COLLOIDS AS THE BUILDING BLOCKS. Yadong Yin, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated a strategy that combines physical

templating and capillary forces to assemble spherical colloids into uniform clusters with well-controlled sizes, shapes, and structures. We have illustrated the capability and feasibility of this approach by assembling polystyrene beads and silica colloids (≥ 150 nm in diameter) into complex structures that include polygonal or polyhedral clusters; linear or zigzag chains; and circular rings. We have also generated hybrid aggregates in the shape of HF or H₂O molecules that are composed of polymer beads having different diameters; polymer beads labeled with different organic dyes; and a combination of polymeric and inorganic beads. In this talk, we will discuss the experimental procedure, and some applications of this procedure in fabricating microphotonic devices such as arrays of microlenses and photonic crystals.

9:45 AM AA1.5/K1.5

PHOTONS CONFINED IN 3D-MICROCAVITIES DOPED WITH QUANTUM DOTS. U. Woggon, M.V. Artemyev, B. Möller, W. Langbein, FB Physik, University Dortmund, GERMANY.

We present the concept of a three-dimensionally confined photonic dot (PD) doped with CdSe quantum dots (QDs) and report on the interplay of 3D-confined cavity modes of single microspheres (the photonic dot states) with photons emitted from quantized electronic levels of single semiconductor nanocrystals (the quantum dot states). We show how cavity modes of high cavity finesse are switched by single, blinking quantum dots. The QDs@PD-structures have been prepared using very small glass spheres covered with a thin polymeric shell containing CdSe QDs. With $R < 5 \mu\text{m}$, the small size of the PD ensures a large mode spacing of a few tens of meV. For the cavity mode widths $\hbar\Delta\omega_{cav}$, values between 250 μeV and 1.5 meV were observed yielding maximum Q-factors ≤ 7500 . Using imaging spectroscopy at the diffraction limit, the emission spectra are analyzed and intensity and polarisation are mapped across a single microsphere with spatial resolution of 0.5 μm . Polarisation-selective detection schemes allow a spatial addressing of nanocrystals at the surface of the cavity exploiting the lifting of degeneracy of TM and TE-modes in a spherical cavity. At low temperatures and homogeneous linewidths of single quantum dots as narrow as the photonic dot modes, we observe an enhancement in the spontaneous emission rate, i.e. the Purcell effect is found for quantum dots inside a photonic dot. For these studies we use two special samples: one is a high-Q glass microsphere, the other a small piece of glass from a broken microsphere. Both are impregnated with CdSe QDs in the same process, thus eliminating all variations arising from chemical preparation. To avoid the influence of nonradiative recombination caused by trap processes we optimized before the preparation route and used only those nanocrystals which exhibit monoexponential decay curves with lifetimes in the range of nanoseconds. The PL-decay times have been studied spectrally resolved, in- and off-resonant to cavity modes. Enhancement factors of the spontaneous emission rate in the 3D-cavity compared to emission in free space varying between 2 and 6 have been obtained.

10:30 AM *AA1.6/K1.6

ON-CHIP ASSEMBLY OF SILICON PHOTONIC BAND GAP CRYSTALS. Yurii A. Vlasov, NEC Research Institute, Princeton, NJ; Xiang-Zheng Bo, James C. Sturm, Princeton University, Dept. of Electrical Engineering, Princeton, NJ; and David J. Norris, NEC Research Institute, Princeton, NJ.

Colloidal assembly can now achieve 3D semiconductor photonic crystals (inverted opals) that theory predicts should exhibit a complete photonic band gap. However, serious skepticism remains whether in practice these materials will 1) actually have a band gap and 2) be useful in any real device. Here, these issues will be addressed by exploring high-quality silicon inverted opals that are assembled directly “on-chip”. These structures are useful both for understanding their photonic properties and potential applications.

11:00 AM *AA1.7/K1.7

PHOTONIC BAND GAP DEVICES. Vicki Colvin, Department of Chemistry, Rice University, Houston, TX.

The gemstone opal exhibits a brilliant visible iridescence due to the regular spacing of sub-micron colloids which comprise its structure. This natural motif can be replicated in the laboratory, and artificial opals can be cast as thin films of controlled thickness using colloidal assembly techniques. The opal motif can also be harnessed in the production of highly regular porous materials. Numerous solids, ranging from polymers to metals, can be cast around the colloidal network and the colloids subsequently removed. The macroporous materials that result have arrays of spherical cavities interconnected by smaller windows. The diffractive properties of these inside-out structures are even stronger than the host opal, making them suitable for many optical filtering applications. The highly monodisperse cavities of macroporous polymers are ideal environments for growing many types of uniform particles, including solid and hollow spheres,

as well as elliptical particles. Finally, we have begun to build optoelectronic devices from conducting polymers prepared with strong photonic gaps.

11:30 AM AA1.8/K1.8

PHOTONIC CRYSTALS OF POLYSTYRENE-TITANIA CORE-SHELL COLLOIDS. Arnout Imhof, Condensed Matter Dept, Debye Institute, Utrecht University, THE NETHERLANDS.

Numerical calculations have shown that photonic crystals assembled from core-shell colloidal particles give rise to some interesting photonic properties such as a widening of the bandgap. A procedure was therefore developed to coat colloidal polystyrene spheres with a smooth and well-defined layer of titanium dioxide. The thickness of the coating can be easily varied from a few nanometers upward and can be increased further by seeded growth. The coated particles were characterized with electrophoresis, thermogravimetric analysis, X-ray diffraction, electron microscopy, and light scattering. The core-shell particles can also be turned into spherical hollow titania shells by dissolution of the polystyrene cores in suspension or by calcination of the dried particles in a furnace. Calcination results in spherical shells composed of a dense arrangement of TiO₂ (anatase) nanocrystals. The composite particles are very monodisperse and self-assemble into colloidal crystals. This way, photonic crystals of coated spheres as well as of hollow titania shells were obtained. We studied the photonic properties of these crystals by means of transmission measurements.

11:45 AM AA1.9/K1.9

METALLO-DIELECTRIC COLLOIDAL PARTICLES FOR PHOTONIC APPLICATIONS. Christina Graf^a, Alfons van Blaaderen^{a,b}, ^aUtrecht Univ, Physics & Chemistry of Condensed Matter, Debye Inst, Utrecht, THE NETHERLANDS; ^bFOM Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

It was shown recently that metallo-dielectric colloidal (MDC) particles are promising candidates to construct photonic crystals with a complete band gap in the visible (Moroz, A. Phys. Rev. Lett. 1999, 83, 5274). Moreover, MDC spheres can also improve applications of photonic crystals, like ns optical switches, that do not rely on a strong index contrast. In addition, single MDC particles can enhance Raman scattering of dyes that are placed close to these particles with factors of 10¹⁵ or larger caused by strong local field enhancements that are due to plasmon resonances in the metal. In this contribution we will show how core-shell MDC particles can be made with tunable optical properties. The particles consist of a monodisperse silica core, a gold shell and an optional silica outer layer. The silica can be labeled with fluorescent dyes and/or nano-crystals. The silica outer shell allows for tuning of the interparticle interaction potential through a reduction in the Van-der-Waals forces and facilitates functionalization of the particle surface; the variable gold shell around an also variable silica core makes the plasmon resonance of the particles adjustable over the whole visible and infrared region of the spectrum. The properties of the particles can be further modulated by controlled anisotropic deformation with high energy ion irradiation. It is also possible to turn the MDC particles into hollow metal spheres. Particle characterization by SEM, TEM and extinction measurements will be discussed. Finally, results on crystallization of the MDC particles into colloidal crystals induced by an electric field (Dassanayake, U.; Fraden, S.; van Blaaderen, A.J. Chem. Phys. 2000, 112, 3851) and/or the charge on the particles and the first optical measurements of these crystals will be presented.

SESSION AA2/X1: JOINT SESSION

Chairs: Bruce M. Clemens, Jerrold A. Floro, Julie A. Kornfield and Yuri Suzuki
Monday Afternoon, November 26, 2001
Grand Ballroom (Sheraton)

12:05 PM *AA2.1/X1.1

THE AGE OF MOLECULAR ENGINEERING. Philip Ball, Nature, London, UNITED KINGDOM.

Our view of the molecular world has changed profoundly in the past several decades. The stochastic picture of ensembles exhibiting statistical regularities has given way to the deterministic idea that we can specify, maintain and monitor the states of individual, selected molecules. The technological implications are enormous, and so far barely tapped. But familiarity with trends such as Moores law has encouraged the idea that this molecular engineering is simply another step in the shrinking scale of technology. It is now looking more likely that engineers of the atomic scale should start afresh that traditional ideas of how devices should be designed, how they operate and how

they might be assembled may no longer be appropriate for technology at the smallest scale.

SESSION AA3/N2: JOINT SESSION
HETEROEPITAXY AND SELF ASSEMBLY
Chairs: Frances M. Ross and Michael J. Aziz
Monday Afternoon, November 26, 2001
Room 306 (Hynes)

1:30 PM *AA3.1/N2.1

CONTROLLING THE GROWTH OF SELF-ASSEMBLED NANOSTRUCTURES DURING HETEROEPITAXY. F.M. Ross, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Control of the shape, size and especially the placement of self-assembled nanostructures during heteroepitaxial growth remains a significant challenge to using these structures in novel devices. Precise control of island size and shape is required for good electronic properties, and islands must be accurately positioned in devices such as cellular automata and single electron transistors. In this presentation we will describe approaches to the control of nanoscale structures, in particular self-assembled islands, based on an understanding of the heteroepitaxial growth process obtained from real-time observations made during growth. Video-rate observations made during deposition of Ge and SiGe on Si(001), a model system which has features in common with other strained layer semiconductor systems, allow us to model island growth as a modified coarsening process and therefore to suggest conditions which optimize the size distribution. Furthermore, by observing island shape changes in real time during growth we can understand the sequence of shapes which form and relate this to the size distribution. Island placement remains the most intriguing factor to control because of the apparently random nucleation, although pre-nucleation fluctuations visible during growth experiments may provide a clue to the important processes. Since island development is dominated by competition between strain and surface energy, modulating the surface strain has a dramatic influence on nucleation: it is well known, for example, that nucleation is enhanced at the relaxed tops of mesa structures. Here we will describe nucleation in the strain field of buried dislocations which provides an opportunity for quantitatively determining the effect of stress without any associated surface topography. Methods for patterning the dislocations will be considered. We will also describe in situ modification of the substrate surface using a focused Ga ion beam, and describe the effect of such modification on the nucleation of nanostructures.

2:00 PM AA3.2/N2.2

SELF ASSEMBLING AND ORDERING OF Ge/Si QUANTUM DOTS ON FLAT AND NANOSTRUCTURED SURFACES. Nunzio Motta, Anna Sgarlata, Adalberto Balzarotti, University of Rome "Tor Vergata", Dept of Physics and INFN, Rome, ITALY; Federico Rosei, Univ Aarhus, Inst. of Physics and Astronomy and CAMP, Aarhus, DENMARK.

We have followed the self assembling in real time of Ge islands on flat and nanostructured Si surfaces. By the use of a variable temperature STM several movies of the wetting layer formation up to the nucleation of 3D islands have been recorded. The shape of the islands is driven by the substrate symmetry, resulting in square based pyramids for Si(100), and truncated tetrahedra for Si(111). These islands evolve into multifaceted nanocrystals, which are stable on Si(100), and transform into atoll-like structures on Si(111). Consistent erosion is found in the substrate surrounding the islands, indicating the presence of a high strain field which act as a driving force for removing the atoms from the wetting layer. The way in which the substrate is eroded can be explained by the phenomenon of the surface melting due to the high pressures determined by the heteroepitaxy, as recently calculated. However, in order to explain the atoll formation, a substantial intermixing reaching the core of the island should be assumed. This intermixing has been measured by our group by the XAFS technique, and the results are in good agreement with the first principles calculation performed by the group of Kelires. The actual shape of the Si(111) surface (step bunching) influences greatly the location of the growing structures, which nucleate firstly on the steps and after on the terraces, forming ordered arrays of islands, whose spacing and dimensions are controlled by the diffusion coefficient as a function of the terrace size. Alternatively, it is possible to nucleate array of ordered dots, controlling also their dimensions, by creating artificial defects on the surface. This way is actually one of the most promising for the future applications.

2:15 PM AA3.3/N2.3

SELF ORGANIZED ARRAY OF QUANTUM NANOSTRUCTURES VIA A STRAIN INDUCED MORPHOLOGICAL INSTABILITY. David Montiel^a, Judith Müller^b, Eugenia Corvera Poiré^a.

^aDepartamento de Física y Química Teórica, Facultad de Química, UNAM. Ciudad Universitaria, México, DF, MEXICO; ^bInstitut-Lorentz, Universiteit Leiden, Leiden, THE NETHERLANDS.

We study the strain induced morphological instability at the early stages of heteroepitaxial growth on a vicinal substrate with regularly spaced steps. We perform a linear stability analysis and determine for which conditions of coverage a flat front is unstable and for which conditions it is stable. We discuss the effect of step energy and the effect of external flux. Our results give an estimation of the size and spacing of a regular array of two dimensional islands aligned along the steps. Technologically, this is crucial to understand the spontaneous formation of quantum nanostructures. We compare our results to the results that Li et al [1] obtain via an energy minimization criteria. This work was partially supported by Conacyt under grant 33920-E and FENOMECC. We thank Hong Guo for having suggested us to look into this area.

[1] Adam Li, Feng Liu, D.Y. Petrovykh, J.-L. Lin, J. Viernow, F.J. Himpsel, and M.G. Lagally, Phys. Rev. Lett. 85, 5380 (2000).

2:30 PM AA3.4/N2.4

IMPROVING THE SIZE DISTRIBUTION OF InAs QUANTUM DOTS ON (100)InP. J. Lefebvre, P.J. Poole, J. Fraser, G.C. Aers, D. Chithrani, R.L. Williams, Institute for Microstructural Sciences, National Research Council, Ottawa, CANADA.

InAs self-assembled quantum dots on (100)InP are attractive because their emission wavelength is centered around 1.5 micron, and moreover their emission intensity depends only weakly on temperature up to 300K. However, this system suffers from the broad distribution of quantum dot size, which is attributed to a smaller lattice mismatch compared with the GaAs system, and to exchange processes between group V species. InAs self-assembled quantum dots have been grown on InP nano-templates fabricated in-situ by chemical beam epitaxy. Electron microscopy on surface quantum dots and photoluminescence on buried quantum dots show a significant improvement of their uniformity. The result is due to spatial ordering of quantum dots.

3:15 PM *AA3.5/N2.5

SELF-ASSEMBLY OF NANOWIRES ON STEPPED SILICON: FROM ATOMIC CHAINS TO INTERCONNECTS. F.J. Himpsel, UW-Madison, Dept of Physics, Madison, WI.

One-dimensional objects, such as strings of atoms, organic molecules, nanodots, and nanowires can be produced on stepped silicon surfaces by self-assembly. Step decoration, strain-induced ordering, lattice match, and a match of the electronic states are among the driving forces. These structures can be used for studying electrons in one dimension, for memory arrays at the atomic limit, and as interconnects. For details see: <http://uw.physics.wisc.edu/himpsel/>

3:45 PM AA3.6/N2.6

STRUCTURAL PROPERTIES IN SELF-ORGANIZED BURIED WIRES. Tomas Roch, Anke Hesse, Julian Stangl, Günther Bauer, Johannes Kepler University, Institute for Semiconductor Physics, Linz, AUSTRIA; Karl Brunner, Technical University, Walter-Schottky Institut München, GERMANY.

Self-organized quantum wires were created during heteroepitaxial growth of SiGe/Si multilayers. The multilayers have been deposited on a (001) Si substrate with 3.5 degree miscut. The multilayer consisted of 20 periods of Si_{0.55}Ge_{0.45}/Si (2.5nm/10nm) and it was capped by 12 nm Si. From TEM investigations, a periodic wire structure along [100] with a average wire distance of 90 nm is apparent. The shape of the buried wires and their mean chemical composition were studied by x-ray scattering. The wire morphology was determined using grazing-incidence small-angle x-ray scattering (GISAXS) which is insensitive to the deformation field induced due to the mismatch of the wire lattice with respect to the Si matrix. Contrary, the wide-angle scattering (grazing-incidence diffraction, GID) is influenced mainly by this deformation field. Therefore, combining these methods with elasticity simulations and using the well-known dependence of the mismatch on the Ge content, we were able to determine non-destructively both the wire shape and their average chemical composition. Using the wire shape obtained by GISAXS, we have simulated both the deformation field of a buried wire and the reciprocal space distribution of the x-ray intensity scattered in a GID experiment. Comparing this distribution with the experimental data we determined the mean Ge content in a buried wire to (50 ± 10)%. From the GID measurements, it also follows that the mean lateral elastic relaxation of the wire structure is rather small and it does not exceed $\epsilon_{xx} \approx 7 \times 10^{-4}$. The mechanism of the wire growth determines the shape of its cross-section. In this study, we have approximated the actual shape of the wire cross-section by a triangle, with its base parallel to the wetting layer. If the wires were created only by a bunching process of the monolayer steps present at the growing vicinal surface, the angle of the longer side of the triangular wire shape would

not exceed the miscut angle. However, from the GISAXS we obtain a value of $(6 \pm 1)^\circ$. This indicates that the process of self-organization cannot be explained by step bunching alone, and another mechanism controlling the surface diffusion of the adatoms must be involved.

4:00 PM AA3.7/N2.7

SELF-ASSEMBLED LATERAL STRAINED QUANTUM WELLS IN MOVPE AlInAs ALLOYS. Andrew Norman, Sebastien Francoeur, Mark Hanna, Angelo Mascarenhas, Mowafak Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

Self-assembled strained InAs-rich lateral quantum wells have been spontaneously formed by phase separation in AlInAs alloy layers grown by metal-organic vapor-phase epitaxy at low temperatures. InAs-rich wells of the order of 10 nm wide, over a micron long, and aligned along the [110] direction have been produced. The resulting structures exhibit a large band gap reduction and strongly polarized optical transitions. We will report how the microstructure and properties of these lateral quantum wells may be altered by growth on offcut (001) InP substrates and discuss possible growth mechanisms for these spontaneously formed nanostructures.

4:15 PM AA3.8/N2.8

SPONTANEOUS PATTERN FORMATION DURING ION BOMBARDMENT WITH AND WITHOUT TEMPLATES. Alexandre Cuenat, Michael J. Aziz, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA.

We study the formation and self-organization of ripples and dots spontaneously appearing during uniform irradiation of Si with energetic ion beams. Features have been produced both with sub-keV Argon ions and with a 30 keV Ga Focused Ion Beam (FIB). Spontaneously self-organized features have been observed at temperatures as low as room temperature. It appears that the edge of the sputtered region influences the patterns formed in this process and we will report on our efforts to guide the self organization by the imposition of lateral boundary conditions on the sputter instability. Comparison with other materials and possible mechanism for the formation of the ripples will be discussed.

4:30 PM AA3.9/N2.9

REAL SPACE ANALYSIS OF COLLOIDAL EPITAXY. Jacob P. Hoogenboom^a, Anja K. van Langen-Suurling^c, Hans Romijn^c, Alfons van Blaaderen^{a,b}, ^aFOM Inst AMOLF, Amsterdam, THE NETHERLANDS; ^bUtrecht University, Physics and Chemistry of Condensed Matter, Debye Inst, Utrecht, THE NETHERLANDS; ^cTechnical University of Delft, DIMES, Delft, THE NETHERLANDS.

Using fluorescently labeled core-shell colloids and confocal microscopy structural and dynamical aspects of 3D crystallization can be studied quantitatively in real-space [1,2]. We performed various experiments using colloidal epitaxy to both grow large, well-oriented 3D-crystals and to study (epitaxial) crystallization [2]. We show that by using patterned substrates, any stacking sequence of hard-spheres can be grown, including a hexagonal close packed crystal that has a higher free energy than any other close-packed hard-sphere crystal structure. Furthermore, we studied the stability of these crystals upon lattice vector stretches in the pattern and we examined the structure and evolution of reconstructions and incommensurate crystals that grow beyond this stability range. Using optical tweezers we can locally manipulate the patterning of colloids on a substrate and study the effects of defects and small (irregular) grains in subsequent 3D crystal growth. Apart from hard-sphere systems under gravity, the effects of patterned walls on the crystallization behavior of charged, density-matched colloids were also investigated and compared to computer simulations [3]. A simple pattern of equally spaced, charged lines was found to induce (110) oriented face centered cubic crystals of charged particles. Colloidal Epitaxy provides not only a means to grow large, well-oriented 3D-crystals with characteristic spacings in the photonic range, but also allows fundamental study of epitaxial crystal growth quantitatively in 3D and in real space. [1] W.K. Kegel, A. van Blaaderen, Science **287**, 290 (2000). [2] A. van Blaaderen, R. Ruel, P. Wiltzius, Nature **385**, 321 (1997). [3] M. Heni, H. Lowen, Phys. Rev. Lett. **85**, 3668 (2000).

4:45 PM AA3.10/N2.10

TIN AND SULFURS' EFFECTS ON THE Pb ON Cu(111) SELF-ASSEMBLING SYSTEM. Richard Plass, Gary L. Kellogg, Sandia National Laboratories, Albuquerque, NM.

As a follow up to the discovery of self-assembly in the Pb on Cu(111) surface (1), we have investigated the effects which sulfur and tin have on this system. The self-assembly of this system involves surface domain patterns of a Pb and Cu surface alloy with no long range order and an incommensurate Pb overlayer reconstruction. We find that very small amounts of sulfur, a common contaminant in Cu

single crystals, significantly enhances the mobility of the surface domains. However fraction of a monolayer amounts of sulfur hinder surface mobility. In the tin case, the Cu(111)-($\sqrt{3} \times \sqrt{3}$)R30° Sn surface alloy assumes the role of the Pb / Cu random surface alloy in the self assembly process and segregates from the lead, which remains in the overlayer phase. While the presence of tin slows down the Pb overlayer domains compared to the pure Pb case, self-assembling patterns still form. I will also discuss some properties of the Cu(111)-($4\sqrt{3} \times 4\sqrt{3}$)R30° Pb Sn, Cu(100)-(5x4) Pb Sn, and Cu(100)-($\sqrt{50} \times \sqrt{50}$)R8.1° Pb Sn reconstructions we have identified. 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) R. Plass, J.A. Last, N.C. Bartelt, and G.L. Kellogg, Nature, accepted for publication.

SESSION AA4/W4: JOINT SESSION
SELF ASSEMBLY

Chairs: Masaaki Oda and Mamoru Senna
Tuesday Morning, November 27, 2001
Back Bay B (Sheraton)

8:30 AM *AA4.1/W4.1

NEW DIRECTIONS IN SOL-GEL PROCESSING: EVAPORATION-INDUCED SELF-ASSEMBLY OF POROUS AND COMPOSITE NANOSTRUCTURES. C. Jeffrey Brinker, Sandia National Laboratories and the University of New Mexico, Albuquerque, NM.

"Classical" sol-gel processing of oxides often results in highly disordered materials like aerogels characterized by a mass or surface fractal dimension. However recently, the combination of sol-gel processing with various self-assembly approaches has enabled the efficient formation of highly organized porous and composite materials in thin film and particulate forms. This talk will review recent work referred to as evaporation induced self-assembly. Starting with a homogeneous solution of inorganic and organic precursors plus amphiphilic structure directing agents like detergents, we exploit evaporation accompanying coating, spraying, or printing to promote the self-assembly of micelles that spatially separate and organize organic precursors (sequestered within the hydrophobic micellar interiors) and inorganic precursors (organized around the hydrophilic micellar exteriors). This presentation will first provide a brief overview of our evaporation-induced self-assembly (EISA) approach and its extension to the preparation of hybrid, organic-functionalized silica frameworks as well as (organic) polymer-silica nanocomposite films, particles and a variety of physically and chemically defined patterns, where we utilize such homogeneous silica/surfactant solutions as inks in rapid prototyping processes like micro-pen lithography, ink-jet printing, and selective de-wetting. Then I will discuss new work concerning the self-assembly of responsive nanocomposites. First by introduction of photosensitive molecules into the inks, we can write arbitrary patterns of photosensitive mesophases. A subsequent lithographic patterning step then can be used to photo-define different structures and functionalities within the parent pattern, establishing a simple route to hierarchically organized functional materials. Second, by using polymerizable surfactants as both structure directing agents and monomers, we can self-assemble nanostructured architectures within which we topochemically polymerize the surfactant to form a conjugated polymer (polydiacetylene)/silica nanocomposite.

9:00 AM AA4.2/W4.2

ENGINEERING OF NANOPARTICLES FOR ADVANCED ARTIFICIAL HETEROGENEOUS 2D AND 3D STRUCTURES. Mamoun Muhammed, Yu Zhang, Maria Mikhailova, Muhammet S. Toprak, German Salazar-Alvarez, Do-Kyung Kim, The Royal Institute of Technology, Dept of Materials Science and Engineering, Materials Chemistry Div, Stockholm, SWEDEN.

Nanoparticles are important building blocks in several applications of Nanotechnology. Beside, the enormous increase of their surface area, the high surface to volume ratio of the nanoparticles results in extraordinary high reactivity, and unusual physical properties (optical, magnetic, etc.). Dispersed nanoparticles are used in several important applications, e.g., catalysis, biomedical applications, etc. Nanostructured materials, prepared by consolidating nanoparticles with a very high density of grain boundary, have shown to have dramatically improved mechanical and physical properties. A recent promising development is the fabrication of systems with nanometer features using self-assembly. Nanoparticles can be used for the fabrication of high hierarchical artificial structures through self-assembly. The nanoparticles can be made of composites with controlled structure. Nanoparticles can be fabricated with different core and shell structures, e.g., metallic core and oxide shell or the reverse. The selection of the composition and structure of the shell layer allows different chemistry to be conducted at the surfaces, e.g.,

inducing biocompatibility, enhanced electrical conductivity, or reactivity. By a proper combination of the chemistry at the surface of the particles and substrate, it is possible to achieve a spontaneous self-positional organisation of the particles on the substrate to form stable 2D and 3D structures. In this talk, a presentation of some of our recent results on the fabrication and self-assembly of composite nanoparticles will be presented together with some examples of applications.

9:15 AM AA4.3/W4.3

3D PERIODIC ARRAYS OF NANOPARTICLES INSIDE MESOPOROUS SILICA FILMS. Sophie Besson, Thierry Gacoin, Jean-Pierre Boilot, LPMC, Ecole Polytechnique, Palaiseau, FRANCE; Catherine Jacquiod, Laboratoire CNRS/Saint-Gobain, Aubervilliers, FRANCE; Christian Ricolleau, LMCP, Universités Paris VI et Paris VII, FRANCE.

Periodic mesoporous materials, discovered in 1992 by Mobil Oil Corporation researchers, are synthesized via the polymerization of inorganic species around a periodic organic template, which could be surfactant micelles, copolymers. After a thermal treatment, a porous material is obtained which pores are the perfect replica of the organic species. Thanks to their porous periodic network, these materials can act as template for the synthesis of periodic 2D or 3D arrays of nanoparticles.

Recently, we have reported the synthesis of fully organized mesoporous silica films by spin-coating on glass plates.^{1,2,3} They have a 3D hexagonal structure, consisting in an interconnected spherical pore network which is oriented with the c-axis perpendicular to the film plane. These films are used as template for the synthesis of semiconductor and metal nanoparticles. Characterizations by X-ray diffraction, UV-visible spectroscopy and high resolution electron microscopy show that 300 nm thick films are totally filled with monodisperse and periodically distributed nanoparticles. The aggregates grow inside the pores without disturbing the structure, and their size (3 nm) and spatial arrangement are controlled by the silica porous matrix.

This is the first synthesis of 3D periodic arrays of nanoparticles inside mesoporous films. The use of such templates for the synthesis of periodic nanoparticulate coatings opens new application opportunities, since large scale synthesis is possible.

¹S. Besson, T. Gacoin, C. Jacquiod, C. Ricolleau, D. Babonneau, J.-P. Boilot, J. Mater. Chem. 2000, 10, 1331.

² S. Besson, C. Ricolleau, T. Gacoin, C. Jacquiod, J.-P. Boilot, J. Phys. Chem. B, 2000, 104, 51, 12095.

³ S. Besson, C. Jacquiod, T. Gacoin, A. Naudon, C. Ricolleau, J.-P. Boilot, MRS Symp. Proc. 2000, 628.

9:30 AM AA4.4/W4.4

SELF-ASSEMBLY AND GROWTH OF ORGANIC MOLECULAR NANOCRYSTALS. Edward Van Keuren, Elena Georgieva, Michael Durst, Georgetown University, Dept. of Physics, Washington, DC.

Nanoparticles of organic molecular crystals may be formed in binary solvents by changing the ratio of solvents, one in which the solubility of the solute is good, the other poor. This method is interesting both as a preparation method for nanoparticle dispersions as well as for studying aggregation and crystallization phenomena in model systems under well-controlled conditions. We report on nanocrystals of anthracene formed in an acetone/water solution. The particle growth above the critical nucleation size was characterized using dynamic light scattering and UV-VIS absorption spectroscopy. A number of points in the ternary phase diagram below the critical size were also investigated for evidence of cluster formation.

9:45 AM AA4.5/W4.5

FABRICATION OF TWO- AND THREE-DIMENSIONAL STRUCTURES OF NANOPARTICLES USING LB METHOD AND DNA HYBRIDIZATION. Takayuki Takahagi, Shujuan Huang, Gen Tsutsui, Hiroyuki Sakaue and Shoso Shingubara, Hiroshima University, Graduate School of Advanced Science and Matter, Higashi-Hiroshima, JAPAN.

Recently, self-organization of nanoparticles has been object of researchers attention as powerful method to make nanostructures. We have also carried out research to self-organization of two-dimensional array of gold nanoparticles. We successfully assembled highly regular and large area two-dimensional array of gold nanoparticles encapsulated by alkanethiol molecule films. We used fabrication methods using Langmuir-Blodgett method. And we observed Coulomb blockade phenomenon at room temperature using this array. And moreover, to assemble material regularly containing much kind of particles, specific chemical reaction is considered to be useful. As the specific chemical reaction, we mention some covalent bond reaction systems like esterification reaction. One of most specific chemical reaction is hybridization reaction between complementary DNA

sequences. Therefore, some workers tried to fabricate various nanostructures using DNA hybridization phenomenon. They demonstrated using gold nanoparticle colloid and DNA oligonucleotides capped with thiol group. DNA was confirmed to be useful for fabrication nanoparticle-structures. But they could not clearly show three-dimensional nanostructure fabrication using DNA. In the present work, we tried to fabricate three-dimensional structure of gold nanoparticles with two sizes using DNA oligonucleotides capped with thiol group. The high-resolution scanning electron microscopy observation confirmed that a three-dimensional structure in which two sizes gold nanoparticles alternately arranged was successfully assembled. The result indicates that the "DNA fabrication" is useful method for assembling the nanoparticles into the three-dimensional nanostructure we aimed. Furthermore, much more complex structure might be able to fabricate with electrical, optical functionality when the chemistry is well established to attach SAMs of DNA to the surface of nanoparticles composed of other kind of elements.

10:30 AM *AA4.6/W4.6

MAGNETIC AND MECHANICAL PROPERTIES OF SELF-ASSEMBLED METAL NANO PARTICLES IN THIN FILM MATRICES. D. Kumar and J. Sankar, Center for Advanced Materials and Smart Structures, Department of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC; J. Narayan, T.K. Nath, and Alex V. Kvit, Department of MS&E, North Carolina State University, Raleigh, NC.

Nanoscale magnetism currently provides a wealth of scientific interest and of potential applications. When the size of magnetic particles is reduced to a few tens of nanometers, they exhibit a number of outstanding physical properties such as giant magnetoresistance, superparamagnetism, large coercivities, high Curie temperature, and low saturation magnetization as compared to the corresponding bulk values. Due to realization of these outstanding physical properties upon size reduction, magnetic nanoparticles are bringing revolutionary changes in a variety of applications. In view of the technological importance of producing magnetic nanocomposites, the synthesis of magnetic systems with characteristic nanoscale dimension has attracted a lot of research attention. In this context, we have developed a novel thin film processing method based upon pulsed laser deposition to process nanocrystalline magnetic materials with accurate size and interface control. Using this method, single domain nanocrystalline Fe and Ni particles in 5-20 nm size range were embedded in amorphous (Al_2O_3) and crystalline (TiN) matrices. For example, at room temperature the coercivity of Fe- Al_2O_3 sample decreases from 100 to 50 Oe as the particle size decreases from 9 nm to 7 nm and finally the sample turns superparamagnetic when the Fe particle size becomes around 5 nm. The average volume (V) of magnetic particles, calculated from the expression: $T_B = KV/25k_B$, (T_B , K , k_B are blocking temperature, magnetic anisotropy and the Boltzmann constant, respectively), is found to be in good agreement with the particle size measured using TEM studies.

11:00 AM AA4.7/W4.7

STRUCTURAL AND MAGNETIC PROPERTIES OF SELF ASSEMBLED Co NANOPARTICLES. H.R. Khan^{a,b} and K. Petrikowski^a, ^aFEM, Materials Physics Department, Schwaebisch Gmuend, GERMANY; ^bPhysics Department, University of Tennessee, Knoxville, TN.

Arrays of magnetic nanoparticles have received considerable attention due to the interest in developing high density magnetic recording media (1,2). The magnetic properties such as such as coercivity (H_c), squareness (Mr/Ms) and magnetic energy product ($B.H$) depend on the composition, diameter, length and spacing of the nanoparticles. Cobalt nanoparticles of diameter in a wide range from 18 to 78 nm with spacing between 40 and 90 nm are electrodeposited into the self assembled pores of Al-1%Mg substrates obtained by anodic oxidation. Different electrolytes were used to obtain the various pore diameters. The anisotropic magnetic properties depend on the diameter and length of the nanoparticles as shown by the hysteresis loops. A strong perpendicular magnetic anisotropy and maximum H_c and Mr/Ms values of 1850 Oe and 0.9 are observed for the for the Co nanoparticle arrays of 18 nm diameter and 0.4 micro-meter length. The values decrease with increasing diameter. The magnetic properties of these arrays of nanoparticles in terms of the interactions between the nanoparticles and the possibility of their application as high density magnetic recording media will be discussed.

1. H.R. Khan, O. Loebich and G. Rauscher, Thin Solid Films 275 (1996)207-209.
2. H.R. Khan and K. Petrikowski, J. Magn. Mater. (In Press). This work is supported by Bundesministerium für Wirtschaft through Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. and grant no AIF 11429 N.

11:15 AM AA4.8/W4.8

MATERIALS BASED ON ORDERED THIN FILM ASSEMBLIES OF NANOPARTICLES. Nicholas A. Kotov, Oklahoma State Univ, OK.

Hybrid polyelectrolyte/nanoparticle thin films are made by the sequential adsorption of (mono)layers of oppositely charged inorganic colloids and polyelectrolytes - the technique also known as the layer-by-layer assembly (LBL). The major advantages of LBL are the nanometer scale controlled thickness of nanoparticle layers and high quality of the films combined with simplicity of the process. The LBL technique can be a convenient method of processing of a variety of aqueous dispersions of nanoparticles into functional materials. The areas of applications currently considered for LBL assemblies include photovoltaics, light-emitting diodes, high-density magnetic memory, non-linear optical switches, nanoscale interconnects, resist layer, sensors, gas separation membranes, optical filters, and others. This presentation will be focused on the effect of ordering of the nanoparticle layers on the materials performance, which will include the control over optical, magnetic, electrical, and mechanical properties of thin films achieved by combining different nanocolloids deposited in predetermined order. The universality of LBL also affords the inclusion of biological entities in nanoparticle assemblies. The effect of stratification in biomaterials prepared from layered protein/nanoparticle assemblies and molecularly engineered thin films will be discussed.

11:30 AM AA4.9/W4.9

SELF-ASSEMBLING OF NANOPARTICLES IN THE FORM OF DOUBLE LINEAR CHAINS AND SUPERLATTICES ON THEIR BASIS. Razmik Malkhasyan, Robert Karakhanyan, Mary Nazaryan, Scientific-Production Enterprise 'ATOM', Yerevan, ARMENIA; Changmo Sung, University of Massachusetts, Lowell, MA.

The self-assembling systems in nanoscale powders of crystalline MoO_3 are disclosed. Particularly, in nanoscale powders of MoO_3 , treated by vibrationally excited molecules of hydrogen (1), for the first time the double linear chain aggregates of MoO_3 nanoparticles were revealed. These chains are composed of two separate chains, which are closely disposed to each other. The transmission electron microscopic studies showed that these chain aggregates consist of arbitrary oriented crystalline MoO_3 nanoparticles with diameter of about 20nm. It is found that linear double chain aggregates form two sorts of superlattice. So the double chain aggregates form a linear superlattice (with parameter of about 1 micrometers) from straight chains with length of about 30 micrometers that are parallel to each other. The double chain aggregates of nanoparticles in these superlattices have transversal branches that in some places reach the neighboring chains. Moreover, the double linear chain aggregates form orthogonal superlattice with the following parameters: $a = 200\text{nm}$ and $b = 300\text{nm}$. Both, double linear chain aggregates and formed on their basis linear and orthogonal superlattices, are considered in present work as self-assembling systems with building blocks of crystalline nanoparticles of MoO_3 . In the first stage of self-assembling processes the spontaneous generation of double linear chain aggregates take place, which then form (again owing to self-assembling processes) linear and orthogonal superlattices. Taking into account the fact that double linear chain aggregates and superlattices of nanoparticles were obtained only in case of powders, which are treated with molecules of hydrogen we can conclude that the mentioned treatment of nanoscale powders can be a possible method of obtainment of long self-assembling chains of inorganic materials with controlled properties.

References:

1. R.T. Malkhasyan. Metastable Phase and Microstructures. Material Research Society. Symposium Proceeding, Boston, Massachusetts, USA, 1995, v. 400, p. 77.

SESSION AA5/HH5: JOINT SESSION
BIO- AND SELF-ASSEMBLED
ORGANIC-INORGANIC HYBRIDS
Tuesday Afternoon, November 27, 2001
Independence West (Sheraton)

1:30 PM *AA5.1/HH5.1

MULTIPHASE ASSEMBLY AND PROCESSING OF COMPLEX COMPOSITE MATERIALS. Michael Wong, Jennifer Cha, Larken Euliss, Scott Curtin, Eric Chapa, Timothy Deming, Dan Morse Galen Stucky, Dept of Chemistry, Materials Dept and Molecular Biology Dept, University of California, Santa Barbara, CA.

Multiphase media combined with block copolymers, block polypeptides and protein molecules provide a particularly useful synthetic approach to the direct, single system assembly and processing of composite structures with multi-scale structural and

functional properties. An added synthesis dimension can be obtained using polymer blends made with combinations such as AB BC or the essentially infinite χ parameter that can be obtained with block copolypeptide or polypeptide - non-ionic polymer linkages. Block copolypeptides and their congeners also provide a convenient route for the incorporation of chirality or cholesteric stereochemistry, and the template use of their secondary structure (beta-pleated sheets or helices) in composite assembly. The processing of block copoly-peptides or polypeptide composite based materials can be carried out with nanoscale extrusion using mesoporous arrays as templates. These combinations can be used to give a large of variety of multicomposition domain configurations. An example is the single step assembly using block copolypeptide polymers with specific binding affinities to metals, metal chalcogenides, metal oxides or organics to arrange nanoparticles of these compositions into well-defined microstructures such that nanoparticles of one composition are spatially oriented in non-aggregated and organized arrays that are completely interior or exterior to nanoparticles or a continuous film of another composition. Some general observations of the multiphase assembly of composite materials will be presented.

2:00 PM *AA5.2/HH5.2

EVOLVING BIOMOLECULAR CONTROL OF SEMI-CONDUCTORS AND MAGNETIC NANOSTRUCTURES.

Angela M. Belcher, Christne E. Flynn, Sandra Whaley, Seung-Wuk Lee, The University of Texas at Austin, The Department and Chemistry and Biochemistry, Austin, TX.

Biological systems have a unique ability to control crystal structure, phase, orientation and nanostructural regularity of inorganic materials. We are currently investigating the principles of natural biological molecular recognition in materials and developing new methods to pattern useful non-biological electronic and magnetic materials on new length scales. A peptide combinatorial approach has been employed to identify proteins that select for and specifically bind to inorganic structures such as semiconductor wafers and semiconductor and magnetic nanoparticles. This approach utilizes the inherent self-organizing, highly selective properties of biologically derived molecules. We are currently investigating peptide recognition and interaction with III-V and II-VI semiconductor materials and magnetic materials. We have selected peptides that can specifically bind to and discriminate zinc-blende III-V semiconductor surfaces. These peptides show crystal face specificity and are being used to organize nanoparticles heterostructures. We have also selected peptides that can nucleate and control particle diameter and aspect ratio of II-VI semiconductor nanoparticles. These peptides are being used to grow nanoparticles and nanowires of specific crystallographic structure and orientation. Using these molecular interactions and specific nanoparticles we are organizing organic/inorganic materials into supramolecular architectures.

2:30 PM AA5.3/HH5.3

PERIODIC POROUS ORGANOSILICAS WITH HEXAGONAL AND CUBIC SYMETRIES : FROM POWDERS TO THIN FILMS. V. Goletto, B. Alonso, F. Babonneau, Chimie de la Matière Condensée, UPMC, Paris, FRANCE; M. Impéror, P.A. Albouy, Physique des Solides, Université Paris-Sud, Orsay, FRANCE; A.R. Balkenende, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Using surfactant-mediated synthesis, a large variety of organic functions can be incorporated in silica-based nanoporous materials in order to create original materials that can find applications in fields ranging from adsorption, ion exchange, catalysis and sensing technology to nanoelectronics. The organic groups can be easily introduced during the synthesis of the templated network, either as pendant or bridging groups using two families of organoalkoxysilanes, (RSi(OEt)3) and (OEt)-2Si-R-Si(OEt)2 respectively. Various powdered samples have been synthesized introducing alkyl or aryl moieties bonded to Si using methyltriethoxysilane, bis(triethoxysilyl) ethane phenyltriethoxysilane, 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 1,3,5-tris(triethoxysilyl)benzene in the presence of cetyltrimethylammonium bromide. Their detailed structural characterization have been performed by means of XRD with synchrotron radiation, one and two-dimensional multinuclear MAS-NMR and adsorption-desorption experiments. Depending on the nature of the precursor and on the experimental conditions (pH, nature of the solvent), 2D-hexagonal (p6m) as well cubic (Pm3n) phases have been obtained, and we have tried to understand the role that the R group could play in the self-assembly process. Then the synthesis was extended to dip-coated thin films using evaporation induced self-assembly, and once again, we investigated the relationships between the film structures mainly determined by 2-dimensionnal XRD techniques, and chemical parameters.

2:45 PM AA5.4/HH5.4

STRUCTURE CONTROL AND IDENTIFICATION OF INORGANIC-ORGANIC COPOLYMER HYBRIDS. A.C. Finnefrock,

G.E.S. Toombes, S.M. Gruner, U. Wiesner, Cornell Univ, Ithaca, NY; R. Ulrich, A. Du Chesne, Max-Planck Institute for Polymer Research, Mainz, GERMANY.

An amphiphilic diblock copolymer, poly(isoprene-b-ethylene oxide) (PI-b-PEO), was used as a structure-directing agent for an inorganic aluminosilicate precursor to generate a variety of highly ordered inorganic-organic nanocomposites. The resulting order and morphology is the consequence of interactions on a hierarchy of length scales, and can be tuned by altering the proportions of the primary constituents. The chemical interaction between the inorganic (IO) component and the ethylene oxide on molecular dimensions leads to a selective swelling of the PEO phase and segregates the three constituents (PI, PEO, IO) into two physical phases (PI, PEO IO) with a length scale of tens of nanometers. This drives the formation of many interesting microstructures (spheres, cylinders, lamella, and ordered continuous structures) with dimensions up to hundreds of nanometers. The ordered continuous structures can be calcined to form mesoporous materials with potential applications in the fields of catalysis, separation technology and microelectronics. The mesoporous microstructures resemble periodic minimal surfaces; discriminating between these similar yet distinct morphologies can be a subtle task. This talk concentrates on the phase identification of the ordered continuous structures using a combination of small-angle x-ray scattering (SAXS), transmission electron microscopy (TEM), and gas adsorption measurements. A.C. Finnefrock et al., *Angewandte Chemie Int. Ed.*, 40(7):1207-1211 (2001).

3:15 PM *AA5.5/HH5.5

BIO-INSPIRED NANOCOMPOSITES: FROM SYNTHESIS

TOWARDS POTENTIAL APPLICATIONS. Tewodros Asefa, Neil Coombs, Hiltrud Grondey, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA; Mietek Jaroniec, Michal Kruk, Department of Chemistry, Kent State University, Kent, OH; Mark J. MacLachlan, Geoffrey A. Ozin, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA.

In recent years, the extraordinary properties of bio-inspired nanocomposites have stimulated great interest in the development of bottom-up synthetic approaches to organic-inorganic hybrid materials in which molecular scale control is exerted over the interface between the organic and inorganic moieties. These developments have led to advanced materials with novel properties and potential use in catalysis, sensing, separations and environmental remediation. Periodic mesoporous organosilica (PMO) materials are an entirely new class of nanocomposites with molecularly integrated organic/inorganic networks, high surface areas and pore volumes, and well ordered and uniform size pores and channels. We have recently extended the approach to include novel single and multi-functional PMO materials that incorporate chiral and heteroatom containing organic functional groups inside the inorganic framework and that may be useful in asymmetric catalysis, enantiomeric separations and heavy metal remediation.

3:45 PM AA5.6/HH5.6

PREDICTING THE MESOPHASES OF COPOLYMER/NANOPARTICLE COMPOSITES. Russell Thompson, Anna Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; Valeriy Ginzburg, The Dow Chemical Company, Midland, MI; Mark Matsen, University of Reading, Polymer Science Center, Reading, UNITED KINGDOM.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends on the characteristics of the copolymers and the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we develop a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, the theory predicts new ordered phases, where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

4:00 PM AA5.7/HH5.7

SELF-ASSEMBLY MECHANISMS INVOLVED IN THE FORMATION OF SiO₂, TiO₂, Al₂O₃, ZrO₂ AND V₂O₅ MESO-STRUCTURED HYBRID FILMS AS REVEALED BY IN-SITU SAXS ANALYSIS. David Grosso, Galo J. de A.A. Soler-Illia, Eduardo Crepaldi, Ludivine Pido, Florence Babonneau, Clément Sanchez, LCMC-UPMC, Paris, FRANCE; Pierre-Antoine Albouy, LPS, Université Paris-Sud, FRANCE; H. Amenitsch, Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Graz, AUSTRIA.

The formation of meso-structured materials, involving the polycondensation of inorganic precursors in solution combined with the structuring effect of surfactant mesophases, is a complex process that is governed by the interactions existing at different levels into such multiphases systems. However, this method has proven to be relatively robust and reproducible as long as the critical parameters can be controlled. The preparation of meso-structured thin films by liquid deposition techniques is further complicated by other parameters which are the liquid phase evaporation, the presence of film/air and film/substrate interfaces and the capillary and shearing forces existing at these interfaces. In this work, we studied the auto-assembly mechanisms taking place during dip-coating of SiO₂, TiO₂, Al₂O₃, ZrO₂ and V₂O₅ templated films exhibiting the p6m 2D-hexagonal structure. Initial solutions were composed of aqueous ethanol solvent in which was dissolved the inorganic precursors and the Brij 58 copolymer structuring agent. If needed, the pH was adjusted by adding hydrochloric acid or ammonium hydroxide. The time-resolved structural formation and evolution of the meso-organization in such thin films was followed by in-situ SAXS through synchrotron radiation. The film thickness profile associated to the advancement of the liquid phase evaporation was simultaneously observed via in-situ interferometry. The self-assembly model deduced from these experiments shows that different type of interactions force the system to evolve at different stages of the drying process, and that the presence of both film/air and film/substrate interfaces play a key role in the orientation of the organized domains.

4:15 PM AA5.8/HH5.8

IN-SITU X-RAY SCATTERING STUDIES DURING EVAPORATION INDUCED SELF-ASSEMBLY OF SILICA-SURFACTANT NANOSTRUCTURES/MESOPHASES. Dhaval A. Doshi, Nanguo Liu, Hongji Chen, Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM; Valerie Goletto, University of Paris, Paris, FRANCE; Darren Dunphy, Scott Reed, Sandia National Laboratories, Albuquerque, NM; Andrew MacPhee, Suresh Narayanan, Jin Wang, Advanced Photon Source, Argonne National Laboratories, IL; Benjamin Ocko, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; Alan Hurd, Los Alamos National Laboratory, Los Alamos, NM; Alain Gibaud, University of Maine, LeMans, FRANCE and Sandia National Laboratories, Albuquerque, NM; C. Jeffrey Brinker, Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

Structure formation via amphiphilic molecules such as lipids is ubiquitous in nature. From the cell membrane to detergent soap bubbles their uses are endless. Kresge and co-workers used surfactants to organize inorganic materials such as silica. Since then various amphiphilic molecules such as lipids, surfactants, block co-polymers have been used to self-assemble a wide spectrum of silica nanostructures. Although such materials have been extensively studied in their final form, very little is known about their formation mechanism. We have conducted in-situ x-ray scattering studies to elucidate the co-operative self-assembly process. Starting from a homogeneous solution of silica, ethanol, water, acid and surfactant solvent evaporation enriches the system in surfactant thereby fostering the self-assembly of the silica-surfactant mesophases. Following such an evaporation process in-situ with x-rays allows us to observe various stages of self-assembly from micellization to mesophase formation. Results from experiments conducted at the synchrotron facilities of Brookhaven national laboratory and Argonne national laboratories will be presented.

4:30 PM AA5.9/HH5.9

NANOFABRICATION OF INORGANIC MATERIALS USING CATIONIC LIPID-BIOPOLYMER SELF-ASSEMBLED SYSTEMS. Hongjun Liang, Thomas E. Angelini, James Ho, Paul V. Braun, Gerard C. L. Wong, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL.

It has been shown that cationic lipid-DNA complexes can self-assemble into a nanoporous lamellar structure, in which 1-D ordered DNA arrays are intercalated between planar lipid membrane sheets. The DNA spacings can be tuned from 2.5nm to 6.0nm, and essentially define an array of pores with tunable sizes. These DNA membrane complexes and other related self-assembled systems can be used as templates for the synthesis of nanostructured inorganic materials, such as quantum dots or quantum wires. Charged metal cations can be confined in the biomolecular self-assemblies described above and subsequently crosslinked. In this work, we employ cationic lipid-DNA complexes to control the formation of CdS and related compounds, by variation of parameters such as the membrane charge density, the relative DNA-lipid membrane stoichiometry, and the number of condensed metal ions. We have characterized these composite self-assembled phases of DNA, membrane lipids, and metal

cations (both before and after crosslinking) in a series of detailed Small Angle X-ray Scattering (SAXS) and optical microscopy experiments. In addition, we have developed a number of new methods that quantitatively measure the density of condensed metal ions in such complexes. Preliminary results on the morphologies of the templated phases as a function of these parameters will be presented.

4:45 PM AA5.10/HH5.10

PHOTOCHEMICAL PATTERN TRANSFER, ENHANCEMENT, AND RECOGNITION IN THIN FILM SILICA MESOPHASES. A.M. Dattelbaum, Laurel Ecke, Robert A. Provencal, Andrew P. Shreve, Atul N. Parikh, Bioscience Division, Los Alamos National Laboratory and Department of Applied Science, University of California, Davis, CA.

We have recently shown that a nominally room temperature photochemical method, simply employing ultraviolet light (187-254 nm) generated ozone environment, provides an efficient method for the removal of surfactant templates for a routine production of well-ordered, mesoporous silica thin films at low temperatures. The treatment concomitantly strengthens the silicate phase by fostering the condensation of unreacted silanols leading to mesoporous thin films with well-defined mesoscopic morphologies. Here, we show that this photochemical "calcination" process lends itself for convenient removal of surfactants in laterally defined regions at micrometer length scales and above allowing for photochemical pattern transfer. We further show that the selective functionalization of exposed regions using etching (HF), surface self-assembly (monolayer and bilayer depositions), and condensation (e.g., by water) leads to significant pattern enhancement and pattern recognition. Potential uses of patterned mesoporous thin films will also be discussed.

SESSION AA6/M5: JOINT SESSION SELF ASSEMBLY

Chairs: Peter C. Searson and J. Woods Halley
Wednesday Morning, November 28, 2001
Room 313 (Hynes)

8:45 AM *AA6.1/M5.1

METAL NANOWIRES BY ELECTRODEPOSITION. Mike Zach, Erich Walter, Reg Penner, Dept. of Chemistry, University of California, Irvine, CA; Fred Favier, CNRS Montpellier, FRANCE.

Metal nanowires with lengths up to 1.0 mm and diameters ranging from 10 nm to 500 nm have been prepared by electrodeposition. These nanowires are obtained by step edge decoration on graphite surfaces. Nanowire electrodeposition is carried out using either of two related procedures: The electrodeposition of a conductive metal oxide at step edges, and the subsequent gas phase reduction of the metal oxide in hydrogen at 500°C (molybdenum, iron, copper). Alternatively, for a few noble metals (palladium, gold), nanowires can be obtained directly by electrodeposition in one step. Electrodeposited metal nanowires may be lifted off the graphite surface by embedding in a polymer film. Topics to be discussed include the kinetics of nanowire growth, the chemical stability of nanowires in air and in aqueous ambients, the grain structure of metal nanowires, and their electrical and mechanical properties.

9:15 AM AA6.2/M5.2

ELECTROCHEMICAL SELF-ASSEMBLY OF Cu/Cu₂O NANOWIRES. S. Kenane, L. Piroux, PCPM, Laboratoire de Physico-Chimie et propriétés des Matériaux de Louvain-la-neuve, BELGIUM.

Arrays of Cu/Cu₂O nanowires were grown by electrodeposition in the nanopores of track-etched polymer membranes. Using appropriate solution, the electrode potential spontaneously oscillates during the application of a constant cathodic current. The period of these oscillations depends on the applied current density. The composition of the nanowires can be simply controlled by varying the applied current. Nanocomposite of copper and cuprous oxide is deposited at applied current over which oscillations occur. In contrast, pure Cu or pure Cu₂O are obtained at deposition current out of the range of oscillation. Preliminary electrical transport measurements were performed on these Cu/Cu₂O nanowires.

9:30 AM AA6.3/M5.3

SELF-ASSEMBLY OF Si NANOWIRES ON Pb-COVERED Si(111) SURFACES STUDIED BY SCANNING TUNNELING MICROSCOPY. Ing-Shouh Hwang, Tien-Chih Chang, and Tien T. Tsong, Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.

Our previous room temperature study of nucleation and growth of Ge

at Pb-covered surfaces indicates that there is a threshold coverage for nucleation of two-dimensional (2D) Ge islands to occur [1]. Below the threshold, Ge atoms and clusters are too mobile for STM to image. Above the threshold, there is ~ 0.1 monolayer of Ge atoms moving rapidly on the Pb-covered surface without getting incorporated into existing 2D Ge islands (covered with a Pb layer) [1,2]. Now we study Si deposition on Pb-covered Si(111) surfaces at sample temperatures from room temperature to $\sim 250^\circ\text{C}$, there is also a threshold Si coverage for the nucleation of 2D Si islands (covered with a Pb layer), and the threshold coverage decreases with the sample temperature. Below the threshold, all Si atoms form 1D nanowires on the Pb-covered surface, and the average length increases with the Si coverage and the sample temperature. Above the threshold, 2D islands are found along with the Si nanowires. We also observed the growth of 2D Si islands at the expense of nanowires after annealing at a higher temperature. This study may help us understand the mechanism at the initial stage of surfactant-mediated epitaxy. [1] I.-S. Hwang, T.-C. Chang, and T.T. Tsong, Phys. Rev. Lett. 80, 4229 (1998). [2] T.-C. Chang, I.-S. Hwang, and T.T. Tsong, Phys. Rev. Lett. 83, 1191 (1999).

9:45 AM AA6.4/M5.4

ELECTROCHEMICAL DEPOSITION OF FeCo AND FeCoV THIN FILMS AND NANOWIRE ARRAYS. Ingrid Shao, P.C. Searson, R.C. Cammarata, Johns Hopkins Univ, Dept of Materials Science and Engineering, Baltimore, MD; P.M. Vereecken, IBM T.J. Watson Center, Yorktown Heights, NY; C.L. Chien, Johns Hopkins University, Dept of Physics and Astronomy, Baltimore, MD.

ELECTROCHEMICAL DEPOSITION OF FECo AND FECoV THIN FILMS AND NANOWIRE ARRAYS Iron-cobalt alloys near the equiatomic composition have superior soft magnetic properties with the highest known saturation magnetization (24 kG), high permeability and low D.C. coercivity. In the field of micro-devices, such as hard disk drives, micro-actuators and micro-inductors, thin film deposition processes have to be developed to generate desirable magnetic materials. Electrochemical deposition is an important processing technology for microfabrication due to its low cost, high yield, low energy requirements, and capability for generating high-aspect-ratio features. However, electrochemical deposition of FeCo alloys has been problematic over the years due to high deposition stress and brittleness of FeCo alloys. We have successfully produced high quality $\text{Fe}_{50}\text{Co}_{50}$ films from an aqueous sulfamate electrolyte with a rotating disk electrode. Samples (7 mm in diameter and about 25 μm in thickness) were deposited at constant current densities between -5 and -400 mA/cm^2 . Knoop hardness, magnetic hysteresis loops, resistivity, microstructure, and composition of these films were characterized. A saturation magnetization about 21 to 22 kG and coercivity about 10 Oe was typical for these as-deposited films. Vanadium has proved to be the most effective element for improving the ductility and machinability of FeCo alloys in metallurgical processes. We successfully codeposited small amount vanadium with FeCo films to further improve the ductility of these electrodeposited films. Magnetic properties of deposited FeCoV alloys were similar to FeCo films. FeCo nanowire arrays were also deposited in nanoporous template electrochemically to study the magnetic shape anisotropy due to the geometry of these FeCo nanowires.

10:30 AM *AA6.5/M5.5

SELF-ASSEMBLY FROM SOLUTION AND UNDER ELECTROCHEMICAL CONTROL COMPARED TO MONOLAYER GROWTH BY VAPOUR PHASE DEPOSITION. Michael Rohwerder, Martin Stratmann, Max-Planck-Institut für Eisenforschung, Dept Interface Chemistry and Surface Engineering, Düsseldorf, GERMANY.

Self-Assembly From Solution And Under Electrochemical Control Compared To Monolayer Growth By Vapour Phase Deposition M. Rohwerder, M. Stratmann Max-Planck-Institut für Eisenforschung Dsseldorf, Germany The growth of monolayer films such as thiol or phosphonate self-assembled films is compared for self-assembly from solution under electrochemical control and for deposition from the vapour phase. The growth kinetics and structure formation of thiol monolayers on gold and iron depends strongly on the electrode potential, owing to the interaction of the solvent and solute molecules with the electric field at the interface. The self-assembly is slow at cathodic potentials, where large domains are formed, and is very fast at intermediate and anodic potentials, where the formed domains are quite small. The difference between film formation from solution as compared to adsorption from the gas phase is greatest in the case of thiol self-assembly on iron surfaces. While thiol molecules adsorb readily - though slowly at the necessarily cathodic potentials- on the reduced iron surface, gas phase adsorption results in a cracking of the thiol molecules at the sulphur/carbon link and well-ordered films are not formed. However, when the iron surface is pre-deposited with a monolayer of oxygen or water molecules, thiol monolayer formation occurs also from the vapour phase. This indicates the important role of one of the main differences between the two environments: the presence of the solvent molecules at the surface.

11:00 AM *AA6.6/M5.6

Cu AND Cd UPD-LAYERS ON Pt(533) STUDIED BY XPS, XAS AND XRD. Hans-Henning Strehblow, Hartmut Prinz, Institut fuer Physikalische Chemie und Elektrochemie, Heinrich-Heine-Universitaet Duesseldorf, GERMANY.

The Pt (533) surface consist of a sequence of 3 atomic rows of Pt in (111) direction followed by a (100) oriented step. Potentiodynamic polarisation curves in Cu_2 containing H_2SO_4 suggest a first decoration of the steps by Cu atoms at $E = 0.63$ V followed by the coverage of the (111) terraces at $E = 0.4$ V. The measured charges of both peaks (175 and 581 mC/cm^2) of the CV yield the expected ratio of 1:3 for the step and terrace sites. Quantitative XPS investigation of emersed Pt electrodes support these results (0.24 and 0.8 nmole/cm^2). Parallel to Cu a coadsorption of sulphate is found. According to in situ XAS studies the near range order of Cu deposits at the steps ($E = 0.55$ V) yields a coordination number 2 for the Cu-Pt ($d = 268$ pm) as well as the Cu-Cu distance ($d = 277$ pm) and a coordination 1 for the Cu-Pt distance of $d = 464$ pm. These results support a linear alignment of the Cu atoms at the edge with a coadsorption of sulphate anions in the energetically preferred angle position as supported by XPS results. The evaluation of XRD truncation rods and their comparison with the data obtained by simulation confirm these results for the long range order structure. For more negative potentials, $E = 0.3$ V, with increasing coverage the coordination number of the Cu-Pt and Cu-Cu shells is increasing to 3.2 or 5.8 respectively corresponding to the growth of 2-dimensional islands on the (111) terraces. The adsorption of Cd leads to an alignments at the steps with a coordination number 2 for the first Cd- (298 pm) and of 1 for the Pt-neighbours (303 nm) as a consequence of their larger radius with respect to the Pt-substrate.

11:30 AM *AA6.7/M5.7

CYCLIC EVOLUTION OF WATER/OH MOLECULES ON SINGLE-CRYSTAL SURFACE OF RuO_2 : ORIGIN OF ULTRA-CAPACITANCE. H. You, Y.S. Chu, T.E. Lister, W.G. Cullen, Z. Nagy, Argonne National Laboratory, Argonne, IL.

Ruthenium dioxide is a widely used electrode material for industrial applications because its special properties such as ultra- capacitance (approximately 10 times the double-layer capacitance). The origin of the ultra-capacitance, however, has not been understood because the molecular-level surface-structure studies were not available. Our synchrotron surface x-ray scattering technique combined with STM and cyclic voltammetry measurements unveils that the ultra-capacitance is a result of surface redox processes accompanying structure transformations of the surface by adsorption/desorption of the water and OH molecules. Two distinctive cyclic-voltammetry features associated with surface redox processes were observed in NaOH solution on the $\text{RuO}_2(110)$ surface and the corresponding structural models are proposed. Also features associated with surface redox processes of other crystallographic surfaces in basic and also in acidic solutions will be discussed.

SESSION AA7/K7: JOINT SESSION
COLLOIDS AND PHOTONIC CRYSTALS
Chair: Willem L. Vos
Wednesday Afternoon, November 28, 2001
Room 201 (Hynes)

1:30 PM *AA7.1/K7.1

TYPE IV SEMICONDUCTOR INVERSE OPALS. F. Meseguer, Unidad Asociada CSIC-UPV Edificio de Institutos II. Universidad Politécnica de Valencia, Valencia, SPAIN, also Instituto de Ciencia de Materiales de Madrid (CSIC) Campus de Cantoblanco, Madrid, SPAIN.

Inverse opals has proven to be an easy and cheap route in the fabrication of Photonic Crystals with an omnidirectional photonic gap along the three directions of the space. Here, we show results on the synthesis of germanium and silicon based inverse opals. To guarantee that full gap appears below the semiconductor absorption edge, large periodicity opals should be employed. In the case of silicon (germanium) we have used templates with particle size of 0.87 (1.2) microns. Through the sintering process we can vary the opal void volume. It constitutes an additional parameter to control the photonic gap. We have used Chemical Vapour Deposition method that allows a layer by layer semiconductor infiltration up to a full loading of the opal void. Therefore, one can tailor gap widths of the composites. By comparing optical data with theory we can find evidences of the opening of a full photonic gap in both inverted structures in the near infrared region, around 1.5 microns (for silicon) and 2 microns (for

germanium). The gap to mid gap value for the silicon inverse opal is 5%, and 7% for the germanium case.

2:00 PM AA7.2/K7.2

ANISOTROPIC DEFORMATION OF PHOTONIC CRYSTALS OF SPHERICAL INORGANIC COLLOIDAL PARTICLES.

Krassimir P. Velikov^a, Teun van Dillen^b, Albert Polman^b and Alfons van Blaaderen^{a,b}; ^aPhysics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS; ^bFOM Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

Spherical SiO₂, ZnS, and core-shell particles of these materials show a dramatic anisotropic plastic deformation under ion irradiation [1]. Individual particles can be turned into oblate and prolate ellipsoids with exact control over the aspect ratio. Here, we report on the fabrication and optical characterization of thin three-dimensional (3D) photonic crystals of spherical particles that were anisotropically deformed by means of ion irradiation [1]. As a result of the now collective deformation process both the unit cell symmetry and the particle form factor were changed. In this manner, the spectral position of a stopgap can be tuned. Colloidal crystals of anisotropically shaped spheres have a reduced symmetry of the Brillouin zone compare to face-cubic-centered, giving rise to a birefringence at long wavelengths, and can also be used as a template to grow inverse structures. [1] E. Snoeks, A. van Blaaderen, T. van Dillen et al., Adv. Mater. **12**, 1511 (2000).

2:15 PM AA7.3/K7.3

OPTICAL PROPERTIES OF Sn AND Pb INFILTRATED OPALS. Gugang Chen, G.U. Sumanasekera, V.H. Crespi, and Peter Eklund, Pennsylvania State University, University Park, PA.

Opals (70 nm and 300 nm) were infiltrated with Sn and Pb by the high-pressure melt injection method. The near normal incidence reflectance of polished surfaces of these photonic materials and the bulk solid was measured at 10 K and 300 K. A Kramers-Kronig (KK) analysis was carried out to determine the effective dielectric function. Shifts in the frequencies of intra- and interband absorption are observed for the infiltrated opal relative to those in the bulk metal. These shifts will be discussed in connection with theoretical model calculations on these systems. This work was supported by NSF MRSEC(PSU).

2:30 PM AA7.4/K7.4

METALLO-DIELECTRIC PHOTONIC CRYSTALS AND GLASSES OF SILVER COLLOIDAL PARTICLES. Krassimir P. Velikov^a, Gabby E. Zegers^a, Willem L. Vos^b, Alexander Moroz^a, and Alfons van Blaaderen^{a,c}; ^aPhysics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS; ^bVan der Waals-Zeeman Institute, University van Amsterdam, Amsterdam, THE NETHERLANDS; ^cFOM Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

Colloidal crystals of metallic and metallo-dielectric spheres in a dielectric host are suitable candidates to achieve tunable photonic bandgaps for optical wavelengths [1, 2]. Photonic gaps exist in many periodic structures and are robust against disorder caused by stacking faults and particle polydispersity. Here we report on the fabrication and characterization of metallo-dielectric photonic crystals and glasses of large (100 - 500 nm in radius) silver (Ag) colloidal particles. The experimental method to create Ag colloidal particles and their characterization by electron microscopy will be discussed. The optical properties on a single particle level are studied by means of light scattering and compared to Mie scattering theory. Silver particles in water tend to self-organize in a charge stabilized colloidal crystal, which displays strong Bragg reflection colors. Optical properties of colloidal crystals and glasses of Ag particles will be discussed and compared to theoretical calculations. [1] A. Moroz, Phys. Rev. Lett. **83**, 5274 (1999); Europhys. Lett. **50**, 466 (2000). [2] W.Y. Zhang, X.Y. Lei, Z.L. Wang et al., Phys. Rev. Lett. **84**, 2853 (2000).

2:45 PM AA7.5/K7.5

PHOTONIC CRYSTALS AT NEAR INFRARED AND OPTICAL WAVELENGTHS. Alexander Moroz, Physics and Chemistry of Condensed Matter, Debye Institute, Utrecht University, TA Utrecht, THE NETHERLANDS.

Photonic-band-gap properties of binary colloidal mixtures (both dielectric and metallo-dielectric) of homogeneous and core-shell spherical particles and of two-dimensional (2D) metallo-dielectric structures of (infinitely long) cylinders are discussed. Results are presented on reflection and absorption, as a function of crystal thickness, in the region of a complete photonic bandgap of 2D and three-dimensional (3D) metallo-dielectric photonic crystals. The

stability of optical properties of a photonic crystal with respect to a stacking disorder is investigated.

3:30 PM *AA7.6/K7.6

INVERSE OPAL PHOTONIC CRYSTALS MODIFY THE EMISSION AND THE PROPAGATION OF LIGHT. A. Femius Koenderink, Juan F. Galisteo, Lydia Bechger, Patrick M. Johnson, and Willem L. Vos, Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Amsterdam, THE NETHERLANDS.

Periodic dielectric composites with length scales of the order of the wavelength of light are known as *photonic crystals*. These complex systems are under intense scrutiny because of the possibility to completely control spontaneous emission and the propagation of light. Self-assembly methods such as those involving colloids, are attractive complements to nano-engineering methods that borrow techniques from the semiconductor industry. Through self-assembly, extended samples can be made in all 3 dimensions simultaneously. A particularly strongly interacting and well-ordered kind of crystal, pioneered in our lab, are inverse opals. These consist of ordered arrays of macropores, or air spheres, contained in a backbone of a material with a high refractive index. We discuss methods to improve crystal quality, and novel x-ray probes [1] to confirm the excellent long-range order of the crystals [2]. Photonic crystals are developed from semiconductors with high refractive indices in the range where band gaps are anticipated [3] and doped with light sources. Optical experiments are performed to study emission and the propagation of light in the crystals. We discuss the modification of spontaneous emission due to the (local) density of states and multiple Bragg diffraction. Multiple Bragg diffraction appears to be essential to understand the formation of band gaps [4]. [1] D.O. Riese, G.H. Wegdam, W.L. Vos, R. Sprik, D. Fenistein, J.H.H. Bongaerts, and G. Grübel, Phys. Rev. Lett. **85** 5460 (2000). [2] M. Megens and W.L. Vos, Phys. Rev. Lett. **86** 4855 (2001). [3] With the groups of J.J. Kelly (Utrecht) and W.E. Buhro (St. Louis). [4] H.P. Schriemer, H.M. van Driel, A.F. Koenderink, and W.L. Vos, Phys. Rev. A **63** (2001) no. 011801 (Rapid Comm.).

4:00 PM AA7.7/K7.7

TUNABLE OPTICAL PROPERTIES OF LARGE GOLD NANOPARTICLE ARRAYS. Beomseok Kim, Steven L. Tripp, Alexander Wei, Purdue University, Department of Chemistry, West Lafayette, IN.

The self-organization of large (16-170 nm) gold nanoparticles into 2D arrays is described. Transmission electron microscopy indicates a trend toward decreasing interparticle spacings with increasing unit particle diameters. The nanostructured arrays exhibit periodicity-dependent plasmon resonances and surface-enhanced Raman scattering (SERS), the latter with empirical signal enhancement factors ranging from 10⁴ to over 10⁷. These enhancements are reproducible and correlate strongly with periodic structure and excitation frequency. The arrays are sufficiently robust to support cell growth and attachment, and are being investigated as chemical and biomolecular sensors.

4:15 PM AA7.8/K7.8

AMPLIFICATION OF SPONTANEOUS EMISSION IN INCOMPLETE OPALINE PHOTONIC CRYSTALS. S.G. Romanov, D.N. Chigrin, C.M. Sotomayor Torres, Institute of Materials Science and Dept. of Electrical and Information Engineering, University of Wuppertal, Wuppertal, GERMANY; N. Gaponik, A. Rogach, A. Eychmüller, Institute of Physical Chemistry, University of Hamburg, Hamburg, GERMANY.

The manipulation of the spontaneous emission (SE) is among the most exciting prospects of photonic crystals (PhCs). While no omnidirectional 3D PhCs have been demonstrated in the visible, studies of emission in incomplete photonic bandgap materials, e.g. opals, provide novel information about light-matter interaction. The angular resolved photoluminescence (PL) of CdTe nanoparticles embedded in thin latex opaline films have been studied. Relative spectra obtained by comparison of PL spectra from the PhC and the similar unstructured sample demonstrate the stop-band in emission. Alternatively, ratio spectra obtained by comparison of PL spectra at different levels of excitation power reveal changes of the emission rate. Both relative and ratio PL spectra show spectral features centered at the Bragg resonance. The minimum in the ratio spectrum, which can be interpreted as a decrease of the emission rate, was observed at low gain. In the case of a higher gain, the minimum in the ratio spectrum is replaced with the maximum, moreover, its magnitude is increased with the gain thus demonstrating the SE amplification. Photons with frequencies in the stop-band can either leave the crystal or come back to the emitter, i.e. the emission intensity acquires an angular pattern. SE in localized modes is prohibited. The number of localized modes is constant for a given sample and, subsequently, the depth of the ratio spectrum minimum is gain-insensitive. In contrast, detailed calculations of 3D vector diagrams reveal in the stop-band a certain

density of slow propagating eigenmodes, which appear due to the super-prism effect. Their group velocity is about 5 times lower as compared with modes propagating in allowed directions. SE coupled to slow modes can be enhanced when PhC has a sufficient gain. This competition of localization and enhancement of SE was detected by the analysis of ratio spectra. This effect opens the possibility of lasing on eigenmodes of an incomplete PhC.

4:30 PM AA7.9/K7.9

GERMANIUM NANOCRYSTALS IN SILICA FORMED BY HYDROGEN REDUCTION OF SILICON-GERMANIUM MIXED-OXIDES: PROCESS MODELING AND OPTICAL PROPERTIES. Gianni Taraschi, Wendy W. Fan, Eugene A. Fitzgerald, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Ge nanocrystals in a silica matrix show potential for the fabrication of high index contrast, non-linear, integrated optical devices. Ge nanocrystals in a SiO₂ matrix were synthesized using H₂ reduction of Si_{1-x}Ge_xO₂ at temperatures between 700°C and 800°C. Experiments were conducted for both Si_{1-x}Ge_xO₂ on Si_{1-x}Ge_x, and Si_{1-x}Ge_xO₂ on SiO₂ to explore the kinetics of the reduction process. Under specific annealing conditions, in particular for a temperature of 800°C and using a 6% H₂/ 94% N₂ annealing atmosphere, the reduction experiments for the Si_{1-x}Ge_xO₂ on Si_{1-x}Ge_x samples showed that Ge can be highly mobile. Under such conditions, all the Ge formed diamond-shaped oriented crystals at the Si_{1-x}Ge_x interface, with no Ge nanocrystals in the oxide, implying a solid state growth process akin to vapor phase growth on crystal surfaces. Similar experiments at 700°C, reveal a significantly slower Ge mobility, leading to the formation of Ge nanocrystals throughout the oxide. The mobility of the Ge is possibly due to the diffusivity of GeO gas, as opposed to the motion of elemental Ge in oxide, which is expected to be very slow, and hence cannot account for the 800°C data. A model incorporating both the thermodynamics of the reduction reaction, and the diffusion of reactants and products was developed to explain the data. Diffusion of water vapor from the reduction is an important rate limiting step incorporated in the model. Based on calculations, an optimized annealing sequence was designed to improve the size uniformity of the Ge nanocrystals, and hence reduce the inhomogeneous broadening of the optical spectra. Slab waveguides consisting of Ge dots in the core region were fabricated to measure optical transmission properties and explore potential integrated optics applications.

SESSION AA8/V10: JOINT POSTER SESSION
SELF ASSEMBLY OF NANOPHASE AND
NANOCOMPOSITE MATERIALS
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

AA8.1/V10.1

NANOSIZED PARTICLES AS BUILDING BLOCKS FOR NOVEL POWDERS. Heinrich Hofmann, Nathalie Jongen, Marcel Donnet, Jaques Lemaitre, Paul Bowen Material Science Department, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND.

Nanostructured materials can be manufactured using very different methods, for examples crystallisation of amorphous metals, severe plastic deformation, self-assembling of supramolecules with or without templates or using nanosized particles. Regarding nanoparticles, beside classical processing routes like ceramic powder processing or coating with suspension, in the last few years an increasing interest regarding the assembling of nanoparticles could be observed. Applications like nanolithography, medical devices, devices for diagnostic etc. needs a very well controlled array of monosized particles with a well controlled shape in one, two as well as in three dimensions. In this presentation, some fundamental aspects regarding the required properties of the particles, the synthesis of such nanoparticles and the important forces and mechanisms dealing with the formation of arrays by self-assembling of nanosized particles will be discussed. If the crystallite size and shape of nanosized particles is very homogeneous, the agglomeration of these crystallites to dense particles with a controlled shape is possible. Our investigations show that with surface modification of the crystallites using organic molecules precipitated nanocrystallites can be agglomerated to spherical, cubic or rod like particles. In this paper, a thermodynamic approach which will explain the mechanisms of particle formation by controlled self-organising of nanocrystallites will be developed. Beside surface energy and interactions of hydrophilic/hydrophobic nature, depletion forces combined with other entropic effects will be taken in consideration. With this example of molecular to micron scale control one can envisage the next step being microstructure control using the micron sized particles as the next building block ending with a well

defined and organised macrostructure from the molecular level. Finally some interesting (potential) applications will be shown.

AA8.2/V10.2

SILVER-POLYIMIDE NANOCOMPOSITE FILMS GIVING SELF-ASSEMBLED HIGHLY REFLECTIVE SILVERED SURFACES. Robin E. Southward, Structures and Materials Competency, Langley Research Center, National Aeronautics and Space Administration, Hampton, VA; D.W. Thompson, C.J. Dean, J.L. Scott, S.T. Broadwater, Dept. of Chemistry, College of William and Mary, Williamsburg, VA.

Highly reflective and/or surface conductive flexible polyimide films have been prepared by the incorporation of soluble silver(I) complexes with the 1,1,1-trifluoro-2,4-pentanedionate and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ligands into dimethylacetamide, diglyme, and dimethylformamide solutions of the poly(amic acid)s and polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride/1,3-bis(aminophenoxy)-benzene, (6FDA/1,3(3)-APB), and 6FDA/2,2-bis[4-(4-aminophenoxy)hexafluoropropane, 6FDA/4-BDAF. Thermal curing of silver(I)-poly(amic acid) films ca. 20 mil in thickness leads to cycloimidization with concomitant silver(I) reduction yielding a reflective and conductive surface-silvered film for silver concentration from 2-13 weight percent. The films are cured to a final temperature of 300 C for several hours. The metallized 6FDA-based films retain the essential mechanical properties of undoped films and have good thermal stability particularly in nitrogen atmospheres. The bulk of the polymer contains nanometer-sized silver particles and is not electrically conducting. Transmission electron microscopy establish that films have surface layers of silver from ca. 20-200 nm in thickness. In general, films prepared with the silver(I)-1,1,1,5,5,5-hexafluoro-2,4-pentanedionate complex are reflective but not conductive, where as films prepared with the silver(I)-1,1,1-trifluoro-2,4-pentanedionate complex are both reflective and electrically conductive, particularly for silver concentration above 10 weight percent. Films prepared from the soluble fully imidized form of the 6FDA-based polymers rather than from the amic acid were in general less reflective and less regular in surface morphology than those prepared from the poly(amic acid). The metallized films were characterized with respect to conductivity, reflectivity, surface morphology, thermal, chemical, and mechanical properties.

AA8.3/V10.3

ANTI-STOKES LUMINESCENCE OF DYE-DOPED MESOSTRUCTURED SILICA THIN FILMS. Michael H. Bartl, Brian J. Scott, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA; Gernot Wirmsberger, Alois Popitsch, Karl-Franzens-Univ of Graz, Dept of Chemistry, Graz, AUSTRIA; Galen D. Stucky, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

Recently, materials showing efficient anti-Stokes luminescence are attracting interest with respect to possible applications such as laser cooling and temperature sensors. Here we report on very efficient anti-Stokes luminescence of the xanthene laser dye Rhodamine 101 incorporated into 2-d hexagonally ordered mesostructured silica thin films prepared by a combination of weakly acidic sol-gel chemistry and block-copolymer templating. Owing to their nanoscopic organic/inorganic phase separation as-synthesized mesostructured compounds are excellent solid host for organic dyes. While the inorganic silica phase gives a rigid porous framework comparable to sol-gel glasses the organic surfactant phase provides an ideal environment for organic dye molecules resulting in high quantum efficiencies comparable to that in liquid solutions. By excitation of the Rhodamine 101 dye doped mesostructured films with the 632.8 nm line of a He-Ne laser several unusual observations associated with the dye luminescence were made. Both the energy position of the emission intensity maximum and the average energy of the emitted photons are higher than the energy of the exciting photons. By varying the intensity of the laser output we found a linear dependence of the sample emission intensity on the power of excitation. This observation is attributed to an up-conversion process involving direct single-photon hot band absorption. Although the mesostructured films were doped with rather high amounts of Rhodamine 101 (ranging from 0.05 to 1.0 wt%) quantum efficiencies as high as 0.84 were obtained.

AA8.4/V10.4

STRUCTURAL INVESTIGATIONS OF SELF-ASSEMBLED NANOPOROUS ALUMINA. Guangwen Zhou, Judith C. Yang, Dept of Materials Science & Engineering; Hong Koo Kim, Dept of Electrical Engineering, Univ of Pittsburgh, Pittsburgh, PA.

Anodic porous alumina is known to be a typical self-ordered nanochannel material. The density difference and volume expansion at the metal/oxide interface leads to compressive stress in the oxide layer, and this usually results in formation of a densely packed pore

array of hexagonal symmetry. Highly regular arrangement of pores, however, occurs only for a small process window, and the domain size is usually limited to a micrometer scale. Recently we have fabricated nanoscale pore arrays on aluminum substrates using an anodic process. Within domains, hexagonal pore arrangements with the same orientation of the pore lattice are observed. We have examined the structure of the nanoporous alumina by SEM as well as by planar and cross-sectional TEM, and will present the results of our structural investigations.

AA8.5/V10.5

LOW TEMPERATURE HYDROTHERMAL SYNTHESIS OF NANOCRYSTALLINE CERIA-BASED SOLID SOLUTIONS WITH IRON DOPANTS. Guangshe Li, R.L. Smith Jr., H. Inomata, Tohoku Univ, Sendai, JAPAN.

Ceria-based solid solutions have several important applications such as fuel cells and sensors. The design of new electrolytes depends primarily on an understanding of conductivity for the dopants with a wider ionic size range. However, it is failed to prepare ceria-based solid solutions with a much smaller iron dopant by solid state reactions. This work reports on the crystallization of ceria-based solid solutions with iron dopants. It is found that under low temperature hydrothermal conditions, single phase fluorite ceria-based solid solutions containing trivalent iron ions could be obtained within the nano-meter scale in a compositional range of 0.00 to 0.20. These nanocrystals showed superparamagnetic behavior. The extremely low concentration of oxygen vacancies for these solid solutions was explained in terms of a structural model of substitutional and interstitial dopings.

AA8.6/V10.6

INVESTIGATING CATALYTIC PROPERTIES OF COMPOSITE NANOPARTICLE ASSEMBLIES. Mathew M. Maye, Yongbing Lou, Jin Luo, Laura Moussa, Wei-Ben Chan, Chuan-Jian Zhong, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Composite nanoparticles such gold and alloy particles in the nanometer-sized range are explored as candidates for highly effective catalysts. The nanoparticles are assembled as interfacial thin films. A key challenge is the effective isolation of the nanosized properties while retaining the nanoscale catalytic properties. Core-shell nanoparticles provide an intriguing pathway because the encapsulating structure enables tailoring of core size and enhancement of stability of nanosized catalysts against aggregation propensity. This presentation reports the results of an investigation of the catalytic activation of the nanoparticle assemblies towards CO and methanol oxidation using a number of techniques including electrochemical, electrochemical quartz crystal nanobalance, scanning probe microscopy and infrared reflection spectroscopy. It is demonstrated that the catalytic activity depends on a number of factors including core size, shape, composition, interfacial mass transport and potential-induced oxidation-reduction of surface oxygenated species. The findings will be discussed along with the core-shell tailoring strategies of the nanosized catalytic properties.

AA8.7/V10.7

SURFACTANT TEMPLATED HIGH QUALITY HEXAGONAL MESOSTRUCTURED CHALCOGENIDE SEMICONDUCTORS. P.N. Trikalitis, K.K. Rangan, M.G. Kanatzidis, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Ordered nano-materials with intimately mixed organic and inorganic components are a special class of nanocomposites that are expected to display novel electronic properties. We are particularly interested in metal chalcogenide porous frameworks with enhanced transport and optical properties. The organic part is typically surfactant molecules with special head groups and may play a role in the properties of these materials beyond merely serving as templating agents. The framework pores of these materials are ordered in the mesoscale regime with sizes of 20-50 Å. We will present our efforts in this area and our synthetic strategy to generate broad classes of these materials. We will also describe several semiconducting solids with hexagonal pore arrangement formed by linking adamantane clusters $[\text{Ge}_4\text{Q}_{10}]^{4-}$ (Q=S, Se) and $[\text{Sn}_4\text{Se}_{10}]^{4-}$ as well as simpler $[\text{SnSe}_4]^{4-}$ and $[\text{Sn}_2\text{Se}_6]^{4-}$ anions with square planar Pd^{2+} and Pt^{2+} ions in the presence of alkylpyridinium surfactant molecules, $\text{C}_n\text{PyBr}\cdot x\text{H}_2\text{O}$ (n=12, 14, 16, 18). The use of these ions as the linkage metal has a huge influence of the self-assembly reaction, and gives rise to highly ordered hexagonal mesostructures based on $[\text{Ge}_4\text{Q}_{10}]^{4-}$ (Q=S,Se) and $[\text{SnSe}_4]^{4-}$. The degree of hexagonal order in these materials rivals or exceeds that of the highest quality MCM-41.

AA8.8/V10.8

CYCLIC MICROHARDNESS BEHAVIOR OBSERVED IN CRYOMILLED NANOCRYSTALLINE Zn. Xinghang Zhang, Haiyan Wang, Jagdish Narayan, Carl C. Koch, North Carolina State University, Dept of Materials Science and Engineering, Raleigh, NC; Magdy Kassem, Suez Canal University, Dept of Materials and Metallurgical Engineering, Suez, EGYPT.

Nanocrystalline Zn has been prepared by a cryomilling technique. Large numbers of small grains (2~6nm) have been found in the very early stages of cryomilling as revealed by transmission electron microscopy (TEM) along with larger grains up to several hundred nanometers. Dynamic recrystallization was used to explain the observed phenomena. Microhardness of cryomilled Zn exhibits cyclic behavior with milling time. The microhardness changes are very reproducible and large changes in microhardness of factors of two are observed. Detailed TEM and HRTEM are carried out for samples milled at critical times with regard to the cyclic hardness. Evidence from XRD and DSC measurements is also used to explain these results. Possible explanations include differences in grain size distribution, dislocation densities within the grains, and activation of non-basal plane slip.

AA8.9/V10.9

STUDIES OF INTERSUBBAND TRANSITIONS IN ARRAYS OF BISMUTH NANOWIRE SAMPLES USING OPTICAL TRANSMISSION. M.R. Black^a, S.B. Cronin^b, Y.M. Lin^a, M. Padi^b, M.S. Dresselhaus^{a,b}, ^aMIT, Department of Electrical Engineering and Computer Science, Cambridge, MA; ^bMIT, Department of Physics, Cambridge, MA.

When a porous anodic alumina template is filled with bismuth, the bismuth forms a self-assembled array of aligned single crystalline bismuth nanowires, which exhibit unusual optical properties. If the diameter of the wires is small enough, for example 49(17)nm at 77K(293K), the bismuth nanowires are quantum confined in two dimensions and hence are one-dimensional conductors. The quantum confinement in the nanowires causes subbands in the electronic band structure to form. Electronic transitions between these subbands give rise to optical absorption features. Using Fourier transform infrared absorption, in an energy range where intersubband transitions are predicted (0.05 to 0.5 eV), intersubband transitions in arrays of bismuth nanowires have been measured. The experimental results are compared to theoretical simulations. The energy of the intersubband transitions as a function of wire diameter and n-type carrier doping are reported.

AA8.10/V10.10

CONTROLLING NANOSCALE ORDERING IN METAL OXIDE THIN FILMS TEMPLATED BY AMPHIPHILIC BLOCK COPOLYMERS. Ryan C. Hayward¹, Peter Alberius-Henning², Karen L. Frindell², Galen D. Stucky², Bradley F. Chmelka¹, Edward J. Kramer^{1,3}, ¹Department of Chemical Engineering, ²Chemistry Department, ³Materials Department, University of California, Santa Barbara, CA.

Templating with amphiphilic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers is a convenient route for the production of metal oxide films with regular nanostructural ordering. These films are promising for applications ranging from optical, electronic and photovoltaic devices, to membranes and sensors. To realize such applications it is important to exercise control over the phase structure adopted by the self-assembled organic/inorganic composite materials. Past studies have frequently focused on the production of one particular phase with a given polymer, despite the rich phase behavior exhibited by these polymeric species in aqueous systems. We will discuss how to exercise rational control over nanoscale morphology in thin films by mapping onto the polymer-water binary phase diagram. By systematically varying the polymer content in the composite films, materials with well ordered lamellar, 2D hexagonal, and cubic morphologies have been prepared using the same organic structure-directing agent. One- and two-dimensional small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) have been used to characterize the nanoscale morphology, domain size, and orientational ordering within the thin films. We focus on the characterization of composite silica/block copolymer films and demonstrate the apparent generality of the method for titania/block copolymer films as well.

AA8.11/V10.11

SYNTHESIS AND CHARACTERIZATION OF GRAPHITE NANOFIBERS FROM THE DECOMPOSITION OF CO/H₂ USING POWERED FeCu CATALYSTS. O. Carneiro, Northeastern University, Dept of Chemistry, Boston, MA; P.E. Anderson, Catalytic Materials Ltd, Holliston, MA; M.S. Kim, Myong Ji, University, Dept of Chemical Engineering, Seoul, KOREA; R.T.K. Baker, Catalytic

Materials Ltd, Holliston, MA; N.M. Rodriguez, Catalytic Materials Ltd, Holliston, MA.

The formation of graphite nanofibers from the catalytic decomposition of carbon containing gases interacting with small metal particles continues to generate immense interest in the research community. The unique structure and chemical properties of these novel carbon materials are now at the forefront of aggressive research for potential electrochemical applications and as catalyst supports. In the present investigation the properties of graphite nanofibers formed from the decomposition of CO/H₂ interacting with powered FeCu catalysts in the temperature range of 550 to 650°C were studied. The surface area of the graphite nanofibers was determined using the BET equation and detailed characteristics of the graphite nanofibers are being investigated by a combination of High-Resolution Transmission Electron Microscopy (HR-TEM), Temperature Programmed Oxidation (TPO) and X-ray diffraction. It has been found that the composition of the catalyst, the reaction temperature and the CO/H₂ reactant gas ratio have a direct impact on the yield of the solid carbon formed, as well as the structural characteristics exhibited by the nanofibers.

AA8.12/V10.12

THE ROLE OF THE INTERFACES IN THE OPTICAL EFFECTS OF LARGE-SIZED SiC_xO_{1-x}N NANOCRYSTALLITES.
K.J. Plucinski, Mil. Univ. of Technology, Dept of Electronics, Warsaw, POLAND, H. Kaddouri, Université du Perpignan, Lab. LP2A, Perpignan, FRANCE, I.V. Kityk, Institute of Physics, WSP Czistochowa, POLAND.

The main goal of the present work was to study the transparency of large-sized (10-25) nm nanocrystallites (NC) of SiC_xO_{1-x}N (0.96 < x < 1.06), both experimentally, as well as theoretically. The band energy structure was investigated using different band energy approaches, as well as modified Car Parinello molecular dynamics simulations of interfaces. In particular, we investigated the influence of nanocrystallite size and carbon excess on the optical absorption of the SiC_xO_{1-x}N nanocrystallites, the contribution of the reconstructed near-interface states to the visible absorption of the NC and the contribution of the carbon sheet interfaces to the absorption spectra observed. Among the many possible NC materials, SiC_xO_{1-x}N crystallites were chosen because the technology for their manufacture with the sizes needed is well developed, the energy gap of SiC_xO_{1-x}N may be manipulated within the large spectral ranges (2 - 4.5 eV), depending on polytype kinds, and because SiC_xO_{1-x}N is substantially more stable than other SiON materials, when external mechanical and thermo-treatments are applied. A thin carbon sheet (of about 1 nm) appears, covering the crystallites. This sheet leads to substantial reconstruction of the near-the-interface SiC_xO_{1-x}N crystalline layers. Electron microscopy, NMR, X-ray diffraction, IR absorption and Raman data were applied in order to gain a full understanding of the structural properties and the optical absorption spectra of both the carbon sheets and the reconstructed SiC_xO_{1-x}N close to the particle surfaces. Numerical modeling shows that these NC may be treated as quantum dot-like SiC_xO_{1-x}N reconstructed crystalline surfaces, covering SiC_xO_{1-x}N crystallites. All band energy calculation approaches (semi-empirical pseudopotential, fully augmented plane waves and norm-conserving self-consistent pseudopotential approaches) predicted the experimental spectroscopic data obtained. In particular, it was shown that the near-the-surface carbon sheet plays a dominant role in the behavior of the reconstructed band energy structure. Independent evidence for the important role of the dot-like crystalline layers are the excitonic-like states, which are not dependent on the particular structure of the SiC_xO_{1-x}N, but are sensitive to the thickness of the carbon layer.

AA8.13/V10.13

REVERSIBLE CHARGING EFFECTS ON OPTICAL PROPERTIES OF POROUS SILICON. Vivechana Agarwal, J.E. Lugo and J.A. del Rio, UNAM, Temixco, MEXICO.

An effective medium approximation predicted that the effect of introducing charge is to decrease the dielectric response of the material. In this work porous silicon samples have been charged and depending on the current intensity, the PLE response can be tuned in the energy range 1.5-2.6 eV. A decrease in the emission intensity with an increase in charging current has been observed. This effect is reversible and the recovery time is found to be in the range of 4-6 min. The variation of charging effect with thickness of porous silicon layer has also been studied. An increase in the lowering of the intensity with an increase in thickness has been observed.

AA8.14/V10.14

FLAME SYNTHESIS OF Fe CATALYZED SINGLE-WALLED CARBON NANOTUBES AND Ni CATALYZED NANOFIBERS: GROWTH MECHANISMS AND CONSEQUENCES.

Randy L. Vander Wal, Lee J. Hall, Gordon Berger, The National

Center for Microgravity Research, The NASA-Glenn Research Center, Cleveland, OH.

Flame synthesis of single-walled carbon nanotubes catalyzed by Fe and nanofibers catalyzed by Ni is demonstrated using a pyrolysis flame configuration. Fe reacts preferentially with CO/H₂/He mixtures to produce SWNTs. In contrast, Ni reacts preferentially with C₂H₂/H₂/He mixtures to yield nanofibers. Both catalyst metals exhibit a high level of size dependent reactivity towards these reactant gas mixtures. A 'yarmaluke mechanism' [Dai et al.] and a carbon solvation/diffusion/precipitation [Baker et al.] account for the different catalyzed products; SWNTs and nanofibers. The consequences of these mechanisms are discussed for a) catalyst particle size evolution, b) catalyst particle deactivation/inertness and c) SWNT and nanofiber structure and morphology.

AA8.15/V10.15

DENDRIMER NANOCOMPOSITES: SYNTHESIS, PROPERTIES AND APPLICATIONS. Lajos Balogh, Dept. of Medicine, Univ of Michigan, MI.

Dendrimer nanocomposites (DNC) are recently developed nanosized inorganic/organic hybrid materials (Chemical Innovation, March 2000, pp. 19-26) displaying unique physical and chemical properties. The primary goal of this presentation is to present the synthesis concept and the unique potential of these nanocomposites and engineered DNC nanostructures to make photonic and other materials. DNCs are synthesized as atomic/molecular level mixtures of organic and inorganic atoms as constituents with no covalent bonds between the components. They can be made in a controlled composition, in a predetermined and uniform size, with adjustable surface functionalities and in various morphologies. Both macromolecular and materials properties are present on this nanoscopic scale, which results in many interesting and unique features. A great variety of these nanocomposites can be built. The uniform DNC building blocks can be further organized into ordered structures, such as 0-D (quantum dots), 1-D (chains), 2-D (ultrathin multilayers) and 3-D nanostructures. These nanomaterials and nanostructures offer numerous application opportunities for photonic materials, optics, electronics, sensors, catalysis, environmental cleanup, bioengineering and medicine just to list a few.

SESSION AA9/Y8: JOINT SESSION
NANOPATTERNING OF ASSEMBLED SYSTEMS
Chairs: Marie Angelopoulos and Elizabeth A. Dobisz
Thursday Morning, November 29, 2001
Back Bay D (Sheraton)

8:45 AM *AA9.1/Y8.1

DIFFUSION OF ALKANETHIOLS IN NANOPATTERNING.
P.E. Sheehan, L.J. Whitman, Naval Research Laboratory, Washington, DC.

The patterning of alkanethiols has become a cornerstone in the burgeoning field of nanotechnology. Several patterning techniques have been developed, the more popular of which include stamping using polymeric masters, known as microcontact printing (mCP) and, more recently, the direct writing of the thiols using an AFM tip, known as Dip Pen Nanolithography (DPN). Importantly, in both techniques, diffusion of the thiol away from the contact area fundamentally limits the spatial resolution obtained. Obtaining the highest resolution possible from these techniques will require a full understanding of the rate and nature of thiol diffusion. To address this need, the radii of octadecanethiol spots deposited via DPN were studied as a function of tip-surface contact time and relative humidity. The increase in spot size with time was well described by two-dimensional radial diffusion from a constant source of finite radius. Fits using this formula revealed a diffusion constant of approximately 250 nm²/s with little dependence on humidity. Analysis of published images showing the spread of hexadecanethiol on gold after microcontact printing leads to comparable diffusion constants. Significantly, these values are four orders of magnitude smaller than that expected for diffusion through a bulk fluid such as water. Finally, the role of the water meniscus in DPN will be discussed.

9:15 AM AA9.2/Y8.2

DIRECTED ASSEMBLY OF ONE-DIMENSIONAL NANO-STRUCTURES INTO INTEGRATED DEVICE ARRAYS. Yu Huang, Charles M. Lieber, Harvard Univ, Dept of Chemistry, Cambridge, MA.

There have been increasing interest in using one-dimensional nanostructures as building blocks for bottom-up assembly of nanoscale electronics because they may serve both as wiring and critical device elements in future device architecture. A number of electronic and optoelectronic devices have been demonstrated using

nanotubes or nanowires as the building blocks so far. The major challenge has been how to organize these one-dimensional nanostructures into integrated device arrays. Here we present a rational approach based on fluidics for the hierarchical assembly of one-dimensional nanostructures into well-defined functional networks. We show that nanowires can be assembled into parallel arrays with control of the average separation, and by combining fluidic alignment with surface patterning techniques that it is also possible to control periodicity. In addition, complex crossed nanowire arrays can be prepared using layer-by-layer assembly with different flow directions for sequential steps. Transport studies show that the crossed nanowire arrays form electrically conducting networks, with individually addressable device function at each cross point. Lastly we will show that these parallel and orthogonal nanowire arrays can be used to construct integrated logic and memory device arrays.

9:30 AM AA9.3/Y8.3

SELF-ASSEMBLY PATTERNING OF COBALT DISILICIDE-NANOSTRUCTURES USING LOCAL STRESS EFFECTS. P. Kluth, Q.-T. Zhao, S. Winnerl, S. Lenk and S. Mantl, Forschungszentrum Jülich, Institut für Schichten und Grenzflächen (ISG-IT), Jülich, GERMANY.

We show a new self-assembly patterning method for generating epitaxial cobalt disilicide-nanostructures with dimensions down to 30 nm. This technique is based on anisotropic diffusion of Co/Si-atoms in a strain field during rapid thermal processing. The strain field is generated along the edges of a mask consisting of 20 nm SiO₂ and approximately 300 nm Si₃N₄. This mask, which is similar to that of the well known LOCOS process, is patterned with conventional optical lithography and dry etching. Single-crystalline CoSi₂-layers grown by molecular beam allotaxy (MBA) on Si(100) or ultra-thin silicon on insulator (SOI) substrates were patterned using this technique. During rapid thermal oxidation (RTO) of the masked silicide structure, a well defined separation of the silicide layer forms along the edge of the mask. These highly uniform gaps are as narrow as 40 nm. Combining this process with selective underetching of the SiO₂ underneath the mask and/or silicide/silicon etching delivers highly uniform CoSi₂ nanowires with diameters down to 50 nm. In addition, two parallel nanowires with a distance of 30 nm were achieved. Overlapping stress fields of two mask edges were used to generate 80 nm wires. The same masking technique was used to create nanogaps during the silicidation reaction forming epitaxial CoSi₂ in a titanium oxide mediated epitaxy process. Here, the mask was deposited on a Co/Ti/SiO₂/Si-structure. Subsequent rapid thermal annealing in forming gas (90% N₂, 10% H₂) leads to the formation of epitaxial CoSi₂ with a gap of approximately 100 nm along the edge of the mask. Simulations to estimate the stress profile generated by the nitride/oxide mask using an ATHENA process simulation tool were performed and are in agreement with our patterning results. The generated structures were used as building blocks for the fabrication of nanoscale MOSFET devices.

9:45 AM AA9.4/Y8.4

INTELLIGENT POLYELECTROLYTE MULTILAYERS: pH-RESPONSIVE DEPOSITION/REMOVAL OF THE MULTILAYER THIN FILMS AND THEIR MICRO-PATTERNING. Sung Yun Yang, Michael F. Rubner, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Recently, we have succeeded to build up multilayer films via the layer-by-layer (LBL) technique using hydrogen bonding. Polyacrylamide (PAAm) was used as a non-ionizable polymer, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) were used as hydrogen bonding partners. Multilayers were prepared by alternate dipping of glass or silicon substrates into the dilute polymer solutions at pH 3. At this pH, most of the carboxylic acid groups exist in the non-ionized form, and are available for hydrogen bonds. The key of this experiment was controlling the pH of all solutions including the solutions used in the rinsing steps in the process. The multilayers are stable at low pH and dissolved at high pH. Importantly, at physiological condition (pH 7.2, phosphate buffered solution) these multilayers dissolved into the buffer solution within a minute. This pH change breaks hydrogen bonds between layers by generating negative charges in the ionizable polymer (PAA and PMA). Thermal treatment of these multilayers, which results in a partial cyclic anhydride formation between carboxylic acid groups in the polymer chains, gives the multilayer a good stability at high pH. FTIR spectroscopy experiments confirm there is a high level of hydrogen bonding between amide and acid groups. Ellipsometry and quartz crystal microbalance (QCM) data of the multilayers with different molecular weights of PAAm were taken. In addition, cell adhesion to these multilayers was studied. Using the pH-dependent stability and UV-curable ability of the multilayers, we have succeeded in micro-patterning the films by ink-jet printing and photolithography. This type of multilayer system has a great potential in nanopatterned materials as well as in drug delivery.

10:30 AM AA9.5/Y8.5

NANOCONTACT PRINTING OF PATTERNED SUBMICRON FEATURES OF SELF-ASSEMBLED THIOL DERIVATIZED POLYMERS. John F. Rabolt, Mei-Wei Tsao, Jianling Li, University of Delaware, Dept. of Materials Science and Engineering, Newark, DE.

Microcontact and nanocontact printing have been used to produce patterned self-assembled monolayers (SAMs) and self-assembled polymers (SAPs) on a variety of substrates such as gold, silver or glass. In this technique, an elastomeric stamp, fabricated from poly(dimethylsiloxane) (PDMS) using a polymer master is wetted with an ink made of a solution of a thiol derivatized polymer. The polymer is then transferred by conformal contact to a substrate. In this talk, we will describe the formation of PDMS stamps from commercially available read-write compact disks (master) that have already been patterned with submicron features. SAMs and SAPs were then deposited on gold surfaces using submicron contact printing and micromolding techniques. Utilizing an atomic force microscope (AFM), these patterned surfaces were characterized and analyzed to determine the fidelity and aspect ratio of the features produced. Polarized FTIR measurements were made on the 5.5 nm. thick transferred polymer films in order to assess the extent of polymer orientation induced by the stamping process.

10:45 AM AA9.6/Y8.6

NANOPATTERNING 2D METALLIC SURFACES BY SOFT LITHOGRAPHY. Muhammet S. Toprak, German Salazar-Alvarez, Do-Kyung Kim, Maria Mikhailova, Mamoun Muhammed, Royal Institute of Technology, Dept of Materials Science and Engineering, Materials Chemistry Div, Stockholm, SWEDEN.

The fabrication of large areas of structured surfaces with feature sizes in the nanometer regime is still a challenge. Modern approaches to structure surfaces in sub-micrometer range involve the use of lithographic techniques, which have limitations regarding the minimum feature size. Nanostructures are made by imprinting methods, in which microcontact printing (μ CP) uses an inked patterned stamp to direct chemical reactions between molecules from the ink and the surface of a substrate. In this study, we report on the development of μ CP technique where the ink used on the surface of the stamp is made of alkanethiol solutions. Si was used as substrate on which self assembled monolayer of nanoparticles was formed at the contact regions. The stamps for μ CP are prepared from polydimethylsiloxane (PDMS) by polymerizing on a master defined by self-assembled colloidal SiO₂ nanosphere surfaces. The regions of contact subsequently used for deposition of metal nanoparticles resulting in 2D patterned metallic surfaces. By changing the size of nanospheres used in the master, it is possible to control the size and distance between contact points, i.e. metal deposited points, on the substrate. The chemical and physical properties of the system are investigated where the printed substrates were characterized by SEM and atomic force microscopy (AFM) technique and deposited particles were characterized by XRD.

11:00 AM AA9.7/Y8.7

FIELD INDUCED PATTERNING OF MECHANICALLY CONFINED POLYMER FILMS. David G. Bucknall, Department of Materials, University of Oxford, UNITED KINGDOM.

At elevated temperatures polymer films on a non-wetting solid surface form quasi-periodic patterns resulting from film rupture and dewetting [1]. This behaviour can be prevented by mechanically confining the film by a capping layer of, for instance SiO_x, to produce a completely different morphology [2]. This paper presents results of our recent studies on the morphological changes which occur to such mechanically confined films when an electric field is applied normal to the film thickness. An electric field applied across a polymer film with a free surface is known to produce structures which are either columnar or replicate the topography of the electrode [3]. By capping the polymer film with a thin metal layer, we produce very different structures. The effect of applying an electric field to these capped polymer films during annealing at elevated temperatures for a few minutes is to produce lateral morphologies which display both anisotropic, highly linear regions as well as areas which are totally isotropic. The effect of the polymer film and capping layer thickness and field strength have on the resultant structures will be presented.

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11:15 AM AA9.8/Y8.8

PLANAR MOLECULAR AND MACROMOLECULAR GRADIENTS: PREPARATION AND PROPERTIES. Jan Genzer,

Deposition of self-assembled monolayers (SAMs) offers one of the highest quality routes of systematically tuning the surface properties of materials: by controlling the chemical composition of the terminal group, the length, and microstructure of the SAM molecule, the chemical and physical properties, including wetting, adhesion, friction, and biosensing, can be successfully tailored. While early studies concentrated mainly on preparing substrates with laterally homogeneous SAMs, recent advances in the field allowed for creating SAMs with two-dimensional chemical patterns. In particular, the microcontact printing (μ CP) technique has proven to be a convenient method for producing chemically patterned substrates. While μ CP is useful for decorating materials substrates with a variety of motif shapes and dimensions, it always produces sharp boundaries between the distinct chemical substrate regions. However, for some applications, it is required that the wetting properties of the substrate change gradually over a certain region in space. This situation can be accomplished by producing surfaces with a gradually varying chemistry along their length. In these so-called gradient surfaces, the gradient in surface energy is responsible for a position-bound variation in physical properties, most notably the wettability. Such gradient surfaces can be particularly useful to study interactions in biological systems, as the influence of the entire wettability spectrum upon protein adsorption or cellular interactions can be obtained in one single experiment. In our presentation we will discuss several methodologies of preparing planar molecular and macromolecular gradients on substrates. We will show that the gradient properties (including the wettability change and chain orientation) can be elucidated by a combination of several complementary experimental tools, including NEXAFS, static and dynamic contact angle measurement, spectroscopic ellipsometry, and FTIR. Moreover, we will demonstrate that the gradient properties (including steepness, position of diffusing front, and wettability) can be fine-tuned by forming the gradients on a flexible (and thus deformable) substrate, such as an elastomeric network.

11:30 AM AA9.9/Y8.9

SOFT CONDENSED MATTER NANO- AND MESOSCOPIC PATTERNS ON SEMICONDUCTOR SURFACES. V. Samuilov, Y.-S. Seo, Department of Materials Science, SUNY at Stony Brook, Stony Brook, NY; V. Ksenevich, Department of Physics, State University of Belarus, Minsk, BELARUS; J. Galibert, Laboratoire National des Champs Magnetiques Pulses, Toulouse, FRANCE; J. Sokolov, M. Rafailovich, Department of Materials Science, SUNY at Stony Brook, Stony Brook, NY.

The most striking property of soft condensed matter is the ability to self-organize - to create spatially oriented or periodic states on nano- and mesoscopic scale [1]. A novel and simple approach of self-organized fabrication of two dimensional mesoscopic networks with the feature size down to 50 nm has been developed. The technique is based on the self-organized patterning in a thin layer of complex liquid (polymer solution) in the presence of humid atmosphere. Two dimensional mesoscopic honeycomb-shaped carbon structures were produced by high temperature annealing of nitrocellulose precursors [2]. The polymer network was also utilized as a mask for further reactive ion etching of surfaces with epi-layer of GaAs [3,4] and GaAs/AlGaAs d-doped heterostructures [5]. These structures can be considered as regular arrays of mesoscopic cells or 2-D photonic band gap crystals. We have used diblock-copolymer system, self-assembled with L-B technique, to produce nano-patterns. These structures were utilized as templates for introducing metal nanopatterns on semiconductor surfaces by reactive ion beam etching for magnetic storage systems [6] and DNA separation on a flat surface [7] devices. DNA molecules positioning on Si surface by simple physical alignment process has been developed. The capillary forces applied by the receding front of the evaporating drop containing DNA molecule were used to align them perpendicularly to the direction of drying front. This alignment was used as a precise DNA molecules loading technique on Si surface in a new method of DNA separation [7]. We determined the resolution related to loading width by the thickness of the line, which was approximately equal to the length of the stretched DNA molecules.

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SESSION AA10/DD11: JOINT SESSION
SELF-ASSEMBLY BY POLYMERIC FILMS
Chairs: Spiros H. Anastasiadis and Georg Krausch
Thursday Afternoon, November 29, 2001
Constitution B (Sheraton)

1:30 PM *AA10.1/DD11.1

STRUCTURE FORMATION AND MOLECULAR DYNAMICS IN THIN LIQUID FILMS. Ralf Seemann, Karin Jacobs, Stephan Herminghaus, University of Ulm, Applied Physics Lab., Ulm, GERMANY.

The principal mechanisms of dewetting and structure formation in thin liquid films are presented and discussed with polystyrene films as a model system. Quantitative agreement of *in-situ* optical and AFM microscopy with theoretical predictions, both analytical calculations and simulations, is obtained. It is found that additivity of van der Waals interactions is a good approximation for computing the effective interface potential. On the basis of the observed features, we are furthermore able to infer the rheological properties of the polymer melt at the small (μ m to nm) scales investigated. This can be applied to a wide range of (complex) fluids, yielding rheological information not easily accessible by other techniques.

2:00 PM AA10.2/DD11.2

MICRODOMAIN STRUCTURE AND DYNAMICS OF SELF-DEWETTING POLYSTYRENE-BLOCK-POLY (ETHYLENE-PROPYLENE) THIN FILMS. A. Horvat, A. Knoll, G. Krausch, R. Magerle, Phys Chem II, Universität Bayreuth, GERMANY.

The structural development of polystyrene-*block*-poly(ethylene-propylene) (PS-PEP) thin films with 28 wt% PS has been studied as a function of film thickness, temperature and annealing time. Above the polystyrene (PS) glass transition temperature various self assembled structures are formed depending on treatment. Tapping ModeTM AFM investigations of spin cast samples reveal a stripe like pattern at the film surface corresponding to the bulk structure of cylindrical microdomains. After annealing at 160°C the film shows a disordered spherical microdomain structure of PS domains in a PEP matrix. Upon annealing at 140°C a transition to irregular structures with dimensions much larger than the microdomain spacing occurs. At longer time scales polymer droplets form and move spontaneously across the surface. This phenomenon was followed in situ by hot stage Tapping ModeTM AFM. The phenomenon is believed to be caused by a delicate balance between the surface and volume contributions to the effective interface potential of the confined polymer film.

2:15 PM AA10.3/DD11.3

SELECTIVE ELECTROLESS METALLIZATION USING MICROCONTACT PRINTING OF FUNCTIONALIZED COPOLYMERS. Tricia L. Breen, Ali Afzali, Sarah J. Vella, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We present a low-cost, additive method that uses microcontact printing and electroless plating to fabricate patterned metal films with minimum feature sizes of ~ 1 micron. Our approach is based on stamping new copolymers that incorporate two types of functional groups: The first group bonds the copolymer to the SiO₂ substrate; the second group ligates catalytic colloids used to initiate electroless metallization. After stamping the copolymer onto a substrate, the patterned film is exposed to a solution of an electroless plating catalyst. The catalytic colloids selectively adhere to the stamped regions of the surface. Subsequent metallization in an electroless plating solution yields a metal film only over the catalyzed copolymer regions. Using this method, we have fabricated patterned nickel and copper films over areas as large as 15 cm².

2:30 PM AA10.4/DD11.4

APPLICATION OF SELF ASSEMBLED MONOLAYER TECHNOLOGY TO INVESTIGATE THE FIBER-MATRIX ADHESION. E. Feresenbet, D. Raghavan, Polymer Division,

Department of Chemistry, Howard University, Washington DC; G. Holmes, Polymer Division, National Institute of Standards & Technology, Gaithersburg, MD.

Adhesion at the fiber-matrix interface of composite is often related to a combination of factors such as mechanical interlocking, physico-chemical interactions, and chemical bonding of the fiber-matrix interphase region. We demonstrate the use of SAMs technology for studying the impact of these interactions on the adhesion process. Through some unique chemistry, functionalized and nonfunctionalized C11 and C3 chloro silane SAMs were deposited on to the glass fiber. The deposited SAM layer was analyzed using atomic force microscopy (AFM), ellipsometry, X-ray photoelectron spectroscopy (XPS), and contact angle measurements. The adhesion of diglycidyl ether of bisphenol-A (DGEBA) cured with meta-phenylene diamine (m-PDA) to chlorosilane SAMs deposited glass fibers was measured by performing single fiber fragmentation test (SFFT). The extent of adhesion between the fiber and matrix was found to be dependent on the deposition process, carbon chain length, the functional group at the end of the SAM layer, and the structure of the epoxy/amine resin network. Furthermore, the contributions to adhesion by physico-chemical interaction and covalent bonding will be discussed.

2:45 PM AA10.5/DD11.5

SURFACE AND INTERFACIAL PROPERTIES IN THIN POLY(*p*-PHENYLENE VINYLENE) MULTILAYERS PREPARED BY SELF-ASSEMBLY METHODOLOGY. C.A.M. Borges, A. Marletta, R.M. Faria and F.E.G. Guimarães, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, São Carlos, BRAZIL.

In this work we studied the influence of different interfaces (metal/film, ITO/film) and surfaces (air/film) on the optical properties of very thin layers (less than 15 nm thick) of poly(*p*-phenylene vinylene), PPV. The PPV films were prepared joining a novel self-assembly method (SA) and a low temperature conversion process for PPV¹. The main advantage of this SA procedure is that thermal conversion may be performed at considerably lower temperatures (80-100°C) in few minutes, producing high ordered PPV films with very low defect incorporation. In addition, Atomic Force Microscopy (AFM) has shown that 0.4 nm thick PPV can be homogeneously deposited layer-by-layer on different metal (50% transmission Au, Cu, Pt, Ag, Cr films) and glass/ITO surfaces. Absorption measurements revealed that the conjugated π - π^* band suffers different blue-shifts for each interface as the PPV thickness decreases, indicating different extension of the interfacial disorder in the PPV layers. The ITO/PPV interface has the highest disorder extension (~12 nm) and surface roughness (RMS~2.5 nm) while the lowest values (~3.5 nm and RMS~0.6 nm, respectively) were found for the quartz/PPV interface. The thermal conversion of 4 nm thick PPV films at different temperatures (100-230°C) and under vacuum conditions demonstrated that a large amount of structural disorder is incorporated when high conversion temperatures are used. Infrared (IR) measurements showed that carbonyl groups are responsible for conjugation length shortening. When the conversion temperature is lowered (around 100°C), no defect incorporation was detected by absorption and IR measurements. Photoluminescence data will be presented for further discussion.

3:30 PM AA10.6/DD11.6

EFFECT OF SOLVENT QUALITY ON THE FRICTIONAL FORCES BETWEEN POLYMER BRUSHES. Aaron Forster, S.M. Kilbey II, Clemson University, Dept of Chemical Engineering, Clemson, SC.

Polymer brushes have shown promise as surface tethered lubricants, and it has been demonstrated that solvent quality strongly influences the frictional forces between two sliding brush layers. It is known that brush layers immersed in a good solvent must be compressed well below their equilibrium height before a frictional force is measured. Conversely, brushes immersed in a solvent at its theta temperature exhibit a frictional force at much lower levels of compression. We used the surface forces apparatus to measure the structural and frictional force profiles between opposing, sliding brush layers as a function of temperature. Three different polyvinylpyridine-polystyrene [PVP-PS] diblock copolymers were used to make PS brushes. The molecular weights (in thousands) of these PVP-PS materials were [114/103]k, [30/70]k, and [60/100]k. Structural and frictional force profiles in toluene and cyclohexane were measured, with the cyclohexane experiments being done at temperatures ranging from the theta-point to 50°C. We found that the structural force profiles agree with well-known behaviors¹. The frictional forces depended strongly on the solvent and the solvent temperature: PS brushes in toluene need to be compressed to ~1/6th their equilibrium height before frictional forces are measured, but this onset of frictional force is detected at a much lower level of compression in near-theta cyclohexane. When the

cyclohexane temperature is raised the onset of frictional forces decreases toward the good-solvent behavior. At 50°C, the onset of frictional forces occurs at a comparable distance to that in toluene, which is a very good solvent for PS. We will compare this behavior in cyclohexane at various temperatures to the behavior of the brushes in another theta-solvent.

1. S.M. Kilbey, H. Watanabe, M. Tirrell, *Macromolecules* 2001, in press.

3:45 PM AA10.7/DD11.7

MORPHOLOGY AND ORDERING BEHAVIOR OF BLOCK COPOLYMER IN BLOCK COPOLYMER/CLAY NANOCOMPOSITES. Jae Young Lee, Hoichang Yang, Jin Kon Kim, Department of Chemical Engineering and Polymer Research Institute, Pohang University of Science and Technology, Pohang, Kyungbuk, KOREA.

Morphology and ordering kinetics of polystyrene-block-polyisoprene-block-polystyrene (SIS) with various block length ratios and total molecular weights in SIS/clay nanocomposites have been investigated using by transmission electron microscopy, rheology, and small and wide angles X-ray scattering methods. One of SISs employed in this study exhibits the order to order transition of hexagonally packed cylinder microdomains to body-centered cubic microdomains (BCC) at 185°C, then becomes disordered micelles at 225°C. All composites showed that the domain spacing of the clay was larger than compared with PS/clay nanocomposites due to the presence of PI block, but there is no sign of the exfoliation of the clay, that is, the intercalation of clay was observed. But, the domain spacing of block copolymer does not change with the amount of the clay. The degree of intercalation of the clay in nanocomposites does not depend on either PS block length ratios in SIS or the amount of block copolymer in nanocomposites. However, the kinetics of the BCC formation from disordered micelles varied significant with the amount of the clay. Finally, an exfoliated structure for the clay was observed for a nanocomposite when a maleic anhydride functionalized polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene is used instead of SIS.

4:00 PM AA10.8/DD11.8

CHARACTERIZATION OF THIN POLYMER BLEND FILMS USING ESEM - NO CHARGING, NO STAINING. I.C. Bache, C.M. Ramsdale, D.S. Thomas, A.C. Arias, J.D. MacKenzie, R.H. Friend, N.C. Greenham, A.M. Donald, Univ of Cambridge, Cambridge, UNITED KINGDOM.

We have developed the application of Environmental Scanning Electron Microscopy (ESEM) to the study of conjugated polymer blends. ESEM has the special advantage that polymers do not need to be coated to prevent charging. Thin films of conjugated polymer blends are increasingly finding application in novel optoelectronic devices, including LEDs and photovoltaics. The use of blends in photovoltaics is driven by efficient exciton dissociation at the interfaces between the two phases leading to improved performance. In order to optimise the device efficiency, it is therefore necessary to understand the interplay between processing (typically spin casting on an appropriate substrate), morphology (especially the nature of the interfaces) and performance. Traditionally a variety of microscopies have been used to study thin film structure. TEM has various limitations, including the lack of contrast between polymer phases in the absence of staining, and the need for substrate removal. AFM, more recently used, can only study the surface of the blend unless etching or dissolution techniques are used to remove one component preferentially. ESEM provides a powerful technique to study blend films. We have demonstrated that polymers can show significant contrast according to their electronic properties. Thus for these optoelectronically interesting polymer blends, contrast can be seen readily between the phases. This means that morphological changes due to processing conditions can readily be studied, even without removing the device from the substrate. In addition, by sectioning the sample, variations in phase separation through the film thickness can also be imaged. Such images show not only how the surface topography is affected by the phase separation - which can be confirmed by AFM - but also whether the phase separation visible at the free surface propagates right the way through the film. Understanding this has important implications for device performance.

4:15 PM AA10.9/DD11.9

EFFECTS OF SELF-ASSEMBLED PHTHALOCYANINE AND POLYMER MULTILAYERS ON PHOTOVOLTAIC PROPERTIES OF CONDUCTIVE AND SEMICONDUCTIVE SURFACES. Lin Song Li, QuanXi Jia, Los Alamos National Laboratory, Materials Science and Technology Division (MST-STC), Los Alamos, NM; Alexander D.Q. Li, Department of Chemistry and Center for Materials Research, Washington State University, Pullman, WA.

The recently developed technique of layer-by-layer (LBL) assembly of

oppositely charged polymeric and organic materials has been used to fabricate multilayers on various substrates. Using this technique, we have deposited multilayers of nickel phthalocyanine (NiPc) and poly(diallyldimethylammonium) (PDDA) onto ITO and TiO₂/ITO substrates, respectively. Kelvin probe and surface photovoltage measurements have been used to probe the electronic and charge transfer properties of these self-assembled multilayers. The results showed an oscillating behavior of the surface potential as the surface layer was alternated between these multilayers on both substrates. The average gap of this surface potential oscillation was around a few hundreds of milli-Volt. These changes of surface potential or work function, induced by self-assembled PDDA or NiPc were due to the modulation of electron affinity rather than band bending at ITO surfaces, which was consistent with the surface photovoltage measurements. In photovoltage experiments, we also found that the spectra of photovoltage were a weak periodic function of the number of layers (PDDA or NiPc).

4:30 PM AA10.10/DD11.10

LIQUID CRYSTALLINE ALIGNMENT OF SIDE-CHAIN SMECTIC HOMOPOLYMER FILMS. Jung-Sheng Wu, Paula T. Hammond, MIT, Dept of Chemical Engineering, Cambridge, MA.

Surface properties have profound influence especially on polymer thin film applications. The understanding of LC alignments in nanoscale thin films becomes critical, when the technology trends towards to diminish the film thickness but keep ordered surfaces. From previous results of morphological studies, lamellar side-chain LC diblock copolymers have been synthesized and examined as thin films. LC terraces with the smectic LC layer spacing are observed on the top surfaces to minimize the surface tension. In order to determine LC alignments, homopolymer films with different thickness are examined to give us an idea about LC alignments and use as model system to describe complicated diblock copolymer systems. LC orientations are determined by both experimental (contact angles, angle-resolved XPS, AFM, X-ray specular reflectivity, ellipsometry, SAXS, TEM, and X-ray single crystal diffractometer) and theoretical (molecular mechanism modeling and group contribution theory) approaches. The LC orientation shows homeotropic in the air interface by the non-polar end group, but planar on the substrate by the mesogen core. We have also investigated morphologies and LC alignments of diblock copolymer thin films with lamellae, cylinders, perforated lamellae, and unusual smectic bilayers. They all show homeotropic LC terraces on the air interface. The fundamental understanding of the self-oriented LC polymer thin film behaviors will be helpful for further nano-patterning, and electrical/optical applications.

4:45 PM AA10.11/DD11.11

STRUCTURAL CHARACTERIZATION OF SEGMENTED POLYURETHANES BY SMALL ANGLE NEUTRON SCATTERING. Loren I. Espada, Lance-12, Los Alamos National Laboratory, Los Alamos, NM; Joseph T. Mang, DX-2, Los Alamos National Laboratory, Los Alamos, NM; E. Bruce Orlor, MST-7, Los Alamos National Laboratory, Los Alamos, NM; Debra A. Wroblewski, MST-7, Los Alamos National Laboratory, Los Alamos, NM; David A. Langlois, MST-7, Los Alamos National Laboratory, Los Alamos, NM; and Rex P. Hjelm, Lance-12, Los Alamos National Laboratory, Los Alamos, NM.

The beneficial mechanical properties of segmented polyurethanes derive from microphase separation of immiscible hard and soft segment-rich domains at room temperature. We are interested in the structure of the domains, how these are affected by hydrolytic aging, and how the structure is modified by low molecular weight plasticizers. Segmented poly(ester urethane) with various weight fraction hard segment content, both deuterated and non-deuterated were synthesized and the morphology assessed using small-angle neutron scattering. We also assessed the distribution of the plasticizer in polyurethane. We have analyzed the results in terms of a simple model in which the contrast, $\Delta\rho = \rho_H - \rho$, between the hard and soft segment-rich domains is varied by the amount of deuterated hard segments or presence of deuterated or hydrogenated nitroplasticizer, using the fact that $I(Q) \sim \Delta\rho^2$. Modeling results give us key information on the domain structure of polyurethane, the segregation of the hard and soft segments in each domain and determined that plasticizer partitions into the soft segment-rich domains.

SESSION AA11/BB11: JOINT SESSION NOVEL PATTERNING SCHEMES

Chairs: Michael F. Rubner and Paula T. Hammond
Friday Morning, November 30, 2001
Constitution A (Sheraton)

NOTE EARLY START

8:15 AM *AA11.1/BB11.1

THIN FILM PROCESSING SCHEMES FOR MANIPULATING ELECTRONICALLY ACTIVE ORGANICS. M.F. Rubner, Department of Materials Science and Engineering, MIT, Cambridge, MA.

In recent years, we have developed a number of simple strategies for manipulating electronically active polymers and small molecule light emitters into thin film devices. For example, we have utilized a layer-by-layer processing approach to form functionally active polyelectrolyte multilayers. Such films show promise as the active elements of light emitting devices, micro-photon devices, thin film sensors and anti-reflection coatings. In addition, we have developed simple blending techniques that make it possible to fabricate high efficiency, red-orange light emitting thin films from the well known Ru(II) complex. Our best devices to date operate at low voltage (ca. 2.5 volts) with high external quantum efficiency (in the 4-5 % range), high brightness and good stability. These performance characteristics are obtained from a simple spin-coated blend system and by using stable electrode materials such as silver as the cathode. Recent developments in these two areas will be discussed.

8:45 AM AA11.2/BB11.2

NANOLITHOGRAPHIC PATTERNING OF ORGANIC ELECTRONIC DEVICES BY AN ADDITIVE METAL COLD WELDING PROCESS. Changsoon Kim and Stephen R. Forrest, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ.

We demonstrate a simple and high resolution patterning technique capable of creating submicrometer structures on organic thin film. Previously, we demonstrated that organic light emitting device cathodes could be quickly and easily patterned by locally removing metal film from the organic layers using a stamping process¹. The new method described here differs from the earlier technique in that the metal film predeposited on a hard stamp is left behind on regions of the organic layers once stamp and organic layers come into contact. This metal-additive process has several advantages over the metal subtractive method reported earlier. For example, it uses a lower pressure which is independent of metal layer thickness. The process proceeds as follows: First, the metal film is deposited on a patterned stamp precoated with an anti-sticking layer such as Teflon, while a very thin (~100Å) layer of the same metal is deposited across the entire surface of the organic film predeposited on a hard (e.g. Si) substrate. Selective cold welding is then induced between the metal films in the area defined by the raised features of the stamp by pressing the stamp onto the substrate. Upon separation of the stamp from the substrate, the metal film on the stamp is transferred to the substrate, resulting in a pattern defined by the shape of the stamp. Next, the thin metal film on the substrate between the patterned regions is removed by a brief exposure to a plasma or other dry etching process. This patterned metal film can be used as an etch mask or can serve as electrodes for electronic devices. We show that this process has a pattern resolution to ~10nm by fabricating a grating line pattern in a polymer where the individual lines are as small as 80nm. Furthermore, using this additive transfer process, we demonstrate fabrication of pentacene thin film transistors where source and drain electrodes are added to the pentacene surface. A mobility of ~0.1cm²/Vs and on/off ratio of ~10⁶ are obtained. Very short gate lengths are demonstrated.

[1] C. Kim, P.E. Burrows, S.R. Forrest, *Science* **288**, 831 (2000).

9:00 AM AA11.3/BB11.3

PHOTOPATTERNING OF PHENYLENE-VINYLENE BASED POLYMERS. Thomas Kavc, Gregor Langer, Wolfgang Kern, Kai Mahler, Franz Stelzer, Gertraud Hayn, Robert Saf, Graz Univ. of Technology, ICTOS, AUSTRIA; Alexander Pogantsch, Emil J.W. List, Egbert Zojer, Graz Univ. of Technology, Institute of Solid State Physics, AUSTRIA; Kurt F. Iskra, Theo Neger, Graz Univ. of Technology, Institute of Experimental Physics, AUSTRIA; Hans-Heinrich Hörhold, Hartwig Tillmann, Univ. Jena, Institute of Organic Chemistry and Macromolecular Chemistry, GERMANY; Gerald Kranzelbinder, ENS Cachan, LPQM, FRANCE; Georg Jakopic, Joanneum Research, Weiz, AUSTRIA.

The patterning of conjugated materials is of general interest for controlling the emission properties of light emitting devices (LEDs). In addition, periodical structures are required for the realization of organic lasers based upon the principle of distributed feedback (DFB). We employed the photoreaction of gaseous hydrazine (N₂H₄) with aromatic polymers to introduce patterns into films of polystyrene (PS), poly(2-vinylnaphthalene) (PVN) and phenylene-vinylene based polymers (PPV). Under UV irradiation in N₂H₄ atmosphere the

aromatic units in PS and PVN were partly transformed into aliphatic units (as evidenced by FTIR). This resulted in a decrease of the refractive index n by 0.04 (PS) and 0.11 (PVN). In the case of the PPV derivatives, the treatment first lead to a saturation of the vinylene units and subsequently to a conversion of the phenylene rings. The mechanisms of these reactions were investigated using model compounds. Spectroscopic studies showed that the photobleaching of the PPV derivatives resulted in a reduced conjugation (blue-shift of absorption spectra). The luminescence quantum yield, however, remained high during the initial stages of the photoreaction. This indicates that this process does not introduce quenching centers, which makes it promising for patterning the emission of luminescent devices. After prolonged UV irradiation under N_2H_4 the energy gap of PPV was shifted to the far UV. Using interference lithography, gratings were enscribed in the PPV films resulting in a periodical modulation of the refractive index and the optical gain. The applicability of these structures for DFB lasing was investigated. As an alternative approach, PPV derivatives and laser dyes were incorporated into photosensitive polymers. Using poly(4-vinylbenzylthiocyanate-co-styrene) as matrix material, refractive index and surface relief gratings were obtained after patterned UV illumination. With these structures optically pumped DFB lasing was demonstrated.

9:15 AM AA11.4/BB11.4

STUDY OF SURFACES PREPARED BY MICROCONTACT PRINTING METHODS USING CHEMICAL FORCE MICROSCOPY. Hiroki Okui, Fuminobu Sato, Uichi Akiba, Kosaku Suga, Masamichi Fujihira, Tokyo Institute of Technology, Department of Biomolecular Engineering, Yokohama, JAPAN.

In the present work, we applied chemical force microscopy (CFM) by mapping adhesive force using pulsed-force-mode atomic force microscopy (PFM-AFM) with chemically modified AFM tips to study mixing of two components in patterned self-assembled monolayers (SAMs). The patterned SAMs were prepared by two types of microcontact printing methods. One is the wet-inking method, in which inking of the stamp was done by placing a thiol ethanol solution on it and then removing the excess solution under a stream of nitrogen. The other is the contact-inking method, in which an inker pad made of polydimethylsiloxane (PDMS) was dipped in a thiol ethanol solution overnight, then the excess solution was removed by a stream of nitrogen, and finally the stamp was placed on the inker pad impregnated with the thiol solution. Contamination due to vapor phase transfer during stamping and defects in printed areas due to insufficient ink transfer were studied by the present CFM in water.

9:30 AM AA11.5/BB11.5

TEMPLATING ORGANIC SEMICONDUCTORS VIA NANOSCALE SELF-ASSEMBLY. James F. Hulvat¹ and Samuel I. Stupp^{1,2,3}, Department of Materials Science and Engineering¹, Department of Chemistry², and Medical School³, Northwestern University, Evanston, IL.

The science and technology of low cost organic electronics could be advanced significantly by utilizing aqueous, self-assembly processes to pattern and control the nanostructure of conducting polymers. This could simplify fabrication and improve efficiency of organic light emitting diodes (OLEDs), organic field effect transistors and other devices. Orientation and isolation of polymer chains enhances charge injection and reduce exciton quenching via interchain charge transfer. We report here a templating strategy utilizing nanoscale dielectric channels in liquid crystals to orient and isolate conducting, light-emissive polymers. The strategy involves confining monomeric precursors within the cylindrical hydrophobic core of a hexagonal lyotropic liquid crystal (LC). The amphiphilic molecule oligo(ethylene oxide)-oleyl ether forms a self-supporting gel in water with a hexagonal (H1) mesophase consisting of two nanometer cores. The hydrophobic nature of these cores allows high concentrations of precursor molecules, such as 3,4-ethyldioxythiophene (EDOT), to be solubilized in an aqueous mesophase without disrupting the LC order. We have electropolymerized this monomer on gold and indium tin oxide (ITO) within the LC gel to form the conducting polymer poly(ethyldioxythiophene) (PEDOT). The PEDOT film produced here precisely mimics the orientation and domain texture of the LC template. When the LC template is removed, the PEDOT remaining on the electrode exhibits a birefringent texture commensurate with the original liquid crystal gel. EDOT electropolymerizes preferentially in LC domains oriented parallel to the applied potential. This novel result indicates the optical anisotropy of the LC mesophase is templated on the growing polymer. The PEDOT film formed is electrochromic, electrochemically dopable, and can be reversibly oxidized and reduced. This facile approach bridges the gap between conventional lithography and molecular self-assembly by confining polymers within a nanoscale liquid crystal template ordered over hundreds of microns. In this process, precursor monomers are isolated, oriented, polymerized and doped in a single step.

9:45 AM AA11.6/BB11.6

MULTILAYER MICROCONTACT-PRINTING OF ELECTRODES FOR SEMICONDUCTING POLYMER DEVICES. M.M.J. Decré, J.B. Giesbers, M.H. Bles, R.J.M. Schroeders, P.P.J. van Eerd and G.H. Gelinck, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Soft lithography has previously been reported for patterning source-drain electrodes of semiconducting polymer transistors, while other layers were relying on either low resolution at typically 50 micron alignments or else standard photolithography for designs requiring better alignment performance. It is however desirable to demonstrate that a single technology can offer solutions for all device layers, including alignment. In our work, both electrode layers are patterned using microcontact-printing, to within a layer-to-layer alignment of 5 micron. We realized electronic devices based on semiconducting polymers. The devices have a so-called "bottom-gate" design: the layers follow a substrate/gate/insulator/source-drain/semiconductor structure. Both electrode layers are made of gold on a thin titanium adhesion layer. Using a rubber stamp (Sylgard 184) impregnated with alkanethiols, we print each electrode with a patterned monolayer and then etch it. The in-layer registration and layer-to-layer alignment allow for a total alignment of 5 micron. The devices have 4 micron channel width and source-drain finger widths. We present results on transistors, ring oscillators and simple bit-encoding devices having a surface of several square-millimeter and tens of transistors. We will address the patterning of vias by soft lithography to offer a complete manufacturing approach.

10:30 AM *AA11.7/BB11.7

APPROACHES TO NONLITHOGRAPHIC ASSEMBLY: FROM POLYMER MULTILAYERS TO COLLOIDAL PARTICLES. Paula T. Hammond, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

Research directions in materials and polymer science include the development of surface-directed assembly that can guide the placement of molecular to micron-scale objects onto substrates in pre-determined arrangements for sensors, electrical and optical devices, MEMS, and 2-D photonic systems. Nonlithographic approaches to these goals such as nano to micronscale printing, molding, and templating, will be key to driving the technologies toward application and commercialization. In our group, we have demonstrated the ability to direct polymers to different regions of a surface based on both electrostatic and secondary interactions between the polymer and the surface. We have now established a set of rules that define the conditions required for selective deposition of different functionalized materials onto specific surface regions. We have successfully expanded this understanding of polyion-surface interactions to mesoscale systems, including functionalized colloidal systems and colloids. This concept of adsorption directed by chemistry is universal, and can be applied to dye molecules, polymers, and nanometer to micron sized functionalized particles. Incorporation of two or more different elements within a pattern or array is one of the challenges in this field. We have used these techniques to build up complex, laterally patterned microstructures on the surface, in which more than one materials system can be selectively placed on a surface. The use of polymer-on-polymer stamping as a means of patterning such materials onto plastic as well as glass and oxide surfaces will also be addressed.

11:00 AM AA11.8/BB11.8

MICRON SCALE PATTERNING OF ORGANIC THIN FILMS VIA ORGANIC VAPOR PHASE DEPOSITION. Max Shtein^{1,2}, Peter Peumans^{1,3}, Anna Chwang⁴, Jay B. Benziger², Stephen R. Forrest^{1,3}; ¹ Center for Photonics and Optoelectronic Materials (POEM), ² Department of Chemical Engineering, ³ Department of Electrical Engineering, Princeton University, Princeton, NJ; ⁴ Universal Display Corporation, Ewing, NJ.

Organic vapor phase deposition (OVPD) is attractive for fabrication of molecular organic devices due to low operation cost and ease of scale-up as compared to vacuum thermal evaporation. In OVPD, organic molecules are delivered from remote evaporation sources by an inert carrier gas (e.g. N_2) into a hot wall reactor at pressures of from 10^{-2} to 10 Torr, where selective deposition occurs on the cooled substrate. For many applications, such as in full color displays, it is often necessary to achieve selective area patterning the organic film on the substrate via deposition through a shadow mask. Using vacuum thermal evaporation, sharply defined pixels are readily achieved, since the molecular mean free path, λ , at 10^{-7} Torr is ~ 1 meter. However, OVPD typically proceeds at pressures $\leq 10^{-2}$ Torr, with $\lambda < 1$ cm, resulting in pixels with diffuse edges. In this work we show that OVPD growth of thin films with pattern definitions $\sim 1\mu m$ can be achieved under the appropriate conditions of substrate temperature

and reactor pressure. We describe Monte Carlo simulations (displayed in video) to determine the pixel pattern evolution in real time and its dependence upon the deposition pressure and the carrier flow rate. The simulations are then tested experimentally, and we find pattern definition as small as 1mm is readily achieved by OVPD growth through shadow masks. The results help identify useful processing conditions, and guide the design of future OVPD systems.

11:15 AM AA11.9/BB11.9

EDGE TRANSFER LITHOGRAPHY. Oksana Cherniavsky, Karl Knutson, Aleksandar Adzic, Ling Zang, David M. Adams, Columbia University Dept of Chemistry, New York, NY.

A simple and general method, edge transfer lithography (ETL), has been developed for large-area patterning of self-assembled monolayers (SAMs) at nanometer resolution. ETL employs standard "ink" and "stamp" microcontact printing (μ CP) techniques and takes advantage of the intrinsic topographic character and discontinuous dewetting behavior of micropatterned elastomeric stamps to selectively apply ink solutions within the recesses of the stamp. A polydimethylsiloxane (PDMS) stamp is used to pattern alkyl silane SAMs on glass with 60-nanometer line width resolution. Molecules are controllably delivered from the stamp to a solid substrate of interest selectively along the edges of the stamp features. Four-way and higher order junctions can be created by multiple applications of the stamp. Patterned SAM surfaces allow for the guided assembly of molecular materials. ETL is a potentially useful method for creating large-area complex patterned nanoscale structures of other materials such as nanoparticles, with applications in nanotechnology, and the biological and surface sciences.

11:30 AM AA11.10/BB11.10

ELECTROWETTING CONTROLLED TUNABLE LIQUID MICROLENS. Tom Krupenkin, Shu Yang, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Tunable liquid microlens capable of adjusting its focal length and lateral position is demonstrated. The microlens consists of a droplet of a transparent conductive liquid placed on a dielectric substrate with a hydrophobic coating. By varying the voltage applied to the structure, both the position and curvature of microlens can be changed. To improve the electrical and optical performance of the microlens, different conductive liquids, dielectric materials, and their surface coatings are studied. The influence of the bulk and surface properties of the materials on the microlens behavior is experimentally investigated and supported by theoretical calculation. Some of the potential physical and technological limitations of the microlens performance are outlined and possible ways to alleviate them are suggested. Several potential applications of the proposed microlens will also be discussed.

11:45 AM AA11.11/BB11.11

MULTI-COLORED ELECTROCHROMIC CONJUGATED P- AND N-TYPE DOPABLE POLYMERS BASED ON ALTERNATING DIOXYTHIOPHENE DONORS AND PYRIDINE ACCEPTORS. C.J. DuBois, Jr., John R. Reynolds, University of Florida, Department of Chemistry and Center for Macromolecular Science and Engineering, Gainesville, FL.

This paper reports on a family of alternating donor-acceptor copolymers based on electron-rich 3,4-ethylenedioxythiophene (EDOT) and electron-poor pyridines, which exhibit low band-gaps and multi-colored redox states. The parent polymer, PBEDOT-Pyr, has a band gap of 1.9 eV and four readily accessible color states: neutral red, oxidized dark blue-purple, reduced purple, and protonated dark blue. Derivatization of the pyridine to enhance its acceptor strength has led to the synthesis of a group of aryl and alkyl derivatized pyridopyrazines (PyrPyr): specifically BEDOT-PyrPyr(Ph)₂ and BEDOT-PyrPyr(Hex)₂. PBEDOT-PyrPyr(Ph)₂ has a band-gap of 1.2 eV and exhibits broad p-type doping electrochemistry centered at 1.1 V vs SCE. PBEDOT-PyrPyr(Ph)₂ also displays two distinct reduction peaks centered at -1.05 V and -1.70 V. Cyclic voltammetry, differential-pulse voltammetry, in-situ conductivity, colorimetry, and spectroelectrochemistry results will be discussed for this family.