

# SYMPOSIUM M

## M: Nontraditional Approaches to Patterning

December 1 - 5, 2003

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\* Invited paper

**8:30 AM M1.1**

**Heterojunctions of Multi-Walled Carbon Nanotubes and Semiconducting Nanocrystals for Electronic Device Applications.** Cengiz Sinan Ozkan, Mechanical Engineering, University of California at Riverside, Riverside, California.

We report the controlled synthesis of multi-walled Carbon Nanotube-Quantum Dot (CNT-QD) heterojunctions with controlled conjugation of water stabilized, amine terminating, ZnS coated CdSe QDs with amine terminal groups to acid treated ends of multi walled CNTs (MWCNT) using the Ethylene Carbodiimide Coupling procedure (EDC). Scanning Electron Microscopy, Transmission Electron Microscopy and Fourier Transform Infrared Spectroscopy were used to characterize the conjugation process. The method developed preserves the electronic properties of the MWCNTs and enables the nanoassembly of heterojunctions. The conjugates obtained can be used as building blocks for nanoscale electronic or optoelectronic devices and three dimensional hierarchical assembly of multilayered systems.

**8:45 AM M1.2**

**Single Crystalline GaN Nanotubes.** Joshua Goldberger and Peidong Yang; Chemistry, UC Berkeley, Berkeley, California.

A novel //epitaxial casting// approach was developed for the synthesis of single crystalline GaN nanotubes (Goldberger, J.; He, R.; Lee, S.; Zhang, Y.; Yan, H.; Choi, H. J.; Yang, P. *Nature* **422**, 599, 2003). In this process, hexagonal ZnO nanowire arrays are used as templates for the epitaxial overgrowth of thin GaN layers in a chemical vapor deposition system. Since ZnO and GaN both have the wurtzite crystal structures with similar lattice constants, GaN can be grown epitaxially on the side (110) planes of these ZnO nanocylinders, thus forming a thin GaN layer that is single crystalline in nature. The ZnO nanowire templates are subsequently removed by thermal reduction and evaporation in an H<sub>2</sub> / NH<sub>3</sub> atmosphere, resulting in ordered arrays of GaN nanotubes on the substrate. These nanotubes have inner diameters ranging from 30 – 200 nm and wall thicknesses between 5 – 50 nm. Electron diffraction indicates these tubes are single crystalline. In addition, the size dependent optical and electronic properties from individual nanotubes will also be discussed.

**9:00 AM \*M1.3**

**Hierarchical Organization of Nanowires for Integrated Nanoelectronic and Nanophotonic Systems.** Charles M. Lieber, Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

(Abstract Not Available)

**9:30 AM \*M1.4**

**Synthesis of Metal and Semiconductor Nanowires By Electrochemical Step Edge Decoration.** Reginald Penner, Qiguang Li, Erich Walter, Ben Murray and Erik Menke; UCI, Irvine, California.

A general method is described for the electrodeposition of long (> 500 microns), nanowires composed of noble or coinage metals including molybdenum, nickel, copper, silver, palladium, and gold. Nanowires of these metals, with diameters in the range from 60 nm to 750 nm, were obtained by Electrochemical Step Edge Decoration (ESED); the selective electrodeposition of metal at step edges. Nanowire growth by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying three voltage pulses in succession: An oxidizing activation pulse, a large amplitude, reducing nucleation pulse, and a small amplitude reducing growth pulse. The activation pulse potential was optimized to oxidize step edges on the graphite surface just prior to deposition. The nucleation pulse had an overpotential for metal deposition of between -200 and -500 mV and a duration of 5-10 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by a time-independent deposition current and consequently, the nanowire radius was proportional to the square root of the deposition time in accordance with the expected growth law. We also describe a method for preparing long (> 100 micron) bimetallic nanowires that are compositionally modulated along the axis of the nanowire. Essentially, the new method described here involves wiring together particles of one metal using nanowires of a second. This is accomplished by combining two new electrodeposition methods that we have recently described: Slow growth for preparing metal nanoparticles that are narrowly dispersed in diameter, and nanowire growth. Using this approach, beaded bimetallic nanowires that are up to a millimeter in

length can be prepared in parallel arrays on a graphite surface. These wires can then be transferred onto a second, insulating surface (e.g., glass) using a method we have previously described. Finally, electrochemically prepared metal or metal oxide nanowires can be used to prepare semiconductor nanowires having correlated attributes of diameter and length. We describe one example involving the synthesis of molybdenum disulfide nanowires from molybdenum dioxide precursors.

**10:30 AM \*M1.5**

**Patterning of Nanocrystals.** Paul Alivisatos, Chemistry Department, University of California-Berkeley, Berkeley, California.

We will present new methods for patterning nanocrystals into small groupings, from 1 to 7. In these groupings, we can specify the composition and positions of the nanocrystals. One strategy involves the use of DNA to create these groupings. A second involves the use of lithographic patterning tools.

**11:00 AM \*M1.6**

**Perspectives in hierarchically ordered multi-component nanocomposite materials.** Edwin Lorimer Thomas, Michael Rainer Bockstaller, Itzak Tsabba and Edwin Chan; MIT, Cambridge, Massachusetts.

Hierarchically ordered composite materials promise a route towards new high performance materials that capitalize on the physical properties of the periodic microstructure and the sequestered component. In my talk I will review recent approaches that utilize the simultaneous self-organization of block copolymers in the presence of ex-situ synthesized 0, 1 and 2 dimensional nanoparticles in order to engineer hierarchically ordered periodic nanostructures. The effective control of the length scale and the spatial organization of block copolymer morphologies renders these materials particularly attractive as scaffolds that facilitate control of the structural characteristics of the sequestered component. I will discuss the relevant morphological and processing parameters that control the spatial connectivity and orientation of the nanoparticles within the composite as well as the relevance of microstructural characteristics on the consequent optical, mechanical as well as permeability properties of the composite.

**11:30 AM M1.7**

**Aqueous Chemical Growth of Micro-Patterned 3-D Arrays of Metal Oxide-based Nanomaterials.** Lionel Vayssieres, <sup>1</sup>Chemical Sciences Division, Lawrence Berkeley National Lab, Berkeley, California; <sup>2</sup>Materials Chemistry, Uppsala University, Uppsala, Sweden.

The ability to develop non-lithographic techniques to pattern, to assemble, and to integrate nanomaterials as functional 3-D networks is an important challenge scientists have to face to develop functional and practical nanodevices. The fabrication of micro-patterned metal oxide 3-D arrays is possible with the aqueous chemical growth thin film processing technique via a general consideration of the chemical, physical, and structural affinities and interactions of substrates, metal precursors, and synthesis conditions. Our approach to control the overall growth of nanomaterials thin films is to tune their direct aqueous hydrolysis-condensation growth onto substrates by monitoring the interfacial thermodynamics of nanocrystals as well as their kinetics of heteronucleation. This is achieved by minimizing the surface energy at the water/oxide interface according to a general quantitative model based on the Gibbs adsorption equation. Indeed, growing materials at low interfacial tension, i.e. at thermodynamically stable conditions, allows the experimental control of the extension and rate of the nucleation stage and therefore different size, shape, and orientations can be generated onto various chemically-activated substrates. Consequently, the design of novel devices with tailored and engineered three-dimensional patterned architecture can be obtained without template or surfactant. Such ideas will be demonstrated on the design of micro-patterned arrays of nanorods and nanowires of zinc oxide and iron oxide with different orientations as well as on bio-nanocomposites.

**11:45 AM M1.8**

**Silicon Oxide Thickness-dependent Growth of Carbon Nanotubes.** A. Cao<sup>1</sup>, R. Baskaran<sup>2</sup>, K Turner<sup>2</sup>, P. M. Ajayan<sup>1</sup> and G. Ramanath<sup>1</sup>; <sup>1</sup>Materials Science & Engineering, Rensselaer Polytechnic Institute, TROY, New York; <sup>2</sup>Mechanical and Environmental Engineering, University of California at Santa Barbara, Santa Barbara, California.

Recent discovery of site-selective chemical vapor deposition (CVD) growth of aligned carbon nanotubes (CNTs) on SiO<sub>2</sub>/Si patterns makes it possible to create meso-scale CNT-architectures for micro-electronic devices. Here we report that besides the selectivity, CNT length and growth rate depend on the thickness and area of the SiO<sub>2</sub> layer. SiO<sub>2</sub> samples with various thicknesses were prepared by

thermal oxidation of Si wafers at 700 to 850 C for 1 to 3 hrs. CVD was carried out at 800 C on these SiO<sub>2</sub> substrates using a mixture of ferrocene/xylenes as the carbon/catalyst source. The CNT lengths were measured by Field Emission scanning electron microscopy (FESEM). Our results show that the length and growth rate of CNTs are similar when CNTs grow on thicker SiO<sub>2</sub> layers (from 50 nm up to 1 μm), however, the CNT growth rate shows a dramatic decrease as the SiO<sub>2</sub> thickness goes down from 25 nm, until 3.5 nm on which no CNTs grow. Also, we observed that as-grown CNTs of all the SiO<sub>2</sub> samples thicker than 6 nm remain vertical alignment, even for very short CNTs of several microns. We propose a bottom-up growth model for this SiO<sub>2</sub> thickness-dependent growth, which involves carbon incorporation into the Fe catalyst particles at the CNT/SiO<sub>2</sub> interface. For very thin SiO<sub>2</sub> layers, the catalytic activity of Fe particles is weakened due to diffusion interfacial silicide formation. This mechanism is consistent with our observation of decreased CNT growth rate for SiO<sub>2</sub> samples below 25 nm. Based upon this understanding, we grow CNT structures with multiple controllable CNT lengths through a single CVD process by using SiO<sub>2</sub> layers of various thicknesses. Three-dimensional CNT structures created by utilizing SiO<sub>2</sub> thickness-dependent growth are promising candidates for field emitters, functional electronic devices, sensors and actuators.

SESSION M2: Soft Lithography I  
Chair: Younan Xia  
Monday Afternoon, December 1, 2003  
Room 310 (Hynes)

### 1:30 PM M2.1

**Wafer-Scale Fabrication of Micro-Optical Components through Micromolding.** Hartmut Rudmann and Markus Rossi; Heptagon, Zurich, Switzerland.

Micro-optical components are already widely used in one- and two-dimensional diffraction gratings, subwavelength gratings, microlenses, and microprisms. For many high-volume applications micromolding is a cost effective fabrication technology. Double-sided optical modules are replicated by precision micromolding of a UV curable polymer. During the replication process the surface topology of a master is duplicated with a PDMS mold into a thin film of a UV-curable epoxy resin on top of a substrate. The substrate typically consists of a standard glass wafer, a high-precision machined refractive optical element or a wafer of opto-electronic components. The master can be an e-beam written etched silica structure or a laser beam written structure. The thickness and uniformity of the replicated epoxy film can be controlled to a few microns over a surface area of several inches in diameter, thus being comparable to the quality of etched components in fused silica. Double-sided micro-optical components are obtained either by a simultaneous replication process on both sides of the substrate or by processing the two sides subsequently. In both schemes the alignment of front- and backside structures is achieved with an active alignment system as is typically used in semiconductor industry. A 4 inch wafer scale production process has been developed that allows the fabrication of hundreds of thousands of optical components. For this purpose, a proprietary step and repeat process based on UV-embossing is being used to recombine a small area e-beam written structure on a 4 inch sub-master wafer. In the subsequent wafer scale micromolding process this recombined sub-master acts as original. Micro-optical component that were fabricated with this process pass harsh environmental testing such as damp heat or temperature shock tests. Consequently, such micro-optical components are of great interest for telecom and datacom applications.

### 1:45 PM M2.2

**Modified Templates for the Fabrication of Structured Wires and Tubules.** Feng Li<sup>1,2</sup>, Ran Liu<sup>1,2</sup>, Chris McArdle<sup>1</sup>, Andrew Bankston<sup>1</sup>, Lianbin Xu<sup>1,2</sup>, Weilie Zhou<sup>2</sup> and John B. Wiley<sup>1,2</sup>;

<sup>1</sup>Department of Chemistry, University of New Orleans, New Orleans, Louisiana; <sup>2</sup>Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

Template methods are well established for the fabrication of nano- and micron-scale wires, tubules, meshes and sphere arrays. Our group is working to develop methods for altering the topology of templates so as to make wires and tubules with modified structures. Specifically we have developed methods that allow the formation of arrays of wires with structured tips, furrows along the circumference of the wires, and wires with extended pore structures. In this presentation we will highlight processing techniques and discuss the general utility of such methods.

### 2:00 PM \*M2.3

**Some Current Research in Soft Lithography.**

George M. Whitesides, Byron Gates, Justin Jiang, Qiaobing Xu, Chris

Love, Daniel Wolfe and Declan Ryan; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Soft lithography is an alternative to photolithography: it uses printing, molding, and embossing to transfer patterns, rather than imaging with light. It is not competitive with photolithography in applications such as fabrication of microprocessors, but when cost and the ability to pattern non-planar surfaces, to pattern large areas, and to accept a wide range of materials are criteria, then it (or related techniques used in patterning polymers) may be superior. It may also have applications in nanofabrication. This talk will discuss new work in soft lithography in several areas of application, especially bioanalysis and nanofabrication.

### 3:00 PM \*M2.4

**3D Photolithography with a Conformable Phase Mask.**

John Rogers<sup>1</sup>, Seokwoo Jeon<sup>1</sup> and Shu Yang<sup>2</sup>; <sup>1</sup>University of Illinois, Urbana, Illinois; <sup>2</sup>Bell Laboratories, Murray Hill, New Jersey.

This talk describes a form of photolithography that uses soft conformable phase masks to generate three dimensional nanostructures. Ultraviolet laser light that passes through such a mask while it is in intimate contact with a thick layer of resist, generates complex, but well-defined and controllable, three dimensional patterns of intensity. Exposing the resist in this fashion, followed by developing and supercritical drying yields structures with features sizes from microns to nanometers over large areas and through depths of tens of microns. This type of approach provides a simple alternative to existing multiple beam laser interference and colloidal sedimentation routes to photonic crystals and other systems. Using the patterned resist as templates for casting suspensions of silica and other inorganic nanoparticles produces nanostructures in a range of materials that are difficult to pattern directly.

### 3:30 PM \*M2.5

**New Nanopatterning Routes Based on the Controlled Generation of Disorder on Functionalized Solid Surfaces.**

Joanna Aizenberg, Bell Labs/Lucent, Murray Hill, New Jersey.

Fabrication of surfaces with complex patterns and small features are important in fields ranging from cell biology to electronics. One of the methods used for controlling surface properties is the functionalization of a solid substrate with self-assembled monolayers (SAMs). Using methods of conventional or soft lithography, these SAMs can be patterned on a micron scale into ordered regions formed from different molecules. The strategy described here is based on a conceptually new approach – controlled generation of disordered regions in a SAM of a single molecule formed on a substrate micropatterned with different materials – metals or photoresists. The SAM at the transition region between the two metals or the metal and the resist has a distinct and disordered character. The size of the disordered region can be regulated over scales of below 20 nm to microns. We show that the increased reactivity of the surface at the transition region can be used for patterning various area-selective processes, such as wetting, crystallization and fabrication of structures with sub-50-nm features in different materials.

### 4:00 PM M2.6

**Tunable Bio-inspired Microlens Arrays in Environmentally Responsive Hydrogels.** Shu Yang<sup>1</sup>, Joanna Aizenberg<sup>1</sup>, Yong-Jin Han<sup>1</sup>, Gang Chen<sup>1</sup>, Ronen Rapaport<sup>1</sup>, Elsa Reichmanis<sup>1</sup>, Chaitanya Ullal<sup>2</sup> and Edwin L. Thomas<sup>2</sup>; <sup>1</sup>Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; <sup>2</sup>Materials Science and

Engineering, MIT, Boston, Massachusetts.

It has been discovered that light-sensitive brittlestars have microlens arrays with integrated pore structures. The combination of microlenses with pores results in a wide range of tunable parameters, including variable field of view, tunable transmission, and wavelength selectivity. Given its speed and simplicity, holographic lithography offers significant advantages over traditional lithographic processes, and enables us to fabricate porous lens arrays that are analogous to the biological structures. By integration of the microlens arrays in environmentally responsive hydrogels, we demonstrate the dynamical tuning of the lens shape and size, thus directly affecting the focal length and light transmission. Such lens arrays may have potential applications in biosensors and biomolecule screening and detection.

### 4:15 PM M2.7

**Three-dimensional and Multilayer Nanostructures Formed by Nanotransfer Printing.** Jana Zaumseil<sup>1</sup>, Matthew A. Meitl<sup>2</sup>,

Bharat R. Acharya<sup>1</sup>, Julia W.P. Hsu<sup>1</sup>, Yueh-Lin Loo<sup>3</sup> and John A. Rogers<sup>2,1</sup>; <sup>1</sup>Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; <sup>2</sup>Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Illinois; <sup>3</sup>Department of Chemical Engineering, University of Texas, Austin, Texas.

Established methods for nanofabrication (e.g. electron beam lithography, deep UV photolithography) are well suited for building two-dimensional (2D) structures on flat surfaces but lack easy access to complex three-dimensional (3D) structures. Newer techniques based on molding, printing and embossing provide similar patterning capabilities with simple, low cost tools (i.e. molds, stamps and presses) that avoid many limitations of conventional methods. These new techniques can also generate certain types of three-dimensional (3D) structures that can be useful for applications in photonics, microelectromechanical systems and electronics. Here we show how nanotransfer printing (nTP), can be used to build a range of complex 3D structures with feature sizes between tens of microns and tens of nanometers over areas of several square centimeters. 3D nTP uses high-resolution stamps (polydimethylsiloxane - PDMS) coated with thin layers of metal (e.g. gold) as 'ink'. Surface chemical bonding interactions between the substrate (e.g. GaAs with a monolayer of octanedithiol) and the metal enable its efficient transfer from the stamp to the substrate by contact printing. Through careful control of the relief geometry of the stamp and deposition of the metal it is possible to fabricate freestanding three-dimensional structures by transferring continuous metal films. These films can in turn serve as underlying substrates for subsequent printing steps. Using this technique, we have successfully fabricated micro- and nanoscale closed channels, suspended beams and nanochannel stacks over large areas - a task that would have been difficult or impossible with other fabrication methods.

#### 4:30 PM M2.8

**Microsystems Manufacturing via Embossing of Thermally Sacrificial Polymers.** Clifford Lee Henderson<sup>1</sup> and William P. King<sup>2</sup>; <sup>1</sup>School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Substantial recent interest in microelectronics manufacturing has motivated significant work on non-traditional processes such as embossing-based lithography. This work has been generally limited to manufacturing conventional microelectronics and producing two dimensional patterned surfaces and structures. To date, little work has been done to produce microelectromechanical systems (MEMS), which can require the production of complex three-dimensional and possibly free standing structures. This paper reports a novel method for manufacturing three-dimensional microstructures that can be freely standing and/or fully released. The method involves the use of thermally sacrificial polymers, i.e. materials that can be cleanly decomposed to gaseous products upon heating at elevated temperatures. Such sacrificial polymers can be directly embossed and subsequently overcoated with a variety of materials including other polymers, dielectrics, semiconductors, and metals. Following the deposition of the overcoat layer, further processing can be performed on the overcoat layer (e.g. selective etching or deposition of additional materials). Finally, the entire structure is heated to the decomposition temperature of the sacrificial polymer which results in the dry removal of the sacrificial layer, thus releasing the desired structures. This type of sacrificial process eliminates the need for wet processing of the device and thus eliminates stiction problems and the need for supercritical drying steps. The various sacrificial materials that have been investigated are polynorbornenes and polycarbonates, and the overlayer materials are polyimides, silicon oxide, and metals. This paper discusses the various properties of these sacrificial materials, the printing and processing conditions for these materials, and the use of this method for the fabrication of a MEMS based porous membrane and released cantilever beams. This novel manufacturing technique meets the needs of MEMS manufacturing in that it can produce three dimensional and free standing microstructures. It permits the fabrication of devices and systems in only a few process steps that would otherwise be either substantially more complicated or impossible to achieve. This process of coating, embossing, and overcoating can also be repeated to build-up complex multi-layered structures.

#### 4:45 PM M2.9

**Microcontact Wave-Printed Polymer Misfetts.** Jochen Schellekens, Dirk Burdinski, Milan Saalmink, Monique Beenhackers, Gerwin Gelinck and Michel M.J. Decker; Research Laboratories Eindhoven, Royal Philips Electronics, Eindhoven, Netherlands.

MISFET devices based on semiconducting polymer have already been realized with soft lithography, but they were either using an unstructured gate substrate or designed for low resolution alignments. It is, however, desirable to demonstrate that a single technology can offer solutions for all device layers, including registration and alignment. In our work, we microcontact-print electrodes using a novel concept termed "wave-printing", that provides multilayer alignment better than 2 micron over 150 mm wafers. The devices have a so-called 'bottom-gate' design: The layers follow a substrate/gate/insulator/source-drain/semiconductor structure. Gold

was used as the electrode material. The finest features in these devices, i.e. finger width and distance of the source and drain electrodes are formed using microcontact printing. A microstructured rubber stamp (Sylgard 184) impregnated with alkanethiols is brought into contact with the second metal layer using the "wave-printer". The thus transferred self-assembled monolayer then prevents wet-etching of the gold underneath, thereby patterning the layer. We routinely obtained feature sizes (both line and spaces) as small as 1 micron over the whole wafer. After spincoating the organic semiconductor, the devices are ready. We realized MISFETs on 150 mm substrates. Transistors with channel length ranging from 20 to 1 micron have been made and analyzed. Their performance is equal to devices made using standard photolithography, demonstrating that wave-microcontact printing offers a viable route to low-cost manufacturing of organic transistors.

### SESSION M3: Soft Lithography II

Chair: Lionel Vayssieres

Tuesday Morning, December 2, 2003

Room 310 (Hynes)

#### 8:30 AM M3.1

**Fabrication of 3D Titania Nano-Architectures Based on Photolithography and Surface Sol-Gel Process: A Nano Copy Approach.** Shigenori Fujikawa and Toyoki Kunitake; Topochemical Design Lab., The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, Japan.

Fabrication of three dimensional structures in the nanometer regime is a major challenging topic in nanotechnology. Laser photo-fabrication and micro-contact printing have been widely studied for this purpose, but their size resolution still remains in the micrometer range. On the other hand, template synthesis has been successfully applied to preparation of nano-objects such as nano-capsule [1] and nano-tube [2], although the resulting architectures of the nano-object could not be much varied due to the lack of proper templates. We have reported the preparation of 3D-structured ultrathin titania films that are templated by 2D assembly of nano particles on solid substrates [3,4]. The results suggested that other templates should be effective for further designing the shape of the 3D-structured titania film. We, therefore, decided to use more flexible lithographic patterns as templates. A line structure (width: 200-1500 nm, height: 500 nm) of a resist polymer (Tokyo Ohka Kogyo: TDUR-P015PM) was prepared on Si wafer, and was first exposed to oxygen plasma briefly (10W, 10 min). The substrate was then immersed in Ti(O-nBu)/heptane (100 mM, 2 min), heptane (1 min) and water (1 min) in this order. The adsorption process was repeated for given cycles, and the organic moiety was removed by oxygen plasma (30W, 1 hr.). For a 10 cycle sample, a rectangular tube consisting of ultrathin titania (thickness 10 nm) film was obtained. The film thickness is a key factor to maintain 3D structures, and more than 10 nm thickness (10 cycles) are required to preserve the shape of original template. In the case of less than 10 cycles of adsorption, the ratio of width and height in a line structure affects the shape of the 3D structure: wider width gives a drooping structure, and narrow one produces a T-shaped structure. Recently, we have proposed **Nanocopying** as a means of 3D nano fabrication. Nano copying is possible by taking advantage of nano-precision, self-sustaining properties of ultrathin titania layer. We demonstrated here that this approach was effective for fine patterns as created by photolithography. References [1] For example, F. Caruso, *Adv. Mater.*, **2001**, 13, 11 [2] For example, W. Shenton, T. Douglas, M. Young, G. Stubbs and S. Mann, *Adv. Mater.*, **1999**, 11, 253. [3] S. Fujikawa and T. Kunitake, *Chem. Lett.*, **2002**, 11, 1134 [4] S. Fujikawa and T. Kunitake, *Langmuir*, **2003**, Web Release Date: May 6, 2003

#### 8:45 AM M3.2

**Selective surfactant-mediated growth for patterned electronic and magnetic media.** Noshir S. Pesika<sup>1</sup>, Peter C. Searson<sup>2</sup> and Kathleen J. Stebe<sup>1</sup>; <sup>1</sup>Chemical & Biomolecular Eng, Johns Hopkins University, Baltimore, Maryland; <sup>2</sup>Materials Science and Engineering Dept, Johns Hopkins University, Baltimore, Maryland.

A major challenge in patterning surfaces is to develop low cost, highly parallelizable techniques. Here we show that soft lithography and electrodeposition can be combined to create 3-D patterned surfaces of magnetic or non-magnetic metals. Using soft lithography, a pattern of a surfactant can be transferred to form a self-assembled monolayer (SAM) on a conducting surface. Depending on the substrate and SAM, a metal can either be deposited preferentially under the SAM or in the surfactant-free region. This is analogous to positive or negative photoresists in lithography and can be applied to a wide range of systems. For example, for a gold surface patterned with octadecanethiol, silver can be selectively electrodeposited beneath the thiol layer. Conversely, nickel deposits preferentially in the surfactant-free regions. Thus, this technique provides a quick and

simple method to pattern magnetic or non-magnetic metals on lateral length scales determined by the features in the patterned SAM, and of aspect ratios determined by the deposition conditions. One can envision using this technique to create 3-D multilayer structures and interconnects, or arrays of MTJs and GMR devices at the micro and nanoscales. Demonstrations of these applications are shown.

#### 9:00 AM \*M3.3

##### First Steps toward Fabricating TFT LCDs using Microcontact Printing and Electroless Deposition.

Emmanuel Delamar<sup>1</sup>, Matthias Geissler<sup>1</sup>, Heinz Schmid<sup>1</sup>, Heiko Wolf<sup>1</sup>, Bruno Michel<sup>1</sup>, Richard Stutz<sup>1</sup>, Hannes Kind<sup>1</sup>, Patrick Schmidt-Winkel<sup>1</sup>, Alexander Bietsch<sup>1</sup>, James Vichiconti<sup>2</sup>, William S. Graham<sup>2</sup>, Paul A. Andry<sup>2</sup>, John C. Flake<sup>2</sup>, Ronald W. Nunes<sup>2</sup>, Shawn A. Hall<sup>2</sup>, Peter M. Fryer<sup>2</sup>, Eugene J. O'Sullivan<sup>2</sup>, Robert L. Wisniewski<sup>2</sup> and Roy H. Magnuson<sup>3</sup>; <sup>1</sup>IBM Zurich Research Laboratory, Ruschlikon, Switzerland; <sup>2</sup>IBM T.J. Watson Research Center, Yorktown Heights, New York; <sup>3</sup>IBM Endicott, Endicott, New York.

We are exploring how to fabricate the gate metal lines of the thin-film transistor (TFT) array of liquid-crystal displays (LCDs) in an entirely new and potentially cost-effective way. This involves depositing the metal layer of the TFT array using electroless deposition (ELD) and by patterning the gates using microcontact printing ( $\mu$ CP). We set the conditions for ELD and  $\mu$ CP separately on 15-inch display glass substrates before combining them in a number of variants. ELD steps encompass grafting silanes functionalized with amino groups from aqueous solution to glass, binding catalytic Pd/Sn colloids to the derivatized glass, and plating  $\sim 120$  nm of NiB or Cu using well-defined conditions. The gate pattern can be defined by either microcontact printing the silanes or the catalyst on glass (an additive process) or by printing a self-assembling monolayer resist on Cu homogeneously deposited on glass (a subtractive process). The latter variant is particularly attractive for manufacturing high-end displays (15-inch diagonal with a resolution of 200 pixels per inch) due to the conductive characteristics of Cu, the large dimensions (typically  $>1$   $\mu$ m) of gate structures, the use of alkanethiols for the ink, and the capability of wet-etching printed Cu very selectively and with control of the sidewall profile. These patterning strategies were developed parallel to optimizing the chemical composition of poly(dimethylsiloxane) stamps, molding large stamps, developing printing tools, and understanding systematic and nonsystematic distortions so that patterns could be printed with an absolute accuracy of  $\pm 3$   $\mu$ m over 15 inches. We predict that  $\mu$ CP is applicable to the patterning of metals that are electroless-deposited on large substrates, and hope that this work will spur the introduction of novel surface chemistry processes into flat-panel-display fabrication.

#### 9:30 AM \*M3.4

##### Unconventional methods for patterning of nanoparticles and glassy carbon nanopillars.

Hong Yang, Saifur Rahman, Xiaowei Teng and Qijie Guo; Department of Chemical Engineering, University of Rochester, Rochester, New York.

Fabrication that does not require extensive cleaning room process is an important characteristic in the unconventional approach to patterning. Most of such nontraditional methods are not only relatively simple in process, but also applied to various materials beyond photoresist on silicon in order to meet the specific application requirements. Recently there are resurrections in using Langmuir-Blodgett techniques in the fabrication of nanomaterials such as nanoparticles and nanowires, and in the creation of nanostructures based on nanoporous templates. In this talk, I will present our recent work on using anodized porous alumina in the synthesis and patterning of glassy nanopillar arrays with the diameter typically in 30-50 nm range, and in the patterning of monodisperse nanoparticles using Langmuir-Blodgett techniques. The structures have been characterized by field emission scanning electron microscope (SEM), transmission electron microscope (TEM), atomic force microscope (AFM), powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS). The properties and applications of the patterned structures will be discussed.

#### 10:30 AM \*M3.5

##### Nanocontact Printing: A High Resolution Patterning Technique and its Applications.

Wilhelm Huck, Hongwei Li and Guillaume Fichet; University of Cambridge, Cambridge, United Kingdom.

Soft-lithographic techniques have made an enormous impact on sub-100 nm scale patterning because of the relatively low capital investment and the great range of materials that can be used. Nanocontact printing is now capable of printing sub-50 nm features of large molecules. Although the fabrication of stamps in this regions becomes a limiting step, contact printing itself should be able to produce smaller features. Combining a number of approaches relying on self-assembly or self-organization (e.g. phase-separation of block

copolymers) we are trying to establish the smallest chemical patterns that can be fabricated. At the same time, printing chemical features is mostly interesting if such features can be used as a chemistry platform. At the same time, printing chemical features is mostly interesting if such feature can be used as a chemistry platform. The printed patterns consist of dendrimers or proteins and can be used as a scaffold for further modification with gold nanoparticles. Polymer brushes can be grown from patterned surface to amplify the initial pattern to make it more chemically and mechanically robust and introduce useful chemical and physical properties to the surface. These brushes can also carry functional side chains which play an active role in device applications. Our initial results on arylamine-containing brushes in photovoltaic devices show that polymer brushes are fully compatible with devices fabrication. This offers a new level of control over the active components in polymeric devices.

#### 11:00 AM M3.6

##### Fabrication Of Unsymmetrical Colloid Particles By

##### Microcontact Printing Techniques.

Vesselin N. Paunov<sup>1</sup>, Olivier Cayre<sup>1</sup> and Orlin D. Velev<sup>2</sup>; <sup>1</sup>Department of Chemistry, University of Hull, Hull, United Kingdom; <sup>2</sup>Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

We present a novel method for preparation of unsymmetrically coated spherical microparticles based on microcontact printing over latex particle monolayers. In the first part of the talk we describe the fabrication of dipolar colloid particles by 'stamping' of an ionic surfactant monolayer (deposited on an elastomer stamp) over a monolayer of latex particles of opposite charge. These colloid particles are expected to have asymmetric (dipolar) distribution of their surface charge due a charge inversion of a part of the particle surface treated by stamping with surfactant monolayer. Both negatively charged particles stamped with cationic surfactant and positively charged particles stamped with anionic surfactants have been examined. We discuss the effects of salt and external electrical field on the aggregation of such dipolar particles in aqueous suspensions. In the second part of this talk we present results from the microcontact printing of one colloidal monolayer over another monolayer of latex particles of an opposite charge. We demonstrate that when the particle diameters in the two colloid monolayers are comparable this method allows fabrication of doublets and triplets of colloid particles. When the particle monolayer is 'stamped' with another colloid monolayer of much smaller particle size we were able to produce complex structures as half-coated raspberry-like particles. Possible applications of these dipolar colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals, and water-based electrorheological fluids.

#### 11:15 AM M3.7

##### Patterned Conjugated Polymer Ultrathin Films via Soft Lithography.

Qing Wang, Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Conjugated polymers combine the optical and electronic properties of semiconductors with advantages of organic materials such as low cost, easy processing, and great opportunities for structural modification. They are being considered as active components in various types of thin-film organic electronic and optoelectronic devices such as light-emitting diodes, field effect transistors, lasers, solar cells, and chemical and biological sensors. While a major effort has been focused on material synthesis to explore new materials with tailored properties, the realization of polymer based electronics and optoelectronics also depends on developing techniques for processing this new class of materials. A critical element in this emerging technology is the spatial deposition of high definition micron and sub-micron scale features of active materials. We describe here several convenient methods for the generation of patterned conjugated polymer films using self-assembled monolayer (SAM) templates. Reactive SAMs presenting carboxylic anhydrides was patterned by microcontact printing and served as templates for the deposition of amino-substituted poly(phenylene vinylene)s (PPV) from solution in pattern. The PPV can also be directly printed onto the surface with the reactive SAMs to generate patterns. Well-defined PPV micropatterns were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), and fluorescence and optical microscopy. The interaction between polymer thin films and the surface was analyzed by polarized external reflectance spectroscopy (EFTIR) and X-ray photoelectron spectroscopy (XPS). The formation of covalent bonds via amidation renders great stability of the resulting functional patterns.

#### 11:30 AM M3.8

##### Wrinkle Patterns: Combining Mechanics and Chemistry to Generate Controlled Nano-Scale Topography in Polymer Thin Films.

Harold T. Evensen<sup>2</sup>, Shuang Zhao<sup>4</sup>, Sorin Manolache<sup>3</sup>, Ferenc S. Denes<sup>5,3</sup> and Robert W. Carpick<sup>1,4,5</sup>; <sup>1</sup>Engineering Physics, University of Wisconsin - Madison, Madison, Wisconsin;

<sup>2</sup>Engineering Physics, University of Wisconsin - Platteville, Platteville, Wisconsin; <sup>3</sup>Center for Plasma Aided Manufacturing, University of Wisconsin - Madison, Madison, Wisconsin; <sup>4</sup>Materials Science Program, University of Wisconsin - Madison, Madison, Wisconsin; <sup>5</sup>Rheology Research Center, University of Wisconsin - Madison, Madison, Wisconsin; <sup>6</sup>Biological Systems Engineering, University of Wisconsin - Madison, Madison, Wisconsin.

We have used a plasma-mediated cross-linking process to generate patterns on polydimethylsiloxane (PDMS) thin film surfaces. The method is fast, inexpensive, and can be uniformly applied to macroscopically large areas in a single procedure. Exposure of pure spin-coated PDMS to an argon plasma leads to the formation of a siloxane network in the near-surface region, as confirmed by surface spectroscopy measurements. This silica-like surface layer is put into compressive stress when the sample cools after removing it from the plasma chamber due to differential thermal contraction, generating a wrinkling pattern to reduce the stress. The wavelength, amplitude, and pattern characteristics are controlled by modifying the plasma conditions, the initial PDMS film thickness, and the PDMS molecular weight. Atomic force microscopy is used to study the nano-scale topography as a function of these parameters. Comparison to a recent analytic model of the wrinkling of compressively stressed films provides a theoretical framework for the results. We use this model to explore the lower bounds on the pattern dimensions imposed by alternate strain relief mechanisms such as plastic deformation. This work was supported by a gift from the 3M Corporation and by a grant from the University of Wisconsin-Platteville.

**11:45 AM M3.9**

**Improved Anti-adhesive Coating for Nanoimprint Lithography by Co-evaporation of Fluorinated Tri- and Monochlorosilanes.** Sunggook Park<sup>1</sup>, Helmut Schift<sup>1</sup>, Celestino

Padeste<sup>1</sup>, Andreas Scheybal<sup>1</sup>, Thomas Jung<sup>1</sup>, Bernhard Schnyder<sup>2</sup>, Ruediger Koetz<sup>2</sup> and Jens Gobrecht<sup>1</sup>; <sup>1</sup>Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland; <sup>2</sup>Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

For nanoimprint lithography (NIL), an emerging patterning technology based on the molding of resists, it is essential to provide stamps with very good anti-sticking surface properties. Fluorinated trichlorosilanes are used as anti-adhesive layers for silicon stamps due to the covalent anchoring of the molecule on the oxidized silicon surface. They provide in many cases satisfactory results. However, for the future high throughput fabrication the properties have to be further improved. Surfaces with extremely low surface energy need the formation of a dense and fully bound film. In many practical cases, e.g. by using trichlorosilanes, this is not easily achieved, because the silanes have some tendency to polymerize to bulk deposits. We have developed a new route to lower the surface energy of silane coatings by co-evaporation of tri- and monochlorosilanes. The silane coatings are performed in the gas phase at a pressure of 30 mbar and room temperature. The bulk polymerization occurring for trichlorosilane coatings is found to be suppressed upon co-evaporation with a monochlorosilane while the surface coverage remains similar to that of trichlorosilane coated surfaces. As a result, the surface with the co-evaporated silanes shows the surface energy of 11.6 mN/m, which is lower than that of surface coatings with respective tri- and monochlorosilanes. The results corroborate very well with those of friction constants and surface work functions, determined by lateral force microscopy and ultraviolet photoelectron spectroscopy, respectively. This finding is interpreted in terms of chemical binding as measured by x-ray photoelectron spectroscopy. The possibility of using this new coating as an anti-adhesive layer will be discussed on the basis of imprint tests performed with nanostructured silicon stamps. Furthermore, the coating is also applied for the production of high contrast chemical patterns via NIL, as demonstrated by friction force measurement.

SESSION M4: Soft Lithography III  
Chair: Wihlhelm Huck  
Tuesday Afternoon, December 2, 2003  
Room 310 (Hynes)

**1:30 PM M4.1**

**A New Class of Procedures for Fabricating Nanostructures.**

Byron D. Gates, Qiaobing Xu and George M. Whitesides; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Two procedures were developed for fabrication of metal structures with nano-scale lateral dimensions of well-defined width and length. The first method uses a combination of conventional photolithography to define arrays of vertical structures and the application of a shear

force to reposition these structures onto one side face. This is a simple technique for fabricating arrays of nano-scale (in-plane) features that could be electrically addressed. A second method converts a thin metallic film, embedded in a polymer matrix, that is thin along the z-axis into a structure that is thin along the x-axis by sectioning the polymer along the first axis. Our approach provides an effective route to nanoband electrodes with tunable dimensions. The flexibility of these approaches was demonstrated by fabricating isolated nanostructures that were also magnetically addressable.

**1:45 PM M4.2**

**Multicomponent Protein Patterning Based on 2-D Colloidal Assembly.** Junsang Doh<sup>1</sup> and Darrell Irvine<sup>2,3</sup>; <sup>1</sup>Department of

Chemical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Department of Materials Science & Engineering, MIT, Cambridge, Massachusetts; <sup>3</sup>Biological Engineering Division, MIT, Cambridge, Massachusetts.

A new patterning method based on mild aqueous-condition photolithography and 2-D colloidal assembly was developed for the surface assembly of multiple fragile proteins into arrays with control over protein distributions on multiple length scales. In this approach, a photoresist polymer coated on top of polyelectrolyte-coated substrate was used as a template for protein-functionalized colloid assembly. The resist was developed by biological buffer either after brief exposure to UV or during exposure to UV by immersing substrate in buffer, and negatively charged regions 4 to 10  $\mu\text{m}$  in diameter were created on the substrate. Protein functionalized colloids with 200-500 nm diameters were assembled on the exposed regions, followed by removal of the remaining photoresist and 'backfilling' with a second type of protein bearing particles. The photoresist polymer was synthesized by copolymerization of o-nitrobenzyl methacrylate with methyl methacrylate (MMA) and methoxy-poly (ethylene glycol) methacrylate (MPOEM) to tune the surface properties of polymer film. The colloids used for protein assembly on these surfaces were positively charged PMMA nanospheres with various diameters, synthesized either by emulsion polymerization or dispersion polymerization. To improve colloidal stability in the presence of physiological ionic strength buffers and functionality, the surfaces of nanospheres were decorated by functional poly (ethylene glycol), and streptavidin was chemically coupled to the ends of a fraction of these chains. Two different fluorescent protein-coupled nanospheres were used for patterning, and the fidelity of colloid patterning was studied by fluorescent microscopy and scanning electronic microscopy. This patterned surface is being used to study the effect of ligand density and spatial distribution on T cell activation to design devices for adoptive T cell therapy.

**2:00 PM \*M4.3**

**Engineering NanoPatterned Interfaces Between Electrodes and Biological Environments.** M. Mrksich, Department of Chemistry, University of Chicago, Chicago, Illinois.

This presentation will describe strategies to tailor the surface chemistry of electrodes to install selective interactions of the substrate with proteins, virus particles and cells. The surface chemistries are compatible with a range of nanopatterning tools and allow the immobilization of multiple ligands at sub-micron length scales. Applications of patterned substrates include chip-based assays, high throughput screening and model substrates for cell adhesion.

**2:30 PM \*M4.4**

**New Approaches to Patterning via Polymer Stamping and Polymer Transfer Printing.** Youn Sang Kim, Juhyun Park, Hiroaki Tokuhisa and Paula T. Hammond; Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nonlithographic approaches which don't rely on photolithography, such as nano to microscale printing, molding, and templating, will be key to driving these technologies toward application and commercialization. In our research group, we have recently been able to guide different organic systems to different regions of a surface upon adsorption, using electrostatic, hydrogen bonding and hydrophobic interactions as a means of surface recognition. This universal approach is currently being applied to a range of applications, including photovoltaics, biosensors and display devices. Current work is centered on the creation of multiple component systems containing 3, 4 or more different systems at predetermined locations on a surface. These approaches are combined with new 'soft' nanofabrication techniques such as polymer-on-polymer stamping, that allow patterning of polymer monolayers on the nanometer length scale over large areas without lithography to produce surfaces for cellular and protein arrays, colloidal arrays, sensors, and other devices. Multilayer transfer printing methods that allow the direct stamping of a functional organic polymer thin film will be addressed. Finally we will discuss a new method of physically and chemically patterning a broad range of polymer films such as polystyrene, polyvinylpyridine, using a polymer spin transfer

approach that allows the formation of sub-100 nm features in dense or non-dense arrays over large areas. The aspect ratios of physical structures created using this technique approach values of 3 and higher. Examples of this new technique will be presented.

### 3:30 PM M4.5

**Liquid Embossing: All-Printed Fabrication of All- Inorganic Logic Elements And Micro-Electro- Mechanical Systems From Nanoparticle Precursors.** Joseph Jacobson and Eric Wilhelm; Media Lab & Center for Bits and Atoms, MIT, Cambridge, Massachusetts.

Present means of chip fabrication comprising vacuum deposition and photolithographic processes require billions of dollars of infrastructure (fabs) and weeks of fabrication time. As such they operate far from the limits which are in principle possible for achieving the metric of nanoscale fabrication per unit time or per unit cost - a metric we have termed *Fabricational Complexity*. In order to more closely approach the limits of fabrication complexity per unit cost we have developed a process called *Liquid Embossing* for the direct all-printed fabrication of both all-inorganic logic elements and micro-electro-mechanical devices from nanoparticle building blocks. Here we report on recent advances using this approach.

### 4:00 PM M4.6

**Build-up of Multilayered Thin Lines using Sequential Adsorption of Polymers in Microfluidic Channels.** Christophe Lefaux and Patrick T Mather; Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

Evolution and revolution of processing methods for micropatterned circuits for modern information technology are areas of active research and highly varied routes are being pursued toward this end. In the present work, we have developed a process for the creation of multilayered self-assembled thin films with fine z-axis resolution (2-5 nm) and modest x-y resolution (1-10  $\mu\text{m}$ ). Our approach is inspired by a coupling of two well-known techniques: layer-by-layer assembly (LbL) and microcontact printing ( $\mu\text{CP}$ ). However, in our case  $\mu\text{CP}$  is not used classically; i.e., as a stamping method to design point-like islands of polymeric assemblies. Rather, our "stamp" defines a microfluidic network ( $\mu\text{FN}$ ) that guides the multilayer deposition through its microchannels while potentially allowing polymer chain extension prior to adsorption. Here, we report on our promising results regarding the achievement of polymeric multilayer assemblies of poly(styrene sulfonate) and poly(allylamine hydrochloride) with prescribed well-defined patterns. Following microscopic characterization of the  $\mu\text{FN}$ s themselves, atomic force microscopy (AFM) confirmed the formation of well-defined thin lines on a silicon substrate where polyelectrolyte solutions were sequentially flowed through the microfluidic devices. Roughnesses of the localized polymeric multilayer assemblies were found to be comparable to those achieved with a standard quiescent LbL process. The influence of such process variables as flow rate and solution composition will be reported, along with discussion of possible applications for the new process.

### 4:15 PM M4.7

**Novel Roll-to-Roll Metal Patterning on Flexible Substrates for Thin Organic Field Effect Transistor Technology.** Dong-Un Jin<sup>1</sup>, Christos G Takoudis<sup>1</sup>, Jie Zhang<sup>2</sup>, Abhijit Roychowdhuri<sup>2</sup>, Paul W Brazis<sup>2</sup> and Dan Gamota<sup>2</sup>; <sup>1</sup>Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois; <sup>2</sup>Motorola Advanced Technology Center, Motorola, Schaumburg, Illinois.

A simple, low-cost patterning technique suitable for high volume manufacturing of thin film transistors (TFT) is proposed. This method utilizes photolithographic templates on plastic substrates to generate high-resolution metal patterns on a variety of flexible substrates. Templates were fabricated on polyimide (PI) and polyethyleneterephthalate (PET) substrates followed by electroless plating to generate copper patterns. A major advantage of the process comes from simultaneous copper deposition and template dissolution that reduces the effective number of process sequences. High resolution (minimum feature size less than 5 micrometer) has been obtained through this method. Since the initial template determines the process resolution, further reduction of feature sizes may be achieved through optimization of the template formation. The proposed technique can be easily adapted for high volume roll-to-roll fabrication, compatible with organic semiconductors, particularly for solution processible and low-cost applications.

### 4:30 PM M4.8

**Micromolding Polyimide (Kapton) Materials.** Anton C Greenwald<sup>1</sup>, Martin U Pralle<sup>1</sup>, Edward A Johnson<sup>1</sup>, James T Daly<sup>1</sup>, Irina Puscasu<sup>1</sup>, Mark McNeal<sup>1</sup>, Nicholas Moelders<sup>1</sup> and

Eugene F Barasch<sup>2</sup>; <sup>1</sup>Ion Optics, Inc., Waltham, Massachusetts; <sup>2</sup>UC Davis Medical Center, Davis, California.

Previously published micromolding methods fashion a master pattern in a silicon wafer using photolithographic techniques, then fabricate a soft mold of silicone based elastomer that can be used as a mold for polyurathane. Polyurathane was chosen as it is available as a liquid monomer that can be used to fill the mold, then cured by ultraviolet light to a solid polymer. There are no corresponding monomers for polyimide based compounds. When these materials are dissolved in a solvent for pouring into a mold, then heated for curing, gasses evolved from the solvents leave bubbles in the cast solid. We found that solutions containing very low concentrations of solvent, available for spin-coating thick films of polyimide for electronic applications, could be pressed into a mold under pressure. When cured, the low volume of gasses evolved were able to be absorbed into the silicone mold leaving a high quality, bubble-free, patterned rigid polyimide solid. We created flat, rigid polyimide structures up to 70mm diameter for applications to gas electron multipliers and microstrip particle detectors. This application demanded the use of polyimide materials with improved electrical resistance, thermal properties and greater mechanical strength compared to polyurathane. This work was partially funded by the Department of Energy.

### 4:45 PM M4.9

**The Wave-Printer: Towards Large-Area, Multilayer Microcontact-Printing.** Michel M J Decre<sup>1</sup>, Ronald Schneider<sup>2</sup>, Dirk Burdinski<sup>1</sup>, Jochen Schellekens<sup>1</sup>, Milan Saalminck<sup>1</sup> and Rine Dona<sup>2</sup>; <sup>1</sup>Research Laboratories Eindhoven, Royal Philips Electronics, Eindhoven, Netherlands; <sup>2</sup>Center for Industrial Technology, Royal Philips Electronics, Eindhoven, Netherlands.

While microcontact printing has previously been reported for patterning electrodes for semiconducting polymer transistors, an accurate and up-scalable multilayer manufacturing technique for large area printable electronics is still lacking. This is due to the combined difficulties of single layer distortion control, multilayer alignment, contact control and defect management. We analyze some mechanical constraints put on large area microcontact printing, particularly those deriving from low filling ratios where printed features of small size are located far from each other. If the printing pressure exceeds a critical value, the squeezing deformation of recessed regions will lead to unwanted contact with the substrate. We have studied experimentally and numerically the critical squeezing pressure, with good agreement. By comparing critical pressures with the pressures resulting from small variations in stamp or substrate thickness, we conclude that large area microcontact printing must abandon conventional printing approaches. A new printing concept, termed "wave-printing", is described that addresses the discussed mechanical constraints and holds the promise of easy alignment and up-scalability. In "microcontact wave-printing", the microstructured rubber stamp (Sylgard 184) is brought in contact with the substrate using a pneumatic pressure wave, that travels across the substrate to achieve complete printing. Since the pressure applied during printing is lower than 10 kPa, very low filling ratios are achieved without unwanted squeezing contact. We present our prototype microcontact wave-printer and discuss results of multilayer printing on gold. Micron-size features were printed on 150 mm wafers with multilayer alignments better than 2 micron.

SESSION M5: Poster Session I  
Tuesday Evening, December 2, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

### M5.1

**Templated Adsorption of Multilayered Thin Films.** Marianne Terrot<sup>1</sup>, Christine Ortiz<sup>2</sup> and Paula T Hammond<sup>1</sup>; <sup>1</sup>Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Ionic multilayer assembly has become an important technique for the formation of organic polymer films. Such films are of great interest for use as optical waveguides, electrochromic devices, power storage devices, biomaterial coatings, and as platforms for nano-scale electronics, proteomic arrays, and sensors based on molecular recognition. In order to produce the micron sized features required for many such applications, our group has pioneered the technique of in-situ micropatterning of polyelectrolyte multilayer assembly. In this approach, charged polymers adsorb only to specific regions of a surface chemically patterned via micro-contact printing; the surface acts as a molecular template for the adsorption of ionic polymer multilayers. Lateral heterostructures can be created by sequential deposition of polyion multilayers with contrasting selectivities. Our

current work focuses on the expansion of selective deposition capacities by identifying and quantifying new surface-polymer interactions and on the design and development of novel devices assembled by templated adsorption. Both absolute and relative selectivity are studied by comparing the adsorption of a range of polyelectrolyte pairs on unpatterned and patterned surfaces. Since adsorption behavior is strongly influenced by environment, we also seek to identify the conditions (ionic strength, pH, solvent composition, temperature) under which selectivity is optimal. Systems of particular interest include perfluorinated surfaces and polymers and systems which interact through hydrophobic or hydrophilic effects in addition to electrostatic effects. We use chemical force microscopy to quantitatively measure the interaction between a given polyelectrolyte and chemical functionality.

### **M5.2**

#### **Mechanical Studies of Nanoimprint Lithography.**

Graham L. Cross, Barry O'Connell and John B. Pethica; Physics, SFI Trinity Nanoscience, Dublin, Ireland.

Nanoimprint lithography is a high resolution, parallel patterning process where rigid stamps form negative replicas in softened material. So far, there have been few detailed studies of the forces and flow patterns during imprinting. We report here on the detailed mechanics associated with the technique. Stamps formed by focused ion beam milling of blank spherical indenters were pressed into thin polymer films. Deformation was measured during displacement and load controlled imprinting by a temperature controlled nanoindenter above and below the glass transition region of the polymer. Contact geometries corresponding to simple flat punching, lateral squeezing, and recessed cavity filling were investigated. Load-displacement-time data and atomic force microscopy images of the transferred patterns reveal the role of both the elastic and viscous response of the polymer films. The conditions for the creation and dissipation of residual stresses and their role in pattern transfer fidelity for isothermal stamping are shown. The results are compared to contact mechanic models of the stamping process.

### **M5.3**

**Rubber stamp contact charge for nanoparticle arrangements.** isao matsui<sup>1,2</sup>, Naofumi Hiraoka<sup>1,2</sup>, Tazumi Nagasawa<sup>1,2</sup> and Yoshiaki Nakamura<sup>1,2</sup>; <sup>1</sup>Advanced materials & devices laboratory, Toshiba R&D center, kawasaki, Japan; <sup>2</sup>Japan Chemical Innovation Institute, Tokyo.

Nanoparticle arrangements in the micronmeter or sub-micronmeter range on a substrate enable the fabrication of photonic or quantum electronic devices. Many approaches to create nanoparticle arrangements have been performed. Among them, arrangement from the gas phase was studied by use of a sliding contact charge with a stainless-steel needle on a silicon substrate and a line of particles with 100nm width and several millimeters long was obtained[1]. Here we show a rubber stamp contact charging method can attain nanoparticle line arrangements with 100 nm resolutions. We used a silicone rubber as a stamp material instead of a metal needle to obtain both large contact charge density and parallel line arrangements over an entire substrate surface at one time. In order to achieve both high resolution and extended area particle arrangements, we set up the positively charged lines by rubber stamp contact on the negatively pre-charged acrylic resin substrate, since the stamp contact area on the substrate were positively charged. Negatively charged 80 nanometer polystyrene particles from the gas phase were aligned over an area of 16 mm<sup>2</sup> acrylic resin flat plate. Particle line arrangements as narrow as a few particles with 3 micronmeter space to the next line were obtained, where the apparent stamping pressure(contact pressure over whole stamp area, 16mm<sup>2</sup>) was set at about 61 kPa and background surface potential was set at about -500V. The stamping pressure and the intensity of negative background were shown to have crucial effects on the resolution of the nanoparticle arrangements. (This research is financially supported by New Energy and Industrial Technology Development Organization.) [1]Krinke, T.J. et al, Appl. Phys. Lett. 78,3708(2001)

### **M5.4**

**Suspended Carbon Nanotube Shadow Lithography: Incident Evaporation Angle Dependence.** Nitin Chopra<sup>1</sup>, Rodney Andrews<sup>2</sup>, Wentao Xu<sup>3</sup>, Lance Delong<sup>3</sup> and Bruce Jackson Hinds<sup>1</sup>; <sup>1</sup>Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky; <sup>2</sup>Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky; <sup>3</sup>Physics, University of Kentucky, Lexington, Kentucky.

Due to micron scale lengths, carbon nanotubes can be manipulated with current microelectric fabrication techniques yet result in nm-scale line widths. Examples of CNT manipulation include self-assembly or catalytically supported CNT growth in areas defined by sub-micron-scale lithography. One promising geometry is

suspended CNTs attached to the top of photolithographically defined posts. Coupled with a line-of-site deposition, this geometry will result in nm-scale line underneath the CNT. The width of the resulting shadow is a function of CNT diameter, incident evaporation angle and height of CNT above the substrate. Reported here is that CNTs were suspended (200-800nm) over a Si<sub>3</sub>N<sub>4</sub> membrane TEM grid by lithographically defined PMMA lines. Aluminum evaporation was performed at well controlled incident angle by slits. Shadows were directly observed by scanning transmission electron microscopy (STEM). For example, CNTs of ~20nm diameter 500nm above Si<sub>3</sub>N<sub>4</sub> membrane and incident angle of 0.4 degrees resulted in shadows of 8 nm. Simple line of site geometry would predict 14 nm line widths, thus significant surface migration from the momentum of incident metal evaporate is observed. Significantly, this incident angle effect requires relatively large diameter CNTs (5-10nm) to form nm-scale lines. This requirement is necessary since the post height must be greater than post separation for suspended CNT growth. These nm-scale lines can be the basis of precisely controlled self assembly processes that would occur only in nm-scale shadow area.

### **M5.5**

#### **Physical and Chemical Nanostructure Transfer in Polymer Spin Transfer Printing and Soft molding.**

Youn Sang Kim and Paula T Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Extensive efforts have been made since the early 1990s to replace photolithography using soft lithography, imprint lithography and dip-pen lithography techniques; recently, soft molding and capillary force lithography have been added to the list. These processes have progressed rapidly; however, there are still some important limitations and challenges regarding the accomplishment of complex, continuous or non-continuous physical nanostructures at high density and chemical or surface functional nanopatterns on various substrates such as Si or SiO<sub>2</sub> wafers, glass, plastic and other flexible polymer films. Here we present an alternative new, unconventional lithographic technique that creates complex physical or chemically defined nanostructures using an elastomer stamp and a polyelectrolyte as the adhesion promotion layer. We demonstrate the pattern transfer of complex physical nanostructures consisting of a variety of polymers (polystyrene, poly(4-vinyl pyridine) and poly(methyl methacrylate) with both moderate hydrophilic and hydrophobic nature; it is also possible to create alternating chemical functionality or surface properties to achieve hydrophobic and positively charged chemical nanopatterns on various substrates using our technique. With this method, we achieve high aspect ratio features as small as 80 nm over centimeter square areas.

### **M5.6**

#### **Fabrication of Poly (ethylene glycol) Microstructures for Protein and Cell Patterning.**

Kahp Y. Suh<sup>1</sup>, Jiehyun Seong<sup>1</sup>, Ali Khademhosseini<sup>2</sup>, Paul E. Laibinis<sup>1</sup> and Robert Langer<sup>1</sup>; <sup>1</sup>Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Division of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We developed a simple, direct soft lithographic method to fabricate poly (ethylene glycol) (PEG) microstructures. This lithographic method involves a molding process in which a uniform PEG film is molded with a patterned polydimethylsiloxane (PDMS) stamp by means of capillary force. The patterned surfaces created by this method provide excellent resistance toward nonspecific protein and cell adsorption. The patterned substrates consist of two regions: the molded PEG surface that acts as a resistant layer and the exposed substrate surface that promotes protein or cell adsorption. A notable finding here is that the substrate surface can be directly exposed during the molding process due to the ability to control the wetting properties of the polymer on the stamp, which is a key factor to patterning proteins and cells.

### **M5.7**

#### **Fabrication of large area ferromagnetic arrays using nanosphere lithography with size variation control.**

Feodor Ogrin, Shemaiah M. Weekes and Andrew Murray; University of Exeter, Exeter, United Kingdom.

Nanosphere lithography [1] is a simple, but very effective technique, which combines advantages of large area fabrication and relatively small dimension magnetic pattern elements. Fabrication of samples using this method is achieved by depositing a single layer of latex spheres, which form a base matrix for further metal deposition in the spacing between the spheres. After the removal of the spheres a pattern of sub-micron size particles is thus achieved. Commercial availability of nanospheres with diameters in the range of 1µm down to 50 nm makes it possible to vary the size and the pitch of the magnetic elements. So far the major disadvantage of this technique is that the coverage of the spheres always contains dislocations, which



result in agglomerations of particles after metal deposition. To avoid this imperfection we introduced a radically new approach, which makes it possible not only to avoid agglomerations, but also to allow us to precisely control the diameter of the deposited particles. In this paper we present our first results on the fabrication and magnetic characterisation of patterns of Ni nanoparticles with the diameters in the range of 50 - 300 nm. Here we show how the hysteretic properties of torque and magnetisation change with the variation of diameter and height of the magnetic elements. Particular attention is given to the patterns where elements boundaries are within close proximity of each other. The results are analysed in terms of the magnetostatic interactions and compared with those produced by a micromagnetic single domain pattern Monte-Carlo simulation. [1]Y. Xia, B. Gates, Y. Yin, Y. Lu, *Advanced Materials* 2000 12 No10 p693

#### **M5.8**

**Nanopatterning of Chemical Vapor Deposited Diamond Films in Room Temperature Nanoimprint Lithography Using Diamond Molds.** Shuji Kiyohara, Hideaki Takamatsu, Taku Motoishi and Katsumi Mori; Department of Electronics and Computer Science, Tokyo University of Science, Yamaguchi, Onoda, Yamaguchi, Japan.

The nanopatterning technique of diamonds is essential to the fabrication of many electronic and optical devices, and micro-gear and motor made of diamond using micromachins. The nanopatterning of chemical vapor deposited (CVD) diamond films in room temperature nanoimprint lithography (RT-NIL) using a diamond mold was investigated. The diamond mold was fabricated by electron cyclotron resonance (ECR) oxygen plasma with Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> octylate mask in electron beam lithography technology. The optimum drawing and oxygen plasma etching conditions were an electron dose of  $5.4 \times 10^{-4}$  C/cm<sup>2</sup>, a microwave power of 300 W and gas flow rate of 3 sccm, respectively. The diamond mold is longer lifetime than SiO<sub>2</sub>/Si molds using conventional NIL because diamond has many unique properties such as high hardness, high thermal conductivity and low thermal expansion. The use of spin-on-glass (SOG) as RT-imprint (mask) resist material which has resistance to oxygen plasma in order to form an oxide film on surface was proposed. Compared to a conventional NIL process using polymethyl methacrylate (PMMA) which require a thermal cycle of the resist, RT-NIL process using SOG has certain advantages, including short step, high throughput and low cost. The compact imprint apparatus using the driving power of DC coreless motors were developed. The apparatus is 15 cm in width and 25 cm in height and has a 10×10 mm<sup>2</sup> mold mask holder and a 60×60 mm<sup>2</sup> stage. The z-positioning accuracy using a DC coreless motor was obtained resolving power of 1 μm. The z axis of a mold holder and x-y axis wafer stage were controlled by three DC coreless motors from a computer. The peltier component was varied from 0 °C up to 200 °C by heating and cooling stage. The pressure of imprint was measured using load cell. The oxygen plasma etching rate of SOG films first increased with increasing gas flow rate and reached maximum rate at 3 sccm, then decreased gradually with increasing gas flow rate. The etching selectivity (CVD diamond/SOG) of 107 was obtained under the ECR oxygen plasma etching conditions of a microwave power of 300 W and oxygen gas flow rate of 3 sccm. The etching selectivity of SOG film was eight times higher than that of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> octylate film because the etching resistance of SOG was high to oxygen plasma. The imprint depth was 0 μm at pressure up to 0.65 MPa and then increased linearly with increasing imprint pressure at 0.65 MPa or more. The optimum imprint pressure and its depth obtained after 5 min impressing time were 0.8 MPa and 0.5 μm, respectively. The resulting CVD diamond nanopatterns were fabricated a lattice with 500 nm linewidth and 5 μm pitch, and holes with 500 nm diameter and 500 nm pitch.

#### **M5.9**

**Direct Formation of Two- or Three-dimensional Patterned Structures of Silicon Nanocrystals.** Xinfan Huang, Feng Qiao, Xiaowei Wang, Wei Li, Kai Chen and Kunji Chen; Dept of Physics, Nanjing University, Nanjing, China.

The research of fabrication technique of patterned nanostructure with high throughput and the low cost is very important in the nanoelectronics and photoelectronics application. In this paper we report a method of direct formation of two-dimensional (2D) or three-dimensional (3D) patterned structures of silicon nanocrystals (nc-Si). The technique is based on the laser interference crystallization (LIC) in ultra-thin a-Si:H single-layer (< 10 nm) or a-Si:H/a-SiN<sub>x</sub> multilayers. The pattern of phase-modulated KrF excimer pulsed (30 ns) laser beam is generated by using 2D phase-shift grating mask (PSGM) with 2 μm periodicity and 248 nm depth. During the LIC treatment, a sample was placed behind the PSGM. Upon laser irradiation a transient thermal 2D pattern are directly formed on the surface of sample. When the local laser intensity exceeds the crystallization threshold value, the crystallization process occurs within the patterned areas of the initial a-Si:H single-layer or a-Si:H

sublayers. Si nanocrystals are directly formed in the discal regions which are patterned with the same 2D periodicity of 2.0 μm as the PSGM. Each discal region is with the diameter of about 300 nm and the height of about the same as the thickness of a-Si:H single-layer or a-Si:H sublayers. For the multilayer samples, we not only get 2D patterned distribution of nc-Si in a-Si:H sublayers, but also in the growing direction of the sample we get ordered distribution of nc-Si with the same periodicity as that of a-Si:H/a-SiN<sub>x</sub>:H multilayers. The results show that the present method can be used to fabricate required patterned nc-Si films for device applications.

#### **M5.10**

**Nanosphere Lithography of Amorphous III-Nitride-Rare Earth Doped Luminescent Films.** Aurangzeb Khan, Hugh H Richardson, P.Greg van Patten and Martin E. Kordesch; Physics and Astronomy, Ohio University, Athens, OH, Ohio.

Nanosphere lithography (NSL) is an inexpensive, simple to implement, inherently parallel, high-throughput and materials-general nanofabrication technique capable of producing well ordered two-dimensional periodic particle arrays (PPA) of nanoparticles. The NSL has been used to form 2D PPA's of 20-1000 nm in size. While metal films are commonly used for NSL, acceptable results have been achieved with sputter deposited amorphous aluminum nitride films. Rare earth doped III-nitrides may be reactively sputtered from metal targets onto a variety of polymer, glass or ceramic substrates at 300K and below, making the sputter deposition process compatible with NSL. We report the fabrication of luminescent 2D PPA's using Tb and Ho doped amorphous AlN thin films.

#### **M5.11**

**Sub-10 nm Fabrication of Large Area Periodic Nanopillars.** Chiung Wen Kuo and Peilin Chen; IASER, Academia Sinica, Taipei, Taiwan.

Here we present a large-area fabrication technique that is capable of producing size-tunable periodic silicon nanopillar arrays with sub-10 nm resolution. Our approach is to transfer the patterns created by nanosphere lithography into silicon substrates, forming nanopillar arrays and modify the size, shape and height of nanopillar arrays by various etching schemes. In this process, nanosphere lithography has been employed to pattern the monodisperse polystyrene beads into close packed structures. By depositing a thin layer of Cr and subsequently dissolving away the polystyrene beads in dichloromethane solution, periodic Cr arrays can be obtained. Then the substrates are placed in a reactive ion etcher to create periodic silicon nanopillar arrays. By adjusting the etching recipes, it is possible to control the shape, and height of nanopillar arrays. After removing the Cr arrays by dipping in a Cr7 solution for 4 min and dried with nitrogen gas, the remaining silicon nanopillars are the oxidized in an oven purged with oxygen at 800 degree. During this process, silicon oxide is formed on the outside wall of nanopillar, and the thickness of silicon oxide on the nanopillars can be controlled by varying the oxidation time. At the end, the oxide layer on the silicon nanopillars was removed in a BOE solution. Our result indicates that it is possible to systematically reduce the size of nanopillar to smaller than 10nm. The quality of the nanopillar arrays fabrication by our method is good enough for nanoimprint lithography. We have successfully employed nanoimprint lithography to replicate nanoparticles with lateral dimension less than 30nm with a density higher than 10<sup>9</sup> particle/cm<sup>2</sup> over a few square centimeter area.

#### **M5.12**

**Direct Polyelectrolyte Multilayer Transfer Printing of Layer-By-Layer Micropatterned Thin Films from PDMS Stamps to Substrates.** Juhyun Park<sup>1</sup> and Paula T. Hammond<sup>2</sup>;

<sup>1</sup>Materials Science & Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Chemical Engineering, MIT, Cambridge, Massachusetts.

Polyelectrolyte multilayer assembly has created an inexpensive route to the formation of electro-optical, conducting, and luminescent thin films. Recent developments include new functionalities such as electrochromic thin films, photovoltaics, ionically conducting systems, and even biologically functional systems for cell templating and drug delivery. For each of these applications, it is critical to be able to control the 2 and 3 dimensional patterning of these films on substrates at a micron scale. We present a new approach to the patterning of polymer multilayers by the creation of electrostatically assembled multilayers atop a polydimethylsiloxane stamp, and the subsequent direct transfer of the entire nanocomposite thin film to substrates, allowing perfect selectivity on virtually any surface, unlike other conventional approaches. In this process, a polyelectrolyte multilayer is fabricated by the alternating adsorption of a polyanion/polycation pair directly onto the surface of a PDMS stamp. The stamp is then placed onto a substrate which is oppositely charged from the multilayer top surface, and the multilayer is transferred in its entirety to the substrate, resulting in a patterned multilayer thin

film on the substrate over large area at 100% selectivity. The ability to transfer the film directly opens up a number of possibilities to achieve nonlithographic patterns at high resolution, to transfer the thin film to a nearly limitless number of substrates with appropriate surface treatment, and of extending the technique to both multi-component arrays and 3-D structures through multiple sequential transfer, or stamping, steps utilizing films of differing functionality to create complete devices or device components.

#### **M5.13**

##### **A Transient Bioscaffolding Route to Chemically-tailored, Nanoparticle-based Assemblies with Complex 3-D shapes and Fine (Meso-to-nanoscale) Features.** Christopher S. Gaddis<sup>1</sup>,

Junping Zhao<sup>2</sup> and Ken H. Sandhage<sup>1</sup>; <sup>1</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

Nature provides elegant examples of organisms that generate three-dimensional (3-D) structures with complex patterns from the macroscale to the nanoscale. For example, diatoms are single-celled aquatic microorganisms that possess intricate 3-D microshells (called frustules) comprised of amorphous silica nanoparticles. Tens of thousands of diatom species exist, with each species possessing a frustule with a unique shape and/or a unique pattern of fine, mesoscale features (10<sup>2</sup> nm pores, channels, protuberances, etc.). Diatom reproduction under ambient conditions can yield enormous numbers of offspring with similar frustules (e.g., 80 sustained reproductions of a single parent diatom would yield 2<sup>80</sup> = 1.2 trillion trillion, or more than Avogadro's number, of descendent diatoms). Such precise, massively-parallel, and direct generation of 3-D nanoparticle structures has yet to be equaled with man-made processes. However, although diatom frustules may possess shapes and fine features appropriate for micro/nanodevices, the use of such natural frustules is limited by the properties of amorphous silica. This chemical limitation has recently been overcome by using diatom frustules as *transient bioscaffolds*. In this paper, diatom frustules have been coated with precursor-bearing solutions (i.e., precursors to polymers, oxides, or carbides). The coatings have been converted into desired materials by evaporation of a solvent, curing, and/or firing. Removal of the underlying silica (e.g., by selective dissolution) then leaves freestanding, chemically-tailored structures that retain the shapes and fine features of the original bioscaffolds. Such a transient bioscaffolding approach has been used to convert capsule-shaped frustules of *Aulacoseira* diatoms into silicon carbide, zirconia, and epoxy microcapsules. By coupling the attractive characteristics of biology (precise, genetically-directed, and massively-parallel generation of 3-D nanoparticle structures) with those of synthetic solution-based processing (low-temperature syntheses of a wide range of ceramic, polymeric, or metallic compositions), this hybrid (biogenic/synthetic) process can yield micro/nanostructures with 3-D shapes and tailored chemistries for a host of applications.

#### **M5.14**

##### **Directing the Self-Assembly of Nanoscale Polymeric Templates.** Seth B. Darling<sup>1</sup>, Deepak Sundrani<sup>2</sup> and S J Sibener<sup>2</sup>;

<sup>1</sup>Materials Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois.

Ultrathin diblock copolymer films have been offered as promising candidates for bottom-up type templates in nanotechnological applications. Their natural tendency to self-organize into laterally alternating domains with a length scale tunable in the range of 10-100 nm is fundamental to their potential in this arena. However, having arbitrary control over the orientation of these domains is equally crucial and, until now, largely unrealized. We will present a novel lithographically assisted self-assembly approach that leads to low defect density domains of mesoscopic dimensions spanning 0.2-2  $\mu\text{m}$  in width, 100  $\mu\text{m}$  in length, and with nanoscopic features down to 20 nm. Square wave gratings are constructed using an electron beam writing process and polystyrene-block-polyethylenepropylene (PS-*b*-PEP) thin films are cast on the gratings and annealed to obtain the desired effect. This technique merges the innate tendency of PS-*b*-PEP to microphase separate and the anisotropic confinement of the grating channels to produce nearly perfect alignment. Potential applications extend from fundamental polymer science to sensor technology, electronics/spintronics, optics, and catalysis. Funding is acknowledged from the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research, the NSF-MRSEC at the University of Chicago, and the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences.

#### **M5.15**

**Novel Nanostructured Carbons through Pyrolysis of Well-Defined Block Copolymers of Polyacrylonitrile.** Shijun Jia, Krzysztof Matyjaszewski and Tomasz Kowalewski; Department of

Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Carbon materials prepared by pyrolysis of organic precursors play an important role in many areas of chemistry and chemical engineering, such as separation processes, electrochemistry, catalysis, energy storage/conversion devices, etc. Well-defined carbon nanostructures have been receiving particular attention since the discovery of fullerenes, followed by carbon nanotubes. Numerous envisioned applications of nanostructured carbons include nanocomposites, gas storage media (in particular hydrogen storage for fuel cells), catalyst supports, and proximal probes. This presentation will describe our recently developed approach to the fabrication of well-defined nanostructured carbons, which is based on controlled pyrolysis of self-organizing condensed phase precursors, such as well-defined block copolymers containing polyacrylonitrile (PAN) [*J. Am. Chem. Soc.* **2002**, *124*, 10632]. Self-organization of PAN blocks, which serve as carbon precursors, is facilitated by their covalent coupling to another linear polymer (auxiliary block), with which they are immiscible. Immiscibility between the blocks leads to the nanoscale phase separation and to the formation of a range of morphologies, dictated by the extent of immiscibility between the blocks and by their relative volume fractions. Following the covalent stabilization of PAN nanostructure through heating in air to  $\sim 230^\circ\text{C}$ , the copolymer is then pyrolyzed by heating under nitrogen atmosphere. PAN domains are converted into the nanostructured carbon, whereas the auxiliary block, which facilitated the formation of the desired nanoscale morphology, is "sacrificed" during pyrolysis. "Classical" morphologies observed in di-block copolymers, range (in the order of increase of the minority phase content) from dispersed spheres, through cylinders to lamellae. Formation of nanostructured carbons exhibiting all these morphologies and derived from block copolymers of PAN will be demonstrated. Some applications of these novel materials will be also discussed.

#### **M5.16**

**Self-Assembly of Two Different Types of Nanoparticles Utilizing Bimodal Mixtures of Diblock Copolymer Micelles.** Byeong-Hyeok Sohn, Seong Il Yoo, Sang-Hyun Yun, Jeong-Min Choi, Dae-Ho Park and Hae-Woong Park; Materials Science and Engineering, POSTECH, Pohang, Kyungbuk, South Korea.

Diblock copolymers composed of two different polymers covalently linked spontaneously self-assemble into structures on the tens of nanometer length scale, whether in bulk or in a solution. In a selective solvent for one of the blocks, nanometer-sized micelles consisting of a soluble corona and an insoluble core are formed above the critical micelle concentration. These micelles can be coated onto substrates by spin coating to form a self-assembled nanostructure in short-range hexagonal order. Moreover, from a mixture solution of diblock copolymer micelles having a bimodal size distribution, we were able to produce an ordered self-assembly of bimodal micelles, in which hexagonally ordered large micelles were surrounded by small micelles. We utilized the bimodal self-assembly of micelles as a structured template for various nanoparticles. For example, we synthesized iron oxide nanoparticles in the core of large micelles and zinc oxide nanoparticles in the core of small micelles, resulting in a mosaic nanopattern of two different kinds of nanoparticles having magnetic and optical functions. Thus, the methodology based on a bimodal mixture of diblock copolymer micelles can be applicable to various pairs of nanoparticles to generate multifunctional arrays with functional building blocks.

#### **M5.17**

**Synthesis and Characterization of Periodic Metal Sphere Arrays.** Lianbin Xu<sup>1,2</sup>, Le Duc Tung<sup>2</sup>, Leonard Spinu<sup>2</sup>, Anvar A Zakhidov<sup>3</sup>, Ray H Baughman<sup>3</sup> and John B. Wiley<sup>1,2</sup>; <sup>1</sup>Department of Chemistry, University of New Orleans, New Orleans, Louisiana; <sup>2</sup>Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana; <sup>3</sup>NanoTech Institute, University of Texas at Dallas, Richardson, Texas.

Three-dimensionally periodic metal sphere arrays were synthesized using a combination of self-assembly and multiple templating methods employing polymerization and electrodeposition. A three-dimensionally periodic poly(methyl methacrylate) (PMMA) mesh was prepared by templating a silica colloidal crystal (opal). After removal of the silica spheres, silica were infiltrated into the void space of the PMMA mesh by electrodeposition. Subsequent removal of the PMMA mesh with organic solvent produced periodic arrays of metal spheres. Details on the preparation and characterization of these materials are presented including electron microscopy, X-ray diffraction and magnetic studies.

#### **M5.18**

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

Raymond R. Unocic<sup>2</sup>, Frank M. Zalar<sup>2</sup> and Kenneth H. Sandhage<sup>1</sup>;  
<sup>1</sup>Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

Appreciable global effort is underway to develop new micro/nanodevices for aerospace, biomedical, telecommunications, and environmental applications. Nonetheless, commercial microfabrication has been largely focused on layer-by-layer (2-D) techniques that are not well-suited for the cost-effective mass production of complex-shaped 3-D devices with submicron features. Nature, however, provides numerous examples of organisms that directly synthesize 3-D structures with meso-to-nanoscale features. Among the most striking examples are the microshells (frustules) of diatoms (single-celled algae). Each diatom species assembles a uniquely-shaped 3-D frustule, comprised of silica nanoparticles, that is decorated with mesoscale pores, channels, or other features arranged in intricate patterns. Given that the number of extant diatom species is 104-105, a dazzling variety of frustule morphologies can be found in nature. The rapid replication of diatoms (via a 2n geometric series) under ambient conditions enables enormous numbers of identical 3-D frustules to be formed. However, the use of diatom frustules as micro/nanocomponents has been limited by the properties of silica. To expand the range of applications, a novel method has been invented to change the frustule chemistry while preserving the frustule morphology: the BaSIC (Bioclastic and Shape Preserving Inorganic Conversion) process. Such shape-preserving conversion has been accomplished with the following types of gas/solid displacement reactions: Oxidation-reduction:  $2\text{Mg}(\text{g}) + \text{SiO}_2(\text{s}) \Rightarrow 2\text{MgO}(\text{s}) + \{\text{Si}\}$  Metathetic:  $2\text{TiOF}_2(\text{g}) + \text{SiO}_2(\text{s}) \Rightarrow 2\text{TiO}_2(\text{s}) + \text{SiF}_4(\text{g})$  where  $\{\text{Si}\}$  refers to a Si-Mg liquid that migrates away from the converted structure. The micro/nanostructures of such converted frustules have been examined by electron microscopy (SEM, TEM). Focused ion-beam milling has also been used to provide 3-D views of internal structures of starting and converted frustules. The influence of reaction parameters on shape preservation will be discussed. The BaSIC process is an enabling technology for the syntheses of a wide variety of patterned 3-D micro/nanocomponents with tailored chemistries.

#### M5.19

**Nanoparticle Assemblies by Fluid Evaporation on Patterned Surfaces to Create Patterned Media.** Fengqiu Fan and Kathleen J. Stebe; Dept. of Chemical and biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

Evaporating fluid films can be used as vehicles to organize nanoparticles suspended within them. When fluid layers evaporate on substrates of patterned wetting, dewetting and contact line pinning can create complex fluid geometries and flow fields within the films. Together, these effects can be used to direct the spontaneous formation of nanoparticle deposition patterns with complex geometries. Here, we create surfaces with patterned wettability in nanometer or micrometer scales using soft lithography. Thin aqueous films containing suspended particles were deposited and evaporated on these substrates. Particle distributions left as residue on the surfaces were studied by SEM and optical microscopy. High resolution arrays of particles were obtained with a variety of features depending upon the relative size of the wetting regions and the particles. When the wetting region is larger than the particles, 3-D arrays and 2-D arrays of ordered particles mimicking the shape of the wetting pattern form, depending on the particle volume fraction. When the wetting region and particle diameters are similar, 1-D arrays along the wet/de-wet boundaries, or 0-D distributions of single particles centered in the wet regions form. When the wetting region is smaller than the particle size, the particle distribution is not influenced by the underlying wetting pattern, and 'coffee ring' distributions form. These results indicate that wetting patterns provide a highly parallelizable means of tailoring the geometry of particle distributions to create patterned media.

#### M5.20

**Swollen Polymers for the Patterning of Inorganic Microstructures.** Daniel Brennan, Paul Sideris and Scott R. J. Oliver; Department of Chemistry, SUNY at Binghamton, Binghamton, New York.

We report here our approach of using swollen polymer matrices as a sacrificial template for highly ordered inorganic materials. While other groups grow metal oxides on polymeric supports, we synthesize metal oxide morphologies within the voids of a solvent-swelled polymer. The procedure involves infiltration of a polymeric support with metal alkoxide, which causes the polymer to swell. The liquid alkoxide creates channels in the polymer as it swells. These voids act to pattern the metal oxide that forms upon initiation of the condensation polymerization of the oxide precursor. The result is a replica of the internal void space of the swollen polymer. The swollen polymer

template can be tuned, for example, through extent of cross-linking in the polymer. Removal of the template is accomplished by thermal or chemical degradation. This nontraditional approach to inorganic pattern formation could lead to new materials applications in catalysis, separation, and semiconductor components of voltaic cells.

#### M5.21

**Abstract Withdrawn**

#### M5.22

**Photochemical-Functional Photonic Crystals Prepared Using A Two-Dimensional Array-Based Template.**

Sachiko Matsushita<sup>1</sup>, Nobuko Fukuda<sup>1</sup> and Masatsugu Shimomura<sup>1,2</sup>;  
<sup>1</sup>Dissipative-Hierarchy Structures Laboratory, RIKEN Frontier Research System, Wako, Saitama, Japan; <sup>2</sup>Nanotechnology Research Center, Hokkaido University, Sapporo, Hokkaido, Japan.

Photonic crystal has gathering much attention since it is a new idea to control photons. Among many preparation methods of photonic crystals, inverse-opal structure, which is a mold of self-assembled particles, became very popular recently because the inverse-opal structure can be fabricated in an easy way, and can be composed of many functional materials. This presentation show that the inverse-opal type photonic crystal composed of TiO<sub>2</sub> anatase type is not only interesting from point of view of photonic crystal, but also from point of view of a photoelectrode. As a particle-assembled structure, two-dimensional (2D) fine-particle arrays, in which fine particles are assembled by means of lateral capillary force and surface tension in liquid thin film, was selected: They can prepare in a short time, their film thickness is controllable, and many functional materials can process to photonic crystal. Monolayers of polystyrene 2D fine-particle arrays were prepared on hydrophilic ITO substrates. These arrays were put into a heater. Partially connecting 2D particle array was used as a working electrode, and a Pt sheet was used as a counter electrode. These electrodes were put in TiO<sub>2</sub> aqua sol. 2D particle arrays after the electrophoresis deposition were put in an electric oven for sintering process. The resulting material have red iridescent colour. This TiO<sub>2</sub> periodic structure was used as a photoelectrode, and the photoelectrochemical property was examined by means of electrochemical system. The relationship of the structure and photochemical properties would be presented.

#### M5.23

**Porous Layers Formed by Silica Nanoparticles Using Emulsion Templating with Microchannel Emulsification Method.** Qingyi Xu<sup>1</sup>, Mitsutoshi Nakajima<sup>1</sup> and Bernie P Binks<sup>2</sup>;

<sup>1</sup>Food Engineering, National Food Research Institute, Tsukuba, Ibaraki, Japan; <sup>2</sup>Chemistry, University of Hull, Hull, United Kingdom.

The possibility of tailoring the size and modifying the surface chemistry of nanoparticles synthesized from a wide variety of materials enables the development of new structured materials with desired functionalities. Highly porous materials formed by self-assembly of nanoparticles possess higher surface area and greater mechanical strength and thus have strong potentials for broad applications in drug delivery, sensors, separation and catalysis. Emulsion templating has been proven to be an effective way to create porous layers formed by nanoparticles. However, conventional emulsion preparation methods such as mechanical agitation usually result in wide droplet size distributions, thus making them difficult to be used as ideal templates for producing porous structures with uniform layer thickness and pore size. Microchannel emulsification method is a moderate method for preparing emulsions with narrow droplet size distributions, providing a way to produce porous materials with uniform structures. We report here on the preparation of porous interfacial layers formed by the aggregates of hydrophilic silica nanoparticles using oil-in-water emulsion templating in a cross-flow type microchannel emulsification device. The detailed preparation and characterization of the interfacial layers will be presented.

#### M5.24

**Preparation and Characterization of Carbonaceous Nanomaterials from Pyrolysis of well-defined Nanostructured Precursor-Polyacrylonitrile.** Shijun Jia, Krzysztof Matyjaszewski and Tomasz\* Kowalewski; Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania.

This communication presents an approach to the synthesis of novel nanostructured carbons, which is based on the self-assembly of polyacrylonitrile (PAN, carbon precursor) and poly(n-butyl acrylate) (PBA, sacrificial phase) diblock copolymers followed by thermal stabilization and subsequent carbonization. It is focused on the evolution of morphology and structure of these materials upon thermal treatment as followed by tapping mode atomic force microscopy (AFM), Raman spectroscopy and thermogravimetric analysis (TGA). AFM revealed that in thin films cast from solution, two block copolymers, with volume fractions of PAN equal to 0.06 and

0.38, displayed typical well-defined nanoscale spherical and lamellar morphologies. Visualization of nanoscale morphology of materials was facilitated by the difference in compliance between low- $T_g$ , soft matrix (PBA) and rigid PAN inclusions, as indicated by the disappearance of contrast when imaging was carried out at set-points close to unity ("light tapping"). The samples were then thermally stabilized by heating in air to 230 °C (this step is necessary) for the preservation of original morphology [*J. Am. Chem. Soc.*, **2002**, *124*, 10632] and subjected to further thermal treatment under nitrogen. TGA measurement showed that main weight loss of the samples occurred in the temperature range between 300 and 450 °C, with the samples losing, respectively 60 and 80 wt% of their original weights. This weight loss corresponded primarily to the thermal decomposition of PBA, which serves in this system as a sacrificial block. Raman spectra showed the gradual evolution of two characteristic bands: D-band, centered at  $\sim 1380\text{ cm}^{-1}$ , corresponding to disordered species and G-band centered at  $\sim 1600\text{ cm}^{-1}$ , corresponding to graphitic structures. The D-band reached its maximum intensity below 500 °C, whereas the relative intensity of the G-band kept increasing with the increase of pyrolysis temperature, indicating the progressive graphitization of material. At all stages, AFM imaging showed the preservation of gross features of surface morphology, defined by the spatial arrangement of PAN phase, turning into increasingly graphitic nanostructured carbon. For samples treated somewhere above 300 °C, the nanostructure could be visualized across the whole set-point range, consistently with the disappearance of soft, sacrificial phase. The degree to which the surface morphology of pyrolyzed materials corresponded to the original PAN morphology depended on the nature of the samples (thick *vs.* ultra-thin films). In thick films, domain spacing decreased to some extent with the increase of pyrolysis temperature, pointing to the partial collapse of the nanostructure necessitated by the mass loss. In contrast, domain spacing was well preserved in ultra-thin films, in which precursor domains remained pinned to the substrate.

#### **M5.25**

**Development of Self-Assembled Patterns in Films of Immiscible Polymer Blends.** Tong Liu, Rahmi Ozisik and Richard W. Siegel; Materials Science and Engineering Department and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Self-assembled patterns of nanometer to micrometer scale were observed in films of immiscible polyetherimide (PEI) and polycaprolactone (PCL) blends. The films were prepared by spin-coating from a common solvent of the two polymers. Phase separation was observed during the spin coating process, which lead to the formation of the self-assembled patterns. The phase separation process is affected by many factors, such as composition of the polymer blend, solvent, polymer concentration in the solvent, substrate, and spin-coating process parameters. We studied the formation of the self-assembled patterns and the influences of polymer composition and spin-coating process parameters on the phase morphology of the films. Different phase morphologies were observed by changing the relative composition of the polymer blend and spin-coating parameters. The formation of self-assembled patterns was governed by different interactions between the two polymers and the substrate, and the difference in the solubility of the two polymers in their common solvent. In addition, the phase separation process was found to be far from thermodynamic equilibrium. A rather long-lived metastable structure was obtained by annealing depending on the phase morphology.

#### **M5.26**

**Template Synthesis of Submicron Nickel Tubes Using Recyclable Organic Molecular Assemblages.** Daisuke Ishii, Masaru Nakagawa, Ken-ichi Aoki, Takahiro Seki and Tomokazu Iyoda; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

We describe here a novel template-synthesis method to prepare nickel tubes possessing a submicron pore using recyclable organic molecular assemblages formed from amphoteric azopyridine carboxylic acids. The amphoteric azopyridine carboxylic acids having a pyridyl group as a hydrogen acceptor and a carboxy group as a hydrogen donor located at each molecular terminal were dissolved in an alkaline aqueous solution due to cleavage of intermolecular hydrogen bonds. Neutralization of the aqueous solution by acidic substance caused the formation of supramolecular assemblages with fibrous morphologies resulting from intermolecular hydrogen bond reformation. Nickel tubular materials were successfully obtained by catalization with an aqueous PdCl<sub>2</sub> solution, nickel electroless plating, and dissolution of the supramolecular template with an alkaline aqueous solution. It was found that the amphoteric azopyridine carboxylic acids were collected readily from the filtrate solution by re-neutralization in yields of 60 - 87 %. In general, tubular metal materials are fabricated by burning metal coated hybrid materials to remove organic templates such as

surfactant-forming micells and electrospinning polymers. Our template-synthesis method has several advantages from industrial and environmental standpoints. First, the organic fibrous template is recyclable because the molecular assembly and disassembly are based on the formation and cleavage of non-covalent hydrogen bonds in aqueous media. Secondly, the organized morphology of the template fiber is hardly affected during successive processes of electroless plating, compared with fluidic rod-like micells formed from surfactants. Thirdly, the morphology of the supramolecular template may be controlled by choice of chemical structure of azopyridine carboxylic acids so that the inner diameter of nickel tubes is tunable in the range of 100 nm to a few  $\mu\text{m}$ .

#### **M5.27**

**Selective Particle Adsorption and Metallization on a Photodegradable Cationic Monolayer.** Nozomi Nawa, Masaru Nakagawa, Takahiro Seki and Tomokazu Iyoda; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Well-defined surfaces at a molecular level to promote or resist adsorption of tiny functional materials from nano to micro meter size have been required increasingly as nanotechnology has progressed. Patterned monomolecular layers to control such surface properties are fabricated mainly by photolithography, soft lithography (micro contact printing), and scanning probe microscope lithography. Among these methods, photolithography is underutilized due to complicated chemical synthesis of layer-forming molecules, organic solvent usage, and limitation on combinations between a layer-forming molecule and a substrate. More sophisticated materials for monolayer photolithography matched to industrial and environmental standpoints should be developed. Here, we demonstrate a novel method to prepare adsorption templates for colloidal particle patterning and selective metallization on silica and poly(ethylene terephthalate) (PET) substrate surfaces by convenient photolithography of an adsorbed monolayer formed from a new photodegradable multivalent cation. A decaphenylcyclopentasilane derivative with plural quaternary pyridinium units as multipoint adsorption sites formed a monolayered film exhibiting desorption-resistance for deionized water on negatively charged SiO<sub>2</sub> and polymer PET surfaces. UV-light exposure caused fragmentation of the cationic adsorbate and reduced the desorption-resistance leading to fabrication of a photopatterned monolayer. Both the adsorbed monolayer fabrication and the pattern formation after imagewise UV-exposure could be carried out in environmentally benign aqueous media. It was found that the positive zeta potential value exhibited by the photodegradable cationic monolayer turned to a negative zeta potential value by the UV-exposure due to removal of the cationic adsorbate from the negatively charged substrate surface. The substrate surface possessing surface-charge photopatterns worked as adsorption templates for site-selective assembly of colloidal tiny materials charged in either positive or negative sign. Colloidal polymer particles of submicron size in diameter were adsorbed selectively on the patterned surface through electrostatic attraction and repulsion. To apply this principal, we noticed a metal particle working as a catalyst in electroless plating. We could fabricate electric circuit boards based on site-selective Ni deposition in accordance with the latent monolayer photopattern.

#### **M5.28**

**A New Application of Atomic Hydrogen for Fabrication of Highly Aligned Nano-Hole and Trench Structures on GaAs (001).** Jong Su Kim, Mitsuo Kawabe and Nobuyuki Koguchi; Nanodevice Group, National Institute for Materials Science, Tsukuba, Japan.

Atomic hydrogen is very interesting element in semiconductors because it is able to be applied to surface cleaning, band gap tuning, hydrogenation, wafer bonding, hydrogen-assisted crystal growing, and passivation in semiconductor processes. For the last two decades, many researchers have confirmed the atomic hydrogen induces surface cleaning to get a high quality and atomically flat surface. Recently, there have been many proposals for nano-structures in device applications and physical models, such as quantum coupling, quantum dot cellular automata, and quantum computation. In particular, for the application of the quantum devices, it is necessary to fabricate site-controlled and highly aligned artificial nano-structures. Many research works for the fabrication of site-controlled nano-structures by artificial techniques have been reported by using electron-beam lithograph, scanning tunneling microscope (STM) tip-assisted patterning, and atomic force microscope (AFM) tip-induced oxide patterning. A number of works demonstrated that an AFM could be used for the oxidation on semiconductors and metal films. In this present work, in order to achieve highly aligned nano-hole and trench structures with atomically flat surface, we combined well-defined AFM tip-induced oxidation and oxide-removal on GaAs (001) by atomic hydrogen cleaning. Highly aligned oxide dot and line structures at the nano-meter scale were patterned by using AFM tip-induced oxidation.

Then, the oxide structures and surface oxides were removed by using atomic hydrogen. Finally, nano-hole and trench structures with atomically flat surface were successfully achieved. The smallest hole diameter obtained in the present work was 13.4 nm with the depth of 0.47 nm. We believe that these hole and trench structures will be also applied to highly aligned quantum dots and wire deposition for quantum dot devices and future applications.

#### **M5.29**

**Hydrothermal Synthesis of Patterned Thin Films of Barium Titanate Ceramic Nano-Tubes at 200 C.** Xuezheng Wei and Nitin P Padture; Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut.

A novel, low-temperature synthesis method for producing BaTiO<sub>3</sub> thin films patterned in the form of nano-tubes ("honeycomb") on Ti substrates is reported. In this two-step method, the Ti substrate is first anodized to produce a surface layer (~200-300 nm thickness) of amorphous titanium oxide nano-tube (~100 nm diameter) arrays. In the second step, the anodized substrate is subjected to hydrothermal treatment in aqueous Ba(OH)<sub>2</sub>, where the nano-tube arrays serve as templates for their hydrothermal conversion to polycrystalline BaTiO<sub>3</sub> nano-tubes. This opens the possibility of tailoring the nano-tube arrays, and of using various precursor solutions and their combinations in the hydrothermal bath, to produce ordered, patterned thin-film structures of various Ti-containing ceramics. These could find use not only in a variety of electronic-device applications but also biomedical applications, where patterned thin films are also desirable.

SESSION M6: SPM-Based Nanolithography  
Chair: Jie Liu  
Wednesday Morning, December 3, 2003  
Room 310 (Hynes)

#### **8:30 AM M6.1**

**Dip-pen Nanolithography with Poly(diallyldimethylammonium chloride).** Bumsu Kim, Georgios Pyrgiotakis and Wolfgang M Sigmund; Materials Science & Engineering, University of Florida, Gainesville, Florida.

Nano-scale manipulation has been intensively researched in order for fabrication to facilitate the size-shrinkage of microelectronic devices. Scanning probe microscope (SPM) nanolithography has attracted much attention because of its ability to fabricate precise nanometer-size structures on the surface. The mechanical force or electric field induced by tips has been utilized in SPM nanolithography techniques for decades. Dip-pen nanolithography (DPN) has been a promising tool since Mirkin et al.'s invention. Here, we report DPN with poly(diallyldimethylammonium chloride) (PDAC). The high molecular weight cationic polyelectrolyte PDAC was used as an ink for DPN. Patterns were generated on the bare silicon wafers directly with PDAC coated tips. The widths and heights of lines increased with decreasing scan rates. At the same scan rate, the widths and the heights of patterning decreased with increasing the molecular weight of PDAC. The dependence of line width on inverse writing speed is consistent with a modified mathematical diffusion model.  $w \approx (4G_1 l_0 / v)^{rac{13}} G = 4\pi r D C_0 / \rho$  where  $\rho$  is the monolayer surface density of PDAC,  $r$  is a radius on the PDAC surface around the AFM tip,  $D$  is the diffusion constant,  $w$  is the line width,  $v$  is the writing speed of the AFM probe during patterning,  $l_0$  is the distance that an AFM tip travels and  $C_0$  is the concentration of PDAC. Although PDAC has a broad distribution of molecular weight, results are a satisfactory fit of the modified model. The ratio of the diffusion constants can be calculated by the equation by the following equation,  $D_1/D_2 \approx G_1/G_2 (R_{G1}/R_{G2})^2$  where  $R_G$  is the radius of gyration. This value will be used to calculate the ratio of diffusion constants of polyelectrolytes with different molecular weights. It is suggested that both the diffusion constant and surface density with different molecular weights are critical factors to control the feature size of patterning.

#### **8:45 AM M6.2**

**Miniaturized electronic noses.** Ming Su and Vinayak P Dravid; Department of Materials Science and Engineering, Institute for Nanotechnology Northwestern University, Evanston, Illinois.

Portable sensor arrays with gas recognition ability are important for the on-site detection of hazardous gases. The advent of nanomaterials and the means to pattern them at smaller length scale have paved the way for the construction of miniaturized sensor arrays. Although nanoparticle film, nanowire or nanotube and mesoporous materials have been explored as sensor materials, the corresponding construction methods lack the required ability in position control, multiple species patterning, which prevent the real sensor application of nanomaterials. We have used dip-pen nanolithography (DPN) to

pattern different semiconductive metal oxide nanostructures between electrodes using sol ink for the construction of miniaturized semiconductor chemical sensors by exploiting the capabilities of DPN in site-specific and multiple ink patterning, and the versatility of sol-gel synthesis to prepare appropriate sol inks. The method allows the construction of fast response and rapid recovery sensors and a combinatorial array in search for good sensor materials. It also paves the way for on-chip electronic sensor array, capable of discriminating various gaseous species with collective reference response from all the sensor elements.

#### **9:00 AM \*M6.3**

**Functional Nanostructures via Dip-Pen Nanolithography.** Chad Mirkin, Chemistry, Northwestern Univ, Evanston, Illinois.

Dip-Pen Nanolithography (DPN) is a lithographic tool for patterning surfaces with chemical complexity on the sub-100 nm length scale using a technique that can be scaled to a high-throughput parallel-probe process. Using DPN, we are now able to pattern surfaces ranging from metals to insulators with nanostructures possessing specific biological, electronic, magnetic, or optical activity through the nanoscale control of the substrate's surface chemistry. This talk will review our recent results in several areas of DPN research, highlight the use of DPN to generate functional nanoscale architectures with unique electronic and electrochemical properties, and review the rapid progress being made toward high-throughput parallel probe DPN systems.

#### **9:30 AM M6.4**

**Controlling the Morphology of Patterned Self-Assembled Monolayers Deposited on Gold Surfaces using Dip-Pen Nanolithography.** Robert J. Barsotti and Francesco Stellacci; D.M.S.E., M.I.T., Cambridge, Massachusetts.

Lithography is the key to develop complex devices in the nano-scale. Dip Pen Nanolithography (DPN) allows for the controlled deposition of molecules on surfaces using contact mode atomic force microscopy (AFM). Patterns can be written with 20 nm resolution. Here we show that, in DPN, by varying the writing speed and the relative humidity it is possible to control the morphology of the written self-assembled monolayers (SAMs) for both hydrophobic and hydrophilic thiolated molecules on a gold surface. By carefully analyzing both AFM height and frictional force images of the written SAMs we found that molecules deposited at slow writing speeds form high (i.e. dense) SAMs, while at faster writing speeds the molecules tend simply to lie flat on the substrate. The monolayer height decays exponentially with the writing speed; at certain humidity levels particular speeds maximize the SAM density. Moreover, it was found that, even at low writing speed, the tilt angle of the written monolayer never reaches the one of the corresponding homogeneous monolayer. Strategies for achieving such angles such as retracing the same feature multiple times will be presented. The control of the morphology of the monolayer formed via DPN is fundamental for applications that require post-writing processing. For example, it is known that monolayer height is proportional to their density; consistently when using these monolayers as masks for selective gold etching denser SAMs act as better resists. Indeed, for a given etching time, we have found that the density of the starting monolayer correlates with the height of the final gold features. Moreover, one of the most powerful tools for complex device fabrication is chemically directed self-assembly. This technique requires control over the orientation of the deposited molecules on the surface. Preliminary results showing templated self-assembly on densely packed SAMs of MHA will be presented.

#### **9:45 AM M6.5**

**Assembly of 1- and 2- Dimensional Virus Arrays by Nanolithography.** Chin Li Cheung<sup>1</sup>, Julio A. Camarero<sup>1</sup>, Bruce W. Woods<sup>1</sup>, Tianwei Lin<sup>2</sup>, John E. Johnson<sup>2</sup> and Jim J. De Yoreo<sup>1</sup>; <sup>1</sup>Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; <sup>2</sup>Molecular Biology, The Scripps Research Institute, La Jolla, California.

The assembly of genetically engineered viruses and proteins on patterned chemical templates has great potential for directing the formation of ordered protein and virus arrays. We present here a general methodology to create nanoscale ordered protein and virus structures with by using patterns of site-specific chemoselective linkers deposited through dip-pen nanolithography and nano-grafting. Chemical templates with dimensions comparable to the size of a target virus were created with these linkers and were used to assemble genetically engineered viruses into pseudo one-dimensional arrays. The kinetics of the assembly of viruses on these templates under difference solution conditions was studied by atomic force microscopy. Preliminary results using these templates to direct the growth of virus crystals and their comparisons with bulk virus crystallization experiments will also be discussed.

10:30 AM M6.6

**Biomimetic Templates Generated via Dip-Pen**

**Nanolithography,** Nicole Onyeneho, Dorjderem Nyamjav, Meng Yu and Albena Ivanisevic; Purdue University, West Lafayette, Indiana.

The identification, fabrication and evaluation of biomimetic templates hold great potential for variety of applications. The generation of templates on these substrates is achieved using an appropriately modified atomic force microscope (AFM) tip. Colloids or cells immobilized onto a surface, and can serve as functional pixels as a result of being modified to have either a negatively- or positively-charged outer layer. AFM tips are modified in a variety of ways to have positively- or negatively-charged molecules at their ends. Dip-pen nanolithography (DPN) is utilized to functionalize individual functional pixels on the surface by moving the AFM tip according to a predetermined blueprint. Such modification is highly dependent upon specific adhesion forces and can be monitored using topography, phase and amplitude imaging and force curves data during the process. By changing the nature of biological and chemical species used for surface and tip modification, we can enhance or decrease the complexity of the generated surface template.

10:45 AM M6.7

**Effect of Alkylsiloxane Monolayers' Alkyl Chain Length on Atomic Force Anodization Nanolithography.** Bumsu Kim, Georgios Pyrgiotakis, Jason Sauer and Wolfgang M Sigmund; Materials Science & Engineering, University of Florida, Gainesville, Florida.

The scanning probe microscopy (SPM) nanolithography has attracted much attention due to its ability to fabricate and control nanometer dimensions precisely for potential nanodevices. Though other conventional techniques, such as photolithography, electron-beam lithography, and soft lithography, are available for nano-size patterning under some conditions, it is still a challenge to control accurate nanometer size patterns. Though many mechanisms of the atomic force microscopy (AFM) anodization were reported, the effect of chain length for AFM anodization nanolithography on different alkylsiloxane monolayers have not been elucidated yet. We demonstrate that the threshold voltage and the line width depend on alkylsiloxane monolayers with different carbon chain lengths by fabricating line and dot patterns. The threshold voltage and line widths were measured on different alkylsilane self assembled monolayers (SAMs). There were similar ranges of threshold voltages between the hexyltrichlorosilane SAM and the octyltrichlorosilane SAM, and between the dodecyltrichlorosilane SAM and the octadecyltrichlorosilane SAM. The wide gap between the octyltrichlorosilane and the dodecyltrichlorosilane SAM may be caused by the electric energy needed to degrade monolayers and the organizations of SAMs with different alkyl chain length in spite of similar energy offset by calculations. The length of the alkyl chain affects the width of lines, with longer alkyl chains yielding narrower patterned lines. Empirical relationships for the dot patterns of octyltrichlorosilane and octadecyltrichlorosilane SAMs, dependent on applied bias voltages and dwell times, were found to describe dot diameters. The patterning results were well fitted into empirical equations. By using these equations, threshold bias voltages for the octadecyltrichlorosilane SAM and the octyltrichlorosilane SAM were estimated. It is suggested that the alkyl chain lengths of monolayers were an important factor to control patterning sizes and threshold bias voltages on AFM anodization nanolithography.

11:00 AM M6.8

**Surface Modifications by Nano-oxidation.** Guangwen Zhou and Judith C Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Controlled nanoscale pattern formation on surfaces has become one of the most important and challenging areas of nanoscience. To-date, two approaches for surface patterning have been pursued: top-down lithographic methods and bottom-up self-assembly methods. Lithographic nanopatterning of large areas is typically a slow process requiring expensive tools of limited availability. In contrast, self-assembly methods rely on intrinsic properties of the system and hold promise for creating complex architectures. In this work, we present the potential for a new method for the production of nanostructured oxide island arrays by nano-oxidation of a model metal surface. Fundamental understanding of the nano-oxidation process provides key insights needed for important advances in a variety of technologies where nano-oxide structures are essential for their potentially novel optical, magnetic and sensor properties. We also investigated the reduction of oxide arrays on surface to form a template surface. Cu films with different orientations were chosen as a typical model system in this study. An in-situ UHV TEM was involved to observe the production and reduction of oxide islands. The dynamic observation of the nucleation/growth of oxide islands shows

completely different oxide structure (disks, nanorods, container pyramids, cellular networks, etc.) can be obtained by altering the oxidation temperature and substrate orientation. The dynamic observation of the oxide reduction processes reveals an effective way to create controlled nano-indentation arrays on metal surfaces by reducing the oxide arrays. The in situ TEM measurements of shape/size evolution of the oxide were used to determine the kinetics/energetics in the oxide production and reduction. Different models based on the generation of epitaxial/growth stresses and their relaxation were proposed to explain quantitatively the formation of some of the novel oxide nano-structures.

11:15 AM M6.9

**Localized Ligand Replacement on Gold Nanoparticle Monolayers: a Novel Method for the Generation of Supramolecular Wires.** Gretchen A DeVries<sup>1</sup>, Gianluca M Farinola<sup>2</sup>, Stefania Cicco<sup>2</sup>, Francesco Babudri<sup>2</sup>, Francesco Naso<sup>2</sup> and Francesco Stellacci<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Chemistry, Univerista' degli Studi di Bari, Bari, (BA), Italy.

Novel synthetic and lithographic methods have allowed the fabrication of nanoscale materials that then have shown unique properties. In nanotechnology, the difficulty often lies in constructing these materials and/or assemblies. The combination of the right materials and the appropriate lithography ultimately leads to the fabrication of electronic and optical devices such as nanotransistors and nanosensors. One of the most promising nanolithographies recently developed is replacement lithography (RL). RL is a technique for nanometer-scale resolution patterning of self-assembled monolayers (SAMs) using scanning tunneling microscopy (STM). In RL, an alkanethiol monolayer is placed in a concentrated (~10mM) dodecane solution of another thiolated target molecule. By applying a suitable voltage to an STM tip, molecules from the SAM exchange with the target molecules in solution. We consistently obtain resolution of less than 10 nm for RL patterns written on flat surfaces. Here, we demonstrate the ability of RL to pattern a wide variety of molecules into a SAM. In particular, we use RL to fabricate 10 nm wide lines composed of  $\pi$ - $\pi$  stacked oligo-paraphenylenevinylenes (PPV). These supramolecular wires show interesting fluorescent properties. Preliminary results about the confinement of light within these wires will be presented. Moreover, it is possible to use RL to change the ligands on surface-bound nanoparticles with a resolution comparable to the nanoparticle size (9 nm). After preparing a nanoparticle monolayer on gold via original methods that will be presented, we selectively change the ligands on certain nanoparticles in the monolayer. This method allows the construction of fluorescent nanoparticle wires. We believe that RL will enable fabrication of complex nanoparticle based devices due to the control it offers over the surface chemistry and thus the electro-optical behavior of specific nanoparticles on a given surface. Finally, extension of RL to other scanning probe microscopies will be demonstrated.

11:30 AM M6.10

**Lithographic Patterning Using Near-Field Scanning Optical Microscopy.** C Veauvy<sup>1</sup>, R E Hollingsworth<sup>2</sup>, J D Beach<sup>1</sup>, A Khandekar<sup>3</sup>, M A Treaster<sup>1</sup>, T F Kuech<sup>3</sup> and R T Collins<sup>1</sup>; <sup>1</sup>Physics, Colorado School of Mines, Golden, Colorado; <sup>2</sup>ITN Energy Systems, Inc., Littleton, Colorado; <sup>3</sup>Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

We report the development of a near-field scanning optical microscope (NSOM) designed specifically for direct write lithography. We also present applications of this microscope to submicron pattern generation including gate lines for quantum point contacts and nucleation sites for arrays of semiconductor microcrystallites. Direct write lithography is ideally suited to research use where rapid turn around, flexible pattern generation and much lower cost than production tools are very important. The advantages of NSOM lithography over other direct write approaches are the ability to use conventional optical photoresists, to combine near-field with far-field optical exposure, and avoidance of high-energy electron beam damage and of vacuum compatibility issues. The microscope also functions in standard NSOM characterization modes allowing, for example, nanoscale topography and reflectance to be measured and used in feature characterization and pattern registration. In this presentation, we will discuss the microscope design, performance tests, and photoresist process development for 100nm scale features and for pattern transfer into semiconductor substrates and metal films. We have used the tool to fabricate masks for electrochemical deposition of Ga dots on silicon substrates. After an arsine anneal of the Ga dots, ordered arrays of GaAs crystallites are produced. The spacing (2-20um) and size (200-1000nm) of the crystallites are then varied to study GaAs formation and subsequent growth using the dots as nucleation sites. We will also present a process for patterning gates on a GaAs/AlGaAs two-dimensional electron gas for the fabrication of quantum point contacts.

**11:45 AM M6.11****Site-Specific Chemical Modification Of Nanowires And Nanodevices Using Dip-Pen Nanolithography.**

Benjamin W. Maynor, Lei An, Chenguang Lu, Jianye Li and Jie Liu;  
Department of Chemistry, Duke University, Durham, North Carolina.

Using Electrochemical Dip-Pen Nanolithography (E-DPN) and Dip-Pen Nanolithography (DPN), GaN nanowires and single-walled carbon nanotubes (SWNTs) were patterned and locally modified to produce nanoscale heterostructures. GaN nanowires were locally modified using KOH "ink" and SWNTs were modified with organic polymers. The electronic properties of these nanostructures were dramatically different before and after chemical modification. By regulating the environmental conditions during the DPN experiment, the morphology of the modifications can be controlled. These experiments demonstrate that, because of their inherent site-specificity, E-DPN and DPN are ideally suited for the modification of nanostructures and for the rational fabrication of nanowire heterojunctions.

## SESSION M7: Self-Assembly I

Chair: Orlin Velev

Wednesday Afternoon, December 3, 2003

Room 310 (Hynes)

**1:30 PM M7.1**

**Alkaline and alkaline-earth metals self-assembled nano-patterns on the Fe<sub>3</sub>O<sub>4</sub>(001) surface.** Guido Mariotto, Shane Murphy, Sergio F Ceballos, Ciaran Seoighe and Igor V Shvets; Physics, Trinity College, Dublin, Ireland.

We have studied the mechanism of nano-pattern formation by self-assembly of impurities aggregated on the Fe<sub>3</sub>O<sub>4</sub>(001) surface. Self-assembly is controlled by thermal diffusion from the bulk of natural and artificial single crystals. We show that the diffusion of potassium and calcium is of fundamental importance to the surface dynamics of magnetite. The self-assembly of Ca impurities, combined with the reduction in oxygen concentration, leads to the formation of nanotrenches that can be identified as a p(1×4) structure. According to our model, the formation of nanotrenches contributes in two ways to the reduction of the surface energy. Firstly, alkaline and alkaline-earth impurities cause a reduction of the strain energy due to their large ionic radius. Secondly, their segregation and the reduction of the O/Fe ratio at the surface cause a reduction of the surface polarity. We expect that this mechanism of nanopattern formation should apply to (001) surfaces of other spinels. The structure of ordered nanotrenches could be used as a template for the deposition of carbon nanotubes, fullerenes and DNA molecules.

**1:45 PM M7.2**

**Organic-inorganic hybrid thin films from block copolymer self-assembly.** Phong Du<sup>1</sup>, Anurag Jain<sup>1</sup>, Carlos B.W. Garcia<sup>1</sup>,

Ligu Wang<sup>2</sup>, Paulette Clancy<sup>2</sup>, Michael O. Thompson<sup>1</sup>, Sol M. Gruner<sup>3</sup>, Detlef-M. Smilgies<sup>4</sup> and Ulrich Wiesner<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York; <sup>3</sup>Physics, Cornell University, Ithaca, New York; <sup>4</sup>Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York.

The routine formation of nanometer size structures remains a challenge that limits advances in many fields of nanotechnology. Increasingly "bottom-up" self-assembly approaches for the nanometer scale patterning of surfaces are competing with traditional "top-down" lithographic processes such as scanning probe lithography or high-resolution e-beam lithography. Block copolymer thin films (<100 nm) are among the more promising materials being examined as they offer ease of processing combined with phase separation induced structure formation on the nanometer scale; recent work with all-organic systems has generated thin films of various different morphologies and chemical compositions. Here we report on the use of small molecule additives (3-glycidioxy-propyltrimethoxysilane and aluminum-tri-sec-butoxide) to a structure directing block copolymer (poly(isoprene-b-ethylene oxide)) to create organic-inorganic hybrid thin films and demonstrate a first application of these films as a template to nanostructure silicon. In addition to retaining the self-assembling behavior of the pure polymer system, this hybrid approach allows for easy access to a wide range of morphologies and provides unique macroscopic properties (mechanical and thermal) that open up pathways for novel processing methods. Studies of the film morphology and surface topography are carried out using atomic force microscopy (AFM), scanning electron microscopy (SEM) and grazing incidence small angle X-ray scattering (GISAXS). AFM, SEM, and GISAXS images along with quantitative modeling of the results demonstrate successful structure formation at the nanoscale over

macroscopic dimensions. The resultant porous films show uniformity in structure dimensions and exhibits medium-range order. These films serve as templates for a laser-induced capillarity-driven filling process to create large arrays of silicon nanopillars. Surface analysis before and after laser treatment shows good registry between the pores and pillars. This method should be extendible to materials other than silicon and to generate geometrically varied structures and thus offers enormous scientific and technological promise in a wide range of fields ranging from nanofluidics, to biosensing and nanoelectronics.

**2:00 PM \*M7.3**

**Progress in the Fabrication of Complex Materials Architectures via Dynamics and Soft-Lithographic Patterning.** Ralph G. Nuzzo, Materials Research Laboratory, University of Illinois, Urbana, Illinois.

Self-assembly has evolved to become a powerful methodology for preparing organic thin films. It is now routinely used to prepare materials with significant utility for applications in technology. Recent progress in research has established this method as an essential tool for micro and nanoscale fabrication, areas in which assembly methods can be used to extend conventional fabrication methods for cases where specific types of chemical functionality are required. This talk will describe recent results that highlight the interesting synergies that can be developed in the melding of physical patterning and self-assembly methods. Of particular interest is the organization of complex structures in organic thin films via the use of driven processes, ones that constrain in some way the critical length scales of an assembly process. I will highlight specific examples that include new examples of Soft-Lithographic patterning and complex gradient arrays and multilayer assemblies—ones that derive at least a part of their functionality and structure from the properties of driven flow fields. These examples will include materials structures of interest for applications in electronics technologies and bioanalytical systems.

**2:30 PM \*M7.4**

**Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates.**

Paul F Nealey<sup>1</sup>, Sang Ouk Kim<sup>1</sup>, Harun H Solak<sup>2</sup>, Mark P

Stoykovich<sup>1</sup>, Juan J de Pablo<sup>1</sup> and Nicola J Ferrier<sup>3</sup>; <sup>1</sup>Chemical Engineering, University of Wisconsin, Madison, Wisconsin; <sup>2</sup>Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, Villigen, Switzerland; <sup>3</sup>Mechanical Engineering, University of Wisconsin, Madison.

Top-down approaches to fabrication such as advanced lithographic techniques are designed to meet severe processing constraints, but may be prohibitively capital intensive or may not offer sufficient control at the nanoscale. Inexpensive bottom-up approaches based on self-assembling materials such as colloidal particles and block copolymers often possess the required nanometer resolution, but the dimensions over which the self-assembled structures are defect-free limits potential applications. Tremendous promise exists for the development of hybrid technologies in which self-assembling materials are integrated into existing manufacturing processes to deliver molecular level control in parallel processes to meet exacting tolerances and margins, and placement of the structures, including registration and overlay, with nanometer precision. Here we demonstrate the integration of advanced lithography with the self-assembly of thin films of block copolymer to induce the epitaxial assembly of densely packed nanoscopic domains. The areas over which the patterns are defect free, oriented and registered with the underlying substrate are arbitrarily large, determined by the size and quality of the lithographically defined surface pattern rather than the inherent limitations of the self-assembly process.

**3:30 PM \*M7.5**

**Assembly of Gold Nanorods.** Catherine J. Murphy, Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina.

Gold nanorods of controlled aspect ratio and constant width (30 nm) are made via a seed-mediated growth approach in water in the presence of a directing surfactant. At high solution concentration, the nanorods spontaneously assemble into liquid crystalline-like arrays, as judged by polarizing optical microscopy, transmission electron microscopy, and small-angle x-ray scattering. Covalent linkage of gold nanorods with biotin-streptavidin linkers yields unusual preferential end-to-end alignment of the rods.

**4:00 PM \*M7.6**

**Inorganic Semiconductor Nanostructures Defined by Self-Organizing Polymers.** Klaus Thonke, Abt. Halbleiterphysik, Universitaet Ulm, Ulm, Germany.

For the definition and production of nanostructures from inorganic semiconductors like Si, GaAs and ZnO, we make use of several types

of self-organized polymer nanostructures. Small structures with typical dimensions of 10 nm can be obtained with the use of micelles formed by diblock-copolymers. In a "bottom-up" approach, these micelles can be used as nanoreactors for the formation of Zn, Cd, or Cu metal dots, which are then transferred in an oxygen plasma directly into ZnO, CdO, or Cu(x)O semiconductor dots. When instead Au dots are formed in the micelles, these Au dots then can be used as catalysts on sapphire substrates in a "vapor liquid solid" process for the growth of ZnO nanopillars with high aspect ratio. In a "top-down" approach, Au dots formed with the aid of diblock-copolymer micelles are used as etching masks on different types of semiconductor substrates for the formation of pillars in highly anisotropic plasma etching processes. When quantum well heterostructures on substrates are used, again quantum dots embedded in the etched pillars result. Larger hole or pillar structures with hexagonal short-range order and typical diameters of 100 nm to 1  $\mu$ m are obtained, when other self-assembled patterns like "breath figures" or ordered imprints of colloids in polymer films are used for the formation of metal masks of different sizes on semiconductors in the first preparation step, and then in a second step again plasma etching is applied. Even ring-shaped (Zn,Cd)O semiconductor patterns were formed starting with nanoporous polymer membranes, which are wetted by appropriate metal salts and then removed in an oxygen plasma, leaving "donut"-like (Zn,Cd)O rings. We also transfer the polymer masks into metal films, thus producing metal nets with holes of 5 nm to 1  $\mu$ m diameter, or hexagonal assemblies of metal nano-disks. The production, the structural and the optical properties of these nanostructures are discussed.

#### 4:30 PM M7.7

**Engineering Self-assembled Nanostructures Using Substrate Topography.** Joy Cheng<sup>1</sup>, Caroline A Ross<sup>1</sup>, Edwin L Thomas<sup>1</sup>, Henry I Smith<sup>2</sup> and G Julius Vancso<sup>3</sup>, <sup>1</sup>Material Science & Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Electrical Engineering & Computer Science, MIT, Cambridge, Massachusetts; <sup>3</sup>Material Science and Technology of Polymers, University of Twente, AE Enschede, Netherlands.

The self-assembly process is simple and low cost method to produce large-area nanostructures, however, self-assembled block copolymer thin films typically have uncontrolled defects and lack long-range order. Topographically patterned substrates made by interference lithography and e-beam lithography were used to guide the formation of nanoscale domains in a subsequently deposited block copolymer film. Well-ordered structures of polystyrene (PS)-*b*-polyferrocenyldimethylsilane (PFS) can be achieved under proper confinement conditions. For example, 9 rows of PFS domains self-assemble in a regular pattern in a groove with width 223-248 nm. Moreover, substrates with various submicron features such as castellated grooves or fishnet patterns have been employed to further elucidate the spatial relation between the positions of PS-PFS microdomains and guiding lithographic structures. With the knowledge of dislocation formation and annihilation of the block copolymer, the position of polymer microdomains and defects in the ordered arrays can be purposefully controlled by the design of the topographical guiding features. Combining bottom-up self-organizing materials and top-down lithographic methods allows self-assembled nanostructures to be fabricated in precise positions on a substrate.

#### 4:45 PM M7.8

**Self-Assembly Patterns Formed by Lateral Capillary Force Within Carbon Nanotube Arrays.** Elijah B Sansom<sup>1</sup>, Jijie Zhou<sup>1</sup>, Flavio Noca<sup>2</sup> and Morteza Gharib<sup>1</sup>; <sup>1</sup>Bioengineering, Caltech, Pasadena, California; <sup>2</sup>NASA-Jet Propulsion Lab, Pasadena, California.

The many unique properties of carbon nanotubes make them ideal candidates for use in working at the nanometer to micron length scales. Though many of their properties have been well studied, one that has not been fully characterized experimentally is their interaction with liquids. Small amounts of various liquid solutions, including pure water, surfactant solutions, and microspheres were applied to vertically oriented, densely packed, well-ordered multi-walled carbon nanotube arrays and then dried in a controlled manner. Observations were made at several stages using optical and electron microscopy. Following drying, interesting rearrangement patterns of the nanotubes were observed of size orders much larger than single nanotubes. Results indicate that there are several requirements for this to occur, including local geometry, liquid penetration of the array, appropriate initiation of drying, and rate evaporation rate. Based on the results, we believe the rearrangements are due to lateral capillary forces causing patterns of nanotube clumping. This is in analogy to previous work done on 2-D colloid crystal formation with latex microspheres in thinning liquid films [1] and mutual attraction of glass micro-capillary tubes placed in close proximity while piercing a liquid-air interface [2]. By elucidation of this process as well as general liquid wetting and flow interactions with

carbon nanotubes, a step is made toward the design of useful devices incorporating liquids and carbon nanotubes, such as biomolecular analyzers, flow sensors, and actuators. [1] Denkov, N. D., O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, K. Nagayama, Mechanism of Formation of Two-Dimensional Crystals from Latex Particles on Substrates. *Langmuir*. 1992. 8(12):p. 3183-3190. [2] Dushkin, C. D., P. A. Kralchevsky, V. N. Paunov, H. Yoshimura, K. Nagayama, Torsion Balance for Measurement of Capillary Immersion Forces. *Langmuir*. 1996. 12(3):p. 641-651. Acknowledgements: NASA: Office of Biological and Physical Research (OBPR), JPL Nanotube Group: Robert Kowalczyk, Michael Bronikowski

#### SESSION M8: Poster Session II

Chair: Jie Liu

Wednesday Evening, December 3, 2003

8:00 PM

Exhibition Hall D (Hynes)

#### M8.1

**Patterning at nanoscale with low-dose focused ion beam and chemical etching.** Andrei Stanishevsky<sup>1</sup> and John Melngailis<sup>2</sup>;

<sup>1</sup>Physics, University of Alabama at Birmingham, Birmingham, Alabama; <sup>2</sup>University of Maryland, College Park, Maryland.

Focused Ion Beam (FIB) is a very useful, ultra-high-vacuum compatible tool for a maskless, direct and local implantation and sputtering of materials at micro- and nano-scale. Although commercially available FIB systems have reached the resolution close to electron beam systems (about 5 nm), the FIB micro- and nano-patterning is a sequential process. It is much slower than the parallel processes of optical or electron beam lithography. The slow processing is the main drawback of FIB and, therefore, this technique is best suited for prototype nanostructure fabrication. We utilized a combination of two processes (low-dose FIB and chemical etching) to fabricate nanostructures in several materials. For nanoscale patterning the appropriate level of interaction between ions and solids is translated towards low dose effects where the high sensitivity of many materials and structures to ion bombardment is observed. We report the results of the investigation of the semiconductor and metal nanopatterns fabrication using selective chemical etching of low-dose focused ion beam (FIB) irradiated substrates. In this approach, the fabrication time is substantially reduced when compared to FIB process alone. It has been known that a high concentration of p<sup>+</sup> doping in Si drastically reduces its etch rate in certain chemical etchants such as KOH and hydrazine. The FIB irradiation of selected regions on Si substrate leads to the same result. The exposure to As<sup>+</sup>, B<sup>+</sup>, Pd<sup>+</sup>, Ga<sup>+</sup> FIB with ion doses >10<sup>14</sup> cm<sup>-2</sup> of selected areas of silicon substrate reduces the etching rate of such areas to a negligible value when compared to bulk Si (100). This approach has been utilized to fabricate various micro- and nano-scale three-dimensional structures, such as membranes and complex shape cantilevers with a sub-100 nm component size. FIB induced surface modification has also the opposite effect and enhances the rate of chemical etching depending on the reactive compound. Titanium and TiO<sub>2</sub> nanowires with the width down to 60 nm and with the length of up to 100  $\mu$ m were produced by etching FIB exposed Ti and TiO<sub>2</sub> films on SiO<sub>2</sub> with appropriate chemical solutions.

#### M8.2

Abstract Withdrawn

#### M8.3

Abstract Withdrawn

#### M8.4

**Fabrication of Micro- and Nanopatterns on Al<sub>2</sub>O<sub>3</sub> Surface Utilizing Novel Room-Temperature Epitaxy of Electron Beam-Induced and Buffer Layer-Enhanced Growth.**

Atsushi Sasaki, Norihiro Tateda, Jin Liu, Shusaku Akiba and Mamoru Yoshimoto; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

$\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) is one of the quite useful single-crystal substrates for functional thin film growth. Previously, we have reported that it is possible to fabricate ultrasmooth sapphire substrates with atomically smooth terrace and atomic step structure by annealing at high temperatures ( $\sim$ 1000°C) (*Appl. Phys. Lett.* Vol. 67 (1995) 2615.) In this work, only on the ultrasmooth sapphire (10-12) substrates (R-plane), we could attain electron-beam-induced epitaxial growth of Al<sub>2</sub>O<sub>3</sub> thin films at room temperature in laser MBE process, i. e., pulsed laser deposition in ultrahigh vacuum. The film in the electron-irradiated region grew epitaxially at room temperature, while an amorphous phase was obtained in the non-irradiated region. This in-plane patterned sapphire surface composed of epitaxial and amorphous phases was also verified to be useful as the template for



patterned epitaxial growth. On the other hand, we examined the possible applicability of this novel epitaxy to the micro- and nanopatterning of not only crystallinity but also morphology on  $\text{Al}_2\text{O}_3$  surfaces. We succeeded in fabrication of microstructures such as microwalls and microgrooves on R-plane sapphire surfaces through selective wet-etching of the amorphous region after the electron-beam-induced epitaxial growth. The height of microstructures could be controlled in a nanometer scale. Next, in order to attain the buffer layer-enhanced room temperature epitaxial growth of  $\text{Al}_2\text{O}_3$  film, several oxide films such as  $\text{NiO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  etc. were deposited as the buffer layer on sapphire (0001) substrate (C-plane). As a result, it was found that  $\text{Al}_2\text{O}_3$  thin films were grown epitaxially on the epitaxial  $\text{NiO}$  (111) buffer layer even at room temperature. These novel room-temperature epitaxy techniques are expected to give us the hybrid devices combined with organic or biological materials.

#### **M8.5**

##### **A New Approach For The Formation Of Size And Site Controlled Metallic Nano Dots Seeded By Focused Ion Beams.**

Alois Lugstein, Bernhard Basnar, Gottfried Strasser and Emmerich Bertagnolli; semiconductor technology, Institute for solid state electronics, Vienna, Vienna, Austria.

We present a new approach for the generation of uniform metallic nano dots, which in contrast to conventional bottom up or top down processes is based on a subtractive self organization process relying on material decomposition induced by focused ion beam exposure and subsequent rapid thermal annealing. Ga and In dots were formed in a size and position controlled fashion on GaAs (100), InAs (100), Si (100) and  $\text{SiO}_2$  substrates using molecular beam epitaxy and focused ion beam techniques. Two dimensional ordered arrays of embedded as well as freestanding metallic dots were fabricated by a site control technique relying on preformed craters and an irradiation mediated migration. The diameters of the dots range from 60 to 850 nm. The formation of these dots is discussed in terms of selective etching of arsenic due to the local energy injection by the ions and further agglomeration. Due to the high energy injection during FIB milling and the low melting point of the metal the precipitations behave like a liquid under milling conditions. Thus, the minimization of surface energy at the enhanced temperatures during FIB exposure calls for a perfect spherical cap shape of the small droplets, as we did observe. The morphological evolution of the sample surface was investigated by in-situ FIB-SEM, AFM and the chemical composition of the pattern was analyzed using high resolution AES. We completed these many-faceted experimental study with optical microscopy and electrical measurements. This technique is a promising way to obtain quantum dot arrays with small and uniform dot sizes and high packaging densities. Since GaAs quantum dot formation from Ga droplets has been reported, our technique is considered to be a candidate for the fabrication of highly ordered quantum dot array structures. Furthermore, this method is expected to apply to various metals apart from Ga and In.

#### **M8.6**

**Topology-Free Nanopatterning of Si to Control Ge Island Nucleation.** Martin Kammler<sup>1</sup>, Robert Hull<sup>1</sup>, Charles T Black<sup>2</sup> and Frances M Ross<sup>2</sup>; <sup>1</sup>Department of MSE, University of Virginia, Charlottesville, Virginia; <sup>2</sup>IBM T. J. Watson Research Center, Yorktown Heights, New York.

The ability to choose the nucleation sites of self-assembled nanoscale islands grown by strained layer epitaxy will open many future device applications, including for example quantum cellular automata. For most applications we also need to encapsulate the islands with an epitaxial overlayer. This grows most easily on a flat surface, and therefore we have focused on the problem of laterally patterning substrates without changing surface topography. We find that focused ion beam (FIB) patterning and use of the strain fields of buried dislocations are both promising tools to control island nucleation. Substrate patterning and growth experiments were performed in an ultra high vacuum transmission electron microscope system giving the possibility of studying in real time the growth of islands on patterned substrates. Using FIB micropatterning, Si(001) samples were irradiated using low doses of  $\text{Ga}^+$  ions and the effect of the FIB patterning on CVD Ge island growth was observed under UHV. We find that Ge islands grow selectively on the Ga-irradiated spots with no islands nucleating in between. Furthermore, in strong contrast to the growth of Ge islands on clean Si(001), Ge islands grown on Ga-implanted spots are smaller and have a steeper aspect ratio, which could be advantageous in applications. We will discuss the influence of the implanted Ga on island growth and compare with growth on unpatterned, Ga-terminated Si(001) surfaces. In addition we will show that Ge islands grow selectively on flat surfaces which are influenced by the strain field of buried dislocations. Here the challenge is to create a well-defined pattern of dislocations. We will show that dislocation nucleation can be controlled by the use of strained SiN pads. We will present real time studies of dislocation nucleation and

compare the dislocation configurations with computer simulations. Beside its application for controlling island nucleation, this method suggests new possibilities for engineering dislocations into novel devices.

#### **M8.7**

##### **Optical control of molecular motion for surface**

**nanopatterning.** Nathalie Sanz, Damien Garrot, Jacques Peretti, Thierry Gacoin, Khalid Lahlil, Georges Lampel and Jean-Pierre Boilot; physique de la matiere condensee, CNRS, PALAISEAU.

We report on the near-field optical patterning of photochromic sol-gel films with nanometric resolution. The experiments are performed on sol-gel samples prepared from functionalized alkoxy-silane monomers bearing bulky carbazole moiety and electron-donor/electron-acceptor substituted azobenzene (DR1). The prepared hybrid sol is deposited by spin-coating on a glass substrate, leading to a hybrid film of thickness that can be varied from 20 to 800 nm. The optical nanopatterning experiments are based on the local illumination of the films through the aperture of a metallized tapered optical fiber. The illumination wavelength is chosen in the visible absorption band of the photochromic DR1 molecules. Due to repeated photoisomerisation cycles of the azobenzene molecules, photo-induced matter migration occurs under the tip leading to the formation of a surface relief. This modification of the surface topography is imaged by in-situ shear-force microscopy. The shape of the photo-induced structure is characteristic of the electromagnetic field distribution and strongly depends on the tip-to-sample distance. In near-field illumination conditions, dots of lateral size as small as 60 nm are currently produced. When repeating this process, artificial controlled patterns can be optically inscribed on the film surface with a resolution at least one order of magnitude lower than the wavelength. These results demonstrate that the optical control of the molecular motion can be used for multi-scale surface nanostructurations.

#### **M8.8**

##### **Three dimensional nano to micro patterning inside**

**transparent materials by a femtosecond laser.** Jianrong Qiu<sup>1</sup>,

Jinhai Si<sup>1</sup> and Kazuyuki Hirao<sup>2</sup>; <sup>1</sup>Photon Craft Project, Japan Science and Technology Corporation, Kyoto, Japan; <sup>2</sup>Graduate School of Engineering, Kyoto University, Kyoto, Japan.

Femtosecond laser is a perfect laser source for materials processing when high accuracy and small structure size are required. Due to the ultra short interaction time and the high peak power, the process is generally characterized by the absence of heat diffusion and, consequently molten layers. Various induced structures have also been observed inside transparent materials after the femtosecond laser irradiation. Here, we report on formation of three-dimensional nano to micro patterns inside transparent materials by the femtosecond laser. 1) formation of optical waveguide with internal loss less than 0.5dB/cm in the wavelength region from 1.2 to 1.6  $\mu\text{m}$ , by translating a silica glass perpendicular to the axis of the focused femtosecond laser beam; 2) nano-scale valence state manipulation of active ions inside transparent materials; 3) space-selective precipitation and control of metal nanoparticles inside transparent materials; 4) self-assembly of nanostructure inside transparent materials. The mechanisms and applications of the femtosecond laser induced phenomena were also discussed.

#### **M8.9**

##### **Formation of ZnO Nanostructure Arrays on Focused Ion Beam-Patterned $\text{SiO}_2$ Substrates.**

Sang-Woo Kim<sup>1</sup>, Masaya Ueda<sup>1</sup>, Shizuo Fujita<sup>2</sup> and Shigeo Fujita<sup>1</sup>; <sup>1</sup>Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; <sup>2</sup>International Innovation Center, Kyoto University, Kyoto, Japan.

In spite of many promising characters of self-organized techniques, a number of problems, e.g., random distribution with fluctuations on their size as well as their position, has prohibited the self-organized semiconductor nanostructures from the application to novel electronic and optic nanoscale devices. In this regard, there have been many attempts to realize the position selection and the size control of semiconductor nanostructures using various lithographical patterning techniques. Focused ion beam (FIB) has been regarded as an attractive approach to the fabrication of nanoscale material structures and electrical interconnections, allowing the formation of complex nanoscale material structures in a single process with nano-scale resolution. In this work, we report on the position control of ZnO nanostructures grown by metalorganic chemical vapor deposition (MOCVD) in terms of the FIB-pattern and the growth conditions. An emphasis is given on the realization of long-range self-organized two-dimensional (2D) nanodot arrays on  $\text{SiO}_2/\text{Si}$  substrates engraved by the FIB of  $\text{Ga}^+$  ions. It was found that one-dimensional ZnO nanodot arrays were formed on a nanopatterned lines. The size of a nanodot was about 80-nm diameter and 6-nm height. At a certain condition, one ZnO nanodot was successfully formed on one nanohole,

achieving complete position control of nanodots. More recently, it became possible to fabricate 2D-arrayed  $4 \times 10^4$  nanoholes in a  $0.2 \times 0.2$  mm<sup>2</sup> patterning area on SiO<sub>2</sub>/Si substrates within 15 min. After the MOCVD growth of ZnO nanodots on the nanopatterned substrate, one nanodot with about 120-nm in diameter and 7-nm in height was formed in one nanohole, resulting in a very well-organized long-range 2D array of nanodots. Depending on the patterning shape and the growth time of ZnO, we could easily control the dimension of ZnO nanostructures (either ZnO nanodots or nanorods). This method could pave a new way to the commercial application of semiconductor nanostructures for realizing semiconductor photonic bandgaps, nanosized photonic elements, nanoscale laser arrays, and multifunctional nanoscale electronic devices.

#### M8.10

**Express Pattern Fabrication - Single Step processing by Direct-write Deposition.** Heinz D Wanzenboeck, Stefan Harasek, Erwin Auer, Helmut Langfischer and Emmerich Bertagnolli; Institute for Solid State Electronics, Vienna University of Technology, Vienna, Austria.

Traditional lithography provides several methods for nanostructure generation on the scale of nm. However, conventional those lithographic techniques require several process steps such as resist patterning and subsequent transfer of the pattern on the material. Direct-write deposition offers an alternative method for fabricating patterned material in the nm range. In contrast to projection lithography no photomask is required for direct-write deposition so that ready-to-use structures are obtained. This one-step ability renders this method a key technology for rapid prototyping in the nm-range. Direct-write deposition is based on a locally confined chemical vapor deposition that is initiated by the energy of a focused particle beam. The deposition process exclusively occurs in the areas that are scanned by the focused beam. With this unconventional approach even three-dimensional structures up to 20 μm height may be deposited. Lateral features in the 100 nm region could be fabricated. Utilizing this local reaction arbitrary, pre-defined nanostructures of silicon oxide were deposited. The essential equipment features and critical process parameters are discussed. The effects of the gas composition and the beam characteristics on the reaction mechanism have been investigated. Especially the composition of the gas atmosphere is shown to significantly influence the chemical composition of the deposited dielectric. Also the electrical properties of the deposited silicon oxide have been studied. With this unconventional approach metallic and dielectric materials may be deposited as well-defined patterns. Nanostructures display interesting and potentially useful properties that include quantized electric phenomena, Coulomb blockade, or single electron tunneling. This nontraditional approach provides a promising strategy for the formation of patterned structures in terms of total fabrication time and cost to produce a single exemplary sample. Novel applications of patterned microscale structures for electronic devices, photonic components, and MEMS can be quickly realized by this technique. Potential applications of this rapid pattern fabrication process for nanoscale electronic devices and for photonic, magnetic or biofunctional structures are discussed in this work.

#### M8.11

**Surface Relief Formation on Liquid Crystalline Azobenzene Polymer Film Induced by Patterned Light.** Takashi Ubukata<sup>1</sup>, Takeshi Higuchi<sup>1</sup>, Nobuyuki Zettsu<sup>2</sup>, Takahiro Seki<sup>3</sup> and Masahiko Hara<sup>1</sup>; <sup>1</sup>Frontier Research System, Local Spatio-Temporal Functions Lab., RIKRN, Wako, Japan; <sup>2</sup>Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan; <sup>3</sup>Applied Chemistry, Nagoya University, Nagoya, Japan.

During the past several years, it has been shown that thin films of azobenzene functionalized polymers (azo polymers) form surface relief gratings due to lateral material migration on micrometer scale under irradiation with an interference pattern of coherent laser beams. Such photogeneration of regular surface on azo polymers has attracted much attention not only from academic interests but also from a viewpoint of practical use for optical device applications. Recently, we have attained more than three orders of magnitude improvement in the sensitivity of surface relief formation in a liquid crystalline azo polymer film irradiated with ultra-violet light in advance. However microscopic mechanism of polymer migration is not fully understood yet. In this study, we aimed at understanding of the azo polymer migration in this high sensitive system, investigating surface relief structure produced by patterned light with different spatial periods. The process of the azo polymer migration could be detected by observation of the surface relief structure produced by step-by-step irradiation through a photomask using an atomic force microscope. Spontaneous lateral polymer migration unexpectedly continued to proceed at the edge of the periodic grating structure even in the dark conditions after switching off the light irradiation. Factors of high-sensitive azo polymer migration mechanism will be discussed in

consideration of these results.

#### M8.12

**Photofabrication of helical surface patterns on azobenzene polymer films.** Mi-Jeong Kim, Sung-Jong Yoo, Chae-Min Chun and Dong-Yu Kim; Dept. of Materials Science and Engineering, Kwang-Ju Institute of Science and Technology (K-JIST), Kwangju, South Korea.

Azobenzene-functionalized polymer films have unique photo-controllable properties such as photoinduced anisotropy, optical patterning of surface relief grating (SRG), and photoinduced chirality using light handedness [1-3]. In this presentation, helical surface patterns aligned in parallel were photofabricated on amorphous azobenzene polymer films by exposure to interference laser beams with handedness. By precise control of polarization state and expose time, we discovered that the well-aligned helical patterns could be obtained in the course of simple linear grating pattern formation, which was characterized by surface probe microscopy. Chiroptical property of the superhelical patterns was investigated by measuring circular dichroism and analyzing polarization states of the diffracted He-Ne laser beam. We could also fabricate superhelical surface patterns with a large surface modulation (> 100 nm) using superposition of interference patterns of laser beams. [1] L. Nikolova et al., *Optical Materials* 1997, 8, 255. [2] G. Iftime et al., *J. Am. Chem. Soc.* 2000, 122, 12646. [3] M. J. Kim et al., *J. Am. Chem. Soc.* 2002, 124, 3504.

#### M8.13

**One-Step Pattern Formation by LPE on Ion-milled Substrate for Magneto-Optic Spatial Light Modulators.** Jaehyuk Park<sup>1,3</sup>,

Jae-Kyeong Cho<sup>2</sup>, Kazuhiro Nishimura<sup>1</sup>, Hironaga Uchida<sup>1</sup> and Mitsuteru Inoue<sup>1,4</sup>; <sup>1</sup>Electrical & Electronic Eng., Toyohashi University of Technology, Toyohashi, Japan; <sup>2</sup>Electronic materials Eng., Gyeongsang National University, Jinju, South Korea; <sup>3</sup>ASTF, Nagoya, Japan; <sup>4</sup>JST-CREST, Saitama, Japan.

We demonstrate a new approach to pattern formation of iron-garnet films by liquid phase epitaxy (LPE) method on ion-milled substrates and its application to magneto-optic spatial light modulators. A spatial light modulator (SLM) is a real-time reconfigurable device capable of modifying the amplitude, phase, or polarization of an optical wavefront as a function of position across the wavefront. Various types of reusable modern SLMs with two-dimensional pixel arrays have been intensively developed over the past three decades. Of these, magneto-optic spatial light modulators (MOSLMs) have the advantages of high switching speed, robustness, nonvolatility, and radioactive resistance. The concept of one-step pattern growth for the MOSLM is based on the combination of a single-crystal epitaxial film growth by LPE and a impeded film growth on a substrate whose surface has been locally damaged and milled by ion bombardment before film deposition. Preparing a one-step pattern growth in an iron-garnet film comprises five process steps: (1) proper treatment of the single-crystal Sm-substituted gallium-garnet substrate (SGGG) to produce an unperturbed surface for epitaxy; (2) formation of a photoresist mask on the substrate; (3) ion-milling of the thickness of 100 nm on the unprotected substrate surface as pixel gap areas; (4) removal of the mask; and (5) LPE of the iron-garnet film onto the bare substrate. The thickness of the grown magnetic garnet film of (BiYGd)<sub>3</sub>(FeGa)<sub>5</sub>O<sub>12</sub> was about 3.5 μm. The rectangular pixels of several sizes of 5, 10, and 15 μm with a pixel gap of 2 μm were formed by one-step growth. The interface between pixel (single-crystal epitaxial area) and pixel gap (perturbed epitaxial area) guides magnetic walls just like a groove. This new method overcomes the disadvantages associated with groove etching of the conventional MOSLM. Thus, this method offers new possibilities for the fabrication of integrated magneto-optic light switch arrays, magnetic waveguides and similar devices. The MOSLM with one-step pixel formation had the layer structure of substrate (SGGG) / magnetic garnet layer with one-step pixel growth / reflective Al layer / insulator layer / bottom conductor line / insulator layer / top conductor line. The one-step grown pixels were 16 μm × 16 μm with pixel gap of 2 μm. The total number of pixels was 16 × 16 = 256. The fabricated prototype MOSLM is switched by applying driving currents of 40 mA for the bottom conductor line and 80 mA for the top conductor line under external bias field of 20 Oe, which is over 2 times smaller than that of the conventional MOSLM. These results strongly suggest that the novel MOSLM can provide higher resolution, simpler fabrication process, more compact systems and lower driving current.

#### M8.14

**SPM Local Oxidation of Ferromagnetic Thin Films.** Jun-ichi Shirakashi<sup>1</sup> and Yasushi Takemura<sup>2</sup>; <sup>1</sup>Department of Electronics and Information Systems, Akita Prefectural University, Honjo, Akita, Japan; <sup>2</sup>Department of Electronics and Information Engineering, Yokohama National University, Yokohama, Kanagawa, Japan.

Local oxidation of metallic and semiconductor surfaces by scanning

probe microscopy (SPM) is a very promising lithographic approach for fabricating electron devices with ultra-fine well-defined nanometer dimensions. It is well known that under appropriate bias conditions, SPMs such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM) can be used to selectively oxidize the surface of metal thin films. The reaction mechanism of the SPM local oxidation is considered to be anodic oxidation, and this oxidation process proceeds through an electrochemical reaction driven by a negative bias applied to the SPM tip. In this way, one can easily obtain metal oxide wires with a feature size of  $\sim 10$  nm, which suggests that lateral tunnel junction devices can be easily obtained using this fabrication process. In this report, we apply this technique to the local oxidation of ferromagnetic thin films for the fabrication of ferromagnetic single-electron transistors (FMSETs). Nanometer-scale surface modification of ferromagnetic thin films was investigated by this SPM-based local oxidation technique in ambient air. Extremely thin Ni films with thickness of  $3\sim 5$  nm were prepared by EB evaporation on  $\text{SiO}_2/\text{Si}$  substrates. Metal-coated  $\text{Si}_3\text{N}_4$  tips were used for the oxidation with the reference force of  $\sim 10^{-9}$  N. Successful surface oxidation of Ni was performed by applying tip-sample voltages of  $> 2\sim 3$  V. The size of the Ni oxide wires was well controlled by changing the applied voltage and scanning speed. With increasing the tip-sample voltage from 3 V to 30 V, the size of the oxidized structure increased, ranging from  $10\sim 30$  nm to 200 nm in width and 0.5 nm to 6 nm in height. The width and the height of the oxidized structures at a fixed tip-sample voltage decreased with increasing the scanning speed of the tip. This implies that by adjusting the applied voltage and scanning speed carefully, the size of the oxidized structures could be precisely controlled using this technique.

#### **M8.15**

**In-situ Assembly of Nanostructured Surfaces During Physical Vapor Deposition of Thin Films.** Chi Zhang and Ramki Kalyanaraman; Dept. of Physics, Washington University, Saint Louis, Missouri.

We have developed a new approach to in-situ assemble surface nanostructures during thin film deposition. One and two dimensional nanostructures of metals like Co and Ag, and compounds like  $\text{TiO}_x$ , have been fabricated on Si surfaces with spacing between 300-2000 nm using this approach. The approach consists of simultaneous film deposition and inhomogeneous surface heating using a high power pulsed laser. The nanostructures form by directed assembly during film deposition and do not require additional processing steps like lithography or the use of chemicals. Further, the size of the lines or dots can be controlled primarily by the amount of deposited material. We have successfully used various physical vapor deposition approaches like pulsed laser deposition and e-beam evaporation to form the nanostructures. The wide range in deposition techniques and the fact that no chemicals or additional processing steps are required makes this an economical and environmentally viable process to manufacture surface nanostructures.

#### **M8.16**

**Spatial Control of Surface Tension Using Inkjet-patterned Weak Polyelectrolyte Multilayers.** Jeeyoung Choi and Michael F. Rubner; Dept. of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Weak polyelectrolyte multilayers assembled by the alternating deposition of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) were employed as patternable platforms to manipulate surface tension for various applications such as microfluidic devices. The top surface of PAA/PAH multilayers was patterned by additive inkjet printing using PAA as an ink to create chemically distinct regions at length scales of 70 microns or larger that are enriched with either PAA or PAH functional groups. An amphiphilic block copolymer, polystyrene-block-poly(acrylic acid) (PS-PAA), was then preferentially adsorbed to the PAH-rich regions of the patterned multilayer surfaces from a tetrahydrofuran (THF) solution, thus rendering the originally hydrophilic PAH-rich regions hydrophobic, in contrast with the remaining hydrophilic PAA-rich regions. The behavior of the additive inkjet-printed polyelectrolyte multilayers, including the effect of post-printing treatments such as rinsing or heating, was also studied. The use of the inkjet-patterned multilayer system for applications such as microfluidics is currently under investigation.

#### **M8.17**

**Abstract Withdrawn**

#### **M8.18**

**Selective Grafting Propyleneimine Dendrimers onto a UV-Exposed Monolayer Surface.** Masaru Nakagawa, Naoyuki Toyoda, Nozomi Nawa, Tomokazu Iyoda, Takahiro Seki and Kunihiro Ichimura; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

As nanotechnology has progressed, well-defined patterned molecular surfaces to control adsorption of tiny functional materials have been required increasingly. We herein described a photoreactive monomolecular layer formed from a new silane coupling reagent bearing a benzyl phenyl sulfone moiety, which can graft amine-terminated dendrimers onto a UV-exposed monolayer surface. By exposure to 254 nm UV light, followed by treatment with propyleneimine dendrimers, the hydrophobic photoreactive monolayer formed from 2-(4-benzylsulfonyl)phenyl)ethylchloro-dimethylsilane turned hydrophilic. A noticeable feature is that the exposure energy making the substrate surface hydrophilic was reduced more, as the generation number of the amine-dendrimers was larger. In the case of a 4th generation dendrimer possessing 32 amino groups, such a hydrophilic substrate surface was obtainable only at an exposure energy of 50 mJ  $\text{cm}^{-2}$ , which was 1/30 in comparison with a 0th dendrimer possessing 2 amino groups. The zeta potential studies and the spectroscopic quantitative analysis of surface densities of surface amino groups on silica substrates chemically adsorbing the amine-dendrimers with different generations suggested that a small quantity of photo-generated sulfonic acid groups could be converted to a large quantity of amino groups by the surface implantation of amine-dendrimers. Surface densities of amino groups were dependent on the number of amino groups that the dendrimers had. It was obvious from the experimental results that the formation of hydrophilic surfaces was a result of dendrimer implantation amplifying photo-generated sulfonic acid groups in the photoreactive monolayer. Using this novel method consisting of the monolayer photoreaction and the dendrimer implantation, we could fabricate well-defined patterned amine-dendrimer surfaces on a silica plate at a micrometer resolution by imagewise UV-exposure.

#### **M8.19**

**Abstract Withdrawn**

#### **M8.20**

**New Template-Free Routes to Functional Macroporous Inorganic Oxides.** Eric S Toberer, Kannadka Ramesha and Ram Seshadri; Materials Department, University of California, Santa Barbara, Santa Barbara, California.

Our research evolves new methods for creating macroporous monoliths through template-free routes. Porosity in inorganic materials has been previously achieved through the use of colloidal spheres as templating agents. Here we present a template-free route that is applicable to a wide range of inorganic materials and is quite scalable. A solid composed of two intimately mixed, immiscible phases is first prepared, and one of the two phases is then leached out, leaving behind a macroporous material. Proof of concept has been demonstrated for several important materials. Metathesis has been used to form macroporous  $\text{PbTiO}_3$ ,  $\text{LaMnO}_3$ , and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . Decomposition of a single-source precursor has been utilized to form macroporous NiO. These materials have potential in catalysis, fuel cells, and acoustic materials.

#### **M8.21**

**Hot Filament Chemical Vapor Deposition of Organic Resists for Solventless Lithography.** Yu Mao<sup>1</sup>, Karen K Gleason<sup>1</sup>, Peter Nguyen<sup>2</sup> and Christopher Ober<sup>2</sup>; <sup>1</sup>MIT, Cambridge, Massachusetts; <sup>2</sup>Cornell University, Ithaca, New York.

Solventless lithography eliminates "wet" processing in conventional lithography through application of an irradiation sensitive thin film by hot-filament chemical vapor deposition (HFCVD) and development of exposed resists using supercritical (sc)  $\text{CO}_2$  fluid. Being an enclosed process, CVD raises no issues of exposure to volatile organic compounds or solvents and no costs or wastes associated with solvents and rinse water. sc $\text{CO}_2$  is envisioned as an "environmentally responsible" solvent and possesses low surface tension and high diffusivities which are beneficial for the development of small, high-aspect ratio features. HFCVD of glycidyl methacrylate (GMA) at high rates ( $> 200$  nm/min) was achieved over a filament temperature range of 500 K to 560 K using a peroxide initiator. The pendent epoxide group was preserved and a linear polymer structure was achieved, as confirmed by FTIR,  $^1\text{H-NMR}$  and X-ray Photoelectron (XPS) spectroscopies. Film molecular weight could be controlled from  $M_n \sim 3,000$  to  $M_n \sim 40,000$  through adjusting process conditions. The HFCVD GMA films are smooth, with RMS roughness less than 0.5 nm, and have high sensitivity ( $< 5$   $\mu\text{C}/\text{cm}^2$ ) to e-beam irradiation. A negative tone 120 nm L/S pattern was achieved through e-beam exposure followed by conventional development. To achieve dry development in sc $\text{CO}_2$ , a fluorine containing monomer, fluoroalkyl acrylate (FAA) was introduced along with GMA as a precursor feed to enhance the polymer's solubility in sc $\text{CO}_2$ . The result was a dry resist composed of the copolymer of GMA with FAA which could be developed by sc $\text{CO}_2$ . Preliminary study demonstrated that films with  $> 60\%$  of FAA in composition is completely soluble in

scCO<sub>2</sub> with 1% EtOH added as cosolvent. A 300 nm L/S pattern was achieved through this solventless lithography process.

#### **M8.22**

**Highly Uniform Carbon Nanotube-Silicon Heterojunction Diode Array.** Marian Tzolov, Baohe Chang, Aijun Yin and Jimmy M. Xu; Division of Engineering, Brown University, Providence, Rhode Island.

Carbon nanotubes are envisioned for electronic device applications, and have indeed shown great promises as functional electronic devices in various lab demonstrations. However, the incumbent silicon electronics is likely to continue to enjoy its dominance for a number of reasons. In light of this, one strategy for advancing nanotube electronics would be to incorporate carbon nanotubes into the silicon electronics platform. One way to meet this desire would be through physical placement of a carbon nanotube device on a silicon substrate and electrically interconnect it a silicon IC. Another way is to develop a technology for controlled growth of carbon nanotubes of desired features or growth of well defined and uniform nanotubes directly on silicon. We report on an initial success in demonstrating the latter, which resulted in, to our best knowledge, the first highly uniform carbon nanotube-silicon heterojunction diode array. It also overcame the difficulty in achieving the control and uniformity as encountered in earlier attempts (e.g. [1]). In addition, an extremely high ON/OFF ratio, as high as  $10^5$ , is measured in this new type of heterojunction diode. The fabrication of highly uniform nanotubes in a vertically aligned periodic array form on silicon was accomplished using a nanopore array formed in anodic aluminum oxide as a growth template. Current-voltage characteristics of this heterojunction measured in dark exhibited pronounced rectifying behavior with an ON/OFF ratio greater than  $10^5$ . Analysis of the current-voltage characteristics shows that at temperatures higher than 100K and/or at voltages greater than 2V the forward current is space charge limited which allowed to derive some parameters of the traps in the CNTs. Charge transport through the CNTs is the limiting mechanism at temperatures higher than 80K, but below this temperature an exponential region due to injection across the heterojunctions was observed. A band diagram of the heterojunction was proposed for the CNT/heterojunction. It explains the rectification of the heterojunction as well as the presence of built-in voltage observed in photocurrent measurements. The model also suggests that the trap states are acceptor type in the CNTs. An estimation of the forward current at 4V shows that the current through an individual CNT to be in the order of  $10^{-11}$  A. This value is lower than that in the previous experiments on single nanotubes [1] showing that there is further potential for improvement of our devices. The realization of a heterojunction array offers an exciting combination between the two dimensional lateral periodicity and functionality and the quasi one-dimensional transport along the perpendicular direction. [1] J. Hu, M. Ouyang, P. Yang, and Ch. M. Lieber, *Nature* 399, **48** (1999).

#### **M8.23**

**Ashing Technique For nano-gaps Fabrication of Electrostatic Transducers.** Marie Ange Eyoum, Emmanuel Quevy, Hideki Takeuchi, Tsu-Jae King and Roger Howe; Electrical Engineering, University of California-Berkeley, Berkeley, California.

During recent years, there has been extensive research and significant progress in the fabrication as well as testing of radio-frequency MEMS resonators. In the case of parallel plate electrostatic transducers, extending the resonant frequency of micromechanical resonators in the Gigahertz range often entails shrinking the gap spacing between the electrodes. Gaps size of 100nm and less are necessary in order to reduce the motional resistance  $R_{eq}$ . Several fabrication methodologies have been previously demonstrated to achieve ultra small gaps in the sub-micron scale. E-beam lithography and sacrificial sidewall spacer techniques were used to achieve lateral electrode to resonator gaps of 100nm [1], [2]. In this work, photoresist (PR) ashing has been implemented, to define sub-micrometer gaps for the fabrication of RF transducers. Resist ashing was reported to be a suitable and useful technique to extend the lithography line width limit for conventional and e-beam lithography [3]. It is generally used in semiconductor industry to define nanometer gate dimensions below optical lithography limitations [4]-[5]. A standard lithographically-defined procedure has the advantage of allowing the gap to be placed very specifically and the device to be built around it, as compared to a spacer technology. This yields a better resolution, larger design flexibility, and simplicity in the fabrication process. A low temperature process flow, using SiGe technology, was developed to pave the way for a modular integration of MEMS with standard CMOS electronics. Work is underway to achieve high aspect ratio  $\geq 10:1$ , and gaps dimensions below 80nm. **References:** [1] J.W. Weigold, A.-C. Wong, T.-C. Nguyen, and S.W. Pang, *IEEE JMEMS*, pp.221-228, September 1999. [2] J. Clark, W.-T. Hsu, T.-C. Nguyen, *IEDM Technical Digest*, pp.493-96, December 2000. [3] J. Chung, M. Jeng, J. E. Moon, A.T. Wu, T.Y. Chan, P.K. Ko, C. Hu, *IEEE Electron Device Letters*, vol.9,

pp.186-8, April 1988. [4] B. Doris, M. Jeong, T. Kanarsky, Y. Zhang et al, *IEDM Technical Digest*, pp.267-270, December 2002. [5] S. Thompson, N. Anand, M. Armstrong, C. Auth, B. Arcot, et al, *IEDM Technical Digest*, pp.61-64, December 2002.

#### **M8.24**

**Abstract Withdrawn**

#### **M8.25**

**The Gel Trapping Technique: A Novel Method For Characterization Of The Wettability Of Microparticles And Replication Of Particle Monolayers.** Vesselin N. Paunov and Olivier Cayre; Department of Chemistry, University of Hull, Hull, United Kingdom.

We have developed a 'gel trapping technique' (GTT) which based on spreading of colloid particles on air-water or oil-water surface and subsequent gelling of the water sub-phase with a non-adsorbing polysaccharide. The particle monolayer trapped on the gel surface is then replicated and lifted up by casting with polydimethylsiloxane (PDMS) elastomer. Using the GTT we have developed a conceptually novel method for determining of the three-phase contact angle of solid microparticles adsorbed at air-water or oil-water interface. The method is applicable for particle diameters ranging from several hundred nanometers to several hundred micrometers. Particle monolayers have been imaged on the surface of the PDMS replica with Scanning Electron Microscope (SEM). The particles position with respect to the air-water interface or the oil-water interface has been determined from the SEM images of the PDMS replica. Particle samples of different size and surface chemistry have been examined. We will present results for the particles contact angles at air-water and decane-water interface obtained by using GTT. Using the same technique we have also been able to prepare unsymmetrically coated colloid particles (Janus particles) by direct evaporation of gold over colloid monolayers partially embedded within the protective PDMS matrix. By direct replication of densely-packed colloid monolayers at liquid surfaces we have been able to produce hexagonal pattern of holes of different spacing on PDMS and other materials with a number of possible applications, including antireflective coatings, surfaces and filters of controlled microporosity, etc.

#### **M8.26**

**Fabrication of 20-nm Zn nanocrystallites by the selective photodissociation of adsorption-phase diethylzinc using a near-field optical chemical vapor deposition.** Jungshik Lim<sup>1</sup>, Takashi Yatsui<sup>2</sup> and Motoichi Ohtsu<sup>1,2</sup>; <sup>1</sup>Tokyo Institute of Technology, Yokohama, Japan; <sup>2</sup>JST, Machida, Japan.

Future optical transmission systems require ultrahigh integration of photonic devices. To meet this requirement, we have proposed nanophotonic integrated circuits that consist of nanometer-scale dots. To fabricate them, nanometer-scale dots must be deposited on a substrate with nanometer-scale controllability in size and position. To achieve this level of controllability, we demonstrated the feasibility of nanometer-scale chemical vapor deposition (CVD) using optical near-field techniques. However, conventional photo-CVD uses a light source that resonates the absorption band of metalorganic (MO) vapor and has a photon energy that exceeds the dissociation energy. Thus, it utilizes a two-step process; gas-phase photodissociation and subsequent adsorption. However, we found that the dissociated MO molecules migrate on the substrate before adsorption, which limits the minimum lateral size of deposited dots. To overcome this difficulty, we demonstrate here a deposition of Zn dots using the selective photodissociation of adsorption-phase diethylzinc (DEZn) with a nonresonant optical near field, where the photon energy is lower than that of the absorption band edge of gas-phase DEZn and higher than that of the absorption edge of adsorption-phase DEZn. Since the absorption band edge energy (E) of the gas-phase DEZn was 4.6 eV, we used He-Cd laser light (E = 3.81 eV) as the light source; it is nonresonant to gas-phase DEZn. Using a sharpened UV fiber probe, we achieved selective dissociation of adsorbed DEZn, as a result, we successfully fabricated 20-nm Zn dots with 65-nm separation on (0001) sapphire substrate. Furthermore, since the nonresonant propagating light that leaked from the probe did not dissociate the gas-phase DEZn, the atomic-level sapphire steps around the deposited dots were clearly observed after the deposition. Since high-quality ZnO nanocrystallites can be obtained by oxidizing Zn nuclei, this technique could be used to produce high-quality ZnO nanocrystallites, which is a promising material for nanophotonic devices.

#### **M8.27**

**Two-Dimensional Arrays of Metal Oxide Nanostructures on Surfaces Fabricated using Templating Techniques.** Matthew J. Cote<sup>1</sup>, Melissa S. Sander<sup>2</sup>, Robert J. Lad<sup>3</sup> and Carl P. Tripp<sup>3</sup>; <sup>1</sup>Chemistry, Bates College, Lewiston, Maine; <sup>2</sup>Institute of Materials Research and Engineering, Singapore, Singapore; <sup>3</sup>LaSST, University of Maine, Orno, Maine.

Dense arrays of metal oxide nanodots and nanotubes on silicon surfaces have been fabricated using porous anodic alumina films as templates for deposition. Tungsten oxide nanodots and titania nanotubes have been created using electron-beam evaporation and atomic layer deposition, respectively. Because the alumina templates were formed directly on silicon substrates, the nanoparticle structures retained their as-created orientation and distribution after template removal. Using this approach, we have produced arrays of nanoparticles with diameters as small as 20nm and heights ranging from several nanometers to several hundred nanometers.

#### **M8.28**

##### **Situ-Growth of A Single Carbon Nanotube on A Silicon Tip for Scanning Microscope Probes.** Zhongping Huang<sup>1</sup>, D. L.

Carnahan<sup>1</sup>, Y. N. Emirov<sup>2</sup>, J. D. Schumacher<sup>2</sup>, M. Beerbom<sup>2</sup>, R. Schlaf<sup>2</sup>, M. Sennett<sup>3</sup> and Z. F. Ren<sup>4</sup>; <sup>1</sup>NanoLab, Inc., Brighton, Massachusetts; <sup>2</sup>University of South Florida, Miami, Florida; <sup>3</sup>U.S. Army Soldier and Biological Chemical Command, Natick Soldier Center, Materials Science Team, Natick, Massachusetts; <sup>4</sup>Boston College, Chestnut Hill, Massachusetts.

The application of carbon nanotubes in scanning probes of microscopes can not only improve imaging resolution and probe strength but also diminish sample contamination and damage. For this reason, situ-growth of a single carbon nanotube on a silicon tip was investigated. To precisely control the site and diameter of the nanotube, a single nickel dot was first prepared on the silicon tip by focused ion beam associated with different techniques such as masking, deep socket, and milling. Hot filament plasma enhanced chemical vapor deposition was applied to achieve a vertically aligned carbon nanotube. The study shows a way to fabricate carbon nanotube scanning probes efficiently and the more reliable and stronger adherence of nanotube can be expected compared with a mechanical attachment.

#### **M8.29**

##### **Micropatterning of Glass and Its Use to Study Near Surface Mass Transport.** Linlin Wang, Cornell University, Ithaca, New York.

At elevated temperatures, glass will tend to re-flow so as to reduce to a minimum the free energy of its surface. There are four processes by which material may be transported to accomplish the change of shape: (a) bulk viscous flow, (b) surface diffusion, (c) volume diffusion, and (d) evaporation-condensation. We can determine which mechanism dominates by following the annealing out of gratings of different wavelengths etched into the surface. The decay of the gratings amplitude can be characterized by an effective time constant  $\tau$ , and the dependence of  $\tau$  on wavelength and annealing time differs for different mechanisms. In this work, we systematically studied the decay of gratings on seven Corning glass samples. These samples are comprised of alumina, calcia, and silica with the silica composition varying from 25mol% to 75mol%. Uniform 1D gratings were produced with wavelengths ranging from 40 $\mu$ m to 4 $\mu$ m via dry etching. These gratings were then subjected to temperatures at least 120°C above the strain point ( $T_s$ ) of the glass compositions. The amplitude data were collected at three or more annealing temperatures, and at more than four different annealing times for each temperature, from which the decay rate constant  $K$  was obtained. Based on equation  $K = \pi\gamma/\eta\lambda$ , we calculated the surface viscosity of the seven glass compositions, and further the activation energy, using Vogel-Fulcher-Tammann equation. Our study demonstrated that the rate of the smoothing of periodic surface perturbations with wavelength from 4 to 40 $\mu$ m is controlled by viscous flow. This technique also allows determination of the viscosity of glasses from 10e+8 to 10e+12 Pa-sec. And alternatively, if the viscosity of the glass is known, it is possible to predict with some accuracy the annealing time required to smooth a scratched glass surface.

#### **M8.30**

##### **Ferroelectric Lithography for Directed Assembly of Functional Nanostructures.** Xiaojun Lei, T. Alvarez and Dawn Bonnell; Material Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

A novel approach for the fabrication of complex structures consisting of multiple classes of nanostructures is presented. The process overcomes the limitation of most directed assembly strategies which operate on one class of materials, as for example in the use of electromagnetic fields to align nanowires. The ability to locate different classes of nanostructures in pre defined positions allows complex nanosized devices to be fabricated. Ferroelectric lithography exploits the fact that ferroelectric domains exhibit chemical specificity in combination with the ability to pattern polarization orientation. Scanning probes, e-beam lithography, and microcontact stamping are used to produce patterns of oriented domains on ferroelectric thin films. These films serve as substrates for subsequent electron exchange

reactions that are mediated by the local electrostatic fields on the ferroelectric surface. A typical functional nanostructure consists of a single ferroelectric domain, two metal clusters, and an organic/biological molecule configured for electronic or opto electronic properties. Nanosized structures with electronic and opto-electronic properties will be illustrated. The approach can be generalized to co assemble nanodots, nanowires, nanotubes, with semiconductors and molecular devices. Strategies for integrating the nanodevices into systems will also be discussed.

#### SESSION M9: Self-Assembly II

Chair: Paul Braun

Thursday Morning, December 4, 2003

Room 310 (Hynes)

#### **8:30 AM M9.1**

##### **Self-Assembled Aligned Carbon Nanotube Arrays with Long-Range Periodicity.** Yang Wang<sup>1</sup>, J. Rybczynski<sup>1</sup>, Wenzhi Li<sup>1</sup>,

B. Kimball<sup>2</sup>, D. Steeves<sup>2</sup>, M. Giersig<sup>3</sup>, Dezhi Wang<sup>1</sup>, K. Kempa<sup>1</sup> and Zhifeng Ren<sup>1</sup>; <sup>1</sup>Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Army Soldier & Biological Chemical Command, Natick Soldier Center, Natick, Massachusetts; <sup>3</sup>Center of advanced european studies and research, Ludwig-Erhard-Allee 2, Bonn, Germany.

Self-assembly of large-area periodic catalyst dots has been used for patterning of aligned carbon nanotubes grown by plasma-enhanced chemical vapor deposition. The patterning of the catalyst dots is precisely controlled by the self-assembly of polystyrene microspheres. The length and diameter of nanotubes are well tuned by growth parameters such as time, thickness of catalytic layer, plasma intensity, etc. These arrays are characterized by scanning electron microscopy and are promised to have significant research value and numerous potential applications including photonic band gap crystal, laser-eye protection, negative index of refraction, etc.

#### **8:45 AM M9.2**

##### **Template-Based Fabrication of Polymeric Membranes.**

Maria M. F. Cortalezzi<sup>1</sup>, Vicki L Colvin<sup>2</sup> and Mark R Wiesner<sup>1</sup>;

<sup>1</sup>Civil and Environmental Engineering, Rice University, Houston, Texas; <sup>2</sup>Chemistry, Rice University, Houston, Texas.

Porous solids were obtained from self-assembled deposits of silica nanoparticles used as templates to form 3-D porous membranes. Deposits of nanoparticles of different sizes were obtained for a variety of conditions in order to control the morphology of the deposits by changing the solvent chemistry. Glass microslides were placed vertically inside suspension of nanoparticles. Upon evaporation of the solvent, deposits were formed on both sides of the microslide. The deposits were imaged using SEM and showed distinctive structures for each of the solvent chemistries, consistently with the DVLO theory and calculations of capillary interaction energy. The deposits were used to fabricate porous polymeric membranes. The void space within the deposit is filled with a monomer and polymerized in a UV chamber. The silica nanoparticles and glass microslides were etched away by immersing the glass-polymer assembly in HF, leaving a porous polymeric film. The obtained membranes were imaged by SEM. They exhibit a high pore volume and relatively lower surface porosity. The effective pore size achieved is related to the size of the particles in the template but significantly smaller; for example, the pore size of polystyrene membranes from templates of 244 nm diameter silica particles was measured in the order of 20 nm. The viscosity of the monomer was found to be another factor in determining the pore size of the membrane.

#### **9:00 AM \*M9.3**

##### **Multifunctional Photonic Crystals Prepared by Colloidal Crystal Templating.** Andreas Stein and Mohammed A. Al-Daous; Chemistry, University of Minnesota, Minneapolis, Minnesota.

Colloidal crystal templating provides a general method of obtaining three-dimensionally ordered macroporous (3DOM) solids of a range of compositions. A number of potential applications have been demonstrated for 3DOM materials, including photonics, sensing, pigments, catalysis, sorption, controlled release, battery materials, and bioactive materials. The main focus of the presentation will be on systems that combine multiple functionality within one material by making use of surface functionalization with organic or inorganic components. For example, inorganic 3DOM structures functionalized with metal oxide nanoparticles were used to optimize sorption, photocatalysis, and photonic effects of the material. Due to the interactions of light with the periodic structure of the walls and pores in 3DOM structures, these materials exhibited photonic stop band effects which were enhanced by the presence of the incorporated nanoparticles. As a result of the stop bands, propagation of light was partially inhibited within the material. Stop band positions could be

shifted by infiltration of the pores with a solvent. The pore dimensions were tuned to result in various degrees of overlap between the stop band and major photoemission lines of the material. The material was then tested as a photocatalyst. The periodicity of the structure was found to influence the rate of photocatalysis. The roles and effects of each component in this system were evaluated in detail.

#### 9:30 AM \*M9.4

##### **On-chip Dielectrophoretic Manipulation of Droplets for Assembly of Microparticle and Nanoparticle Structures.**

Orlin D Velev, Ketan H Bhatt and Brian G Prevo; Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

Dielectrophoresis, particle polarization and mobility in alternating electric fields, allows manipulation and precise control of the interactions and assembly of colloid particles. We have developed tools for dielectrophoretic manipulation and assembly of microparticles and nanoparticles by planar on-chip electrodes. The on-chip dielectrophoresis can also be used as a means to transport and manipulate droplets in a novel liquid-liquid microfluidics system. Water droplets suspended on the surface of a denser liquid were driven by alternating or constant electric fields created by addressable arrays of electrodes immersed in the oil. This manipulation of droplets on chips opens a range of materials synthesis applications that are not available with conventional microfluidic devices. The droplets could serve as self-contained templates and reactors for the assembly of particles with advanced structure. Controlled on-chip mixing and drying of droplets from suspensions was used to form supraparticles from colloidal crystals, and anisotropic assemblies. Precipitation of inorganic salts lead to the synthesis of crystal shells and balls. The formation of oil-water and polymer-water capsules was demonstrated. The liquid-liquid chips allow automated on-chip fabrication, combinatorial synthesis and massive parallelization.

#### 10:30 AM \*M9.5

##### **Micropatterned Colloidal Assemblies by E-field Guiding.**

Ilhan Aksay and D. A. Saville; Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

(Abstract Not Available)

#### 11:00 AM \*M9.6

##### **Heterogeneous Surface Patterning with Nanosized Channel Lattices.**

Lifeng Chi, Physics, University Muenster, Muenster, Germany.

Surface patterning with microscopic structures received an increasing interest in the past decade as a consequence of their potential applications in different scientific and technological fields. In this regard, a number of techniques have been invented and engaged in producing micron, sub-micron till nanoscale structures. We have demonstrated a different approach to form regular line patterns by transferring a Langmuir monolayer from air/water interface to solid substrate under proper conditions. The resulting surface is a heterogeneously structured with periodic regions of alternating wettability, arranging from 300 - 1600 nm. Compared with other lithography methods, the Langmuir-Blodgett (LB) based preparation shows its advantage of low costs, fast, and an unusual ratio between the width and the length of the linear structures (the line width can be as small as 100 nm, and the length is in principle unlimited). Recently, we expand the concept to form stable patterns on silicon surfaces. It turns out that chemically active structures can be built onto Si/SiO<sub>2</sub> surfaces based on template directed self-assembly by using structured LB monolayers as a template. This method provides an easy and fast route to get chemically patterned surfaces with different chemical activities over large areas. Structured surfaces of several cm<sup>2</sup> can be easily produced within several minutes although there is no theoretical limitation in the area. The surface exhibits different surface free energies and chemical activities, which gives rise to anisotropic wetting phenomena thus allow a further a parallel nanofabrication on large-areas. Furthermore, the patterns create with LB method can be transferred into silicon by chemical etching till a depth of 300 nm. The smallest lateral features that we were able to etch were less than 25nm.

#### 11:30 AM M9.7

##### **Synthesis and Spectroscopic Properties of Optically Activated Planar Open-Surface Titania Inverted Opals.**

Michael H. Bartl<sup>1</sup>, Frank Tsung<sup>1</sup> and Galen D. Stucky<sup>1,2</sup>; <sup>1</sup>Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California; <sup>2</sup>Materials Department, University of California, Santa Barbara, Santa Barbara, California.

Open-surface planar inverted opals are a particular interesting class of photonic band gap structures, since they provide a means to precisely confine and manipulate light in ways that were previously impossible

and thus are considered as the key components for a new generation of opto-electronic devices and all-optical integrated circuits. We present here a simple single step sol-gel approach that results in such planar inverted opals of titania with a flat and half-periodic completely open surface. Our method thus eliminates additional processing steps to remove the excess surface coating of the backfilling material, which are necessary in order to avoid unwanted photonic surface states. Furthermore, this technique enables us to combine natural colloidal microsphere assembly with cooperative molecular mesoscale self-assembly strategies. This multiple length scale (nano/meso- and photonic length scales) templating allows for both controlling the optical properties (refractive index, photonic band structures) of the final photonic crystal structure as well as artificially constructing hierarchically ordered photonic crystals doped with optically active species (e.g., dyes, rare earth ions). Examples of such optically activated planar titania inverted opals are presented together with their photonic properties.

#### 11:45 AM M9.8

##### **Directed Assembly of 3-D $\mu$ -Periodic Structures using Bio-Inspired Polyelectrolyte Inks.**

Gregory M Gratson and Jennifer A. Lewis; Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois.

We have developed a novel approach to patterning complex architectures in three dimensions via directed assembly (Langmuir, 2002; Adv. Mater., 2002). Here, we demonstrate a new ink design based on a binary mixture of anionic and cationic polyelectrolytes that permits the directed assembly of three-dimensional (3-D) periodic structures with micron-sized features. Our novel approach requires an ink capable of flowing through fine deposition nozzles (diameter of 0.5 to 10  $\mu$ m) and then solidifying in-situ to maintain its shape while spanning unsupported regions of the structure. We have created a polyelectrolyte ink that experiences a rapid solidification reaction by mimicking the mechanism used to regenerate spider silk fibers. Three-dimensional structures were patterned by depositing the ink into a reservoir that promotes solidification by increasing the strength of interaction between the oppositely charged polyelectrolytes. Here, we report on the assembly of 3-D  $\mu$ -periodic structures that may find potential application as tissue engineering scaffolds, drug delivery systems, novel membranes, or templates for photonic band gap materials. The influence of reservoir composition, polyelectrolyte MW, and polyacid:polybase ratio on this assembly process has been investigated.

#### SESSION M10: 3D Planning I

Chair: Paul Braun

Thursday Afternoon, December 4, 2003

Room 310 (Hynes)

#### 1:30 PM M10.1

##### **Fabrication and Metallization of Three-Dimensional Microstructures.**

Tommaso Baldacchini<sup>1</sup>, C N Lafratta<sup>1</sup>, R A Farrer<sup>1</sup>, AC Pons<sup>1</sup>, Z Bayindir<sup>2</sup>, J Stewart<sup>3</sup>, M C Teich<sup>3</sup>, B Saleh<sup>3</sup>, M J Naughton<sup>2</sup> and J T Fourkas<sup>1</sup>; <sup>1</sup>Eugene F. Merckert Chemistry Center, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Department of Physics, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts.

Three-dimensional microstructures having complex topology have been fabricated recently by different groups by means of two-photon-absorption (TPA) induced polymerization. This technique presents a unique advantage in its ability to localize polymerization in a small volume, the position of which can be controlled in three dimensions. The nature of the materials used (generally acrylic or epoxy resins) poses the greatest limitation in the fabrication of sensors and actuators, in part because of their lack of electrical conductivity and their relative incompatibility with standard techniques for patterning electronic circuits. In this work we present a method for coating three-dimensional microstructures fabricated by TPA polymerization with conductive metallic patterns in a selective manner. We have developed homemade resins that feature a commercially-available photoinitiator that undergoes efficient TPA polymerization using just a small fraction of the output of a mode-locked Ti:sapphire laser. The composition of the resin can be changed so as to tailor the physical properties of the polymer such as hardness, shrinkage and refractive index. Once the microstructures with the desired three-dimensional geometry are fabricated, we can render their surfaces conductive through multiphoton induced deposition of metals. The methodology described above allows us to fabricate structures that have optical, mechanical, electrical and other functionalities.

1:45 PM **M10.2**

**3-D Submicron Regional Control of Bioactivity Through Multi-photon Excited Crosslinking and Polymerization.**

Paul J. Campagnola and Swarna Basu; Physiology/CBIT, University of Connecticut Health Center, Farmington, Connecticut.

We demonstrate regional control of bioactivity and lateral mobility through the use of multi-photon excited photochemistry. Using a custom laser-scanning microscope this technique has been used to cross-link three-dimensional matrices of alkaline phosphatase, bovine serum albumin, and polyacrylamide, and combinations thereof on the micron size scale. The mechanism of cross-linking these proteins via two-photon excitation of the photo-initiator, Rose Bengal, was found to proceed through the singlet oxygen pathway. Using a fluorescence-based assay (ELF-97) the enzymatic activity of alkaline phosphatase has been studied using a Michaelis-Menten analysis and we have measured the specificity constant  $k_{cat}/K_M$  in both protein and polymer environments to be on the order of  $10^6$  to  $10^7$  M<sup>-1</sup>s<sup>-1</sup> and comparable to known literature values, indicating little protein denaturing was occurring. The specificity constant in 25% polyacrylamide was 5 fold larger than for either protein due to an increase in  $k_{cat}$ , most likely arising from an increase in diffusion and availability of the active site. Under similar crosslinking conditions, the specificity constant in 15% polyacrylamide was yet 6 fold larger due to increased diffusion in the thinner gel. The relative reaction rate of alkaline phosphatase entrapped in BSA was measured as a function of BSA crosslink density and was found to decrease in the more tightly formed matrices, indicating decreased diffusion in the matrix. Upon normalizing to the rose Bengal two-photon cross section, similar rates were obtained at 800 and 750 nm excitation, indicating no significant denaturing of the enzyme through 3 photon absorption was occurring even at the shorter wavelength. Diffusion coefficients were measured in the fabricated protein and polyacrylamide matrices through the use of the fluorescence recovery after photobleaching (FRAP) technique. The lateral mobilities of Rhodamine B, Texas Red, and Rhodamine B dextrans were examined and diffusion coefficients were found to decrease asymptotically with the crosslinking density of the matrix. As expected, the measured values in protein gels are approximately 10-100 fold slower than those reported in solution. These measurements also show that the diffusion coefficient of Texas Red (~1100 amu) is slower than the 10 kD Rhodamine dextran, suggesting the existence of anomalous diffusion for the former within the BSA matrix. This most likely arises from long-range interactions between the hydrophobic groups on the Texas Red chromophore and the surface of the BSA host molecules. The diffusion coefficients were also measured at different levels through the 3D structures and were found to be highly location independent, demonstrating the uniformity of the fabrication process. The results here suggest that multi-photon excited photochemistry is a viable approach to the fabrication of 3D biological devices to be used in applications such as controlled release.

2:00 PM **\*M10.3**

**Two-Photon Lithography.** P N Prasad, H Pudavar, P Markowicz and J M O'Reilly; Institute for Lasers, Photonics and Biophotonics and Department of Chemistry, The State University of New York at Buffalo, Buffalo, New York.

This talk will focus on the use of two-photon excitation to conduct photo-lithography. Two-photon excitation in the far-field allows one to have volume access with a high degree of spatial localization, allowing one to conduct 3D microfabrication. With the availability of highly efficient two-photon absorbing molecules, this two-photon technology holds promise for many applications. Three examples will be provided in this talk. One deals with the fabrication of 3-dimensional optical circuits. 3-D stacks of channel waveguides with mode control have been fabricated. 1xN splitters and volume grating couplers have been produced. Another example is the use of two-photon lithography to produce photonic crystals. Our focus is on optically nonlinear photonic crystals for enhanced nonlinear optical response and on engineering of defects in a self assembled photonic crystals. Two-photon lithography was used to create lines (intentional defects) inside a silica photonic structure. The third example is in the development of multilayer high capacity data storage where storage density reaching terabit per cm<sup>3</sup> have been achieved. Both digital and analogue storage have been demonstrated. Another application being pursued is fabrication of plastic based MEMS. A new area being developed is two-photon near field lithography for nanostructure fabrication.

2:30 PM **\*M10.4**

**The Convergence of Top Down and Bottoms-Up Processing: Formation of 3D Structures.** Mingqi Li<sup>1</sup>, Xuefa Li<sup>1</sup>, Katsuji Douki<sup>2,1</sup> and Christopher K. Ober<sup>1</sup>; <sup>1</sup>Materials Science &

Engineering, Cornell University, Ithaca, New York; <sup>2</sup>JSR Micro, Inc., Sunnyvale, California.

Lithography and the processes associated with it are the backbone of

the nanotechnology revolution. Several developments are occurring simultaneously: a drive to reduce minimum feature size for advances in microelectronics, the use of lithographically patterned structures to prepare devices for photonics, biotechnology and other forms of nanotechnology and finally the drive to create 3-dimensional structures for device and new materials creation. The controlled formation of nanometer scale structures in 2 and 3 dimensions is of increasing interest in many applications ranging from biotechnology to nanotechnology. This paper will discuss new approaches for the construction of small-scale structures using methods based on advanced chemically amplified lithography. New tools derived from 2 photon processes for the formation of complex images and the development of patterned structures will be described. Finally in the production of 3 dimensional patterns, the possible role of self-assembly coupled to lithography will be examined. Photodefinable block copolymers with erodable microstructures have been successfully used to form mesoporous materials and will be discussed.

3:30 PM **\*M10.5**

**Two-Photon 3D Lithography: Materials And Applications.**

Joseph W. Perry<sup>1</sup>, W. Haske<sup>1</sup>, S. R. Marder<sup>1</sup>, M. Rumi<sup>1</sup>, K. Braun<sup>2</sup>, S. M. Kuebler<sup>2</sup>, F. Stellacci<sup>2</sup>, J. Wang<sup>2</sup>, W. Zhou<sup>2</sup>, T. Yu<sup>3</sup> and C. Ober<sup>3</sup>; <sup>1</sup>School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Department of Chemistry, University of Arizona, Tucson, Arizona; <sup>3</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, New York.

Two-photon laser excitation allows for the patterning of materials in three-dimensions with <200 nm feature size. We have developed compounds with large two-photon absorption cross sections and can undergo efficient photochemical processes, such as photo-acid generation, via sensitization of electron transfer. Using these compounds, high-sensitivity two-photon active polymeric resists (positive and negative tone) and metal nanoparticle based composite materials have been developed. These materials allow for the fabrication of 3D polymeric microstructures and the direct writing of 3D metallic structures within a polymer matrix, respectively. The application of two-photon 3D lithography to the fabrication of various passive and active microstructures will be discussed.

4:00 PM **M10.6**

**Physical Characterization of Novel Two-Photon-Fabricated 3-D Polymer Structures.** Zeynel Bayindir<sup>1</sup>, Y. Sun<sup>1</sup>, T.

Baldacchini<sup>1</sup>, J. Stewart<sup>2</sup>, B. Saleh<sup>2</sup>, M. Teich<sup>2</sup>, J.T. Fourkas<sup>1</sup> and M.J. Naughton<sup>1</sup>; <sup>1</sup>Dept. of Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Boston University, Boston, Massachusetts.

We have fabricated true 3D microstructures using two-photon absorption photopolymerization using a laser with custom polymer and photoinitiator, with present feature size ~200 nm. Structures in a cantilever geometry were fabricated in order to characterize the elastic properties (bulk and Young's moduli). We have made cantilevers of nominally 3 micron thickness and 60 to 120 microns length, and thus with a range of spring constants, and report on measurements on their properties using an AFM. In addition, we have measured the magnetic susceptibility, thermal expansion coefficient, and the frequency-dependent dielectric constant, in the range 4K to 300K, in order to assess the potential for cryogenic functionality of planned 3D microsystems using this fabrication method. This work was supported by the National Science Foundation, Grant number ECS-0088438.

4:15 PM **M10.7**

**Holographic 3-D Photonic Crystal Templates.**

Robert G. Denning<sup>1</sup>, Christopher F. Blanford<sup>1</sup>, David N. Sharp<sup>2</sup>,

Emma R. Dedman<sup>2</sup>, Jan Scrimgeour<sup>2</sup> and Andrew J. Turberfield<sup>2</sup>; <sup>1</sup>Inorganic Chemistry Laboratory, Oxford University, Oxford, United Kingdom; <sup>2</sup>Physics Department, Oxford University, Oxford, United Kingdom.

Holographic methods have several desirable characteristics for the fabrication of 3D photonic crystals - (a) all Bravais lattice types are possible (b) the crystallographic basis can be engineered (c) in principle, the method is defect free and "interferometrically" precise, and (d) lattice definition, in a volume that can contain numerous devices, requires a single brief optical exposure. Only small local photochemical changes, which can be made by two-photon writing, are then required to create microcavity and waveguide features. The lattice parameters that can be achieved are constrained because the length scale of the interference pattern is set by the wavelength, and this is linked to the energy of the photons that initiate photochemical change. We discuss the requirements for, and progress towards, amorphous silicon photonic crystals that offer a large omnidirectional photonic bandgap in the 1.5 micron telecommunications band, and devices fabricated within this photonic crystal matrix.

4:30 PM **M10.8**

**Direct Patterning of Barium and Strontium Titanate Films by Laser Activated Electro-chemical Reactions in Aqueous Solutions.** Tomoaki Watanabe, Michiyo Kamiya, Ryo Teranishi, Takeshi Fujiwara and Masahiro Yoshimura; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Patterning of ceramics films has been established generally by [1] classical lithography after fabrication of continuous films by dry or wet methods, [2] direct printing of source materials in powder or their precursors, and then laser firing, [3] direct drawing of patterns with an ink or slurry, and then fixing, mostly by firing, etc. Those processing consists of sophisticated multi-steps, which require large amount of energies and resources and then leave most of those energies as exhaust a lot of wastes. However, our challenges toward "direct patterning of ceramics" have been succeeded to fabricate several ceramics films by a single step using solid-liquid interfacial reaction. Locally laser activated reactions with electro-chemical current in aqueous solutions can allow on-site synthesizing, patterning and fixing at the same time and can fabricating crystallized ceramic films with  $\mu\text{m}$ -size patterns in a single step. In this presentation, we will demonstrate a novel fabrication method of patterned ceramic thin films on titanium substrates using local hydrothermal-electrochemical reactions by a laser irradiation. Using this laser patterning system, crystallized barium and strontium titanate films were patterned directly on the titanium substrate in the barium and strontium hydroxide aqueous solutions at a room temperature.

4:45 PM **M10.9**

**157nm Immersion Lithography For Nanoscale Patterning; Capabilities and Materials Needs.** Roger H French, Robert C Wheland, Weiming Qiu, Michael F Lemon and Sheng Peng; DuPont Central Research, Wilmington, Delaware.

157 nm immersion lithography is being evaluated for inclusion on the semiconductor industry roadmap as a novel optical extension technology with potential applications at feature sizes below 45 nm. These feature size generations are 45, 32 and 22 nm and correspond to printed gate lengths in production of 25, 18 and 13nm and physical (post-etch) gate lengths of 18, 13 and 9 nm. The possibility of Immersion Lithography working for these feature size generations represents the forefront of novel lithography. 157 nm Immersion lithography requires low absorbance fluids with high index of refraction, low birefringence,  $dn/d$ ,  $dn/dT$ , and viscosity, which are compatible with both optical scanners and photoresist and its processing. For immersion lithography at 157 nm, the working distance in the scanner is expected to be 1mm, leading to an optical absorbance specification of 0.2/cm (50,000 times more transparent than a 157 nm photoresist). We have surveyed many classes of candidate fluids for use in 157 nm immersion lithography. Essential to the application are the materials properties and processing, since chemical purity, and control of extrinsic absorbers, such as organic, metallic and gaseous absorbers, can play a large role. We have identified various materials classes with 157 nm absorbances below 3/cm which could have utility as 157nm immersion fluids with further optimization.

SESSION M11: 3D Planning II  
Chair: Shu Yang  
Friday Morning, December 5, 2003  
Room 310 (Hynes)

8:30 AM **M11.1**

**Surface Patterning by Laser Interference induced direct treatment.** Frank T. Muecklich, Kaiwen Liu and Claus Daniel; Materials Science, Functional Materials, Saarland University, Saarbruecken, Saarland, Germany.

Interfering laser beams of a high power pulse laser give the opportunity to apply a direct lateral interaction with the surface microstructure in a micro/nano scale based on photo-thermal, photo-physical or photo chemical nature respectively, depending on the type of material. Detailed thermal FEM simulations allow the optimized exploitation of the threshold for the various kinds of direct patterning. Thus, it confirms the experiments for the pattern formation in PVD layers and multilayers. This might be interesting for the structuring of high resolution libraries in high throughput experiments. On the other side, it also works in terms of surface functionalization by means of lateral metallic/intermetallic composite formation. In the latter case, measurements of periodic nano hardness show effects up to 300%. The friction tests show promising consequences for the wear behavior of such surfaces. For polymers the dominating photo chemical interaction produces rather precise topography pattern in polymers. This was found to be a tool to investigate systematically the influence of various surface topography

features e.g. on cell adhesion.

8:45 AM **M11.2**

**PDMS Replication and Magnetic Actuation of 3D Microstructures Made by Two-Photon-Induced Polymerization.** Christopher N LaFratta<sup>1</sup>, T Baldacchini<sup>1</sup>, R A Farrer<sup>1</sup>, M C Teich<sup>3</sup>, B. E. A. Saleh<sup>3</sup>, M J Naughton<sup>2</sup> and J T Fourkas<sup>1</sup>; <sup>1</sup>Chemistry, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Physics, Boston College, Chestnut Hill, Massachusetts; <sup>3</sup>Electrical and Computer Engineering, Boston University, Boston, Massachusetts.

Two-photon absorption (TPA) induced polymerization has proven to be a powerful method for the fabrication of complex 3D microstructures that would be difficult to produce using standard lithographic techniques. However, TPA induced polymerization is a serial process, and is therefore considerably slower than standard lithography techniques. We present a method that combines the advantages of TPA and soft lithography. A master microstructure, fabricated by TPA polymerization, is molded in poly(dimethylsiloxane) (PDMS), and then single photon polymerization is used to replicate the microstructure. In a matter of minutes, replicas can be formed with sub-micron resolution. This technique allows facile replication of high-aspect-ratio microstructures as well as those that have relief or undercut surfaces, and therefore could not be reproduced using a non-elastomeric mold. The mold also allows microstructures to be created from materials that could not be used in TPA polymerization. This molding technique could ultimately permit rapid production of parts for functional devices. Functional devices require actuation however, and the actuation of polymeric microstructures thus far has been limited to optical manipulation by laser trapping. A novel method is presented for the external actuation of microstructures using magnetic fields. Such manipulation is useful for both the characterization of the microstructures mechanical properties and for its application as a useful mechanical device.

9:00 AM **M11.3**

**A High-Q Photonic Bandgap Crystal Fabricated by Femtosecond Laser Direct Writing Method.** Ming Li<sup>1</sup>, Kiyotaka Mori<sup>1</sup>, Jimmy Jia<sup>1</sup>, Xinbing Liu<sup>1</sup>, Yoshimasa Sugimoto<sup>2</sup>, Naoki Ikeda<sup>2</sup> and Kiyoshi Asakawa<sup>2</sup>; <sup>1</sup>Panasonic Boston Lab, Cambridge, Massachusetts; <sup>2</sup>The Femtosecond Technology Research Association, Tsukuba, Japan.

A one-dimensional (1D) photonic bandgap crystal was fabricated using a frequency-tripled femtosecond laser. During this investigation, we achieved a hole positioning accuracy of  $\sim 10$  nm and record-breaking feature size of  $\sim 100$  nm for laser direct writing method. The fabricated device supports a microcavity with a 10-nm-wide transmission window, centered at  $\sim 1490$  nm. An amplified Ti:Sapphire laser, which was operated at a pulse width of 150 fs, a wavelength of 258 nm (frequency tripled), a pulse repetition rate of 1 kHz, was used as the machining tool. The laser beam was focused to a  $\sim 400$  nm spot size with our delivery system on the Si-on-SiO<sub>2</sub> waveguide, which was mounted on a computer-motorized XY stage with nanometer resolution (Queensgate). A microscope imaging system was incorporated into the setup to monitor the sample surface and drilling in real-time. Using this setup, we fabricated a 1D structure on 571 nm Si waveguide with  $< 200$  nm hole-size, 400 nm pitch-size and a defect ratio of 1.4. The standard deviation of the hole position is  $\sim 10$  nm. As predicted by theory, a sharp transmission peak appeared in the forbidden gap. The full-width-half-maximum of the peak was  $\sim 10$  nm, which would yield a Q value of 150. Both the machining accuracy and the Q value of the microcavity are very comparable with that obtained with lithographic methods. The structure we fabricated can be used as narrow band filter, an add/drop filter for wavelength division multiplexing, or an optical delay generator for time-division-multiplexing in current telecommunication industry. Acknowledgment: This work was performed under the Femtosecond Technology Research Association FESTA, which is supported by the New Energy and Industrial Technology Development Organization (NEDO).

9:15 AM **M11.4**

**Triply Periodic Bicontinuous Structures Through Interference Lithography: A Level Set Approach.** chaitanya ullal<sup>1</sup>, Martin Maldovan<sup>1</sup>, Shu Yang<sup>2</sup> and Edwin L Thomas<sup>1</sup>; <sup>1</sup>Materials Science, MIT, Cambridge, Massachusetts; <sup>2</sup>Bell Laboratories, Murray Hill, New Jersey.

Interference lithography holds the promise of fabricating large area, defect free structures on the submicron scale both rapidly and cheaply. There is a need for a procedure to establish the connection between the structures that are formed and the parameters of the interfering beams. There is also a need to produce self-supporting 3D bicontinuous structures. A generic technique correlating parameters of the interfering beams to the symmetry elements present in the



resultant structures via a level set approach is developed. A particular space group is ensured by equating terms of the intensity equation to a representative level surface of the desired space group. Single and multiple exposure techniques are discussed. The beam parameters for certain cubic bicontinuous structures relevant to photonic crystals, viz. the diamond, the simple cubic P, and the chiral gyroid are derived utilizing either linear or elliptically polarized light.

**9:30 AM \*M11.5**

**3-D Periodic Patterns Formed in Polymer Dispersed Liquid Crystals.** Timothy J Bunning, Lalgudi V. Natarajan, Vincent P Tondiglia, Richard L Sutherland and David W Tomlin; AFRL/MLPJE, Materials and Manufacturing Directorate, WPAFB, Ohio.

Conventionally, 1 D holograms are recorded by the interference of two coherent beams. We have written both transmission and reflective 1 D Bragg holograms in polymer dispersed liquid crystals (PDLC) by using formulations containing multi-functional acrylate monomers and nematic LCs. Recently, we extended this concept to the simultaneous recording of three dimensional gratings using at least four laser beams. By this technique, a spatially ordered 3-D array of individual LC droplets in solid polymer is produced with a structure that is analogous to an orthorhombic P crystal. We have also demonstrated a simple and rapid method for fabricating switchable photonic crystals of orthorhombic F symmetry. The crystals exhibit Bragg diffraction and can be switched with an electric field of  $\sim 8\text{-}10\text{ V}/\mu\text{m}$ . We also attempted 3-D and 2-D patterns using thiol-ene photopolymerization. The PDLC photonic crystals compare favorably with colloid crystals imbedded with LC.

**10:30 AM \*M11.6**

**Multiphoton Polymerization of Waveguide Structures and Other Optical Functions in Self-Assembled Photonic Crystals.** Paul V. Braun, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Self-assembled 3-D photonic crystals offer the potential for the manipulation of light in unique and highly amplified ways. However much of this functionality will require embedding of complex features including wave guides and cavities within the interior of the photonic crystal. Here we demonstrate multiphoton writing of such features followed by refractive index enhancement through infilling of selenium. The colloidal crystal matrix supports the polymerized features, thus no shrinkage or cracking was observed. This methodology enabled the fabrication of complex 3-D patterns within the colloidal crystal with an edge resolution of 100 nm. The high dielectric contrast necessary for wave guiding was generated through the melt imbibing of selenium followed by removal of the colloidal crystal with HF. Critical also for realization of photonic crystal devices will be the creation of 3-D photonic crystals with low defect densities and defined orientation with respect to the substrate. We will present our recent progress in using nanoparticles to organize colloidal crystals with very low defect densities. We will present results on 3-D photonic crystal based sensors, where strong changes in diffraction result from small changes in structure driven by trace chemical compounds and biomolecules.

**11:00 AM M11.7**

**Membrane Photolithography: UV Light-directed Micro-patterning and Manipulation of Fluid Phospholipid Membranes in the Aqueous Phase.** Chanel K Yee, Meri L Amweg, Annapoorna Sapuri and Atul n parikh; Applied Science, UC Davis, Davis, California.

A wet photolithographic route for micro-patterning fluid phospholipid bilayers is demonstrated in which spatially-directed illumination by deep ultraviolet radiation results in highly localized photodecomposition of the exposed lipids. Unexposed parts of the bilayer retain their intrinsic fluidity and stabilize the newly formed holes. The mechanism appears analogous to a recently proposed bactericidal pathway in which holes in the bacterial cell walls are produced locally at the sites of antigen-antibody union by ozone and singlet molecular oxygen. Using this method, we can directly engineer stable patterns of hydrophilic voids within a fluid membrane and create isolated membrane corrals over large substrate areas. Furthermore, the lipid-free regions can be refilled by the same or different lipids and lipid-mixtures which establish contiguity with the existing membrane, thereby providing a synthetic means for manipulating membrane compositions, probing 2D lipid-lipid mixing, engineering metastable membrane micro-domains, and designing protein arrays. Following this route, new constructs can be envisaged for high through-put proteomics, membrane-protein arrays, biosensors, and spatially directed, aqueous-phase materials synthesis. The work is supported by the NSF Center for Biophotonics Science & Technology and Los Alamos National Laboratory.

**11:15 AM M11.8**

**Micropatterning of Inorganic Film by Laser-induced Pyrolysis using Organometallic Precursor.** Akira Watanabe<sup>1</sup>, Tomokazu Tanase<sup>2</sup>, Yoshio Kobayashi<sup>2</sup>, Mikio Konno<sup>2</sup>, Shinji Yamada<sup>3</sup> and Takao Miwa<sup>4</sup>; <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; <sup>2</sup>Department of Chemical Engineering, Tohoku University, Sendai, Japan; <sup>3</sup>Advanced Research Laboratory, Hitachi, Ltd., Hitachi-shi, Japan; <sup>4</sup>Hitachi Research Laboratory, Hitachi, Ltd., Hitachi-shi, Japan.

A novel low-temperature processing of crystalline lead zirconate titanate (PZT) film was developed by laser-induced pyrolysis using organometallic precursor film in this study. PZT has been extensively studied in recent years because of a variety of applications using the remarkable dielectric and ferroelectric properties. One of the problems in the application of the PZT to an integrated electronic devices is the high-temperature annealing at about 650 °C to obtain a crystalline PZT phase because the crystallization of the PZT enhances the dielectric properties and induced the ferroelectric properties for practical applications. However, integration of PZT thin films in an electronic device requires a low-temperature processing in order to minimize the oxidation of the electrodes. Thus, processing temperatures not significantly higher than 450 °C are highly desired. The sol-gel process is effective to prepare a PZT film at a low temperature. However, the crystallization of the film also requires the high-temperature annealing above 450 °C. In this study, we applied the laser-induced pyrolysis method to a sol-gel derived PZT precursor film and achieved the low temperature processing of crystalline PZT. The experimental setup used for the laser-induced pyrolysis consisted of laser source (Ar ion laser), optical microscope, and PC controlled xyz-stage. The laser beam was focused on a PZT precursor film through an objective lens. Development of the film using an acidic solution gave the PZT micropattern. This process has the additional advantage that micropatterns of the crystalline PZT can be obtained by the spatially selective pyrolysis using the focused laser-beam without any other photoresist processing. The structural characterization of the PZT pattern was made by micro-Raman spectroscopy. The PZT belongs to the perovskite family and has a cubic structure in the paraelectric state. In the ferroelectric phases below its Curie temperature, two crystal structures, either rhombohedral or tetragonal phase, can be formed. The features of the Raman spectrum for the PZT micropattern agreed with those of the tetragonal phase which shows two Raman bands located at 500 and 600  $\text{cm}^{-1}$ , however, the broadness at around 550  $\text{cm}^{-1}$  suggests the coexistence of the rhombohedral phase. In conclusion, we achieved the low temperature processing of crystalline PZT film and the direct micropatterning by laser-induced pyrolysis of a sol-gel derived film. The laser-induced pyrolysis is spatially selective even in the direction to the film thickness because of the focal depth of the objective lens, which enable to decrease the thermal damage of a substrate and electrodes. These features are advantageous for applying the PZT to integrated electronic devices.

**11:30 AM M11.9**

**A Nanoscale Approach to Stamp Fabrication in Hard Materials Using High Intensity Ultrafast Lasers.**

Yousuf Neelam Picard<sup>1,2</sup>, Joel P McDonald<sup>2</sup>, Joseph C Pentland<sup>2</sup>, Hsiao-Hua Liu<sup>2</sup>, Lingjie J Guo<sup>3</sup> and Steven M Yalisove<sup>1,2</sup>; <sup>1</sup>Materials Science and Engineering, Univ. of Michigan, Ann Arbor, Michigan; <sup>2</sup>Center for Ultrafast Optical Science, Univ. of Michigan, Ann Arbor, Michigan; <sup>3</sup>Electrical Engineering and Computer Science, Univ. of Michigan, Ann Arbor, Michigan.

Fabrication of stamps with nanoscale features in hard materials can be accomplished with femtosecond laser machining. Two key characteristics that set femtosecond pulse length lasers apart from longer pulse lengths and continuous wave lasers is: 1) confinement of laser induced damage to very near the irradiated area and 2) the deterministic behavior of the intensity threshold to generate damage. The latter characteristic permits machining features that are well below the diffraction limit of the light. By adjusting the peak of the Gaussian distributed light at focus to be just above this deterministic threshold, a feature size that is smaller than 15 percent of the diffraction limit is possible. Femtosecond laser machining will work in a wide variety of materials including, glass, alumina, diamond, silicon, refractory metals, etc. The limitation is not the material but rather our understanding of the physics of the ultrafast ablation process. We will focus our presentation on the ultrafast ablation process in semiconductors to illustrate the opportunities that this new approach offers to the nano-stamping community. A variety of patterned micron and sub-micron features have been produced using 120 fs pulse length, 800 nm wavelength laser radiation in silicon. Features are characterized using SEM and AFM.

**11:45 AM M11.10**

**Material Property Change of Bulk Si Under Irradiation by a Femtosecond Laser.** Jimmy Yi-Jie Jia<sup>1,2</sup>, Ming Li<sup>1</sup> and Carl V

Thompson<sup>2</sup>; <sup>1</sup>Panasonic Boston Lab, Cambridge, Massachusetts; <sup>2</sup>Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

It has been demonstrated that laser ablation of silicon using femtosecond-scale laser pulses allows drilling of nanometer-scale holes. However, the mechanism for this nanomachining processes is not well understood, and the condition of the material adjacent to the holes has not been well characterized. We report on cross-sectional transmission electron microscopy (TEM) of ablation sites. A frequency-tripled Ti:Sapphire ultrafast laser (258 nm, 150fs) was used to drill holes in silicon layers on silicon-on-insulator wafers (180nm-thick single crystal <100> films on 200nm-thick amorphous SiO<sub>2</sub> layers on <100> wafers) The fluence was near the single pulse threshold for Si ablation. A series of ~200-nm-wide ~100-nm-deep holes were drilled through the Si layer with 5 pulses/hole. Cross-sectional TEM samples were prepared using focused ion beam (FIB) sectioning. In bright-field TEM imaging mode, a 20-30nm thick apparently amorphous layer was observed immediately adjacent to the holes. This suggests rapid melting and resolidification, at rates that exceed the maximum crystallization rate for Si. The characteristics of these microstructural features will be determined for different fluences and numbers of pulses. Acknowledgements This work was performed under the Femtosecond Technology Research Association (FESTA), which is supported by the New Energy and Industrial Technology Development Organization (NEDO).

SESSION M12: Other Methods  
Chair: Tim Bunning  
Friday Afternoon, December 5, 2003  
Room 310 (Hynes)

#### 1:30 PM \*M12.1

**Direct Fabrication of Functional Ceramic Patterns without Post-Firing: Second Stage Development in Soft Solution Processing.** Masahiro Yoshimura, Tomoaki Watanabe, Takeshi Fujiwara, Ryo Teranishi and Hao Wang; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

The present human society is supported by the tremendous consumption of resources, energy and advanced materials. Thin and thick films of functional materials, including ceramics, have traditionally been fabricated by processes requiring huge amounts of energy and resources, some of which are wasted to the environment. We are proposing an innovative concept and technology, Soft Solution Processing (SSP) for ceramics, which aims to achieve direct fabrication of shaped, sized, located, oriented ceramic materials from solutions without firing and/or sintering. We have successfully fabricated thin and thick films of BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaWO<sub>4</sub>, SrMoO<sub>4</sub>, LiCoO<sub>2</sub>, and LiNiO<sub>2</sub> by SSP in aqueous solutions from room temperature to 200 °C. In these experiments, interfacial reactions between a solid reactant (substrate) and component(s) in a solution have been designed and realized. By locally activating the reaction and moving the reaction point dynamically in these reactions we can produce patterned ceramics directly in solution without masking, etching, pattern forming, or any post-heating such as firing or sintering. In this paper we present recent results for patterned ceramic films of PbS, CdS, and LiCoO<sub>2</sub>. The processes used to produce these films are entirely new, and represent the first examples of successful direct patterning of ceramics from solutions. Carbon patterning also could be realized in organic solvents. In previous reports, heating processes have been essential for synthesis and/or sintering of powders and precursors to obtain patterns in ceramic materials. Such processes inevitably cost environmentally and economically. In contrast, our method, where no firing is needed, provides an environmentally and economically less expensive alternative. References: (1) M. Yoshimura, et al, MRS Bulletin (Sept. 2000), Special Issue of Soft Processing, pp. 12-16 and 17-25 (2) M. Yoshimura, et al., J. Mater. Chem., 9, 77 (1999) (3) M. Yoshimura, et al., Solid State Ionics (SSP Special Issue of SSP), 151, 11, 41, 97, 147, 419 (2002) (4) M. Yoshimura, et al., MRS Proceeding, in press (2003)

#### 2:00 PM M12.2

**A direct-write lithography technique for the fabrication of nano-circuit interconnects.** Vidyut Gopal<sup>1</sup>, Eric A Stach<sup>1</sup>, Rong Fan<sup>2</sup> and Peidong Yang<sup>2</sup>; <sup>1</sup>National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; <sup>2</sup>Department of Chemistry, University of California, Berkeley, California.

To date, significant progress has been made in the bottom-up fabrication of nanoscale building blocks, such as nanowires and nanotubes. However, there have been fewer efforts in interconnecting them to fabricate functional electronic circuits. We present a simple and versatile direct-write nanolithography technique for the

fabrication of planar interconnects. Decomposition of a metal organic precursor gas injected in the path of a focused electron beam resulted in localized deposition of conductive platinum (Pt). Thus, Pt metal lines were patterned by controlling the shape of the raster area in a scanning electron microscope (SEM). Through combined electrical and microstructural characterization we have optimized these nanoscale interconnects to allow fabrication of reproducible ohmic contacts to silicon nanowires. Since the in-situ metal deposition can be conveniently combined with SEM imaging, nanocircuits with several interconnected semiconductor nanowires were fabricated. This direct-write technique represents an alternative to conventional e-beam lithography, with the potential to greatly simplify the fabrication of prototype nanocircuits.

#### 2:15 PM M12.3

**Electrospinning of Polymeric and Ceramic Nanofibers as Uniaxially Aligned Arrays.** Dan Li, Yuliang Wang and Younan Xia; Department of Chemistry, University of Washington, Seattle, Washington.

Electrospinning has been applied to prepare uniaxially aligned nanofibers made of organic polymers, ceramics, and polymer/ceramic composites. The key to the success of this method was the use of a collector consisting of two pieces of electrically conductive substrates separated by a gap whose width could be varied from hundreds of micrometers to several centimeters. As driven by electrostatic interactions, the charged nanofibers were stretched to span across the gap and thus to become uniaxially aligned arrays over large areas. Because the nanofibers were suspended over the gap, they could be conveniently transferred onto the surfaces of other substrates for subsequent treatments and various applications. Materials that have been successfully incorporated into this procedure include conventional organic polymers, graphite carbon, and metal oxides. We will present some applications of these aligned nanofiber arrays.

#### 2:30 PM M12.4

**Sol-Gel Synthesis of Monodisperse BaTiO<sub>3</sub> Nanocrystalline Particles and Fabrication of Patterned Nanostructured BaTiO<sub>3</sub> Films by Cathodic Electrodeposition.**

Makoto Kuwabara, Juan Li, Hidetaro Tanaka and Chia-Wen Wu; The University of Tokyo, Tokyo, Japan.

We have succeeded in synthesizing single-crystalline barium titanate (BaTiO<sub>3</sub>) particles of 10-15 nm in diameter via a sol-gel method using a high concentration of Ba,Ti alkoxides solution (1.0 mol/L). The alkoxides solution was hydrolyzed at -20°C and then hydrothermally treated at 90°C for 1 h, resulting in transparent BaTiO<sub>3</sub> bulk gels broken into several pieces. Sonication of the BaTiO<sub>3</sub> bulk gels in 2-methoxyethanol added with a small amount of acetylacetone yielded a clear suspension of BaTiO<sub>3</sub> crystalline nanoparticles. Using this suspension, we fabricated patterned nanostructured BaTiO<sub>3</sub> thin films with a thickness of 100-10000 nm on Pt/Ti/SiO<sub>2</sub>/Si substrates, on which resist molds were formed, by cathodic electrodeposition, which was carried out by applying an electric field of 1-20 V/cm for various times of 1 to 30 min. The obtained BaTiO<sub>3</sub> thin films have been confirmed to have a dense structure and smooth surface, though when the film thickness exceeded a certain value (around 1000 nm) cracking occurred in the films after dried. We sintered the electrodeposited BaTiO<sub>3</sub> thin films at 700°C in air to obtain ceramic thin films. We report the dielectric properties of the obtained BaTiO<sub>3</sub> ceramic thin films and the grain structure evolution of the films during sintering.

#### 3:15 PM \*M12.5

**Directed Assembly of 3D Periodic Structures.**

Jennifer A. Lewis, University of Illinois, Urbana, Illinois.

We have developed novel approaches to patterning 3D periodic structures via directed and self assembly of colloidal, nanoparticle, and polyelectrolyte building blocks. This talk will feature highlights from our work and collaborative efforts on the directed assembly of gel-based inks for patterning 3D periodic structures with feature sizes ranging from 500 to 1 micron. Our approach relies on creating self-supporting, concentrated inks that can flow through fine deposition nozzles and yet "set" almost instantaneously to provide shape retention as they span gaps in the underlying layers. These 3D structures may find application as composites (Langmuir, 2002), fluidic networks (Nature Mat., 2003), and templates for photonic materials.

#### 3:45 PM \*M12.6

**Photoinitiated Switching in Holographic Polymer Dispersed Liquid Crystals.** Augustine M. Urbas, Jay R. Klosterman,

Timothy J. Bunning, Lalgudi V. Natarajan, Vincent P. Tondiglia, Richard L. Sutherland, David Tomlin and Osamu Tsutsumi; Air Force Research Laboratory, WPAFB, Ohio.

We have made photoresponsive HPDLC gratings by incorporating

azo-benzene containing liquid crystal mesogens. Typical HPDLC photonic structures exhibit reflective or diffractive properties, which can be modulated by an applied voltage. These normal HPDLC properties are enhanced by the ability to change the spectral characteristics of the holographic grating by exposure to suitable light wavelengths through the use of photo-chromic azo-LC components. The azo-LC components undergo trans-cis isomerization on exposure to appropriate wavelengths inducing an isothermal nematic-isotropic transition. This transition affects a change in the effective dielectric properties of the LC rich HPDLC phase. Both ON-OFF type behavior and modulation with exposure are observed in our system. Self-switching of a given wavelength and thermal vs optical restoration will also be discussed.

**4:15 PM M12.7**

**Organic vapor jet printing for direct patterning of small-molecule organic-based electronics.** Max Shtein<sup>1,2</sup>, Peter Peumans<sup>3,2</sup>, Jay B Benziger<sup>1,2</sup> and Stephen R Forrest<sup>3,2</sup>; <sup>1</sup>Chemical Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Center for Photonic and Optoelectronic Materials, Princeton University, Princeton, New Jersey; <sup>3</sup>Electrical Engineering, Princeton University, Princeton, New Jersey.

We demonstrate Organic Vapor Jet Printing (OVJP) - a novel method for the direct printing of thin films of low molecular weight organics (e.g. Alq3, pentacene) for optoelectronic devices. OVJP is an extension of organic vapor phase deposition,[1] where an inert carrier gas transports organic molecules from the source to the substrate. In contrast, OVJP employs collimated gaseous jets to directly print patterned organic thin films on substrates without shadow masks or post-deposition lithography. The technique is analogous to ink-jet printing of polymers, replacing the liquid solvent with a hot inert carrier gas. We have successfully patterned organic thin films for optoelectronic devices at deposition rates >1000 Angstroms/second and resolution of ~20 microns. We will show how resolution varies with process parameters, such as nozzle-to-substrate distance, nozzle size and pressure drop across the nozzle. The OVJP technique is adaptable to rapid deposition on substrates of virtually arbitrary size and shape, and, due to the nearly 100% efficient use of source materials and a simplified device fabrication sequence, can potentially result in more rapid device processing than competing methods. [1] "Micropatterning of small molecular weight organic semiconductor thin films using organic vapor phase deposition" M. Shtein, P. Peumans, J.B. Benziger, S.R. Forrest, Journal of Applied Physics, 93, 4005, (2003)

**4:30 PM M12.8**

**Abstract Withdrawn**

**4:45 PM M12.9**

**Patterning of Polymer Structures by Guided Anisotropic Dewetting.** Haoli Zhang and David G Bucknall; Department of materials, Oxford University, Oxford, Oxfordshire, United Kingdom.

Patterning polymer thin film into desired nano-scale morphology on a surface is of great importance to science and technology with diverse applications such as microelectronics, photonic materials, high-density data storage devices, and sensors. Many advanced lithographic technologies that are capable of high resolution fabrications, such as EUV and e-beam lithography, require expensive and sophisticated facilities. Recently, approaches such as nanoimprint and soft lithography have attracted great interest since they promise the possibility of patterning large areas with a low cost and high throughput. The nanoimprint and soft lithography approaches are generally based on transferring a pattern from a prefabricated master mold or stamp to a solid substrate by conformal contact. In these approaches, the resulted feature size is normally identical to those on the master, but giving a pattern that is the opposite to that of the master. In this presentation, we will demonstrate a simple method that allows making polymer patterns with features size much smaller than those on the mold. In this approach a elastometric mold is used to pattern a thin polymer films. Because the polymer is chosen that it has higher affinity to the mold than to the substrate, when heated above its glass transition temperature (T<sub>g</sub>) the polymer dewets under the guidance of the mold. By tuning the morphology of mold and the substrate surface properties, regular dots and lines with characteristic feature size beyond that of the mold can be obtained. This approach can be applied to very large areas and has shown good reproducibility.