

# SYMPOSIUM Z

## Patterning Soft Materials—From Methods to Applications

April 18 – 20, 2001

### Chairs

**Milan Mrksich**  
Dept of Chemistry  
Univ of Chicago  
Chicago, IL 60637  
773-702-1651

**John A. Rogers**  
Lucent Technologies, Bell Labs  
Rm 1C-365  
Murray Hill, NJ 07974  
908-582-4742

**Seth R. Marder**  
Dept of Chemistry  
Univ of Arizona  
Ste 300  
Tucson, AZ 85747  
520-574-0456 x13

**David J. Beebe**  
Dept of Biomedical Engr  
Univ of Wisconsin-Madison  
CAE Rm 274  
Madison, WI 53706-1608  
608-262-2260

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\* Invited paper

**8:30 AM \*Z1.1**

DIP-PEN NANOLITHOGRAPHY AND COMBINATORIAL NANOTECHNOLOGY. Chad A. Mirkin, Seunghun Hong, Linette Demers, Dana Weinberger, Northwestern University, Chemistry Department and Institute for Nanotechnology, Evanston, IL.

Methods for doing massively parallel Dip-Pen Nanolithography (DPN) will be described. DPN is a scanning probe method for patterning hard substrates with soft materials (organic and biological) with 10 nm linewidth and 5 nm spatial resolution. This tool can be used to generate complex patterns of a diverse set of chemical inks, thereby providing a means for generating combinatorial arrays that can be utilized in addressing many issues in chemistry (e.g. catalysis and biorecognition) and materials science (e.g. solid-state electronics fabrication and colloidal crystal growth).

**9:00 AM \*Z1.2**

NANOFABRICATION OF SELF-ASSEMBLED MONOLAYERS AND PROTEINS USING SCANNING PROBE LITHOGRAPHY. Gang-yu Liu, Song Xu, Nabil A. Amro, Kapila Wadu-Mesthrige, Yile Qian, Department of Chemistry, Wayne State University, Detroit, MI.

Scanning probe lithography-based methods have been developed to produce nanometer-sized patterns within self-assembled monolayers (SAMs). The key to achieving high spatial precision is to keep the tip-surface interactions sufficiently strong and very local. In this presentation, the following nanofabrication methods are introduced: (1) two AFM-based methods, nanoshaving and nanografting, which rely on the local force; and (2) two STM-based techniques, electron-induced diffusion and desorption, which use tunneling electrons for fabrication. Compared with other techniques used to fabricate microstructures of SAMs, scanning probe lithography offers the highest spatial precision. In addition, nanostructures can be characterized with molecular resolution in situ using the same tip. Using nanografting, one can also quickly change and/or modify the fabricated patterns in situ without changing the mask or repeating the entire fabrication procedure. Automated lithography is also under development for high throughput applications. Two applications of scanning probe lithography will also be discussed: (1) production of protein nanopatterns and (2) study of surface reaction under nanometer-confined conditions. In combination with protein immobilization techniques, we used scanning probe lithography to produce nanometer-sized protein patterns. Proteins within these nanopatterns maintain their bioactivity. Nanostructures produced in these studies offer a good opportunity to investigate size-dependent properties such as mechanical properties and chemical reactivity. New phenomena such as spatially confined surface reactions have been observed in the process of nanofabrication.

**9:30 AM \*Z1.3**

NANO-SCALE STRUCTURES FABRICATED BY ALL-ADDITIVE AFM-ASSISTED NANOASSEMBLY. Brian Hubert, Aggelos Bletsas, Joseph Jacobson, Massachusetts Institute of Technology, Media Lab, Cambridge, MA.

A new all-additive method for direct liquid fabrication of nano-scale two dimensional and three-dimensional structures using the tip of an atomic force microscope (AFM) and a material reservoir is proposed. The technique works with a broad range of materials and liquids and does not require any special substrate-liquid interactions such as self-assembling chemistry and is thus the first technique, to our knowledge which is generally applicable to building three-dimensional structures using the AFM. We have shown that liquid phase and solid phase materials can be transferred from a reservoir to a deposition area by a sharp silicon tip moving under computer control. Gold, silver, and organic structures with 45 nm line-width and 1:2 height:width aspect ratio have been directly fabricated onto glass and silicon substrates. Liquid and solid volumes as small as  $10^{-12}$  picoliters ( $10^{-24}$  L) have been delivered with 10 nm repeatability over a 100x100 micron area. We will report on structures that have been constructed using this approach.

**10:15 AM \*Z1.4**

NANOPATTERNING BY NANOIMPRINT LITHOGRAPHY AND LITHOGRAPHICALLY-INDUCED SELF-ASSEMBLY. Stephen Y. Chou, NanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ.

Two new nanopatterning technologies will be presented: nanoimprint lithography (NIL) and lithographically-induced self-assembly (LISA). Both of them are based upon principles fundamentally different from that of conventional lithography. NIL patterns a resist by physical

deformation of the shape of the resist with embossing, rather than by modification of the resist chemical structures with radiation. NIL has demonstrated sub-10 nm feature size, 40 nm period, excellent uniformity and submicron alignment over a large area. A variety of NIL machines (such as planar, roller, and step-and-repeat NIL), masks and processes have been developed. Many electronic, optic, and magnetic nanodevices have been fabricated using NIL. LISA creates patterns by using a large feature on a mask to induce and guide the self-assembly of much smaller patterns in a resist. A unique advantage is that, contrary to conventional self-assembly, the location of each self-assembled feature in LISA can be predetermined and controlled precisely, and an entire ensemble of the LISA patterns can be a single domain. Both NIL and LISA are high-throughput and low cost nanopatterning technology and will play an important role in future development and manufacturing of nanostructures.

**10:45 AM Z1.5**

NANOPOROUS ALUMINA IMPRINTING MASKS - NANOSTRUCTURING OF COMPLEX SHAPED SURFACES.

Thomas Sawitowski, Steffen Franzka, Matthias Levering, University of Essen, Department of Inorganic Chemistry, Essen, GERMANY.

The fabrication of large areas of structured surfaces with feature sizes in the nanometer range is still a challenge. Modern approaches to structure surfaces in the micrometer and sub-micrometer range (randomly or even ordered) involve the use of versatile lithographic technologies like electron beam lithography, self-assembling methods, scanning probe techniques or novel imprinting methods based, for instance, on soft-lithography. Each of those technologies has advantages and disadvantages, respectively, regarding minimal feature size, structural ordering, and technological effort involved in structuring larger surface areas. For instance, using electron beam lithography, structures of perfect shape and order can be made down to very small sizes, while the effort to perform the process is very high, due to the equipment needed. On the other hand, nanostructures, made by imprinting methods, show impressive variability in shape and order. Sizes down to 30 nm are available by these methods, but to generate the master, electron lithography is still involved. The mask material presented here to create nanometer sized pillars on polymeric or metallic surfaces is nanoporous alumina, made by anodic oxidation of aluminium, a process which is known over decades. The most important aspect is the unique control over the pore size by changing the applied voltage leading to pores from less than 10 nm up to more than 250 nm with small size distributions. Even more, by using pre-structured surfaces highly ordered porous layers have been made. While size and shape of these porous layers are in principle unlimited, this material could serve as an ideal stamp to nanostructure surfaces in the range between 10 nm and 250 nm. Examples of nanostructured metallic and polymeric surfaces, made by using alumina membranes, are presented and the change in surface properties will be discussed.

**11:00 AM Z1.6**

HIGH RESOLUTION PATTERNING USING ACRYLATE

POLYMER NETWORK STAMPERS. Kenneth R. Carter, Bruce D. Terris, Gary M. McClelland, Margaret E. Best, IBM Almaden Research Center, San Jose, CA.

Hopes for high density patterned magnetic media rely in part on innovative, inexpensive ways to pattern nanoscopic features. Contact lithography techniques, such as nanoimprint lithography and step-and-flash lithography, show great promise in the ability with respect to image transfer in an efficient, economic fashion. One of drawbacks of these contact techniques is the lack of availability of suitable, inexpensive, high resolution stampers from which the initial image is pressed. We report the use of siloxane-modified acrylate networks as stampers for contact nanolithography. We have found the networks composed of a mixture of photopolymerizable acrylates can be cast against hard masters, photochemically cured, then in turn, be used repeatedly as stampers in the replication of nanometer sized features into an appropriate imaging layer. The low surface energy siloxane constituent imparts good contact and release character to the stamp. The siloxane-modified stampers were used to transfer pattern smaller than 100nm into a photopolymer layer.

**11:15 AM Z1.7**

NANOSCALE CHARACTERIZATION OF THE LATENT IMAGE

FORMED IN CHEMICALLY AMPLIFIED RESISTS. F.A. Houle,

W.D. Hinsberg, M.I. Sanchez, J.A. Hoffnagle, IBM Almaden Research Center, San Jose, CA.

Chemically amplified resist systems have proven to be extremely versatile and manufacturable, and will be likely be used for patterning many types of films and substrates regardless of excitation source for the foreseeable future. These resists have the characteristic that the steps of initial latent image formation by irradiation and developable image formation by heating are separate. This means that for any means of imaging - photons or electrons, scanned probe or large area

exposure - it is possible to determine how the deposited energy will result in a pattern if the fundamental processes taking place during the post-exposure heating step are understood. In this talk we will describe an experimental study of the detailed chemistry and physics of the image transformation process that has enabled us to determine how coupled reaction and diffusion lead to a developable pattern in a chemically amplified resist. We have placed particular focus on how resist components such as photoacid generator, polymer, and added base work together to affect the final image at the nanometer scale. A series of resists were prepared and exposed using both blanket and interferometric lithography and the image transformation process was followed spectrophotometrically. Physically accurate simulations of the experiments enabled the influence of resist composition and process conditions on extent of reaction to be determined, and yielded full visualization of the resulting latent image. The factors affecting image formation at the 50 nm scale and below will be discussed.

#### 11:30 AM \*Z1.8

3D PATTERNING OF POLYMERS AND METALS USING TWO-PHOTON PROCESSES. J.W. Perry, K. Cammack, S.M. Kuebler, S.R. Marder, M. Rumi, F. Stellacci, T. Watanabe, W. Zhou, University of Arizona, Dept of Chemistry, Tucson, AZ; T. Yu, C. Ober, Cornell Univ., Dept of MS&E, Ithaca, NY.

Recent progress in the development of materials for 3D microfabrication of polymeric and metallic structures by two-photon laser scanning direct writing will be presented. High sensitivity two-photon radical and acid generating initiators and their use in two-photon patterning of polymer microstructures will be described. We will also describe a new approach to the direct writing of 3D metallic structures within a polymer matrix. Prospects for applications, the extension of this approach into the nanoscale, and for the preparation of hierarchically structured materials will be discussed.

#### SESSION Z2:

Chair: Gang-yu Liu

Wednesday Afternoon, April 18, 2001

Olympic (Argent)

#### 1:30 PM \*Z2.1

MULTIDIMENSIONAL VOLUME HOLOGRAPHIC LITHOGRAPHY. M. Campbell, D.N. Sharp, M.T. Harrison, A.J. Turberfield, Oxford University, Clarendon Laboratory, Oxford, UNITED KINGDOM; R.G. Denning, Oxford University, Inorganic Chemistry Laboratory, Oxford, UNITED KINGDOM.

Periodic microstructure on a micron or sub-micron scale can be formed conveniently by converting a holographic-defined intensity pattern into insoluble cross-linked polymer. Both two- and three-dimensionally periodic structures can be readily fabricated in this way. We discuss the design criteria for suitable photoresists, and the potential for incorporating additional aperiodic structural elements into the pattern. It is shown that a single 355nm UV wavelength can be used to define a several face-centred cubic structures with different lattice parameters (as well as other lattice types), and that the choice of the optical polarisation of the writing beams enables a wide variety of crystallographically distinct bases to be realised.

#### 2:00 PM \*Z2.2

THREE-DIMENSIONAL SUB-MICRON FABRICATION WITH BIOACTIVE PROTEINS BY MULTIPHOTON EXCITATION. Steven L. Goodman, University of Connecticut Health Center, Center for Biomaterials and Department of Physiology, Farmington, CT; Paul J. Campagnola, University of Connecticut Health Center, Center for Biomedical Imaging Technology and Department of Physiology, Farmington, CT.

The incorporation of biomolecules into engineered devices can provide critical functionalities in technologies as diverse as biomaterials, tissue engineering, drug delivery, biosensors, bioMEMs, and integrated labs-on-chips. However, lithographic and stamping fabrication methods, and commonly used organic chemical processes, have some limitations with respect to building such devices. These include, i) maintaining biomolecular (protein) bioactivity, ii) positioning multiple biomolecules in different locations, iii) producing submicron features and iv) fabricating complex 3-D structures. We have recently introduced a 3-D fabrication methodology that enables the directed assembly of bioactive proteins, and is capable of <250 nm resolution. This methodology utilizes the intrinsic 3-D confinement of nonlinear optical processes to locally initiate photoactivation-induced cross-linking and/or polymerization. Current instrumentation is based upon a laser scanning confocal microscope (Biorad MRC600) modified for near-infrared excitation provided from a pulsed Ti:Sapphire laser

(Coherent 900-F). To maintain protein bioactivity, and to facilitate the use of structures in biomedical applications, crosslinking and polymerization reactions are photo-initiated in aqueous solutions using non-toxic dyes such as Rose Bengal. With this methodology, submicron structures have been assembled by cross-linking many different proteins, and by locally polymerizing several types of synthetic polymers into complex 3-D structures. Examples include 300 nm enzyme-based structures that exhibit a high level of bioactivity, submicron to >100 um structures fabricated from adhesive proteins that direct cellular adhesion, and micron-scale sustained release (drug delivery) devices assembled from both hydrogels and proteins. Also demonstrated is the capability to build protein and hydrogel structures >100 um deep within porous collagen networks, and the capability to precisely position fabrication with respect to existing structures. This methodology can therefore enable the 3-D patterning of bioactive proteins and other agents into complex biomedical devices such as tissue engineering scaffolds, and can be readily utilized to incorporate biofunctional proteins into other bio-nanotechnological devices.

#### 2:30 PM Z2.3

ACTIVE MANIPULATION OF ORGANIC AND INORGANIC OBJECTS BY USING OPTICAL MICRO BEAMS. Mihrimah Ozkan, Mark M. Wang, Sangeeta Bhatia<sup>a</sup> and Sadik C. Esener Electrical and Computer Engineering Department. <sup>a</sup>Bioengineering Department, University of California at San Diego, San Diego CA.

Vertical cavity surface emitting lasers and near infrared diode lasers are used to transport micron size objects. Electrokinetically formed micro cellular arrays have been manipulated by using photonic momentum transfer that is exerted by micro optical beams. Pre-patterned mouse 3T3 fibroblasts on a transparent substrate have been picked and placed by optical micro beams to a new location on the chip. Active manipulation of 3x1 array of polystyrene spheres is achieved concurrently by VCSEL driven optical multi-micro beams. Each optical micro beam has been driven with 12 mA of current and the distance between the micro beams is about 18 μm. Fibroblasts are transported with the speed of 5-10 μm/sec with VCSEL driven optical micro beams. Optical transport can be advantageous in that it can provide precise and individual manipulation of single cells or other biological samples regardless of their charge. Preliminary tests of cell viability after exposure to the VCSEL tweezers have been performed. Live cells in a defined sampling area on a microscope slide were each exposed to the optical tweezers beam for 60 sec where the VCSEL driving current was 14 mA. The cells were then return to the incubator and observed to grow and reproduce normally over several days. No dead cells were found within the sampling area. Higher optical power exposures of approximately 18 mW for 15 sec were also tested using a higher powered 850 nm diode laser, and similar results were observed.

#### 3:15 PM \*Z2.4

SOLUTION DEPOSITION OF ORGANIC TRANSISTOR SEMICONDUCTORS. H.E. Katz, A.J. Lovinger, Ch. Kloc, T. Siegrist, Bell Laboratories-Lucent Technologies, Murray Hill, NJ.

The main advantages envisioned for organic-based electronics are the lower cost and larger area processing options. Transistors in such circuits will need to meet performance requirements such as high on-conductance and on/off ratio, and low threshold voltage and subthreshold slope. At the same time, the transistor semiconductors will have to be deposited without the capital-intensive processes generally associated with silicon technology. This talk will describe progress in the design of semiconductors where both performance and ease of fabrication are optimized. In particular, molecular solids that function effectively as semiconductors after facile deposition from solution will be emphasized.

#### 3:45 PM \*Z2.5

NON-PLANAR MICROFLUIDIC ARRAYS HOLD GREAT PROMISE AS AN ENABLING TECHNOLOGY FOR MICROFABRICATION. Ralph G. Nuzzo, Jennifer Monahan, Kari Fosser, William Childs and Andrew A. Gewirth, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL.

In this talk I will describe the application of rapid prototyping based on polymer molding as method for generating active stencil masks for microfabrication using wet chemical processing. Of particular interest in this work are structures of interest for applications in microelectronic and optical component technologies as well as several unconventional materials architectures that we are developing for applications in chemically sensitive detection. A central issue of concern in this work is the development of strategies and enabling chemistries for creating complex multilevel structures with micron-scale design rules in a very broad range of materials, including semiconductors, metals, organic thin films, and functional polymers.

**4:15 PM Z2.6**

**MICROPATTERNING POLYMER FILMS ON A SPHERICAL SURFACE VIA LETTERPRESS PRINTING.** Scott M. Miller, Anton A. Darhuber, Sandra M. Troian, Princeton Univ, Dept of Chemical Engineering, Princeton, NJ; Sigurd Wagner, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

We have investigated the direct printing of patterned polymer films onto both flat and spherical surfaces using a letterpress printing technique. The letterpress stamp is made of a polyimide foil with a surface relief pattern prepared by conventional microfabrication methods. Polymer melt is deposited onto the raised structures from a flat, spin cast film. The melt transfer process is then repeated to transfer the polymer pattern onto a target workpiece. We have successfully printed features smaller than 5 microns onto a flat substrate using both planar printing plates and roller-style plates. Printing onto a spherical surface was accomplished by inflating the printing plate into the shape of a spherical cap. Polymer structures printed by this technique are suitable as resist materials for both wet and dry etch processes. Post-printing spreading of the polymer ultimately determines the maximum resolution achievable by this method. We discuss experimental results for the spreading of printed polymer structures and compare to models of spreading droplets. Flow instabilities that occur during the printing process lead to thickness non-uniformities in the printed polymer film. We discuss the effect of feature size on these non-uniformities and show that they can be eliminated for small structures.

**4:30 PM Z2.7**

**A FACILE SOFT LITHOGRAPHIC TECHNIQUE TO FABRICATE RIDGE WAVEGUIDE DISTRIBUTED FEEDBACK LASERS OF DYE-DOPED MESOSTRUCTURED COMPOSITES.** Brian J. Scott, University of California, Santa Barbara, Dept of Chemistry, Santa Barbara, CA; Gernot Wirsnberger, Karl-Franzens-University Graz, Dept of Chemistry, Graz, AUSTRIA; Michael D. McGehee, Stanford University, Dept of MS&E, Stanford, CA; Bradley F. Chmelka, University of California, Santa Barbara, Dept. of Chemical Engineering, Santa Barbara, CA; Galen D. Stucky, University of California, Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

Currently, there is considerable effort to produce compact solid state lasers, waveguides and switches. One way to provide the resonant feedback that is needed for lasing to occur is to incorporate a grating in a waveguide that causes light with the Bragg wavelength to be reflected. Lasers of this type, known as distributed feedback (DFB) lasers, are typically made with holographic lithography, etching and vapor deposition. We have developed a much simpler technique for making DFB lasers that uses elastomeric molds, soft lithography, to pattern dye-doped mesostructured materials into ridge waveguides that have gratings in their top surface. Mesostructured materials have higher gain than dye-doped sol-gel glasses. This results from processing dilute solutions that undergo evaporation induced co-self-assembly of the laser dye/silica/block-copolymer nanocomposites that simultaneously organize both the 2D-hexagonal silica/block-copolymer framework and the laser dyes in the nanocomposite such that they do not aggregate and quench their own luminescence. These dilute solutions are amenable to fabricating structures by MIMIC and micromolding techniques. DFB lasers have been fabricated by such techniques that have as few as two lasing modes with FWHM of less than 0.5 nm.

**SESSION Z3:**

Chair: John A. Rogers  
Thursday Morning, April 19, 2001  
Olympic (Argent)

**8:30 AM \*Z3.1**

**MICRO- AND NANOPATTERNING OF POLYMERS THROUGH LIQUID CRYSTAL, COLLOID CRYSTAL, AND SURFACE MEDIATED GROWTH.** Paul V. Braun, Yun-Ju Lee, Univ. of Illinois at Urbana-Champaign, Dept of MS&E, Urbana, IL.

Recently we demonstrated that lyotropic liquid crystals formed by self-assembly of surfactants and water, and colloidal crystals formed from either polymeric or silica colloidal particles can be utilized to drive the formation of nanometer and micrometer scale structure in II-VI semiconductor materials. We report here that lyotropic liquid crystals and colloidal crystals can also drive the formation of meso- and macrostructures in bulk and thin film conducting polymers. Micron-sized mesoporous polypyrrole particles were oxidatively polymerized at the interface between lyotropic liquid crystals containing pyrrole and the oxidizing agent iron (III) chloride. Spongy mesoporous thin films of polypyrrole and polyaniline were formed through electrochemical polymerizations on ITO using as an electrolyte lyotropic liquid crystals doped with the appropriate

precursors. In related work, we demonstrated that contact printed self-assembled monolayers could be utilized to drive the deposition of sub-micron colloidal particles with better than 50 nm resolution onto the surface of a substrate. The deposition process is driven first, by low-resolution electrostatic interactions between the charged colloidal particle and the oppositely charged patterned monolayer, and second, by high-resolution capillary forces upon solvent removal.

**9:00 AM \*Z3.2**

**BLOCK COPOLYMER LITHOGRAPHY: LARGE AREA DENSE PERIODIC NANOSCALE PATTERNING.** Miri Park, Lucent Technologies, Murray Hill, NJ; Christopher Harrison, M. Trawick, P.M. Chaikin, Princeton University, Department of Physics, Princeton, NJ; Richard A. Register, Princeton University, Department of Chemical Engineering, Princeton, NJ; Douglas H. Adamson, Princeton University, Princeton Materials Institute, Princeton, NJ.

This talk describes the use of block copolymer thin films as nanolithography templates as an inexpensive, fast, and versatile means of producing dense periodic structures at the 3-100 nm scale over large areas.

Well ordered periodic patterns on the order of 10 nm were generated by the self-assembly of the microdomains in the copolymer thin films. The chemical and physical differences between the microdomains permit selective processing of the copolymer film. The pattern-transfer of the microdomain patterns to the underlying silicon or silicon nitride was achieved by two complementary techniques that resulted in opposite tones of the patterns. Furthermore, by taking advantage of the block copolymer templating and semiconductor processing techniques, and by effectively integrating them, we have developed a tri-layer pattern transfer method and have fabricated metal dot arrays with an area density of  $\sim 10^{11}/\text{cm}^2$ . The method provides a viable route for highly dense nanoscale patterning of different materials on arbitrary surfaces.

Understanding the self-assembly properties of block copolymer thin films and controlling them are important for the successful application of block copolymer lithography. Specially, controlling the order, grain size, and alignment is of high interest since many device applications would require a two dimensional registry of the periodic structures. This talk will also address these issues in the context of using the copolymer films as lithographic templates. For example, the block copolymer microdomain monolayer film structures may vary on different substrate materials. We will present the preliminary results on microdomain alignment along step edges, such as steps defined by patterning a metal structure or steps formed in a cleaved mica film.

**9:30 AM Z3.3**

**NANOPATTERNING USING BLOCK COPOLYMERS: PHYSICAL AGEING AND A NANODEVICE APPLICATION.** Sanjun Niu, Eric Stumb, Ravi F. Saraf, Department of Chemical Engineering, Virginia Tech, Blacksburg VA.

Since the invention of nanopatterning using block copolymer by the Princeton group (M.Park et al., Science, 276 1401 (1997)), there has been considerable interest in using this approach to fabricate nano-scale features such as, lines and holes. The purpose of this presentation is two folds: (i) Study the aging phenomena of the block copolymer monolayer at ambient conditions. Such spontaneous changes may affect the effectiveness of the monolayer films as a mask to fabricate nanostructure. (ii) Develop a periodic array of 'polystyrene hills' of characteristic diameter in 10-30 nm range. The interest here is to utilize the nanoarray of polymeric features to design and fabricate a DNA chip for gene sequencing. The presentation will discuss quantitatively the measurement and analysis of the ageing phenomena, and some preliminary results on the nanodevice for DNA gene sequencing.

**10:15 AM \*Z3.4**

**FORMATION OF POLYMER AND POLYMER-NANOPARTICLE COMPOSITE NANOSTRUCTURES THROUGH SPECIFIC NONCOVALENT INTERACTIONS.** Faysal Ilhan, Andrew K. Boal, Vincent M. Rotello, Department of Chemistry, University of Massachusetts, Amherst, MA.

Coupling of highly specific molecular recognition processes with phase separation behavior provides a potentially versatile approach to structural engineering, integrating the 'lock and key' selectivity inherent in molecular recognition with the 3-dimensional morphological control provided by polymer self-assembly. In our studies, we are using polymers functionalized with complementary and self-complementary hydrogen bonding units to create polymer films displaying a wide variety of structural motifs. We are further expanding upon this diversity through the formation of polymer-nanoparticle composites; both of these assembly strategies will be discussed.

**10:45 AM Z3.5**

SELF-ORGANIZED SUPERSTRUCTURES OF FLUORINATED METAL NANOPARTICLES. Tetsu Yonezawa, Shin-ya Onoue, Nobuo Kimizuka, Dept of Applied Chemistry, Kyushu University, Fukuoka, JAPAN.

Preparation, purification, characterization, and self-assembly characteristics of fluorocarbon-stabilized metal nanoparticles are discussed. In the case of silver nanoparticles, in ethanol/water mixtures, well-developed fibrous aggregates were formed. When they are cast on solid supports from fluorocarbon dispersions, regular hexagonally packed monolayers with a high order and highly regularly ordered mesoscopic honeycomb structures were produced, depending on the concentration and atmosphere.

**11:00 AM Z3.6**

ELECTRIC FIELD INDUCED SELF CONSTRUCTION OF POLYMER MICROSTRUCTURES. Cengiz S. Ozkan, Huajian Gao, Stanford University, Mechanical Engineering Dept, Stanford, CA.

We have developed a method for fabricating polymer microstructures based on electric field induced self assembly and pattern formation. A dielectric fluid placed in between two conductive plates experiences a force in an applied electric field gradient across the plates, which can induce a diffusive surface instability and self construction of the fluid surface. This process is exploited for fabricating self assembled polymer structures as well as replicated patterns through the use of pre-patterned plates or electrodes. We have used silicon wafers and transparent ITO (Indium-Tin-Oxide) coated quartz substrates to fabricate the capacitor structures. The bottom silicon plate is spin coated with a 100-200 nm thick PMMA (polymethylmethacrylate) film. The ITO substrate was placed over the polymer surface at a distance to leave a thin air gap using spacers. For directed pattern transfer, patterned ITO substrates were used. The capacitor setup was heated above the glass transition temperature of the polymer and a voltage was applied across the plates (25-100 volts), which induces electric fields on the order of  $10^7$ - $10^8$  volts/m. The capacitor setup was quenched to observe the structures using optical and atomic force microscopy. The method described can be used to fabricate a variety of structures in the micron and nanometer scales including bio-fluidic MEMS, polymer optoelectronic devices and patterned templates for nanolithography.

**11:15 AM \*Z3.7**

SOFT PLUMBING FOR MICROFLUIDIC DEVICES. Stephen R. Quake, Dept of Applied Physics, Caltech.

We have been using soft lithography to make microfluidic chips for ultrasensitive analysis of single DNA molecules and cells. There are numerous advantages to fabricating chips out of polymeric materials, and as a result we have been able to rapidly and inexpensively fabricate active devices with moving parts, such as pinch valves and peristaltic pumps. We have also developed a microfabricated flow cytometry chip as a replacement for analytical pulsed field gel electrophoresis. Assays with these chips are two orders of magnitude faster than pulsed field gels and use a million times less material. Because they are detecting single molecules, their sensitivity is comparable to PCR based techniques. We have also developed a microfabricated fluorescence activated cell sorter and demonstrated its use in screening bacterial cells. The novel valve and pump components for on-chip fluidic manipulation that we developed in the course of this research will be useful for fabricating more complex chip designs for a variety of biotechnological applications.

**11:45 AM Z3.8**

CONSTRUCTION AND APPLICATIONS OF PDMS CILIA-LIKE STRUCTURES. Glenn M. Walker, David J. Beebe, Univ of Wisconsin-Madison, Dept of Biomedical Engineering, Madison, WI.

It is desirable to create practical microscale structures using the most convenient methods possible. We have successfully used syringe filters to create microscale cilia-like polydimethylsiloxane (PDMS) structures by applying soft lithography (i.e. making a mold from a master). To remove the filters, we have investigated mechanical and chemical methods. The mechanical method is to peel off the filter while the chemical method uses NaOH to dissolve the filter. Cilia sizes depend on the filter used and vary from 3 to 14  $\mu\text{m}$  in diameter and 6 to 10  $\mu\text{m}$  in height with densities from  $5 \times 10^4$  to  $2 \times 10^5$  per  $\text{cm}^2$ . Applications for cilia-like structures include filtering or particle positioning, flow visualization and applications requiring high surface area. We have demonstrated the use of the cilia to create a restriction region in a microfluidic channel to trap individual particles while maintaining flow past the particles. By varying the size and density of the cilia we can control the size of particles allowed to pass. Another application of the cilia is flow visualization. One problem with analyzing fluids in microchannels is that their velocity is often difficult to observe. If one wall of a microchannel is lined with cilia

then as a fluid flows through the channel the cilia will bend an amount proportional to the velocity of the fluid. One final application of PDMS cilia is something nature also uses cilia for — to increase surface area. PDMS cilia structures with microscale dimensions that are easy to manufacture should find a wide variety of applications in microfluidics.

**SESSION Z4:**

Chair: Vincent M. Rotello  
Thursday Afternoon, April 19, 2001  
Olympic (Argent)

**1:30 PM \*Z4.1**

SOFT LITHOGRAPHY AND SURFACE ENGINEERING IN BIOLOGY. Emanuele Ostuni, George M. Whitesides, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA; David C. Duffy, Enoch Kim, Olivier Schueller, Surface Logix, Brighton, MA.

Microfabrication and surface engineering are key technologies for fabricating miniaturized systems used in basic research and drug discovery. We will describe two technologies — soft lithography and self-assembled monolayers (SAMs) — that we believe are enabling in these systems. Soft lithography is a set of techniques that allows rapid and inexpensive fabrication of microstructures that are useful for applications in these areas. The techniques of soft lithography overcome some of the limitations of conventional microfabrication by using materials and methods that are compatible with delicate biological media. Surface engineering with SAMs is making it possible to study and design biological interfaces at the molecular level. The combination of soft lithography with surface engineering has made it possible to develop methods that: i) manipulate and pattern proteins and cells in a meaningful manner, and ii) probe single cells in ways that were not possible before — for example, creating intracellular gradients of small molecules.

**2:00 PM Z4.2**

APPLICATION OF SOFT LITHOGRAPHY. Klint A. Rose, MIT, Boston, MA; Peter Krulvitch, Livermore Center for Microtechnology, Livermore, CA.

In this paper, we present three microfluidic systems fabricated using soft lithographic processing. The flexibility afforded by this technique enabled us to meet various design constraints encountered with the different devices. In all cases, glass substrates were photo-lithographically patterned using wet chemical etching to form masters for molding PDMS (Sylgard 184, Dow Corning). The PDMS was bonded to either glass or PDMS substrates to create sealed channels, using an ethanol clean and oxygen plasma surface treatment. For two devices, electrodes were patterned on the glass substrates. Metallization also was successfully demonstrated on PDMS using an e-beam evaporated chromium adhesion layer and gold conductive film, with patterning accomplished using a shadow mask. Fluidic vias were made by boring holes through the PDMS. In the first application, merging laminar flow microchannels were fabricated for single molecule DNA manipulation and processing. Brewer et al. [1] developed this technique using glass flow cells to demonstrate protamine-induced condensation and decondensation of single DNA molecules. The objective was to develop an approach for fast turn-around of new flow cell designs. In addition to rapid processing PDMS offers a number of advantages including low background fluorescence, the ability to directly bond the coverslip to seal the channels, and straightforward interconnects. In the second application a piezo-electric actuated micropump prototype was fabricated within four days within conceptualization. The pump utilizes the flexibility of the PDMS material allowing it to be actuated by the attached piezoelectric. The fluid channels were etched into glass, providing a hard surface for the PDMS to seal against. In the final example, devices were made in conjunction with a counter biological warfare project aimed at developing a miniaturized sample preparation module. Technologies used in these devices include magnetohydrodynamic (MHD) pumping developed, and dielectrophoretic (DEP) trapping of particles. A PDMS based DEP device was used to manipulate particles within an electric field. Electrodes were integrated on a glass substrate. PDMS was then used to form channels over the electrodes. The room temperature bond avoided difficulties such as channels collapsing, a problem encountered with glass-glass and polymer-based fusion bonding.

[1] R.L. Brewer, M. Corzett, and R. Balhorn, Science 286 (1999) 120.

**2:15 PM Z4.3**

CHEMICALLY PATTERNED SURFACES AS TEMPLATES FOR BIOLOGICAL MICROARRAYS. S.D. Gillmor, C.E. Mason, M.G. Lagally, University of Wisconsin-Madison, MS&E Dept, Madison, WI.

As the focus has shifted from sequencing the human genome to interpretation of it, the task of drawing meaningful conclusions requires millions of comparisons between standard and stressed samples, usually the cDNA, RNA, or proteins within cells. For such a project, high information-density, high purity DNA arrays are required. We describe novel methods to construct biological microarrays, using a chemically patterned surface to create the array. The significant advantage of the arrays described here is the use of this chemically patterned surface, which makes possible both small array element sizes and arrays containing long strands of high-purity DNA. The substrate chemical patterning allows a great degree of control and greater precision in loading the solutions as compared to spotted arrays. The DNA can in our case be pre-purified; this purity, relative to other approaches, reduces errors in detection and analysis. The use of chemically patterned surfaces is not limited to DNA arrays. Such surfaces can be modified to accept a variety of terminal groups separated by an inert background, making possible a host of applications in which high information content and reliability are issues.

\*Research supported by NSF and DARPA.

#### **2:30 PM Z4.4**

**PATTERNING HYBRID SURFACES WITH SUPPORTED LIPID BILAYERS AND PROTEIN.** Li A. Kung, Lance Kam, Jennifer S. Hovis, Steven G. Boxer, Stanford University, Department of Chemistry, Stanford, CA.

Two methods for patterning surfaces with immobilized protein and supported lipid bilayers are described. In the first method, proteins are used to fabricate corrals for supported lipid bilayers. Poly(dimethylsiloxane) (PDMS) stamps are used to deposit arbitrarily-shaped patterns of thin layers of immobilized protein onto glass surfaces and followed by formation of supported lipid bilayers via vesicle fusion into the uncoated regions. In the second method, supported bilayer membranes are blotted to remove patterned regions of the membrane, and the blotted regions are filled in (or caulked) with protein from solution. In both cases, the lipid bilayer regions exhibit lateral fluidity, but each region is separated by protein layers of similar heights to the membrane, as shown by AFM. These two methods can be combined and used iteratively to create arrays with increasing lateral complexity in both the fixed protein and mobile supported membrane regions for biophysical studies or cell-based assays.

#### **3:15 PM Z4.5**

**ULTRA RAPID PROTOTYPING OF MICROFLUIDIC SYSTEMS.** Christopher Khoury, David J. Beebe, University of Wisconsin, Dept of Biomedical Engineering, Madison, WI.

The ability to rapidly iterate device and system designs is becoming of increasing value for a variety of reasons. The realities of the present economy demand adaptability. At the same time, collaborative approaches to research are critical if we are to address the complex multi-disciplinary questions faced in the life sciences. Thus, the ability to rapidly build microfluidic systems in minutes instead of days, weeks, or months, will facilitate advancements in basic research as well as allow industry to react more quickly to changing market demands. Microfluidics research has benefited from rapid prototyping (RP) of devices using materials such as poly(dimethylsiloxane). Advancements have been made in reducing the expenditure and time in mask making. However, the mold making process still requires the use of clean room equipment (spin coater, ultraviolet exposure tool) and materials (photoresist, developer). Making the mold can be time consuming (hours to days) and cumbersome because the process relies on traditional methods from the semiconductor processing field. We have developed ultra rapid prototyping (URP) to allow the user to go from concept to prototype in as little as 1 h from the time one has finished the mask design (via CAD software) to device realization. The advantage of URP lies in the ability to create the mold quickly and economically in a standard life sciences laboratory environment (e.g. hot plate, scale, UV source), without the use of a clean room. An additional advantage is the flexibility of URP structures. The mold can lie on a flat substrate, as a curved structure, or as a free-standing released structure. URP uses a photodefinable liquid-phase pre-polymer solution comprising of Isobornyl Acrylate, Tetraethylene glycol dimethacrylate and 2,2-dimethoxy-2-phenyl-*e* to create 2-D or quasi 3-D molds by masking areas of the solution.

#### **3:30 PM Z4.6**

**PATTERNING OF CHEMICALLY SENSITIVE AND BIOLOGICAL MATERIALS USING A PARYLENE BASED DRY LIFT OFF.** B. Ilic, H.G. Craighead, Cornell Univ, Dept of Applied Physics and Nanobiotechnology Center, Ithaca, NY.

In recent years, there has been a growing interest in patterning of chemically sensitive and biological materials. The ability to generate mesoscopic (0.1 $\mu$ m to 10 $\mu$ m) large areal patterns of biomolecular

materials offers new applications in the field of cell culturing, tissue engineering, biosensor technology, drug discovery, and nanotechnology. We have developed a new approach, using a Parylene based dry lift off, to pattern micrometer sized biomolecular surfaces. Using a combination of projection lithography and reactive ion etching, a Parylene coated surface is patterned and subsequently coated with a biochemical layer. Parylene is then peeled from the substrate and the desired chemical pattern is formed. We have patterned antibodies, poly-L-lysine, and aminopropyltriethoxysilane self assembled monolayers. These surfaces were respectively used to pattern *Escherichia coli* serotype O157:H7 bacteria cells, cultured rat basophilic cells, and 20nm diameter aldehyde-sulfate fluorescent polystyrene beads. Furthermore, we have also patterned protein A, laminin, fibronectin and carbon nanotubes. Prototype arrays of 5mm long parallel lines of bacteria with widths varying from 2 $\mu$ m to 20 $\mu$ m. Such patterns can be made over large areas, and we demonstrate this on areas up to 3cm<sup>2</sup>. Scanning electron and atomic force microscopy were used to investigate the topography and morphology of the patterned surfaces.

#### **3:45 PM Z4.7**

**NEURON-ELECTRODE INTERFACES AND PATTERNING WITH PEPTIDES.** Cristian Ionescu-Zanetti, UC Santa Cruz Physics Dept, Santa Cruz, CA; Lindsay Hink, UC Santa Cruz Biology Dept, Santa Cruz, CA; Sue Carter, UC Santa Cruz Physics Dept, Santa Cruz, CA.

Understanding the function of neurons in connected networks has suffered from our inability to directly record changes in the membrane potential for a large neuronal ensemble. While now electrode arrays can be fabricated on the spatial scale of single neurons, the simultaneous recording of large numbers of interconnected neurons has yet to be achieved. The major obstacles have been patterning of the neurons on top of the electrode arrays and controlling the neuron-electrode interface. Here we present work aimed at assembling peptide layers on the active sites of the electrode arrays. This study will presents not only the resulting directed growth of neurons on a variety of surfaces, but the dependence of the neuron-electrode coupling on the surface chemistry of the electrode. The aim is a thorough understanding of the neuron-electrode interface.

#### **4:00 PM Z4.8**

**DEPOSITION AND PATTERNING OF AgAr THIN FILMS ON SILICON FOR BIO-ELECTRONIC SUBSTRATES.** J.F. Muth, D.P. Nackashi, P.D. Franzon, Dept of Electrical and Computer Engineering, North Carolina State University, Raleigh, NC.

The ability to culture living cells on substrates such as silicon and glass offers the potential to integrate biological processes with current microfabrication technologies. This potentially allows cellular measurements to be made on small groups of cells or even individual cells. A universal problem is maintaining cell viability upon the bioelectronic substrate. The focus of this work is to describe techniques explored for the deposition and patterning of agar, a cellular nutrient media, on the surface of silicon and glass. This provides a thin film of nutrient media that the cells can live in or on, with optical or electronic sensors in close proximity to be embedded in the silicon substrate. The agar films are deposited using a spin-on technique. Precise control of agar film thickness are obtained by varying the melted agar viscosity, the spin time and spin rate. Surface tension effects are an important parameter in obtaining uniform films. Millimeter-scale patterning of the agar films is performed using glycol and other polyhydroxy alcohols as etchants. Finally, the deposition and patterning of gold electrodes on the agar film and subsequent electrical measurements of the agar are discussed.

#### **4:15 PM \*Z4.9**

**DIRECT PATTERNING OF CERAMIC FILMS BY SOFT SOLUTION PROCESSING.** Masahiro Yoshimura, Tokyo Institute of Technology, Center for Materials Design, Materials and Structures Laboratory, Yokohama, JAPAN.

We are proposing an innovative concept and technology, Soft Solution Processing (SSP) for Ceramics<sup>1</sup>, which aims "direct fabrication of shaped, sized, located, oriented ceramic materials from solution(s) without firing and/or sintering". We have succeeded to fabricate thin/thick films of BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, BaWO<sub>4</sub>, SrMoO<sub>4</sub>, LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, etc., by SSP in aqueous solutions of RT-200°C<sup>2</sup>. In those fabrications, interfacial reactions between a solid reactant (substrate) and component(s) in a solution have been designed and realized. When we have activated locally and moved the reaction point dynamically in those reactions, we can get patterned ceramics directly in solutions without any post-heating, pattern forming, firing nor sintering. Just recently we have succeeded to fabricate several patterned ceramic films i.e. BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbS, CdS, LiCoO<sub>2</sub>, carbon, etc. They are completely new processings for "direct patterning of ceramics", which seems to be the first success from/in solutions<sup>3</sup>. In previous reports, Patterning of Ceramics means pattern

forming of powders or their precursors, thus heating for synthesis or sintering has been regarded to be essential. They should cost environmentally and economically. Our methods where no firing are needed to fabricate patterned ceramics should be "soft" (low cost) environmentally and economically.

#### References:

<sup>1</sup> M. Yoshimura, et al., MRS Bulletin (Sept., 2000), Special Issue of Soft Processing, pp. 12-16 and 17-25.

<sup>2</sup> M. Yoshimura, et al, J. Mater. Chem., 9, 77 (1999).

<sup>3</sup> M. Yoshimura, et al., Proc. of Int. Symp. on Soft Solution Processing, Dec. 11-13, Tokyo (It will be published in the Special Issue of Solid State Ionics).

#### 4:45 PM Z4.10

TEMPLATE-DIRECTED PATTERNING OF ORGANOSILICA SOL-GELS. Bakul Dave, Rituparna Paul, Mukti Rao, Southern Illinois Univ, Dept of Chemistry and Biochemistry, Carbondale, IL.

Sol-gel-derived silicates exhibit gradual yet reproducible variations in their physical state along the sol-gel-xerogel structural coordinate. Thus, starting from a molecular precursor, one can obtain a liquid sol which has the ability to condense into a solid transparent glass. As such these materials provide unique opportunities for patterning by means of external templates as structure-directing agents such that the geometrical features of the template can be easily imprinted onto the viscous sol prior to gelation. Once the gelation takes place, the physical imprint of the template becomes permanent on the surface of the glass. This presentation will focus on recent results obtained in our lab for introducing structural and geometrical order into organosilica materials by means of using preformed templates. The physical and morphological characterization of these micro-patterned surfaces and evaluation of structural features will be discussed in this presentation. Finally, some of the novel application of these materials as optical microdevices will be elaborated.

#### SESSION Z5:

Chair: Seth R. Marder  
Thursday Evening, April 19, 2001  
8:00 PM  
Metropolitan Ballroom (Argent)

#### Z5.1

MICROCONTACT PRINTING USING STAMPS WITH CURVILINEAR CROSS-SECTIONS. Ramona L. Myers, David P. Adams, Rachel K. Giunta, John A. Emerson, Sandia National Laboratories, Albuquerque, NM; Michael J. Vasile, Louisiana Tech University, Ruston, LA.

Microdevices are becoming increasingly important in many fields. Microcontact printing is a valuable technique in the development and fabrication of microelectronic, optical, and microfluidic devices. Soft lithography is a microcontact printing method that patterns a self-assembled monolayer by transfer printing. The thin patterned layer can be an etch resist or a foundation to build new types of microstructures. The limiting time step in the fabrication of printed features by microcontact printing is the fabrication of a mold from which a stamp is made. Additionally, molds have been restricted to rectilinear or prismatic cross-section features. A single stamp, however, can be highly versatile by customizing the cross section of the stamp's features - for example, making the cross-section curved rather than rectangular. In the present work, we replicate curvilinear features formed by focused ion beam (FIB) sputtering of silicon. Ion milling of prespecified, curvilinear features is accomplished by controlling the beam pixel dwell times and accounting for the sputter yield angle dependence, sputter yield material dependence and ion beam intensity distribution. The patterned silicon becomes a mold for a PDMS stamp. Since the stamp is compliant and the features of the stamp have a curved cross-section, the width of features replicated with a self-assembled monolayer "ink" vary with the pressure applied to the stamp. We will demonstrate the versatility of this method through stamps that incorporate parabolic, hemispherical, triangular, and sinusoidal cross-sections and stamped features that vary dimensionally with stamping pressure.

This work supported by U.S. DOE Contract DE-AC04-94AL85000.

#### Z5.2

INTERCONNECTING CIRCUITS ON A SPHERICAL SURFACE. Rabin Bhattacharya, Pai-Hui Iris Hsu, James C. Sturm and Sigurd Wagner, Department of Electrical Engineering, Princeton University, Princeton, NJ.

The fabrication of integrated circuits on spherically curved surfaces is a fascinating new field that calls for new patterning techniques, in addition to the marriage of integrated circuits with deformable substrates. Applications of spherical electronics include photosensor

arrays that combine high resolution with a large field-of-view, and conformal large-area electronics that are shaped to permanently fit to master carriers with spherical surfaces. Our approach is to (1) fabricate rigid circuit islands on plastically deformable substrates, (2) deform these structures to spherical surfaces, and (3) fabricate the interconnect wiring on the spherical surface. The structure is designed such that the substrate takes up all plastic deformation, with strains in the inter-island substrate that exceed the critical strain of metallization. Addressing the circuit islands requires a two-dimensional matrix of wires, similar to the addressing scheme for the cells of a random access memory or the pixels of an active matrix liquid crystal display. Conventionally, this matrix is set up by first fabricating the X wires, then applying an interlevel insulator, and finally fabricating the Y wires. In our process, we build the wiring crossovers into the circuit islands as part of step (1). Before deformation, while the substrate is still flat, a flexible sacrificial pattern is overlaid on the entire surface. In step (2) this pattern is deformed along with the islands and the substrate. The pattern serves as the mask for metal deposition, and after development, leaves the entire interconnect wiring matrix as the result of step (3). To date we have achieved 10 micron line widths along with line thicknesses of 0.15 microns. We are experimenting with the sacrificial layer, the alignment of metal lines to the circuit islands and the reduction of metal line width to expand the capability of this new technique for forming interconnects.

#### Z5.3

SURFACE-INITIATED FREE RADICAL POLYMERIZATION OF POLYSTYRENE MICROPATTERNS ON A SELF-ASSEMBLED MONOLAYER ON GOLD. Jinho Hyun, Ashutosh Chilkoti, Duke Univ, Dept of Biomedical Engineering, Durham, NC.

We describe in this paper the in situ synthesis of nanometer thick films of polystyrene on a self-assembled monolayer (SAM) on gold by surface-initiated free radical polymerization, and further demonstrate that polymer patterns with micrometer lateral resolution can be microfabricated by combining surface-initiated polymerization (SIP) with microcontact printing ( $\mu$ CP). We have implemented SIP onto SAMs on gold using a sequential approach to couple a free radical initiator to a COOH-terminated alkanethiol SAM on gold, followed by polymerization of styrene initiated from the surface-bound initiator. Each step of SIP was characterized by X-ray photoelectron spectroscopy (XPS), surface plasmon resonance reflectometry (SPR), imaging ellipsometry and atomic force microscopy (AFM). We synthesized thin, 10-20 nm homogeneous films, as well as patterned polymer films on a SAM on gold with micrometer lateral resolution either by reactive  $\mu$ CP of the initiator or by  $\mu$ CP of the COOH-terminated alkanethiol. We have also investigated two potential applications of SIP in biomaterials research: (1) label free, real time monitoring of protein adsorption on polymers by surface plasmon resonance (SPR) reflectometry on nanometer thick, homogeneous polymer films synthesized on SAMs on gold, and (2) control of cell-surface interactions by nanoscale control of the topography of microstructured surfaces.

#### Z5.4

LIQUID PHASE CONSTRUCTION OF MICROSTRUCTURES. Joseph M. Bauer, Theoretical and Applied Mechanics Department, University of Illinois at Urbana-Champaign, Urbana, IL; David J. Beebe, Department of Biomedical Engineering, University of Wisconsin-Madison, Madison, WI.

The construction of microscale structures using methods borrowed from the integrated circuit industry has led to the development of Micro Electrical Mechanical Systems (MEMS). These methods are largely limited to the creation of two-dimensional or pseudo three-dimensional (orthogonal) structures. There are, however, many other geometries in nature. Methods to construct non-orthogonal shapes (smooth curves, etc.) at the microscale are limited. Two-photon polymerization has been demonstrated at this scale, but it requires expensive equipment and is slow, as one must 'write' the geometry piece by piece. We have developed a liquid phase construction process that allows for the rapid construction of smooth three-dimensional geometries. Our process is based on the interactions between solids, liquids, and gasses that give rise to smooth curves. For example, if one brings a solid into contact with a liquid surface and then moves the solid either into the liquid or pulls the solid back from the liquid surface, smooth curves defined by the liquid/air interface are created. If the liquid is solidified in this configuration, the result is a solid three-dimensional structure with curved features. We accomplish the solidification by using a liquid that cures upon exposure to ultraviolet radiation. The liquid consists of isobornyl acrylate, tetraethylene glycol dimethacrylate, and a photoinitiator. Placing multiple solid objects in contact with the liquid surface prior to polymerization forms complex connected structures. Interactions between the liquid shapes make it possible to form channels with curved sidewalls or combinations of individual volcano-like structures.

Modifying the size, shape, and properties of the solid objects or the viscosity of the liquid creates various surface tension interactions, and, therefore, the ability to form diverse, curved, three-dimensional structures.

#### **Z5.5**

**FABRICATION AND TESTING OF PATTERNED MICROFLUIDIC DEVICES FOR MEASURING THE FLOW PROPERTIES OF VISCOUS LIQUIDS.** Rachel K. Giunta, Douglas R. Adkins, Ramona L. Myers, David P. Adams, John A. Emerson; Sandia National Laboratories, Albuquerque, NM.

Bonding of microassemblies gives rise to a variety of technical barriers, including dispensing and application of organic adhesives. At these minute length scales, erudition of the flow dynamics becomes critical in forming good and reliable structural bondlines. Capillary forces are the main driving mechanics for filling micron size gaps. Flow properties of viscous liquids that mimic adhesives are determined from distance/time measurements. Liquid flow through small channels made from either mechanical machining or trench etching as defined by soft lithography is probed. Comparison of these two techniques, using a capacitance measurement as the fluid flows between parallel plates and flow visualization, show similar results. The construction of consistent and parallel channels present challenges for microfabrication. In particular, the effects of surface smoothness and contours are critical.

This work supported by U.S. DOE Contract DE-AC04-94AL85000.

#### **Z5.6**

**FORMATION OF MESOSCALE STRUCTURE IN CONDUCTING POLYMERS USING LYOTROPIC LIQUID CRYSTALS.** Yun-Ju Lee, Paul V. Braun, Univ of Illinois at Urbana-Champaign, Dept of MS&E, Urbana, IL.

Recently it has been demonstrated that lyotropic liquid crystals formed by self-assembly of surfactant in water can be utilized to drive the formation of mesoscale structure in a variety of II-VI semiconductor materials. We report here that lyotropic liquid crystals can also drive the formation of mesoscale structure in conducting polymers both in bulk and thin film form. Polypyrrole particles with ~30nm diameter pores were oxidatively polymerized at the interface between lyotropic liquid crystals containing pyrrole and the oxidizing agent iron (III) chloride. Spongy mesoporous thin films of polypyrrole and polyaniline were formed through electrochemical polymerizations on ITO using lyotropic liquid crystals doped with the appropriate precursors as the electrolyte. Current research is focusing on characterization of the chemical structure of these mesoporous conducting polymers, on improving the fidelity of templating, and on the use of other self-organized template materials.

#### **Z5.7**

**PATTERNING BIOMATERIALS INSIDE ENCLOSED MICROFLUIDIC SYSTEMS AND ON SILICON DIOXIDE SUBSTRATES.** Reid N. Orth, A.M.P. Turner, Cornell University, Dept of Applied Physics and Nanobiotechnology Center, Ithaca, NY; T. Clark, Cornell University, Dept of Microbiology and Immunology, Ithaca, NY; H. Craighead, Cornell University, Dept of Applied Physics and Nanobiotechnology Center, Ithaca, NY.

High-resolution micron-scale biomolecular patterning methods have been developed using avidin-biotin technology to immobilize functional proteins on the inner surfaces of silica glass tubes for microfluidic affinity chromatography/biosensor systems and on silicon dioxide substrates for biosensor applications. The functionality of the bound biomolecules was verified using fluorescently labeled materials: primary antibodies, secondary antibodies, NeutrAvidin, and protein coated spheres. Additionally, bacterial cells were successfully bound to a planar patterned silicon dioxide substrate. Protein-A coated spheres and bacterial cells served as model target antigens for the biosensor systems. Features below 5µm were realized. Proteins were patterned in the following manner. First, the substrates were incubated in 3-aminopropyltriethoxysilane (3-APTS) to obtain a self-assembled monolayer with free amines making up the new chemically active surface. Second, photoactivatable biotin was pipetted onto the surface. The N-hydroxysuccinimide (NHS) ester of the photobiotin covalently bound to the surface upon irradiation through a photomask by 350 nm light from a 1000W-mercury arc lamp. Third, NeutrAvidin was pipetted over the substrates binding specifically to the bound biotin. Fourth, biotinylated antibodies were introduced to the system and bound to the NeutrAvidin molecules. In order to demonstrate the feasibility of the biosensor systems, target antigens (bacterial cells, protein-coated spheres, etc.) were then introduced to the systems and bound to the target specific antibodies. Competitive and multi-analyte studies were conducted with different antibodies and antigen to confirm the specificity of the patterning systems. The advantages of these biomolecular derivitization methods are the versatility of binding any biotinylated protein and freedom from

harmful pH, chemicals, or salinity. Furthermore, the inner surface of enclosed vessels may be patterned after their fabrication without the need for high temperatures or anodically bonded glass covers. These techniques can be easily incorporated into silicon, glass, quartz, and plastic micro- and nanofluidic systems.

#### **SESSION Z6:**

Chair: Milan Mrksich  
Friday Morning, April 20, 2001  
Olympic (Argent)

#### **8:30 AM \*Z6.1**

**NANOPATTERNING OF ORGANIC DEVICES EMPLOYING COLD-WELDING FOLLOWED BY LIFT-OFF.** S.R. Forrest, C.S. Kim, P. Peumans, Dept of Electrical Engineering, Princeton University, Princeton, NJ.

We report a new technique for the nanofabrication of organic devices such as organic light emitting devices and organic transistors using the process of cold-welding followed by lift off of the metal cathode. The process is based on fabricating a stamp consisting of a hard material (e.g. Si or stainless steel) which is pre-patterned into the desired contact configuration. The stamp is then coated with the same metal as the cathode material deposited onto an organic multilayer device structure. By applying pressure that forces the stamp against the cathode, the cathode metal cold-welds with the metal on the stamp. Applying further pressure induces fracture in the cathode at the edges of the stamp. Removal of the stamp also separates the cathode from the organic film, leaving the desired pattern. This technique is demonstrated to result in a pattern definition less than 100 nm. It has been used to fabricate organic electroluminescent displays and other devices, and may be a general technique for large scale and rapid patterning of a wide range of organic devices. The patterning mechanism and the limitations of the technique will be considered in this talk.

#### **9:00 AM \*Z6.2**

**POLYMER BASED DEVICES.** Nir Tessler, Electrical Engineering Dept., Technion, Haifa, ISRAEL.

We describe recent progress in fabrication and characterisation of several device configurations as LEDs and FETs. As part of integrating various devices and their optimisation self-consistent modelling will be presented as well.

#### **9:30 AM Z6.3**

**LITHOGRAPHIC AND NON-LITHOGRAPHIC ELECTRO-PATTERNING OF CONJUGATED POLYMERS ON CONDUCTING SURFACES USING THE PRECURSOR POLYMER APPROACH.** Rigoberto C. Advincula, Chuanjun Xia, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL; Seiji Inaoka, Daniel Roitman, Agilent Technologies, Palo Alto, CA.

We report our recent results on the formation and electro-patterning of conjugated polymer films by a novel electrochemical approach consisting of: 1) Synthesis of specialized precursor soluble oligomers, polymers and co-polymers; 2) Electro-deposition of films from these polymers on specific sites of substrates and in specific sequences. This involves molecularly ordered cross-linked and network "precursor" polymer systems primarily demonstrated in polyfluorenes. The synthesis of polymers containing electroactive monomeric units such as thiophene, aniline, fluorene, etc. is currently being undertaken. Simultaneously, we are investigating the deposition, film characteristics, patterning, and device fabrication - PLED's and TFTs. We have investigated a range of feature sizes using this method with features below micron size and hopefully in the near future, in the nano-size range. We have also been investigating the formation of unique blend film structures, with emphasis on light emitting materials with different wavelength characteristics. Our results indicate that the overall optical and mechanical quality of the films are superior compared to previously reported systems. This new approach will allow us to fabricate patterned devices, e.g. PLED, transistors, etc. with fine resolution (ca 10 micron features) without using conventional spin casting and photolithographic techniques.

#### **10:15 AM \*Z6.4**

**DIRECT PRINTING APPLIED TO SILICON DEVICES.** Sigurd Wagner, Helena Gleskova, James C. Sturm, Dept of Electrical Engineering; Sandra M. Troian, Dept of Chemical Engineering, Princeton University, Princeton, NJ; Paul H. Kydd, Parelec Inc, Lawrenceville, NJ.

New technologies are calling for radical innovation in the ways silicon can be grown and processed to circuits. For one, large-area electronics has vastly expanded our capability of deploying semiconductor silicon

over large surfaces. Two, silicon is leaving the confines of the integrated circuit as the boundary between IC functionality and high-level packaging begins to blur. These new directions necessitate the patterning of silicon circuits over large areas but with few process steps. Direct printing techniques offer an attractive solution since they are capable of applying functional materials in designed patterns. Direct printing can furnish the intrinsic electronic function together with the extrinsic layout of a material, all in a single process. We will begin by describing our research on the application of digital non-impact printing to the fabrication of silicon thin film transistors and address a number of practical issues encountered when integrating direct printing techniques with device fabrication. Efforts to control and solve these difficulties will then be discussed. We conclude by defining the fundamental assets of a successful technology for direct printing. Our experience is based on the electrophotographic printing of toner etch masks and silver metallization, as well as the fabrication of copper metallization from inkjet printed precursor patterns. Practical issues include the availability of printers, pattern resolution, edge definition and area coverage, pattern registration, contamination of the silicon device, and the mechanical and thermal properties of the substrate. Success in directly printing silicon devices will require identification of a single printing technology for all fabrication steps, and the choice of compatible "inks" that can be processed into each of the desired device materials. This work is supported by the DARPA HDS and MLP programs and by NSF.

**10:45 AM \*Z6.5**

**TOWARDS ELECTRONIC PAPER: AN ELECTRONIC INK/ ORGANIC TRANSISTOR DISPLAY ON PLASTIC FILM.**

Karl Amundson, Jay Ewing, Robert Zehner, Peter Kazlas, Paul Drzaic, E Ink Corporation, Cambridge, MA; John Rogers, Zhenan Bao, Kirk Baldwin, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We report on the design and fabrication of a flexible 256 pixel prototype display incorporating an array of organic thin film transistors constructed using soft lithography and a microencapsulated electrophoretic display medium. The display is built on plastic substrates, has an ink-on-paper appearance, and consumes very little power. We discuss an active matrix drive scheme for addressing electrophoretic materials, and show how this technology could be extended toward a high-resolution display. This display demonstrates several features desirable in an electronic paper display: low power, flexibility, excellent viewing characteristics, and construction using inexpensive materials.

**11:15 AM Z6.6**

**NANOTECHNICS: DIRECT FABRICATION OF ALL-INORGANIC LOGIC ELEMENTS AND MICRO-ELECTRO-MECHANICAL SYSTEMS FROM NANOPARTICLE PRECURSORS.**

Colin Bulthaupt, Eric Wilhelm, Brent Ridley, Joseph Jacobson, Massachusetts Institute of Technology, Media Lab, Cambridge, MA.

The reduced melting point and high solubility of inorganic nanoparticles have been shown to be useful in the low-temperature solution-based fabrication of semiconductor devices. These inks have been patterned using various techniques to form inorganic logic elements and multi-layer structures. Here we report advances in the printing and syntheses of such nanoparticle inks.

**11:30 AM Z6.7**

Abstract Withdrawn.