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
SESSION Z1
Chair: Milam Mrkisch
Wednesday, April 18, 2001
Olympic (Argent)

8:30 AM *Z1.1
DIP-PEN NANOLITHOGRAPHY AND COMBINATORIAL NANO-TECHNOLOGY. Chantal Glemarec, Romain Houpert, Lucette Demers, Danna 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 Matshige, 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, nanohaving and nanografting, which rely on the local force; and (2) two STM-based techniques, electron-induced diffusion and adsorption, 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 nanohaving 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
NANOSCALE STRUCTURES FACILITATED BY ALL-ADDITIVE AFM-ASSISTED NANOLITHOGRAPHY. Brian Huber, Angelos Bletsas, Joseph Jacobson, Massachusetts Institute of Technology, Media Lab, Cambridge, MA.

A new all-additive method for direct liquid fabrication of nanoscale 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 1.2:1 height width aspect ratio have been directly fabricated onto glass and silicon substrates. Liquid and solid volumes as small as 10^{12} picoliters (10^{-12} 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 NONPRINT 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: nonprint 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-10nm feature sizes, 40 nm period, over a large area. NIL's unique process flow results in 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, optical, 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
NANOFOCUS ALUMINA IMPRINTING MASKS - NANO-STRUCTURING OF COMPLEX SHAPED SURFACES. Thomas Sawicki, Steffen Frenzel, 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 10 nm, while the process is still expensive and due to the equipment needed. On the other hand, nanostructures made by imprinting methods, show impressive variability in shape and order. Sizes down to 10 nm are available by these methods, but to generate the master, electron lithography is still involved. The material presented her to create nanostructured pillars on polymeric or metal surfaces is nanostructured aluminum, 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 prestructured surfaces highly ordered porous layers have been made. While size and shape of these porous layers are 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 aluminium membranes, are presented and the change in surface properties will be discussed.

11:00 AM Z1.6
HIGH RESOLUTION PATTERNING USING ACRYLATE POLYMER NETWORK STAMPS. Kenneth H. 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 nonimprint lithography and step-and-flash lithography, show great promise in the ability with respect to image transfer in any future, economic, electronic domain. Drawbacks of these contact techniques is the lack of availability of high resolution stamps from which the initial image is pressed. We report the use of silica-modified acrylate networks as stamps for contact lithography. We have found that the networks composed of a mixture of photopolymerizable acrylates can be cast against hard masters, photochemically cured, then in turn, be used repeatedly as stamps in the replication of nanometer sized features into an aggregate imaging layer. The low surface energy silicone constituent imparts good contact and release character to the stamp. The silica-modified stamps were used to transfer pattern smaller than 100nm into a photopolymer layer.

11:15 AM  Z1.7

Chemically amplified resist systems have proven to be extremely versatile and manufacturable, and will be likely used for patterning many types of films and substrates regardless of excitement source for the foreseeable future. These resists have the characteristic that the step initial latent image formation by irradiation is translate into a visible image formation by heating are separate. This means that for any of 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 baking step are understood. In this talk we will describe an experimental study of the detailed chemistry and physics of the imaging and etching processes that has enabled us to determine how a patterned image is formed. The factors affecting the resolution and contrast of the resulting pattern are complex and depend on the parameters of the imaging and etching processes.

11:30 AM #218

Recent progress in the development of了一台材料用于3D微加工的光刻技术。具有高灵敏度的两光子和酸引发器的两光子图案光子微结构的使用和在两光子图案光子微结构的形成过程中，我们将描述对现有构图技术的直接扩展，以实现3D光子结构的制备。为达到这个目的，我们已经开发出一种新的方法，通过使用光子微结构的两光子吸收特性，可以实现对单个355nm UV光波长的可编程控制，定义为几个尺寸中心的立方体结构。与不同的几何尺寸（包括不同的光子类型），并由此导致的光学极化的改变使得光学波长能够覆盖大范围的栅格结构。这些结构被认为是能够被实际应用的。
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 polyamide foil with a surface relief pattern prepared by chemical or mechanical 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 substrate. We have successfully printed features smaller than 5 micrometers in size onto substrates using both planar printing plates and roller-extruded plates. Printing onto a spherical surface was accomplished by infusing 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 effects of feature size on these non-uniformities and show that they can be eliminated for small structures.

Currently, there is considerable effort to produce compact solid state lasers, waveguides and switches. One of the reasons that 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, excimer laser deposition 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-assemble the dye molecules/metal nanoparticles in the mesostructured silica. The nanoparticles are simultaneously organized into the 2D-hexagonal silica/block copolymer framework and the laser dyes in the mesostructured silica such that they do not aggregate and quench their own luminescence. These dye solutions are amenable to fabricating structures by direct laser writing processes. The laser dyes 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 (Anglers)

8:30 AM *23.1*

MICRO AND NANOPATTERNING OF POLYMERS THROUGH LIQUID CRYSTAL, COLLOID CRYSTAL, AND SURFACE MEDiated GROWTH. Paul V. Braun, Yuan-Ju Lee, Univ. of Illinois at Urbana-Champaign, Dept. of MSE, Urbana, IL.

Recently, we demonstrated that lyotropic liquid crystals formed by self-assembling monomers and water, and colloidal crystals formed from either polymeric or silicate colloidal particles can be utilized to drive the formation of nanometer and micrometer scale structures in H-2VI semiconductors. 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. Micro-sized mesoscopic polypyrrole particles were oxidatively polymerized to form structures between lyotropic liquid crystal containing pyrrole and the oxidizing agent iron [III] chloride. Spongy mesoscopic thin films of polypyrrole and polyaniline were formed through electrochemical polymerizations on ITO using as an electrolyte lyotropic liquid crystal doped with the appropriate precursors. In related work, we demonstrated that contact printed self-assembled monolayers could be utilized to drive the deposition of submicron lines 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 *23.2*

BI-DOPOLYMER LITHOGRAPHY: LARGE AREA DENSE PERIODIC NANOSCALE PATTERNING. Mir Park, Lucent Technologies, Murray Hill, NJ; Christopher Harrison, M. Trzeciak, P. M. Chabin, Princeton University, Department of Physics, Princeton, NJ; Richard A. Bogue, Princeton University, Department of Chemical Engineering, Princeton, NJ; Douglas H. Adamson, Princeton University, Princeton Microstructure 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 sides of the patterns. Furthermore, by taking advantage of the block copolymer templating and semiconductor processing techniques, we have developed a trilayer pattern transfer method and have fabricated metal dot arrays with an areal density of ~107 cm2. The method provides a viable route for high density nanoscale patterning of different materials on identical substrates.

Understanding the self-assembly properties of block copolymer thin films and controlling them is important for the successful application of block copolymer lithography. Specially, controlling the order, grain size and alignment in of high interest since many device applications would require a two dimensional registry of the periodic structures. This talk will address these issues in the context of using the copolymer films as lithographic templates. For example, the block copolymer microdomain 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 microfilm.

9:30 AM *23.3*

FORMATION OF POLYMERS AND POLYMER-NANOPARTICLE COMPOSITE NANOSTRUCTURES THROUGH SPECIFIC NONCOVALENT INTERACTIONS. Faisal Illan, Andrew K. Beal, Vincent M. Rotello, Department of Chemistry, University of Massachusetts, Amherst, MA.

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-fold. (i) Study the aging phenomena of the block copolymer monolayer as a function of time. Such structural 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 15-30 nm range. The interest here is to utilize the microarray of polymeric features to design and fabricate a DNA chip for gene sequencing. The presentation will discuss quantitatively the measurement and analysis of the aging phenomena, and some preliminary results on the nanodevice for DNA gene sequencing.

10:15 AM *23.4*

FORMATION OF POLYMER AND POLYMER-NANOPARTICLE COMPOSITE NANOSTRUCTURES THROUGH SPECIFIC NONCOVALENT INTERACTIONS. Faisal Illan, Andrew K. Beal, 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, and self-assembled nanostructure formation that is distinctively different from 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.
11:00 AM Z3.0 ELECTRIC FIELD INDUCED SELF CONSTRUCTION OF POLYMER MICROSTRUCTURES. Congzi S. Oskou, Huijuan 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. Anodic electric fluid placed in between two conductive plates exhibits a force in an applied electric field gradient across the plates, which can induce a diffuse 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 held at a fixed temperature of the polymer and a voltage was applied across the plates (25-100 volts), which induces electric fields of the order of 10^-4 V/cm. The capacitor setup was questioned 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 ultramicroanalysis 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 cytometer chip that can sort individual cells by 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 conventional lab on a chip 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 have 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 Z3.6 CONSTRUCTION AND APPLICATIONS OF PDMS CLINA-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 clina-like polystyrene [PDMS] structures by applying soft lithography (i.e. making a mold from a master). To remove the filter, 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 μm in diameter and 6 to 10 μm in height above the glass from 5 x 10^7 to 2 x 10^8 per cm². Applications for clina-like structures include filtering or particle positioning, flow visualization and applications requiring high surface area. We have demonstrated the use of the cilin 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 cilin we can control the size of particles allowed to pass. Another application of the cilin 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 cilin then a fluid flows through the channel the cilin will bend an amount proportional to the velocity of the fluid. One final application of cilia is also using cilia for surface area. PDMS cilin structures with microscale dimensions that are easy to manufacture should find a wide variety of applications in microfluidics.

SESSION 24: 1:30 PM Z24.1 SOFT LITHOGRAPHY AND SURFACE ENGINEERING IN BIOLOGY. Eugene O. Otafu, George M. Whitesides, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA; David D. Duff, Enoch Kim, Olivier Schueller, Surface Logic, Brighton, MA.

Microfluidic 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 insensitive 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 Z24.2 APPLICATION OF SOFT LITHOGRAPHY. Kevin A. Rose, MIT, Boston, MA; Peter Krulwich, 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 (Silgard 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 was successfully demonstrated on PDMS using an e-beam evaporated chromium adhesion layer and gold conductive film, with patterned completing using a shadow mask. Fluidic vias were made by boring holes through the PDMS. In the first application, emerging luminescence microchannels were fabricated for single molecule DNA manipulation and processing. Brewer et al. [1] developed this technique using glass flow cells to demonstrate protein-induced condensation and decondensation of 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 coverglass 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 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 temperature, the temperature was controlled in order to achieve the same conditions as in the previous paper. The problem encountered with glass-based and polymer-based fusion bonding.

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 the 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 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 P M 24.4
PATTERNING HYBRID SURFACES WITH SUPPORTED LIPID BILAYERS AND PROTEIN. Li A. Kung, Lance Kam, Jennifer S. Hovis, Steven G. Becker, 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 unoccupied regions. In the second method, supported bilayers are formed by removing 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 height 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 P M 24.5
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 days 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 (also known as rapid prototyping or rapid polymerization). Advancements have been made in reducing the expenditure and time in mask making. However, the mold making process still requires the use of sophisticated equipment (spin coater, ultraviolet exposure tools, and materials (photoreact, developer). Making the mold can take 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 utilization. The advantage of URP lies in the ability to create the mold quickly and economically. Standard life sciences, laboratory equipment (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 be on a flat substrate, as a curved structure, or as a free-standing released structure. URP uses a photopolymerizable liquid phase pre-polymer solution comprising of Isobornyl Acrylate, Tetramethyleryglic dimethacrylate and 2,3-dihydroxypropyl e to create 3D or quasi 3D molds by mixing of the solution.

3:30 P M 24.6
PATTERNING OF CHEMICALLY SENSITIVE AND BIOLOGICAL MATERIALS USING A PARYLENE BASED DRY LIFT OFF. Eliza C. Big, H. G. O. Winpenny, Cornell University, Dept of Applied Physics and Nanotechnology 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 nm to 10 μm) large area 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 etched. Parylene is then planarized over the substrate and the designed chemical functionalization is formed. We have patterned antibodies, poly-L-lysine and 4-aminohippuratehexosulose self-assembled monolayers. These materials were respectively used to pattern a biocompatible silicon substrate and a Parylene-coated silicon substrate. The Parylene patterned silicon substrates were used to investigate the topography and morphology of the patterned surfaces.

3:45 P.M 24.7
NEURONELECTRODE INTERFACES AND PATTERNING WITH PEPTIDES. Cristian Ionescu-Zaretti, 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 scale of single neurons, 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 neuronal-electrode interface. Experiments present work using self-assembling peptide layers on the active sites of the electrode arrays. This study will present not only the resulting directed growth of neurons on a variety of surfaces, but the dependence of the neuron-electrode complex on the surface chemistry of the electrode. The aim is a thorough understanding of the neuron-electrode interface.

4:00 P.M 24.8
DEPOSITION AND PATTERNING OF AgAR THIN FILMS ON SILICON FOR BIO-ELECTRONIC SUBSTRATES. J.F. Muth, D.P. Naxaish, P.D. Franko, 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 is critical in 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 photolithography and other polymeric materials to create direct, or time-resolved, measurements of the agar film are discussed.

4:15 P.M 24.9
DIRECT PATTERNING OF CERAMIC FILMS BY SOFT SOLUTION PROCESSING. Masayo 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, which aims "direct fabrication of shaped, sized, located, oriented ceramic materials from solution(s) without firing and/or sintering". We have succeeded to fabricated thin/thick films of BaTiO3, SrTiO3, BaWO4, SrMoO4, Li2Co2O4, Li2O3, etc., by SSP in aqueous solutions of HT-200°C. In these 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 reaction point dynamically in those reactions, we can get patterning effects directly in solutions without any post-heating, pattern forming, firing nor sintering. Just recently we have succeeded to fabricate several patterned ceramics films i.e. BaTiO3, SrTiO3, PbO, CdS, Li2Co2O4, etc, they are completely new processing for "direct patterning of ceramics", which seems to be the first success from in solutions. In previous reports, Patterning of Ceramics means pattern
form of powders or their precursors, thus heating for synthesis or sintering has been regarded as being essential. They should coat environmental and economic aspects. 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 strain in the interconnect substrate that exceed the critical strain of metal alloy. Addressing the circuit islands requires a two-dimensional matrix of wires, similar to the addressing scheme for the microcombs of a random access memory or the pixels of a 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 the fabrication of the circuit substrate, while the substrate is still flat, a flexible sacrificial layer is overcoated 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 thickness 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 MICRO PATTERNS ON A SELF-ASSEMBLED MONOLAYER ON GOLD Jinho Ha, Ashutosh Chilkoti, Duke Univ, Dept of Biomedical Engineering, Durham, NC

We describe in this paper the in situ synthesis of a monolayer 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 (µCP). We have implemented SIP onto SAMs on gold using a sequential approach to couple a free radical initiator to a COOH-terminating alkane thiol 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).

Z5.4 LIQUID PHASE CONSTRUCTION OF MICROSTRUCTURES Joseph I. 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 shown to vary with the presence of a phase change. 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 varying pressure.

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

Z5.5 INTERCONNECTING CIRCUITS ON A SPHERICAL SURFACE Rabin Bhattacharya, Pan-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 method that calls for new patterning techniques, in addition to the marriage of integrated circuits with deformable substrates. Applications of spherical electronics include photodetector arrays that combine high resolution with a large field-of-view, and conformal large-area electronics that are shaped to permanently fit to moving carriers. 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 interconnect substrate that exceed the critical strain of metal alloy. Addressing the circuit islands requires a two-dimensional matrix of wires, similar to the addressing scheme for the microcombs of a random access memory or the pixels of a 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 the fabrication of the circuit substrate, while the substrate is still flat, a flexible sacrificial layer is overcoated 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.

SESSION Z5
Chair: Seth R. Marder
Thursday Evening, April 19, 2001
8:00 PM
Metropolitan Ballroom (Argent)
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.


Bonding of micromembranes gives rise to a variety of technical barriers, including dispensing and application of organic adhesives. At these minute length scales, evaporation of the solvents 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 the time measurement of 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.

25.6 FORMATION OF MESOSCALE STRUCTURE IN CONDUCTING POLYMERS USING LIYOTROPIC LIQUID CRYSTALS. Yan-Ju Lee, Paul V. Braun, Univ of Illinois at Urbana-Champaign, Dept of MSE, 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 structures in a variety of I-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 (III) chloride. Spongy mesoporous thin films of polyester and polystyrene 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.

25.7 PATTERNING BIOMATERIALS INSIDE ENCLOSED MICROFLUIDIC SYSTEMS AND ON SILICON DIODE SUBSTRATES. 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 silicon 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 antibodies, 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. NeutrAvidin was used to bind the spheres, proteins were patterned in the following manner: First, the substrates were incubated in 3-aminopropyltriethoxysilane (3-APTS) to obtain a self-assembled monolayer with freely moving up the newly chemically active surface. Second, photoreactive biotin was pipetted onto the surface. The NH₂-propanesuccinimide (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 functionality of the biotin-antigens (bacteria, protein-coated spheres, etc.) were then introduced to the system and bound to the target specific antibodies. Competitive and multi-analyte studies were conducted with different antibodies and antigen to control the specificity of the patterning systems. The advantages of these biomolecular derivation 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 temperature bonding glues. These techniques can be easily incorporated into silicon, glass, quartz, and plastic micro- and nanofluidic systems.

SESSION 26: Chair: Milton Groshick
Friday Morning, April 20, 2001


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 organic 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 *26.2 POLYMER-BASED DEVICES. Nir Teashler, Electrical Engineering Dept., Technion, Haifa, ISRAEL.

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

9:30 AM 26.3 LITHOGRAPIC AND NON-LITHOGRAPIC ELECTRO-PATTERNING OF CONJUGATED POLYMERS ON CONDUCTING SURFACES USING THE PRECURSOR POLYMERIC APPROACH. Rigoberto C. Advincula, Chuanjun Xin, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL; Seiji Inokuchi, 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 polyelectrolytes. The synthesis of polymers containing electroactive monomeric units such as thiophene, thienylene, fluorene, etc. is currently being undertaken. Simultaneously, we are investigating the deposition, film characterization, patterning, and device fabrication. PLEDs 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 (~10 micrometers) features without using conventional spin casting and photolithographic techniques.


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 aspects 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 Kunis, 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*
NANOTECTONICS: DIRECT FABRICATION OF ALL-INORGANIC LOGIC ELEMENTS AND MICRO-ELECTROMECHANICAL SYSTEMS FROM NANO-PARTICLE PRECURSOR.
Colin Balkcom, 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 synthesis of such nanoparticle inks.

11:30 AM *Z6.7*
Abstract Withdrawn.