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

Symposium Support
E-Ink Corporation
Lucent Technologies, Bell Laboratories
Surface Logix

*Invited paper
SESSION Z1
Chair: Milan Mrksich
Wednesday, April 18, 2001
Olympic (Argent)

8:30 AM #21.1
DIP-PEN NANOFLUIDOGRAPHY AND COMBINATORIAL
NANO-TECHNOLOGY: PROF. RANDY HORTON, Linette
Demers, Dana Weinberger, Northwestern University, Chemistry
Department and Institute for Nanotechnology, Evanston, IL.

Methods for doing massively parallel Dip-Pen NanoFluidography (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, such as
providing a means for generating combinatorial arrays that can be
utilized in addressing many issues in chemistry (e.g. catalysis and
biore cognition) and materials science (e.g. solid-state electronics
fabrication and colloidal crystal growth).

9:00 AM #21.2
NANOFABRICATION OF SELF-ASSEMBLED MONOLAYERS
AND PROTEINS USING SCANNING PROBE LI THOGRAPHY,
Gang-yu Liu, Song Xu, Nabil A. Amro, Kapila Wadu Meethirige, 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 nanofluidography 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
dissolution, 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 nanostructures 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
nanostructures 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-ADITIVE
AFM-ASSISTED NANOSCLPY. Brian Hubert, Angelos Bletias,
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 AFM
and a microfluidic 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 by 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 to width aspect ratio have been directly fabricated onto glass and
glass substrates. Liquid and solid volumes as small as 10⁻¹²
picoliters (10⁻¹⁵ 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 #21.4
NANOPAT Temg BY NOAPRINT LITHOGRAPHY AND
LITHOGRAPHICALLY-INDUCED SELF-ASSEMBLY,
Stephen Y. Chou, Nanostructure Laboratory, Department of
Electrical Engineering, Princeton University, Princeton, NJ.

Two new nanopatterning techniques will be presented: nanoprinting
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
definition of the shape of the resist with embossing, rather than by
modification of the resist chemical structures with radiation. NIL has
defined minimum size 10 nm feature, excellent over a large range of
linearity 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
computing nanotechnology platforms used on the entire substrate.

10:45 AM #21.5
NANORODS ALUMINA IMPRINTING MASKS - NANO-
STRUCTURING OF COMPLEX SHAPED SURFACES.,
Thomas Sawicki, Steffen Franka, Matthias Levering, University of
Eck, Department of Inorganic Chemistry, Eick, Germany.

The fabrication of large areas of structured surfaces with feature sizes
in the nanometer range is 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, which can be used to fabricate microstructures
by serial techniques. The highest spatial precision is achieved using
electron beam lithography, structures of perfect shape and order can be
made down to the smallest details, while the process is very high,
due to the equipment needed. On the other hand, nanostructures
made by imprinting methods, show a better scalability in shape and
order. Sizes down to 50 nm are possible with these methods, but
together with the need for very high pressures and the high cost of
equipment. 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.

11:00 AM #21.6
HIGH RESOLUTION PATTERNING USING ACRYLATE
POLYMER NETWORK STAMPERS. Kenneth H. Carter, Bruce D.
Terry, 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 nanoinprint lithography and
step-and-flash lithography, show promise in the ability with reduced image transfer in any direction, economic aspects, etc. A key drawback of these contact techniques is the lack of availability of
suitable, inexpensive, high resolution stampers from which the initial image
is pressed. We report on a low-cost method for making stampers to be
used in nanoimprint lithography. We have found that the networked
mixture of a similar polymerizable acrylate can be cast against hard
dictators, photochemically cured, then in turn, be used repeatedly as stampers 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 silicone-modified stampers were used to transfer pattern
smaller than 100 nm into a photopolymer layer.

11:15 AM #21.7
NANOSC SLE CHARACTERIZATION OF THE LAT E IMAG E
FORMED IN CHEMICALLY PRODUCED AMPLIFIED RESISTS. E.A.
Koelsch, W.D. Hinshaw, M.I. Sanchez, J.A. Hoffnung, IBM Almaden
Research Center, San Jose, CA.

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 excitation source for
the foreseeable future. These resists have the characteristic that the
initial latent image formation by irradiation is invisible, and only visible
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 formation process that has enabled us to determine how coupled reaction and diffusion lead to a developable pattern in a chemically amplifiable system. We have placed particular focus on how resist components such as photosensitive generator, polymer, and added base work together to affect the final image in the nanometer scale. A series of resists were prepared and exposed using both blanket and interferometric lithography and the image formation 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 #21.8

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 using high intensity focused laser pulses. Prospects for applications, the extension of this approach into the nanoscale, and for the preparation of hierarchically structured materials will be discussed.

SESSION 22
Chair: Guangyu Lui
Wednesday Afternoon, April 18, 2001 (Oncent)

1:30 PM #22.1
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 a volume of polymer. This so-called volume holographic lithography (VHL) allows three-dimensionally periodic structures can be readily fabricated in this way. We discuss the design criteria for suitable photoreists, and the potential for incorporating additional apodization into the holographic image. It is shown that the single 355nm UV wavelength can be used to define a novel face-centred cubic structures with different lattice parameters (as well as other lattice types), and that the choice of the optical polarization of the writing beams enables a wide variety of crystallographically distinct bases to be realised.

2:00 PM #22.2
THREE-DIMENSIONAL SUB-MICRON FABRICATION WITH BIOACTIVE PROTEINS BY MULTIPHOTON EXCITATION. Steven L. Goodman, University of Connecticut Health Center, Center for Biomechanics and Department of Physiology, Farmington, CT; Paul J. Connolly, University of Connecticut Health Center, Center for Biomedical Imaging Technology and Department of Physiology, Farmington, CT.

The incorporation of biocatalysts into engineered devices can provide critical functionalities in technologies as diverse as biocatalysts, tissue engineering, drug delivery, biosensors, bioMEMs, and integrated lab-on-chips. However, holographic and stamping fabrication methods, and commonly used organic chemical processes, have some limitations with respect to building such devices. These include, i) maintaining biocatalytic (protein) bioactivity, ii) positioning multiple biocatalysts in different locations, iii) producing submicron features and iv) structures complex 3D 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 photoinitiated cross-linking and/or polymerization. Current instrumentation is based upon a laser scanning confocal microscope (Hirox MRC600) modified for non-infrared excitation provided from a pulsed Ti: Sapphire laser (Coherent 900F). 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 a single image. Our present work focuses on how resist components such as photosensitive generator, polymer, and added base work together to affect the final image in the nanometer scale. A series of resists were prepared and exposed using both blanket and interferometric lithography and the image formation 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.

2:30 PM #22.3
ACTIVE MANIPULATION OF ORGANIC AND INORGANIC OBJECTS BY USING OPTICAL MICRO BEAMS. Mehrinah Ozkan, Mark M. Wang, Sangeet Bhattachar and Sadik C. Ersen Electrical and Computer Engineering Department, *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. Electromagnetically focused and cellular arrays have been manipulated by using resonant momentum transfer that is exerted by micro optical beams. Pre-patterned metal 3T3 fibroblasts on a transparent substrate have been picked and placed by optical micro beams to a new location on this stage. Active manipulation of 3D arrays of polyacrylamide 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 while the VCSEL driving current was 14 mA. The cells were then returned 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 #22.4

The main advantages envisioned for organic-based electronics are the low 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, high threshold voltage and subthreshold slope. At the same time, the transistor semiconductor 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 in semiconductors after facile deposition from solution will be emphasized.

3:45 PM #22.5
NON-PLANAR MICROFLUIDIC ARRAYS HOLD GREAT PROMISE AS AN ENABLING TECHNOLOGY FOR MICROFABRICATION. Ralph G. Naziro, Jennifer Monahan, Kari Fassler, 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, which we are developing for application in chemically sensitive detection. A central topic of concern in this work is the development of strategies and enabling chemistries for creating complex multilevel structures with micro-scale design rules in a very broad range of materials, including semiconductors, metals, organic thin films, and functional polyester.
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 wafer. We have successfully printed features smaller than 5 micrometers on a substrate using both planar printing plates and roller-type plates. Printing onto a spherical surface was accomplished by immersing the printing plate into the shape of a spherical cap. Polymer structures printed by this technique are suitable as mask 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 *22.7

A NEW SOFT LITHOGRAPHIC TECHNIQUE TO FABRICATE RIDGE WAVEGUIDE DISTRIBUTED FEEDBACK LASERS OF DYE-DOPED MesoSTRUCTURED COMPOSITES. Brian J. Sootz, University of California, Santa Barbara, Dept of Chemistry, Santa Barbara, CA; David M. Goban and J. Robert Hlavacek, Institute for Molecular Science, Graz, Austria; Michael D. McGehee, Stanford University, Department of Chemistry, Stanford, CA; Bradley F. Chmelka, University of California, Santa Barbara, Dept of Chemical Crystals, 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 necessary 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 (DBF) lasers, are typically used with holographic lithography, electron beam lithography, and vapor deposition. We have developed a simple technique for making DBF 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 self-assembly of the dye/fullerene/black polymer system. This process is diphasic (2D-hexagonal silica/block copolymer framework) and the laser dyes are incorporated into the mesostructure such that they do not aggregate and quench their own fluorescence. These dilute solutions are amenable to fabricating structures through a variety of techniques including dip coating, spin coating, and other immobilization methods. DBF lasers have been fabricated by such techniques that have as few as two lasing modes with FWHM of less than 0.5 nm.

SESSION 26
Chair: John A. Rogers
Thursday Morning, April 19, 2001

10:15 AM *23.8
FORMATION OF POLYMER AND POLYMER-NANOPARTICLE COMPOSITE NANOSTRUCTURES THROUGH SPECIFIC NONCOVALENT INTERACTIONS. Fuayr Ilhan, 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, in which the topographic diversity 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.
11:00 AM Z3.0
ELECTRIC FIELD INDUCED SELF CONSTRUCTION OF POLYMER MICROSTRUCTURES. Congzi S. Zhao, Huijun 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 10-1500 nm thick PVA (polyvinyl alcohol) 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 transition temperature of the polymer and a voltage was applied across the plates (25-100 Volts), which induces electric fields on the order of 10–1000 Volts/m. The capacitor setup was then used 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.

11:00 AM Z3.6
ELECTRIC FIELD INDUCED SELF CONSTRUCTION OF POLYMER MICROSTRUCTURES. Congzi S. Zhao, Huijun 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 10-1500 nm thick PVA (polyvinyl alcohol) 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 transition temperature of the polymer and a voltage was applied across the plates (25-100 Volts), which induces electric fields on the order of 10–1000 Volts/m. The capacitor setup was then used 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.
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 test 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 specifically patterned surfaces to create the arrays. 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 PM 24.4
PATTERNING LIPID BILAYERS AND PROTEIN. Li A. Kang, 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) layers 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 removed from patterned regions of the membrane, and the blanked regions are filled in (or caulked) with protein from solution. In both cases, the lipid bilayer regions exhibit intrinsic fluidity, but each region is separated by protein layers of similar thickness 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 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 research needs creative and if we are to address the complex multidisciplinary questions faced in the life sciences, this ability to rapidly build [inexpensive] prototypes [or “lab on a chip”s] in short time will facilitate advances 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 and systems (such as PDMS techniques and wax molds). This has lead to reductions in the production time and cost of microfluidics devices. Advancements have been made in reducing the expenditure and time in mask making. However, the mold making process still requires the use of expensive equipment (such as photoresist and ultraviolet exposure tools and materials). 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 a rapid prototyping (URP) to allow the user to go from concept to prototype in as little as 1 hour from the time one has finished the design (in a CAD software) to device realization. The advantage of URP lies in the ability to create the mold quickly and economically using standard life science 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, or as a curved structure, or as a free-standing released structure. URP uses a photoresistible liquid phase pre-polymer solution comprising of isobornyl Acrylate, Tetraethanolamyl glycol dimethacrylate and 2,6-dimethoxy-2-phenyl ethanol to create 3D or quasi 3D molds by making use of the solution.

3:30 PM 24.6
PATTERNING OF CHEMICALLY SENSITIVE AND BIOLOGICAL MATERIALS USING A PARYLENE BASED DRY LIFT OFF. El-Barghouty, H. C., G.R. Eiltraut, 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 (0.1µm to 10µm) large real 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 biomolecular layer. Parylene is then peeled from the substrate and the desired chemical pattern is formed. We have patterned antibodies, poly-L-lysine, and aminepropyltrimethoxysilane self-assembled monolayers. These layers were respectively used to pattern biotinylated streptavidin, functionalized fluororescent dextran particles, and 20nm diameter alkaline-phosphatase fluorescent polyacrylamide beads. Furthermore, we have also patterned protein A, laminin, fibronectin and carbon nanotubes. Prototype arrays of fixed and mobile single cell ligands were then patterned on a 384 well plate format. This study was conducted in an effort to create a versatile surface chemistry for the development of microfluidic devices.

3:45 PM 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 new 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 neuron-electrode interface. A recent present work has been focused on self-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.

4:15 PM 24.8
DEPOSITION AND PATTERNING OF AgAR THIN FILMS ON SILICON FOR BIO-ELECTRONIC SUBSTRATES. J.F. Muth, D.P. Nookaishi, P.D. Francon, 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 bioelectric substrates. The focus of this work is to describe techniques explored for the deposition and patterning of agar, a cellular nutrient medium, on the surface of silicon and glass. This provides a thin film of nutrient media that the cells can live in or on, with or without an electronic sensor to be embedded in the silicon substrate. The agar films are deposited using a spin-on technique. Precise control of agar film thickness is achieved by using a range of tagged agar concentrations. The agar film then functions as a mask for patterning the underlying silicon substrate. This method allows the surface to be electrically monitored while the cells are cultured. A second method allows direct observation of the cells, which are cultured on the substrate. The cells can be observed using a range of techniques, including both optical and scanning electron microscopy.

4:15 PM 24.9
DIRECT PATTERNING OF CERAMIC FILMS BY SOFT SOLUTION PROCESSING. Masahiro Yoshihara, Tokyo Institute of Technology, Center for Materials Design, Materials and Structures Laboratory, Yokohama, JAPAN.

We are proposing an innovative concept and technology, Soft Solution Printing (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, LiCoO2, LiNiO2, etc., by SSP in aqueous solutions of HT-200°C. In these preparations, 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 ceramics films i.e. BaTiO3, SrTiO3, PbO, Cd, LiCoO2, etc. They are completely new processings for direct patterning of ceramics, which seems to be the first success from/in solutions1. 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 environment efficiently. Our approach is to (1) fabricate patterned ceramics should be ‘soft’ (low cost) environmentally and economically.

References

4:45 PM ZA.10
-template-directed patterning of organosilica sol-gels. I. Baked Dave, Rituparna Paul, Mikiro Sato, 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-kerosene 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 using microfabrication techniques. 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. Mrad
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. Guinta, John A. Emerson, Sandia National Laboratories, Albuquerque, NM; Michael J. Vard, 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 mask 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 pre-specified, 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 and the micropatterned silicon match, the width of the printed line depends on the geometry of the pre-patterned silicon. 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 sputtering pressure.

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

Z5.2
Interconnecting circuits on a spherical surface. Rablin Bhattacharya, Pui-Hui Iris Hsu, James C. Sturm and Signal 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 larges area electronics that are shaped to permanently fit to moving carriers. Our approach is to (1) fabricate rigid circuit segments 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 for material failure. Addressing the circuitry may require a two-dimensional matrix of wires, similar to the addressing scheme for the pixels of a random access memory or the pixels of a memory matrix liquid crystal display. Conventionally, this matrix is set up by first fabricating the X wires, then applying an interleaved insulator, and finally fabricating the Y wires. In our process, we build the wiring crossovers into the circuit array as part of step (1). Before deformation, the substrate is flat, a flexible sacrificial pattern is overlaid on the entire surface. In step (2) this pattern is deformed along with the substrate. The pattern serves as a mask for metal deposition and after deformation, leaves the entire interconnect wiring matrix as the result of step (3). To date we have achieved 10 micron wire 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 array 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 poly(I-vinyl substitution) A SELF-ASSEMBLED MONOLAYER ON GOLD. Jin Heun Hwang, 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-terminated 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). 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 µCP of the initiator or by µCP of the COOH-terminated alkane thiol. 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 a 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. The formation of deformable microstructures such as planar polymer films or monolayer liquid bilayers is limited to two orthogonal planes. However, expensive equipment and small-scale may not be possible to achieve. For example, 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 contains tetrahydrofurfuryl 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 distorted curved surfaces and combinations of individual volume-like structures.

Bonding of microassemblies gives rise to a variety of technical challenges, including dispensing and application of organic adhesives. At these microscopic length scales, emulsion dynamics becomes critical in forming good and reliable structural bondlines. Capillary forces are the main driving mechanisms for filling micron size gaps. Flow properties of viscous liquids that mimic adhesives are determined from the time dependent fluid flow. Flow through small channels made from either mechanical machining or thermal 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 fluid 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. Yu-Ju Lee, Paul V. Braun, Univ of Illinois at Urbana-Champaign, Dept of MSE, Urbana, IL

Recently it has been demonstrated that lyotropic liquid crystal formed by self-assembly of surfactant in water can be utilized to drive the formation of mesoscale structure in a variety of IL–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. Polydye particles with ~30 nm diameter pores, were oxidatively polymerized at the interface between lyotropic liquid crystals containing polydye and a coordinating agent (III) chloride. Spongy mesoporous thin films of polydye and polyamine were formed through electrochemical polymerizations on ITO using lyotropic liquid crystals doped with the appropriate precursors as the electrolyte. Current research is focused 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. J. Robert D. Stockert, A. M. Turner, Cornell University, Dept of Applied Physics and Nanotechnology Center, Ithaca, NY; T. Clark, Cornell University, Dept of Microbiology and Immunology, Ithaca, NY; H. Craighead, Cornell University, Dept of Applied Physics and Nanotechnology Center, Ithaca, NY

High-resolution micro-scale biocompatible 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 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. NeutrAvidin coated spheres were patterned in the following manner. First, the substrates were incubated in S-aminopropyltriethoxysilane (APTS) to obtain a self-assembled monolayer with free amines making up the new chemically active surface. Second, photocleavable biotin was pipetted onto the substrate. The N-hydroxysuccinimide (NHS) ester of the photobiotin covalently bound to the surface upon illumination 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 biocompatible systems, target antigens (bacteria, 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 control the specificity of the patterning systems. The advantages of these biomolecule derivatization 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 bonded glass covers. These techniques can be easily incorporated into silicon, glass, quartz, and plastic micro- and nanofluidic systems.

SESSION 26: Chair: Milan Mrkische Friday Morning, April 20, 2001 Olympic (Argent)


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 fabrication 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 metal 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 1.00 nm. It has been used to fabricate organic electrochromic 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 Teasler, Electrical Engineering Dept., Technician, 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 LITHOGRAPHIC AND NON-LITHOGRAPHIC ELECTRO-PATTERNING OF CONJUGATED POLYMERS ON CONDUCTING SURFACES USING THE PRECURSOR POLYMERIC APPROACH. Rigoberto ADVINCULA, Chunjun XIN, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL; Seiji Innok, Daniel ROITMAN, Aigilet Technologies, Palo Alto, CA, USA

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 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 characteristics, patterning, and device fabrication – PLED’s and TFT’s. We have investigated a range of feature sizes using this method with features below micron size and hopefully in the near future, in the nanoscale 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 (on 10-20 micron features) without using conventional spin coating and photolithographic techniques.


New technologies are calling for radical innovation in the way 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 leading the confines of the integrated circuit to 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 26.5
TOWARDS ELECTRONIC PAPER: AN ELECTRONIC INK/ORGANIC TRANSISTOR DISPLAY ON PLASTIC FILM
Karl Amundson, Jay Ewing, Robert Zehner, Peter Kueh, 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 26.6
NANOTECHNICS: DIRECT FABRICATION OF ALL-INORGANIC LOGIC ELEMENTS AND MICRO-ELECTRO-MECHANICAL SYSTEMS FROM NANOPARTICLE PRECURSORS
Colin Bukholm, 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 26.7
Abstract Withdrawn.