SYMPOSIUM U

Printing of Materials in Photonics, Electronics, and Bioinformatics

April 13 - 15, 2004

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* Invited paper

SESSION U1: Patterning Techniques with Applications in Organic Electronics
Tuesday Morning, April 13, 2004
Room 3022 (Moscone West)

8:30 AM U1.1
Polymer field-effect transistors defined by self-aligned inkjet printing with submicrometer resolution. Christoph Sele[1], Timothy von Werne[2], Wilhelm T.S. Huck[3] and Henning Sirringhaus[1,2]; [1]Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; [2]Plastic Logic Ltd, Cambridge, United Kingdom; [3]Chemistry, University of Cambridge, Cambridge, United Kingdom.

The field of plastic electronics has experienced impressive growth in recent years and promises the realisation of flexible displays and smart labels. Inkjet printing is a promising patterning method for polymeric field-effect transistors, the basic building blocks of flexible circuits. It enables the fabrication of multilayer structures by additive deposition of solution-processable materials. For the fabrication of all-polymer electronic circuits it is desirable to minimize the channel length of the underlying transistors. This enables satisfactory switching speeds, despite the lower mobilities of many polymeric semiconductors compared to amorphous silicon. The achievable resolution using standard inkjet printing is limited to approximately 20 microns by droplet flight variations. Increased resolution has been demonstrated previously but requires pre-patterning of the substrate into hydrophilic and hydrophobic regions to confine the ink droplets. We present here a new self-aligned inkjet printing technique capable of submicrometer printing without the need for high-resolution lithography. The method is based on using the surface repulsion between a first inkjet printed conductive pattern, for example, of a conducting polymer, such as poly(3,4-ethylenedioxithiophene)/ poly(styrenesulfonate) (PEDOT/PSS), and subsequently deposit ink droplets of a second conductive pattern. The latter dewet from the surface of the first pattern but dry in very close proximity to the first pattern to produce sub-100nm gap structures for FET devices without the need for any high resolution lithography. We use this powerful & simple printing-based nanostructuring method to reproducibly pattern source- and drain electrodes with channel lengths of less than 100 nm, for all-polymer field-effect transistors.

8:45 AM U1.2
Studying Charge Transport in Ink-Jet Printed All-Polymer Transistors. Yvonne Y Deng and Henning Sirringhaus; Optoelectronics Group, Department of Physics, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom.

Organic field-effect transistors (FETs) have been of increasing academic and commercial interest recently. In the quest for materials which combine high performance with the stability required for ink-jet printing in ambient conditions, poly(9,9'-dioctylfluorene-co-bithiophene)(F8T2) has emerged as a promising semiconducting polymer. All-polymer FETs made entirely by ink-jet printing and spin-coating have been demonstrated, however, the charge transport physics at polymer-polymer interfaces is not well understood. Charge Modulation Spectroscopy (CMS) is a powerful tool to study the nature of charge carriers that give rise to the current flow in a polymer FET. The technique records changes of the optical absorption of a semitransparent FET upon gate-voltage-induced modulation of the charge carrier concentration in the accumulation layer of the FET. Thus it allows direct observation of the polaronic relaxation of the charges in the FET channel. The technique is very sensitive to the properties of the semiconductor-dielectric interface and we present here, for the first time, the charge-induced absorptions of polaronic charge carriers in the accumulation layer of an ink-jet printed all-polymer FET. Clear evidence for the formation of a clean accumulation layer is seen, similar to that formed at hybrid interfaces with inorganic dielectrics, such as SiO_2. We have performed CMS measurements on uniaxially aligned F8T2 films to investigate the polarisation of the observed charge-induced absorptions parallel and perpendicular to the alignment direction. Two different transitions are observed, one polarised, one unpolarised. Further, we have studied the dependence of the absorptions on the roughness of the active interface, using both, annealing treatments and variations of the dielectric solvent. We have also investigated the changes of the CMS spectrum upon bias stressing of the FETs, yielding valuable information about the mechanisms for threshold voltage shifts commonly observed in organic FETs.

9:00 AM *U1.3
Electronic Materials printed by Thermal Ink Jet. Thomas Lindner, Hewlett-Packard Company, Corvalis, Oregon.

Hewlett-Packard's successful thermal ink jet technology is sometimes perceived as limited to water based inks. In fact thermal ink-jet can print a large variety of materials. Examples are organic solvent based systems, colloidal dispersions of nanoparticles, inorganic solutions, polymer light emitting materials, color filters, and adhesives. The presentation will address the fundamental materials latitude, show examples of printed devices, and outline the path to commercial print systems and applications.

9:30 AM *U1.4
Combinatorial Inkjet Printing for Organic Optoelectronics. Ghassan E. Jabbour and Yuka Yoshioka; Optical Sciences Center, University of Arizona, Tucson, Arizona.

Organic functional materials are key enablers for future generations of smart nano-thick devices. In fact, these materials are already being used to fabricate commercial light-emitting displays having active organic layers of only several tens of nanometer in thickness. These materials also have the promise to be used in transistors, solar cells, memory storage and many other areas. Combinatorial (combi) and high throughput techniques can have significant impact and could propel the advancement of these areas, rapidly. In this regard, not only the materials synthesis benefits from combi-type approaches, but also the device fabrication and optimization. We will discuss the use of combinatorial inkjet techniques to control the sheet resistivity of conducting polymers currently used in organic light-emitting devices and solar cells. With this approach a library of electrodes with various sheet resistivity can be made in few seconds, a result that is otherwise difficult, if not impossible, with traditional fabrication methods.

10:30 AM *U1.5
New Approaches to Nanofabrication. George M. Whitesides, B. Gates, Q. Xu, R. Boulatov, C. Love and D. Wolfe; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Nanofabrication has three components: top down, bottom-up, and integrated (often through self-assembly). This talk will examine new techniques for nanofabrication (and for microfabrication, in some circumstances) that exploit "unconventional" methods of nanofabrication. These methods include soft lithography, edge lithography, and templated synthesis.

11:00 AM U1.6
The Effect of Surface Treatment on Drop Placement and Film Levelling in OLED Devices Fabricated by Ink-jet. Paul Mahon[1], Neil Tallant[1], Steve Yeates[1], Juergen Steiger[2] and Stuart Speakman[3]; [1]Avecia Research Centre, Avecia Ltd., Manchester, United Kingdom; [2]Covion Organic Semiconductors GmbH, Frankfurt, Germany; [3]MicroDevice Science Ltd., Chelmsford, United Kingdom.

Drop-on-demand piezoelectric ink-jet promises to be a flexible and economical manufacturing tool for the fabrication of pixelated polymer OLED devices. For this technology to become a realistic commercial proposition, the process needs to reliably meet the very exacting specifications this application imposes. Two particular challenges are drop placement accuracy and subsequent film levelling. Much work has gone into tackling these issues through development of hardware and ink formulations. Here we will show how effective surface treatment of the display substrate can be used to enhance process reliability and performance. This paper will present results on the use of experimental design to optimise CF_4 and O_2 plasma treatments that are used to modify the surface wettability of an OLED display substrate. The relative importance of the varying process parameters on the contact angles of PEDOT and solvent-based light emitting polymer solutions on both ITO and photoresist material will be discussed. The ability to then control the drop placement properties and film levelling abilities of the fluids by tuning the wetting properties of the substrate materials will be demonstrated. Additionally, computational fluid dynamics (FLOW-3D® free-surface CFD modelling code) has been used to develop a simple model to describe the impact of an ink-jet droplet on a structured, differentially wetting surface. This has been used to rationalise the experimental data obtained and has provided further insights into the influence of fluid properties, substrate treatment and jetting directionality on drop spread and ink retention within pixels.

11:15 AM U1.7
High-performance inkjet-printed pentacene transistors for ultra-low-cost RFID applications. Steven Molesa, Steven K Volkman, Mark Chew, David Redinger, Brian Mattis, Paul Chang, Ali Niknejad and Vivek Subramanian; Electrical Engineering and Computer Scienece, University of California Berkeley, Berkeley, California.

Printed electronics will enable the development of ultra-low-cost RFID circuits for use as electronic barcodes, since it eliminates the need for lithography, vacuum processing, and allows the use of low-cost web manufacturing. Recently, there have been several demonstrations of printed transistors; however, the performance of these has generally

been inadequate for RFID applications. The two most widely printed organic semiconductors are polythiophene and F8T2; both have mobilities well below 0.1cm^2/V-s in inkjetted devices, which is too low for RFID applications. Furthermore, there have been no studies on the AC performance of these materials. Since RFID will likely require operating frequencies of either 135kHz or 13.56MHz, knowledge of the AC performance of these devices is crucial. Last year, we reported on the development of an inkjettable pentacene precursor. Here, we report optimization schemes for the same via control of jetted film thickness and morphology, and demonstrate transistors with mobilities as high as 0.2 cm^2/V-s and Ion/off as high as 10^5. We also measure fmax to be as high as 1MHz in an unoptimized geometry. This inkjetted transistor technology thus provides the highest reported performance for an inkjetted transistor to date, with AC characteristics that are likely adequate for RFID applications.

11:30 AM U1.8
Printed Polymeric Transistor Arrays for Display Backplanes.
Ana Claudia Arias, Kateri E Paul, Steve Ready, William S Wong, Michael Chabinyc, Alberto Salleo, Raj Apte and Robert Street; PARC, Palo Alto, California.

Printing technologies promise to reduce the cost and complexity of the fabrication of display backplanes, because printing can replace conventional photolithographic subtractive patterning methods and can directly deposit active materials. We have developed a method to fabricate polymer TFT backplanes without using conventional photolithography. We report on the fabrication of 64x64 active matrix TFT arrays with 330 micron pixel size, using a regioregular polythiophene polymer semiconductor. The method to fabricate polymeric TFT arrays uses jet-printing for subtractive and additive patterning. First, digital lithography replaces photolithography by directly printing a wax mask onto the layer that needs to be patterned. Once the wax mask is printed, the metal layer is patterned by etching and the wax is removed. This subtractive method is used to define metal gate, source and drain features of the array. Additive jet printing was chosen as the preferred method of polymer deposition in order to achieve semiconductor isolation and reduce the cross talk leakage between transistors in the array. The polymer solution is jetted from a piezo-ink-jet head. The jetted polythiophene semiconductor exhibits TFT mobility of 0.1 cm^2/Vs, ON/OFF ratios of 10^7, and minimal bias-stress. Measurements find a high yield of TFTs with a reasonably narrow performance distribution across each array. The TFT parameters approach the performance of amorphous silicon transistors and meet the requirements for addressing displays. Integration of display media to the array will be discussed. The technology has been applied to both rigid and flexible substrates and can be scaled to large areas.

11:45 AM U1.9
Polymer for phosphor in PDP Binding Application.
Byungkyun Kim, Ki Jun Kim and Dong Sik Zang; SAMSUNG SDI CO., LTD, Yongin-City, Gyeonggi-Do, South Korea.

In the manufacture of PDP panels, the phosphors are applied to an inner panel surface by screen-printing patterns of pastes containing red, green, and blue-emitting phosphors, respectively. But, paste should be formulated to minimize any negative effects on phosphor brightness during panel manufacturing. The organic components of the paste are burned out during panel manufacturing by heating the panels to about 500°C in an oxygen-containing atmosphere for about 1-2 hours. This burn out step can severely impact the brightness and color coordinate of the PDP phosphors, particularly, those phosphors which contain activator ions susceptible to oxidation, e.g., BaMgAl10O17:Eu2+. BAM phosphor has a few problems to overcome for the application to PDP. For instance, a typical brightness loss for this blue-emitting PDP phosphor can be greater than 20% following burn out in air. Simultaneously, the chromaticity is changed from blue to green-like along with the degradation of its phosphor efficiency. Therefore, it is the object of the present research to minimize the decrease in the brightness and the change of color coordinate of PDP phosphor resulting from the burn out of the organic paste components. To overcome those problems, ethylcelluose, poly(butyl methacrylate), poly(butyl methacrylate-co-methyl methacrylate), poly(ethyl methacrylate), polyanhydride, poly(vinyl butyral), polyethylene oxide, polypropylene carbonate, poly(methyl methacrylate), poly(ethyl vinyl acetate), poly(isobutyl methacrylate), and poly(α-styrene) etc. were investigated. However, since polyethylene oxide (PEO) carries its own oxygen enough to burn itself, it is possible to burn out the phosphorous paste in N2 atmosphere. The paste for PDP comprising a phosphor dispersed in an organic paste containing PEO retains at least about 98% of its initial brightness after binder has burned out and little change of color coordinate. Upon decomposition, it leaves very low ash residues with complete burnout of carbon. The TGA data showed that 3% binder content in the initial powder mixture results in a final part with residual ash content of less than 2ppm. In addition, PEO is soluble in many common solvents, such as water, benzene, alcohols, chloroform, esters, etc. The preferred paste composition, which maintained about 98% efficiency (relative to the brightness of the original phosphor) of the blue PDP phosphor, BAM, has the following composition: 40 50wt.% phosphor, 50 60wt.% solvents, 0.5 5wt.% PEO, and additives such as antioxidants, dispersant, plasticizer, and leveling agents 0.1 5 wt.%. This binder also can be used to print the carbon nanotube in FED cathode in order to increase its current density.

SESSION U2: Soft Lithography
Tuesday Afternoon, April 13, 2004
Room 3022 (Moscone West)

1:30 PM *U2.1
Novel Materials for Dry Printing Electronic Devices.
Graciela Blanchet[1], John Rogers[3], Colin Nuckolls[2], Greg Jaycox[1], Michael Lefenfeld[2] and Jueh-Lin Loo[4]; [1]DuPont, Wilmington, Delaware; [2]Columbia University, New York, New York; [3]University of Illinois, Urbana/Champaign, Illinois; [4]University of Texas, Austin, Texas.

Organic electronic systems offer the possibility of lightweight, flexibility and large area coverage, properties not easily achievable with standard silicon technology, and at potentially lower manufacturing costs. DuPonts approach to the fabrication of organic electronic devices is thermal transfer, a laser assisted imaging technique appropriate for their early commercialization. Since complex multi-layer circuits are fabricated by the sequential printing of solid films, the material options is considerably broadened and the stringent solvent compatibility issues faced by wet techniques like micro-contact printing and ink jet are effectively circumvented. We continue to focus on the development of conducting and semiconducting organic composites that allow for the printing of active and passive electronic devices at good process speeds and high resolution. The feasibility of using laser ablation for large area printing of organic electronic devices was demonstrated by fabricating a 32 inch diagonal thin, flexible and ultra-light weight organic transistors array backplane.

2:00 PM U2.2
Printing of Polydiacetylene Vesicle Patterns on Glass.
Dong June Ahn[1], Sang Hoon Lee[1], Hee-Yong Shim[1], Sung Min Woo[1], Eun-Kyung Ji[2] and Jong-Man Kim[2]; [1]Department of Chemical & Biological Engineering, Korea University, Seoul, South Korea; [2]Department of Chemical Engineering, Hanyang University, Seoul, South Korea.

Polydiacetylene-based vesicles are interesting materials in view of application to chemical and biological sensors. These vesicles are unique in changing color from initial blue to red upon specific binding events, caused by shortening of delocalization lenth of π-electrons along diacetylenic backbones. Various binding events including viruses, toxins, glucose, and ionic interactions have been reported detectable. However, simultaneous screening of various binding events has not been possible with solution-phase vesicles. Recently, we were successful in immobilization of the polydiacetylene vesicles on glass substrates without losing their unique color changing property (Adv. Mater. **2003**, 15, 1118). In this presentation, we report on printing of polydiacetylene vesicles on glass substrates by using a conventional spotter to make microscale dot patterns. Each dot is found to possess the color-changing property as well as the fluorescence emission. This technique allows us, for the first time, to fabricate biochips based on polydiacetylene vesicles and to screen binding events simultaneously.

2:15 PM *U2.3
Soft Lithography for Ultraminiaturized Biological Assays.
Emmanuel Delamarche, David Juncker, Sandro Cesaro-Tadic, Heinz Schmid, Marc Wolf, Heiko Wolf, Bruno Michel and Walter Riess; Science & Technology, IBM Zurich Research Laboratory, Ruschlikon, Switzerland.

Depositing proteins as small spots on surfaces opens the way to miniaturizing bioassays with the attendant benefits of economizing reagents, detecting analytes in parallel with high-quality signals and in minimal time. We have developed methods based on soft lithography to pattern proteins down to the level of a single protein molecule. The proteins are patterned on surfaces for bioanalytical applications. Soft lithography refers to a set of techniques that utilize a soft element to pattern a substrate with small molecules, polymers or biomolecules. This element is typically a micropatterned elastomer, and it can be placed reversibly onto a surface without damage. In so-called microcontact printing, the element is a stamp, and it is simple to adsorb proteins from solution onto the stamp for printing on a variety of substrates with submicrometer accuracy. For example, micrometer-wide areas of a silicon surface can be printed with a thousand antibody molecules and used for surface immunoassay

experiments. In so-called affinity contact printing, stamps are tailored to have an affinity for specific proteins from an ink via antibody-antigen-specific binding. Antibodies attached to the stamp bind antigens from solution. The captured antigens dissociate and transfer to the substrate where desired during printing. An alternative to printing is to seal a microfluidic network reversibly to a surface to define microchannels inside which a solution of protein can be drawn. The geometry and wetting properties of the microfluidic networks suffice to move liquids from one part of the device to another using capillary forces only. Hence, these microfluidic networks are free of external pumping elements. They are thus ideal for conducting sandwich immunoassays in a combinatorial fashion on a planar surface with high-resolution and contrast using submicroliter quantities of samples and reagents, and on a time scale of a few minutes. These biopatterning methods stand as proof-of-concepts, and it will be very exciting to try to implement them for advanced bioassays.

2:45 PM U2.4
Patterned Poly(N-isopropylacrylamide) Brushes Prepared by Surface Initiated Polymerization on Silica. Huilin Tu, Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We have fabricated patterned poly(N-isopropylacrylamide) brushes on oxidized silicon wafers by the micro-contact printing of a self-assembled surface initiator followed by the surface initiated atom transfer radical polymerization (ATRP) of N-isopropylacrylamide (NIPAAm). The patterning of the surface initiator was achieved by micro-contact printing of octadecyltrichlorosilane (OTS) followed by backfilling with aminopropyltriethoxysilane and then the exposed amino group was reacted with bromoisobutyric acid. The surface initiated ATRP of NIPAAm was carried out in methanol/water mixture using CuBr/pentamethyldiethylenetriamine(PMDETA) as the catalyst system. By adjusting the polymerization time, the PNIPAAm brush thickness can be varied from a few nanometers up to about 50 nm. The chemical structure of the PNIPAAm brushes was confirmed with X-ray Photoelectron Spectroscopy and Fourier Transform Infrared Spectroscopy, and the physical properties have been characterized with ellipsometry, contact angle measurements, and X-Ray Reflectometry. Atomic Force Microscopy and Fluorescence Microscopy have confirmed the success in the micro-patterning of the PNIPAAm brushes. The fluorescence emission spectra of Prodan in the PNIPAAm brushes have indicated that the local chemical environment of PNIPAAm is very similar to that of DMF. In the fluorescence microscopy image of Prodan in patterned PNIPAAm brushes grafted on silica cover slip, the intensity of Prodan emission is stronger than that on OTS because the Prodan molecules can be incorporated into the thick PNIPAAm brushes. Our experimental results are significant to the design and application of patterned "smart" polymers on oxidized silicon wafers. The patterned PNIPAAm brushes on oxidized silicon wafers or silica substrates may be useful for many applications including surface-confined molecular delivery, biomolecular sensing, and molecular separation.

3:30 PM *U2.5
Directed self-assembly of nanoparticle building blocks onto charged based receptors. Heiko Otto Jacobs, Chad R. Barry and Aaron M. Welle; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Nanoparticles are considered potential building blocks for the fabrication of future devices. This article reports on a new tool to direct the assembly of nanoparticles onto surfaces using electrostatic forces. We demonstrate directed self-assembly of nanoparticles onto charged surface areas (receptors) with a resolution of 100 nm. The charged based receptors required for this type of directed self-assembly were fabricated using a parallel method that employs a flexible, electrically conductive, electrode to charge a thin-film electret. The flexible electrode was brought in contact with a thin-film electret on an n-doped silicon substrate. The charge pattern was transferred into the thin-film electret by applying a voltage pulse between the conductive electrode and the silicon substrate. A new electrode design that is based on a 10 micrometer thick flexible membrane has been developed. Areas as large as one square centimeter were patterned with charge with 100 nm scale resolution in 10 seconds. Charge based receptors, 100 nm x 100 nm in size, contained 100 elementary charges. These charge patterns attract nanoparticles. A liquid-phase assembly process where electrostatic forces compete with disordering forces due to ultrasonication has been developed to assemble nanoparticles onto charged based receptors in 10 seconds. A gas-phase assembly process has been developed that uses a transparent particle assembly module to direct and monitor the assembly of nanoparticles. Nanoparticles were generated using a tube furnace by evaporation and condensation. A process is also being developed to enable the patterning of any organic and inorganic material with sub 100 nm resolution. Currently, the electrostatically directed assembly of 10 - 100 nm sized metal and 30 nm - 3000 nm sized carbon particles is accomplished. Metal nanoparticles less than 100 nm in size can be printed at a resolution of 100 nm.

4:00 PM *U2.6
Additive Contact Printing of Conductors for Thin Film Electronics. Yueh-Lin Loo, Kwang Seok Lee and Kimberly C. Felmet; Dept of Chemical Engineering, University of Texas-Austin, Austin, Texas.

Developments in contact printing technologies have been fueled by the high costs associated with lithography tools and techniques. More importantly, contact printing, unlike conventional lithography, promises to be compatible with a wide range of materials and substrates. Recently, we have developed two contact printing schemes for i) directly patterning conductive polyaniline from an aqueous dispersion and ii) additive printing of copper. These methods are straightforward yet versatile; we have fabricated electrical components for functional thin film electronics with them. Further, these methods are additive in operation so sacrificial resists, developers, and etchants are no longer required. Conductive polyaniline (PANI) is an attractive candidate for all-polymer electronics because of its chemical and environmental stability. Yet, due to its intractability, fabricating functional PANI electrical components remains challenging. Our patterning scheme involves a water-soluble PANI formulation and begins with patterned deposition of octadecyltrichlorosilane (OTS) on a hydrophilic substrate. The treated substrate is then dip-coated with the PANI formulation. Due to specific interactions between the polymer and the substrate, PANI only adheres to the untreated, hydrophilic regions. Conductive PANI patterns, with feature sizes as small as 20 microns, can be routinely produced using this technique. The ability to additively pattern Cu is highly sought after because copper - unlike gold - is compatible with current silicon and CMOS technologies. In this respect, we have recently extended nanotransfer printing to print Cu. Specifically, thiol-terminated molecular layers are incorporated as adhesives to transfer Cu patterns from the raised regions of a stamp onto a substrate. In doing so, we found the conductivity of the Cu patterns to be highly dependent on the chemical nature of the stamp but with suitable processing conditions we have achieved conductivities comparable to evaporated Cu films of similar thicknesses.

4:30 PM U2.7
Programmable Ferrofluid Masks for Lithographic Applications. Benjamin Biron Yellen and Gary Friedman; Electrical and Computer Engineering, Drexel University, Philadelphia, Pennsylvania.

Fabrication of heterogeneous substrates, like the kind used for combinatorial chemistry, genomic microarrays, and drug discovery, requires multiple lithographic patterning steps with appropriate alignment between the patterns in each step. Such heterogeneous substrates have been successfully fabricated by photolithography in the past, however traditional photolithographic techniques are expensive, chemically intensive, and laborious, typically requiring multiple steps to produce even a single pattern. Furthermore, manual alignment of many different masks to the substrate becomes increasingly difficult to control when the critical feature size is microns or even sub-micron in resolution. A novel soft masking method is presented here that employs programmable alignment marks built into the substrate to define and automatically align sequences of masking patterns. This method uses ultra-fine iron oxide grains suspended in fluid (ferrofluid) to protect or de-protect selected areas of a magnetically patterned substrate according to a programmable sequence. Ferrofluid can act as both an optical mask and a diffusion mask. Its ability to act as an optical mask is first demonstrated with commercially available positive and negative photoresist. Ferrofluid is allowed to assemble into a thin film on top of thin photoresist. The competition between external bias fields and the fields produced by the alignment marks causes ferrofluid masks to assemble only over designated poles. After exposure to 354 nm radiation, the ferrofluid mask is rinsed away and the photoresist patterns is developed. The resulting photoresist patterns are used by the lift-off process to produce an array of evaporated metallic islands with typical spot size of 8-μm. Because the masking is self-aligned, the spots are uniformly positioned on top of the alignment marks with sub-micrometer resolution. However, the lithographic applications of ferrofluid masks are not limited to just optical masking. Ferrofluid can be also be applied as a diffusion mask directly to the surface during solution-based synthesis, thereby combining mask formation and material deposition into a single step. Moreover, ferrofluid masks are easily dissolved without intensive chemical strippers. This gentle synthesis approach can potentially be used to pattern multiple layers of delicate biological materials like proteins and cells.

4:45 PM U2.8
Charge Patterning and Decay on Polymethylmethacrylate (PMMA) Films on Different Substrates - a Template for

Guided Assembly. Fengting Xu and John A Barnard; Department of Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Unique opportunities exist for utilizing nanoscale charge patterning for directed electrostatic assembly of complex functional nanostructures from discrete charged/polarized nanoparticles (e.g., colloidal spheres) or macromolecules. In this work, amine-terminated poly(amidoamine) (PAMAM) dendrimers with positively charged end groups were used as the assembled species. First, conductive atomic force microscopy (AFM) tips were used to charge writing/reading polymethylmethacrylate (PMMA) films spin-coated onto n-type doped Si (111) and mica substrates. The substrates effects on the charging process and its decay over time were studied. Both the positive and negative charged dots on both substrates exhibited significant charge dissipation over a period of hours although the positive storage on PMMA/Si was still evident for a few days. The measured time scales are appropriate for guided assembly processes. Second, the charged patterns of PMMA films were submerged into a dendrimer containing solution and the pattern formation due to the electrostatic force between the negative charged regions on the PMMA films and positive charged dendrimer end groups were investigated.

SESSION U3: Poster Session
Tuesday Evening, April 13, 2004
8:00 PM
Salons 8-9 (Marriott)

U3.1
Microcontact printing and slective atomic layer deposition. Mi H. Park, Ki Y. Ko and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

We demonstrate a selective atomic layer deposition (ALD) of TiO2 thin films on patterned self-assembled monolayers formed by microcontact printing. This technique has been used successfully to deposit TiO2 features with sizes ranging from 5 to 0.15 um on technologically important substrates including silicon and gold. The patterned monolayers on these surfaces define and direct the selective deposition of the TiO2 thin film using atomic layer deposition with titanium isopropoxide and water as the precursor. The patterned SAMs and TiO2 thin films have been investigated by atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), contact angle analysis, x-ray diffraction (XRD), transmission electron microscopy (TEM), and UV spectrometer.

U3.2
A new soft lithographic method by using cohesive mechanical failure patterning of PDMS decal stamp. Eun K. Seo, Kyung S. Park and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

Decal transfer microlithography (DTM) is a new soft lithographic method for micro/nanopatterning. We have demonstrated micro/nano scale patterning via cohesive mechanical failure (CMF) version of DTM. In this decal pattern transfer process, the features of a patterned PDMS decal stamp are physically torn from it via a cohesive mechanical failure. CMF is a remarkably versatile technique for fabricating patterned submicrostructures of PDMS on a variety of solid substrates. High-resolution patterns can be formed by CMF. We demonstrate a selective atomic layer deposition of TiO2 thin films on patterned polymeric micro/nanostructures formed by CMF. The patterned polymeric structures can be also used as resists in the wet etching of underlying films.

U3.3
An Affordable and Flexible Hot Embosser Design. Robyn R. Reed, Joanna L. Payne, Nisha D. Patel, Karen E. Legal and Diana D. Glawe; Engineering Science Department, Trinity University, San Antonio, Texas.

Hot embossers can be used to imprint patterns into polymers for microfluidic and optical applications, among others. As part of a senior design project, a group of four students have designed a relatively inexpensive automated hot embossing machine based on a commercial hydraulic press platform coupled with custom designed platens, hydraulic control, and sensor configuration. The hot embosser is controlled using a desktop computer and LabView software, both of which are commonly available at research institutions. Using LabView to control the system permits the integration of additional sensors, thus adding flexibility to the system. The total cost of the equipment, excluding the desktop computer and LabView software, is on the order of $1000, making this an affordable design compared to similar devices.

U3.4
Photo-patterning of poly(3-dodecylthiophene) by means of photoinduced surface relief formation as a molecular conveyer. Nobuyuki Zettsu[1,3], Takashi Ubukata[2], Masahiko Hara[2] and Takahiro Seki[3]; [1]Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [2]Frontier Research System, RIKEN, Wako, Japan; [3]Nagoya University, Nagoya, Japan.

π-Conjugated polymers are promising as active materials in many application areas such as microelectronics and photonics. Their imaging is a key technology in device fabrication processes. Patterning of π-conjugated polymers has been achieved through some advanced techniques such as micro-molding in capillaries (MIMIC), micro-contact printing (μCP), inkjet printing and so on. Most of such techniques required, however, complicated processes. We have previously shown that highly photosensitive surface relief formation (instant mass migration) in liquid crystalline azobenzene polymer films can be accomplished only with short exposure time (in the order of seconds). Sinusoidal undulations originate from photoinduced polymer chain migration at micrometer levels. Construction of micro relief structures in this instant mass migration system is advantageous for facile and all optical step fabrication. Here we focus on the possibility for patterning of π-conjugated polymers using this light-driven instant mass migration system as a molecular conveyer. The micro relief structures were made directly on the polymer blend films which consist of a liquid crystalline azobenzene polymer and poly(3-dodecylthiophene). The surface relief gratings were inscribed by two ways: 1) exposing the blend films to an interference pattern of s-polarized argon ion (Ar) laser beams at 488 nm with 5mW cm-2, and exposure to an incoherent non-polarized blue light at 436 nm (g-line of mercury lamp) through a photomask attached to the film. The inscriptions were characterized by atomic force microscopy, fluorescence microscopy and microscopic fluorescence spectroscopy. The clear fluorescence patterns corresponding to the higher part of the relief structures were observed. This result led to the conclusion that poly(3-dodecylthiophene) was transferred together with liquid crystalline azobenzene polymer with short exposure period. We could obtain various patterns of poly(3-dodecylthiphene) with all optical processes resulting from the use of this Instant mass migration system, in which the photo active host materials conveys other functional guest materials.

U3.5
Solventless Polymerization to Form Conducting Polymers in Nanochannels. Hongwei Gu and Bing Xu; Dept. of Chem., Hong Kong University of Science & Technology, Hong Kong, NA, Hong Kong.

Here we report a simple solventless polymerization procedure to form linear conducting polymers in nanochannels. When the surfaces of nanochannels of a template are covered with a Grubbs's catalyst, vapor of cyclooctatetraene polymerizes inside the channels as highly oriented conducting polymers, whose electrical properties will also be described.

U3.6
Fabricating Arrays of Isolated Single-walled Carbon Nanotubes by Dry Deposition. Kyle Ritter[1] and Joseph Lyding[2]; [1]Materials Science and Engineering, University of Illinois, Urbana-Champaign, Illinois; [2]Electrical and Computer Engineering, University of Illinois, Urbana-Champaign, Illinois.

Creating ordered arrays of single-walled carbon nanotubes (SWNTs) is critical for the realization of integrated carbon nanotube-based electronics. Utilizing a novel dry deposition technique, aligned SWNTs have been observed on the Si(100) surface by atomic-force microscopy (AFM) in under ambient conditions. The dry transfer process is first performed under ultrahigh-vacuum (UHV), where solid phase HiPco SWNTs are deposited onto pristine UHV-prepared Si(100)-2x1:H surfaces [1]. A fiberglass applicator uniformly coated with SWNTs is brought into gentle mechanical contact with the Si sample, delivering predominantly individual SWNTs to the surface with minimal contaminants (catalysts and carbon residue). After removal from UHV, large area AFM scans show that the SWNTs exist almost entirely in the form of aligned arrays. The mechanisms underlying these observations will be discussed. An important aspect of the dry deposition process is that it can be generalized to the deposition of almost any species to surfaces that are not compatible with ambient exposure. One example of this that we will show is the ability to deposit SWNTs onto UHV-cleaved GaAs(110) surfaces and then achieve atomic resolution UHV STM images of both the SWNTs and the substrate [2]. Current experiments include using AFM and STM to characterize SWNTs on different surfaces, as well as to studying the effect of changing different variables in the dry transfer process. AFM will be also be used to determine the effects of using dry transfer under ambient conditions and its effect on the alignment of SWNTs. [1] P. M. Albrecht and J. W. Lyding, Appl. Phys. Lett. (in press). [2]

L. B. Ruppalt, P. M. Albrecht and J. W. Lyding, unpublished.

U3.7
Rapid Screening of Polymers by A Novel Polymer Array System. P. Sidney Sit and Joachim Kohn; Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey.

Although synthetic polymers have shown promise as viable alternatives for tissue repair and replacement, a shortage of suitable polymers remains due to the slow process of material development. As a first attempt to expedite polymer development, we propose and develop a polymer array system for the rapid screening of polymers for potential biomedical applications. Silanated tetraethylene glycol (STEG) was prepared for the modification of glass surface. It was synthesized by adding an undecenyl moiety to TEG monomethyl ether, followed by addition of dichloromethylsilane to the double bond. Then, cleaned glass surfaces were modified with STEG. The silane layer serves a dual role for providing protein resistance on the background (TEG moiety) and a hydrophobic domain for polymer attachment (undecenyl moiety). Eight tyrosine-derived polymers with a systematic variation in the chemical composition and physical properties were used. They were synthesized according to published procedure and dissolved in dimethylsulfoxide (DMSO) (1 wt percentage). Polymers were printed onto STEG-modified glass surfaces by a microarray printer. During the process, the first polymer was transferred from the bulk reservoir to the silanated surface by microarray pins, which were then washed by DMSO and water before printing a second polymer. The cycle was repeated for all test polymers. The polymer spots were then let dry at room temperature and found to be stable under aqueous conditions. An immunofluorescence assay was used to obtain the adsorption profile of fibrinogen and fibronectin on individual polymers. During the assay, polymer arrays were incubated in a single protein solution (150 microgram/ml) for two hours, washed with phosphate-buffered saline and blocked by bovine serum albumin (1 wt percentage). The surface-bound proteins are then recognized by fluorescence-tagged polyclonal antibodies (0.25 v/v percentage). The fluorescence signals on various polymer spots were analyzed by a built-in algorithm of the fluorescence scanner. Using the relative intensity of the fluorescence as an indicator, the protein adsorption profile on various polymer spots was determined simultaneously in a rapid fashion. Without the application of proteins to the polymer spots, there was no significant fluorescence suggesting the specificity of the antibodies. Results indicate that the adsorption profile of fibrinogen is different on individual polymers. A similar trend is also observed for fibronectin. Moreover, adsorption profile of fibrinogen is different from that of fibronectin on the same polymer. Current results suggest that polymer array may used to rapidly identify possible lead polymers for further investigation by using relative small amount of materials, including polymers, proteins and antibodies. (Supported by the New Jersey Center for Biomaterials and National Institute of Health (HL 60416 and P41 EB 000922-001))

U3.8
Production of silver nanoparticles and subsequent formulation of an ink for use in DOD inkjet printing.
Angela Dearden[1], Patrick Smith[2], Dong-Youn Shin[2], Brian Derby[2] and Paul O'Brien[1]; [1]Department of Chemistry, Manchester University, Manchester, United Kingdom; [2]Materials Science Centre, UMIST, Manchester, United Kingdom.

Silver inks with low sintering temperatures for use with drop on demand inkjet printers have been formulated. The inks have been developed for the printing of conductive silver circuits on various substrates, including polyimide. The inks were formulated from a range of silver nanoparticles and a variety of solvents. The silver nanoparticles have been synthesised from the silver salts of fatty acids. The chain length of the fatty acid was the variable, ranging from C11 up to C18. Decomposition of the silver salts under nitrogen for 90 minutes at 250 degrees C produced silver nanoparticles. The size range of the nanoparticles is 6 nm to 10 nm, and they have been characterised by TEM, XRD, UV/vis, elemental analysis and TGA.

U3.9
Laser Writing of Copper Lines in a Metal-Organic Precursor Film.
David Conklin[1], Richard P Martukanitz[2], Sigurd Wagner[1] and Anye Li[1]; [1]Electrical Engineering, Princeton University, Princeton, New Jersey; [2]Applied Research Laboratory, Pennsylvania State University, State College, Pennsylvania.

We describe the direct writing of copper lines with a digitally programmable technique. The copper lines are produced by the laser annealing of a metal-organic compound, copper hexanoate. Films of this metal-organic precursor with thicknesses of 1.6 and 3.2 micrometers are spun onto a glass substrate. The films are then scanned with a Nd:YAG laser beam (1064 nanometer wavelength), which thermolyzes the films to a copper-copper oxide mixture. For full conversion to metallic copper the films are annealed at 200 degrees C in hydrogen. We obtained various stages of film morphologies between two phases. One is a fine crystalline and powdery film, with an appearance under the scanning electron microscope that suggests nucleation and growth of copper or copper oxide from a solid phase. The second phase is a frozen melt, indicating liquefaction as part of the conversion of the precursor. Both phases are electrically conducting. Our results demonstrate the feasibility of direct digital writing of copper conductors. This work is supported by ONR.

U3.10
Programmable Electric Nanocontact Lithography to Pattern Charge and Topography in E-beam Sensitive Resists.
Heiko Otto Jacobs, Jie Gu and Chad R. Barry; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

ABSTRACT: We report on a programmable, reconfigurable, printing approach for parallel nanofabrication of two different types of structures: patterns of charge for nanoxerographic printing, and patterns of e-beam resist for nanofabrication. The developed tool is based on previous knowledge in the area of Conducting Scanning Probe Lithography, which uses a conducting probe to electrically expose and modify a surface. Our tool makes use of the same physical principles, however, instead of using a single electrical point contact, a conductive flexible electrode is used. This electrode is based on a flexible membrane that forms multiple electric contacts of different size and shape to the surface, exposing the entire surface to electrons and electric fields in a single step. The electrodes are used to expose e-beam sensitive resists to generate patterns of charge and patterns of topography with 100 nm resolution. Compared to the commonly used e-beam lithography, the electric nanocontact lithography provides a route to enable programmable, reconfigurable nanofabrication.

U3.11
Selective, Controllable, and Reversible Aggregation of Polystyrene Latex Microspheres via DNA Hybridization.
Antoine Calvez[1], Jackson Crews[1], Phillip Rogers[1], Alistair Wood[1], James K. O. Lau[2], Bradley Roberts[2], Eric Michel[3], David J. Pine[3] and Peter V. Schwartz[1]; [1]Physics, Cal Poly, San Luis Obispo, California; [2]Materials Engineering, Cal Poly, San Luis Obispo, California; [3]Chemical Engineering, UCSB, Santa Barbara, California.

Single stranded DNA is covalently attached to polystyrene latex microspheres and the resulting surface coverage is measured for different attachment protocols. Increased DNA surface coverage improves charge stabilization (reduction in nonspecific aggregation of microspheres) resulting from increased electrostatic repulsion. DNA derivatized microspheres aggregate in the presence of a DNA strand, the opposite ends of which are complementary to strands bound to the microspheres. In a mixture of microspheres derivatized with different sequences of DNA, microspheres with complementary DNA form aggregates, while microspheres with noncomplementary sequences remain suspended. The process is reversible by heating, absence of salt, and ultrasonic agitation.

SESSION U4: Direct Printing and Writing
Chair: James W. Stasiak
Wednesday Morning, April 14, 2004
Room 3022 (Moscone West)

8:30 AM U4.1
Materials Requirements for Successful Drop-On-Demand Ink Jet Deposition.
Michael Grove, David Wallace and Donald Hayes; MicroFab Technologies, Inc., Plano, Texas, Texas.

The increasing use of instruments utilizing drop-on-demand, or demand mode, ink jet technology for the fabrication of micro-scale electronic, photonic, optical, biomedical, and pharmaceutical devices or products is leading to a growing interest among experimenters in these fields in this materials deposition process. This paper intends to discuss the materials requirements for the process that lead to successful ink jet printing experiments. While ink jet technology became a success in the 1980s and 1990s in the color printing of PC generated documents in the office and home environments after having gone through decades of research and development, it had a parallel development, if on a much modest scale, as a technology for the precise printing of pico-liter drops of fluids that were not aqueous solutions of acid dyes, cosolvents, glycols, stabilizers, and biocides. Non image producing ink jet printing developments include the fabrication of micro-lenses, the printing of DNA and polypeptide diagnostic arrays on chips, the printing of molten solder on microprocessor bonding pads for flip chip assembly, printing of interior thick film resistors for PWB assemblies, conductive strips, organic field-effect transistors, conductive polymer structures, light

emitting polymers for OLEDs, and drug containing injectable microspheres for trans-dermal controlled release drug delivery among others. The fluids for the ink jet fabrication of each of these devices or products must satisfy certain functional requirements of the ink jet drop generation device in order to be successful. Characteristics of the fluids for successful interaction with ink jet drop generation devices will be discussed. The fluids covered include both aqueous and non-aqueous solutions of low molecular weight and polymeric solutes, hot-melt printing of organic and metal melts, printing of nano materials, and printing of dispersions and suspensions. Acceptable and unacceptable rheology will be examined. Successful ink jet deposition processes depend on achieving the desired mateials interactions between the fluid and the substrate as well as between the fluid and the jetting device. Substrates used in the above listed examples will be mentioned.

8:45 AM *U4.2
Inkjet Printing Of Multilayers And Self-Assembling Polymers For Structures And Devices. Paul Calvert[1], Yuka Yoshioka[2] and Ghassan Jabbour[2]; [1]Textile Sciences, University of Massachusetts, Dartmouth, Dartmouth, Massachusetts; [2]University of Arizona, Tucson, Arizona.

Inkjet printing is familiar as a method for forming 2-dimensional patterns. With a typical ink and substrate, a dried droplet has a diameter of 50-100 microns and a thickness of 100 nm. Much thicker layers can be formed by overlapping drops to form lines, lines to form layers and then multiple layers to form thick films or truly 3-dimensional structures. The small thickness of each layer allows rapid mixing of materials if two different inks are superimposed. As a result it is possible to build structures by sequential printing of complementary self-assembling polymers. In this case the final structure shows a complex dependence on the molecular weights, substrate wetting and deposition sequence. Examples will be given including building thick layers of conducting polymer and forming insoluble gels from self-assembling cationic and anionic polymers.

9:15 AM U4.3
Inkjet printing of conductive silver tracks. Patrick J Smith[1], Angela L Dearden[2], Dong-Youn Shin[1], Brian Derby[1] and Paul O'Brien[2]; [1]Manchester Materials Science Centre, UMIST, Manchester, United Kingdom; [2]Department of Chemistry, University of Manchester, Manchester, United Kingdom.

A drop-on-demand inkjet printer has been used to print conductive silver tracks on glass and polyimide film substrates. A range of inks containing silver carboxylates were formulated to meet printability parameters, e.g. viscosity and subsequently printed. Thermal processing after printing yielded a continuous silver metal track, which was then characterised in terms of conductivity as a fraction of bulk silver, height, width and surface finish. The processing steps required to obtain conductive silver tracks were also optimised.

9:30 AM *U4.4
Inkjet patterned polymeric field effect transistors and circuits. Janos Veres, Simon Dominic Ogier, Stephen Yeates, Giles Lloyd, Stephen Leeming and Domenico Cupertino; Electronic Materials, Avecia, Manchester, United Kingdom.

The great attraction of organic semiconductors is the possibility to fabricate electronic devices by printing techniques. In this paper we describe the fabrication of organic field effect transistors (OFETs) by an interesting inkjet technique. The resolution currently achieved is 50 microns without any pre-patterning. Source/drain electrodes and transistor arrays were formed using metal electrodes as well as high conductivity polyaniline (PAni) tracks. Simple circuits such as inverters and ring oscillators have been prepared, the latter presently being optimised to achieve device uniformity and eliminate defects for correct operation. The latest high perfprmance triarylamine polymers were used as the semiconductor in the OFETs, offering increased mobility and on/off ratio. Using optimised semiconductor and dielectric materials remarkable device stability is achieved during operation, coupled with very low bias stress. Static, transient and high frequency operation of the devices is also discussed.

10:30 AM U4.5
Inkjet Printing of Embedded Passive Components. Erik Moderegger[1], Guenther Leising[1], Harald Plank[2], Stefan Gamerith[2], Gernot Mauthner[2], Thomas Piok[2], Martin Gaal[2], Christoph Gadermaier[2], Oliver Werzer[2] and Emil J W List[2]; [1]Science & Technology Scientific, AT&S AG, Leoben, Austria; [2]Christian Doppler Laboratory for Advanced Functional Materials, Graz, Austria.

The printed wiring boards (PWB) industry has used screen-printing processes since its beginnings about 75 years ago. Firstly, conductive silver ink was screen-printed onto organic and ceramic substrates. This approach suffered from adhesion and uniformity problems, and was too expensive to become a commercial success. As a successor to this technology, the indirect approach of printing of etching-masks on unstructured metal sheets on a plastic or ceramic carrier was developed. It is still in use today for relatively coarse structures down to 200 μm. For finer structures, photo-lithography is used. In parallel to this evolution, it became interesting to integrate passive electronic components such as resistors and capacitors and even active devices such as transistors or chips into the PWB. Key driving factors for this technology are the need to further minimize the size of devices and to increase the circuit density, while at the same time product performance and reliability have to increase. The development of inkjet printing technology as a means to deposit finely defined quantities of material to a substrate offers the potential for printing technology to regain ground in the fabrication of electronic devices on the production scale. While there are commercial solutions for inkjet-deposited etch masks and solder masks, our research focus is centered around electronically functional materials, such as resistors and capacitors. This approach is motivated by the resolution, tolerance and cost-performance of these components in comparison to other processes such as sheet deposition and structuring or screen printing. In this paper we discuss the demands on inkjet technology and ink formulation from our point of view as a leading PWB producer. We will present results on the electrical properties and surface morphology of inkjet printed resistors based on novel material concepts.

10:45 AM *U4.6
Combinatorial Nanotechnology Through Massively Parallel Dip-Pen Nanolithography. Chad A. Mirkin, Institute for Nanotechnology, Northwestern University, Evanston, Illinois.

Dip-Pen Nanolithography (DPN) is a scanning-probe techniques that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its uses to generate and study a wide variety of nanostructures made from materials ranging from oligonucleotides to proteins to conjugated polymers.

11:15 AM U4.7
The Effect of Environmental Conditions on Dip-Pen Nanolithography of Mercaptohexadecanoic Acid. Erik Peterson[2], Ivan Hromada[1], Matt Leyden[1], Cheuk Tang[4], Brandon Weeks[3], James De Yoreo[3] and Peter V. Schwartz[1]; [1]Physics, Cal Poly, San Luis Obispo, California; [2]Chemistry, Cal Poly, San Luis Obispo, California; [3]LLNL, Livermore, California; [4]Materials Engineering, Cal Poly, San Luis Obispo, California.

The direct patterning of mercaptohexadecanoic acid (MHA) from an AFM tip by Dip-Pen Nanolithography (DPN) is investigated as a function of humidity, temperature, total elapsed time, and protocol for coating the AFM tip. The patterning process is directly observed by means of scanning electron microscopy (SEM). Like the DPN patterning of Octadecanethiol (ODT), MHA can be patterned under a dry atmosphere in apparent absence of a water meniscus. Unlike ODT, the molecular transport rate of MHA both decreases in a near exponential fashion with an approximately 1-hour decay time, and substantially increases at very high relative humidity as a water meniscus is formed.

11:30 AM U4.8
Direct-Writing of Biological Materials Via Maskless Mesoscale Material Deposition (M3DTM) Technology. Gregory J. Marquez, Marcelino Essien, Bruce King and Michael J Renn; M3D Technologies, Optomec Inc., Albuquerque, New Mexico.

Fundamental understanding of structure-function relationship is paramount to development of engineered biological tissue substitutes. This initiative has led to development of several suitable biomedical alternatives to native tissue transplantation. Microfabrication methods used for assisting this effort are being investigated to expand current capabilities. These include various printing technologies utilized in the assembly and patterning of biological material building blocks. One such method has recently been developed for direct-writing of biological materials, previously termed DWB [1]. This method is an extension of the Maskless Mesoscale Material Deposition or M3DTM technology. It features deposition of biological materials in computer-defined patterns on a variety of biocompatible substrates. Like the M3DTM process, an aerosol is first generated. Materials are then delivered to the desired target surface using a deposition head that generates a co-axial flow between the aerosolized material and a sheath of inert gas used for aerodynamic focusing. Stock solutions containing biological molecules such as functional

catalytic peptides and enzymes, somatic extracellular matrix, immunoreactive and fluorescing proteins, or oligonucleotides have demonstrated post-process functionality. This is indicative of the wide range of biological molecules compatible to this direct-write deposition method. Hence, aerosols containing biologically active materials can be deposited into micro-patterned features and structures without loss of functionality due to denaturing. In addition, development of this process for whole cell deposition aims to provide additive value to computer-aided engineering of embedded architecture tissue constructs. The intention of this work is to elucidate the progress made in these areas.

11:45 AM U4.9
New Materials for 3D Printing of Bone Graft Substitutes with Controlled Internal Structures. Stephan H. Irsen, Hermann Seitz and Barbara Leukers; rapid prototyping, research center caesar, Bonn, Germany.

Bone grafts have been used for a long time to repair osseous defects from trauma or disease. While autografts are limited and difficult to shape, allo- or xenografts require extensive processing to minimize disease transmission. Thus, the development of a safe synthetic bone replacement is a worthy objective. Today different synthetic bone replacement materials are available. Normally these materials are produced in simple geometries like blocks, pins or splines. Rapid Prototyping and especially 3D Printing is well suited to generate custom ceramic bone replacement implants from patients X-ray data in a short time. Here a vat filled with a ceramic powder is printed with a special binder solution layer by layer. The powder is bonded in the wetted regions. After all, unglued powder can be removed and a ceramic green body remains. This green body obtains its desired mechanical properties by sintering. Different Apatits have been used as bone replacement materials. We use synthetic Hydroxyapatite (HA) powders for the fabrication of the 3D printed scaffolds. For bone replacement, HA is a promising ceramic material because of the similar chemical and morphological structure in comparison to the mineral portion of human hard tissue. From the process point of view 3D printing requires a powder with good flowability, a controlled particle size distribution and a suitable and strong binder interaction. Commercial HA powders do not fulfill these demands in general. We use various coating and agglomeration techniques e. g. spray drying and fluidized-bed technologies to produce granules suitable for the printing process. With these techniques we fabricate HA powders with a high flowability and bulk density and a mean particle size between 60 and 100 mu. These powders are processed in combination with different water based binder solution which are optimized in means of surface properties and viscosity. For a good osteointegration and resorbability of the fabricated implants the internal structure of the macroscopic bodies and the used materials is very important. For a good osteointegration a mean pore diameter of 500 μm is discussed. We produce 3D printed samples with a controlled internal pore network and a channel diameter between 600 and 800 μm. In addition to this printed pore network the ceramic parts posses a microporosity in the range between 10 and 100 μm. This is realized by modification of the powder materials. The mechanical strength of the sintered parts I was tested and is comparable to commercial available xenografts. To ensure the safety of the ceramics,
biological tests of the sintered parts and the base materials are pending.

SESSION U5: Nanoimprint Lithography and Direct Printing
Chair: Ghassan E. Jabbour
Wednesday Afternoon, April 14, 2004
Room 3022 (Moscone West)

1:45 PM *U5.1
Photonic and Biological Applications of the Nanoimprinting Technique. L. Jay Guo, University of Michigan, Ann Arbor, Michigan.

Nanoimprint Lithography (NIL) has emerged as a promising nanopatterning technology in recent years. NIL uses a hard mold to mechanically deform the polymer resist material to create nanoscale patterns, which completely free itself from the resolution-limiting factors such as light diffraction or beam scattering that are often inherent with other more traditional approaches. The nanoimprinting technique not only has the ability to pattern precise nanoscale features, it is also compatible with polymer material processing. Based on these characteristics, we have applied nanoimprinting to several polymer based photonic devices, including nanostructures in nonlinear optical polymers, high-resolution OLED pixels, and polymer waveguide devices. For the latter devices, we will discuss a specific type, namely polymer micro-ring resonators, fabricated by a direct imprinting technique, and its new application for biochemical sensing. Based on the principle of NIL, we have also developed a new approach to fabricate nanofluidic channels with well controlled dimensions, and have studied the behavior of DNA molecules in such confinement channels. The nanochannels were fabricated by imprinting a channel template into a thin polymer film cast on a glass cover slip in a single step, offering a much higher throughput than previous methods. It is easy to control the nanochannel dimensions by a simple relationship involving the initial polymer layer thickness and the mold pattern configuration. We demonstrated effective DNA stretching in these nanochannels, which could lead to applications of quick mapping of genomic DNA segments in short time using very small amount of DNA samples. This method provides a simple and practical solution for low-cost fabrication of nanofluidic channels, which may serve as a useful tool for chemical analysis system in the nanoscale.
Furthermore, the use of polymer materials for nanofluidic channels also opens up opportunities for exploiting rich polymer chemistry in nanofluidic applications. In addition, I will describe the application of the nanoimprinting in nanoscale protein patterning. The ability to selectively localize proteins to patterns or specific locations is important for development of biosensors, bioMEMS, and basic proteomic research. We will present a flexible technique for selectively patterning bioactive proteins with nanoscale resolution using nanoimprinting and surface functionalization. We have successfully created protein patterns with sub-100 nm resolution, and have demonstrated that the biological functionality of patterned target proteins is retained by using antibody experiment.

2:15 PM U5.2
Barium-doped and Aluminum-doped Silica Gradient-Index (GRIN) Lenses by Slurry-based Three Dimensional Printing (S-3DP^{TM}). Hong-Ren Wang[1], Michael J. Cima[1], Brian D, Kernan[2] and Emanuel M. Sachs[2]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The traditional slurry-based three-dimensional printing (S-3DP^{TM}) process has been used to fabricate complex structure materials by printing organic binders in selective positions of each printing layer. This process has been modified to fabricate functional graded materials, such as gradient index (GRIN) lenses, by depositing different concentrations of dopant solution into selective positions. Two material systems, Al_2O_3-SiO_2 and BaO-SiO_2, have been chosen to demonstrate the fabrication of GRIN lenses. Aluminum nitrate and barium chloride, which decompose into alumina and barium oxide during heat treatment, are dissolved in deionized water and printed into the silica powder bed as the source of dopant. Continuous dopant jets and Drop-on-Demand (DoD) printing heads are used to control the dopant concentration profile in one dimension and two dimension, respectively. GRIN lenses with different concentration profiles are fabricated. The alumina-doped silica powder beds are dehydrated at 1000 ^{0}C for 24 hours and sintered to optical transparency at 1650 ^{0}C for 30 minutes. The barium-doped silica powder beds are treated at 985 ^{0}C for 48 hours and sintered to optical transparency at 1700 ^{0}C for 30 minutes. Both sintering are done in a vacuum furnace ($5x10^{-6}$ torr). The dopant distributions after sintering are measured by electron probe microanalysis (EPMA) and compared with the design profiles. The resulting optical effects are examined by measuring the effective focal lengths of the GRIN lenses. The effects of alumina and barium oxide on the refractive index change are also compared.

2:30 PM U5.3
Direct Patterning of Functional Ceramics Films In/From Solution Without Post Firing. Masahiro Yoshimura, Tomoaki Watanabe, Takeshi Fujiwara, Michiyo Kamiya, Yasuaki Yamakawa, Ruwan Gallage and Ryo Teranishi; Tokyo Institute of technology, Yokohama, Japan.

Patterning of ceramic films has been established generally by [1]classical lithography after fabrication of continuous films by dry or wet methods, [2] direct printing of source materials in powder or their precursors, and then laser firing, [3] direct drawing of patterns with an ink or slurry, and then fixing, mostly by firing, etc. Those processing consists of sophisticated multi-steps, which consume large amount of energies and resources and then leave most of those energies and materials as exhausts and/or wastes. We are proposing an innovative concept and technology, Soft Solution Processing (SSP) for Ceramics(1), 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 solution of RT-200°C(2) In those fabrications, interfacial reactions between a solid reactant (substrate) and component (s) in a solution have been designed and realized. When we have activated locally and moved the reaction point dynamically in those reactions, we can get patterned ceramics directly in solutions without post-heating, pattern forming, firing nor sintering. Recently we have succeeded to fabricate several patterned ceramics films i.e. BaTiO3,

SrTiO3, PbS, CdS, LiCoO2, carbon, etc. They are completely new processing for "direct patterning of ceramics," which seems to be the first success from/in solutions(2,3) References: (1) M. Yoshimura, et al., MRS Bulletin (Sep., 2000), Special Issue of Soft Processing , pp.12-16 and 17-25 (2) M. Yoshimura, et al., Solid State Ionics, 151 (Special issue of SSP)11, 41,97 &419 (2002) (3) M. Yoshimura, et al., MRS Symp. Proc. Vol. 758,65 (2003)

2:45 PM U5.4

Phase Separation Micro and Nano Molding. Laura Vogelaar[1], Jonathan Barsema[1], Lydia Bolhuis-Versteeg[1], Wietze Nijdam[2], Cees van Rijn[2] and Matthias Wessling[1]; [1]Membrane Technology Group, department of science and technology, University of Twente, Enschede, Netherlands; [2]Aquamarijn Micro Filtration, Zutphen, Netherlands.

Phase separation micro and nano molding (PSμ/nM) is a generic replication method, which covers an unprecedented range of materials. Virtually any soluble polymer can be applied in phase separation, including e.g. biodegradable polymers and high Tg polymers. Furthermore, by additional processing PSμ/nM can also be utilized for the fabrication of ceramic and carbon microstructures. During the phase separation, the replication process benefits from intrinsic shrinkage, which facilitates the fabrication of for instance open microstructures. Moreover a small gap between the mould and the structure evolves due to shrinkage. Therefore problems during the release of the structure from the mould, e.g. sticking or breaking of the structure, have not been observed. The process is highly reliable: the microstructures are defect free and exhibit a high uniformity across centimetres squared, even at high aspect ratios. The present maximum aspect ratio is approximately 5:1. A minimum feature size of 150 nm is achieved. Both minimum feature size and maximum aspect ratio have until now been restricted by the mould rather than by the PSμM process, and therefore the boundaries evoked by the process are still unknown. PSμM is an easy and cost effective process. A polymer solution is applied on a mould, and brought into contact with a miscible non-solvent. The solution will phase separate in a polymer rich part and a polymer lean part. The polymer rich part solidifies and assimilates the relief structure on the mould. Phase separation is applied for decades in the fabrication of polymer membranes. The mass fabrication of these membranes is performed in roll-to roll processes, and we anticipate on up scaling of PSμM in a similar process. Phase separation can yield a porous polymer structure, and therefore PSμM enables the fabrication of porous microstructures. The porosity can be utilized for catalytic or absorptive functionality. The possibility to introduce porosity in a microstructure also opens avenues for mass transport through the microstructure, which is an important prerequisite in e.g. tissue engineering. Recently, the fabrication of a simple three-dimensional structure by using PSμM is demonstrated. The structure originates from the controlled inclusion of air bubbles in the process, and does not require extra processing steps in the PSμM process. PSμM combines an easy and cost effective process with a broad range of materials, high reliability and new possibilities. PSμM therefore complements the present spectrum of micro fabrication techniques well.

3:30 PM U5.5

Nanometer Thick Fluorocarbon Films for Nano Imprinting. Nam-Goo Cha[1], Nam-Kyun Kim[1], Jin-Hyung Lee[1], Jin-Goo Park[1], Jun-Ho Jeong[2] and Eung-Sug Lee[2]; [1]Metallurgy and Materials Engineering, Hanyang University, Ansan, South Korea; [2]Precision Machining Group, Korea Institute of Machinery & Materials, Daejeon, South Korea.

Fluorinated carbon surface has been widely used as an anti stiction layer for imprint process because of its low coefficient of friction, low adhesion force and high hydrophobicity. This hydrophobic surface has been commonly prepared by self assembled monolayer (SAM), spin coating, and chemical vapor deposition (CVD). Liquid phase deposition such as SAM can not be used for the mold with nano structure and is not compatible with wafer scale manufacturing process due to its lacks of reproducibility and controllability. New PECVD method was developed to deposit nanometer thick fluorocarbon (FC) films on mold structure by using inductively coupled plasma (ICP) source. C_4F_8 was supplied to chamber to deposit FC films. Contact angles of DI water and diiodomethane (CH_2I_2) were measured to calculate the surface energy. In order to investigate nano-tribological characteristics of FC films, atomic and lateral force microscopy (AFM/LFM) have been used for the measurements of adhesion forces and the friction force. FC coated AFM tip was used to measure adhesion forces. Fourier transform infrared spectroscopy (FTIR) was used to analyze chemical structure of the FC thin films. Variable angle spectroscopic ellipsometry (VASE) was used to measure thickness and optical properties. The deposition of FC films was carried out at an optimized condition of 5 sccm of C_4F_8, 30 W RF power and 110mTorr as a function of substrate position at rates of 1 to 5 nm/min. Static contact angle and surface energy of FC films were over 105° and around 12 dynes/cm, respectively. Adhesion force was measured between coated/uncoated Si_3N_4 AFM tip and coated/uncoated surfaces. The adhesion force between bare Al and bare tip was measured to be around 9.6 nN. The adhesion force between coated Al and coated tip was reduced to be around 2.9 nN. Spectra of FC films show at near 1229 cm^{-1} which has been reported to be a symmetric stretch of CF_2 group. Relatively weak adsorption was observed at 1781 cm^{-1} and 740 cm^{-1}, which represent $CF{=}CF_2$ and CF groups respectively.

3:45 PM *U5.6

Fabrication and Electrical Characterization of Single-wall Carbon Nanotube Array Based Thin Film Transistors. Yangxin Zhou, Anshu Gaur, Matt Meitl, Coskun Kocabas and John A. Rogers; Dept of MS&E, Beckman Institute and Seitz Material Research Laboratory, University of Illinois, Urbana-Champaign, Urbana-Champaign, Illinois.

We fabricate single-wall carbon nanotube based thin film transistors (CNT-TFT) by using e-beam lithography and nanostamps. Carbon nanotube thin films are grown by chemical vapor deposition or spin-cast with functionalized HiPCO nanotubes. CNT-TFT devices are built through different approaches including e-beam lithography, soft contact lamination, and transfer printing. Latest characterization results on these devices will be presented.

4:15 PM *U5.7

Manufacturing Organic Electronics Using Graphic Arts Printing Technologies. Jie Zhang[2] and Daniel Gamota[1]; [1]Physical Realization Research Lab, Motorola, Schaumburg, Illinois; [2]Advanced Technology Center, Motorola, Schaumburg, Illinois.

Low-cost high-volume manufacturing processes will enable the market introduction of electronic products driven by organic semiconductor circuitry. Products such as smart cards, RFID tags, flexible displays, personal-area and body-area networks have been mentioned in the press as potential early applications of organic circuitry. This study is investigating the use of graphic arts printing technologies, contact and non-contact printing platforms, to fabricate organic transistors in a non-clean room manufacturing environment without the use of vacuum processes. The materials and transistor designs were based on graphic arts printing requirements. A series of material property characterization and printing process studies were conducted to fabricate devices demonstrating optimal performance. Several hundreds of feet and several hundreds of sheets of all-printed organic transistors were fabricated that showed tight electrical performance tolerance.

SESSION U6: Nanopatterning and Printing
Chair: Ghassan E. Jabbour
Thursday Morning, April 15, 2004
Room 3022 (Moscone West)

8:30 AM *U6.1

Nanoimprint Lithography Patterning of Nano-Environments for Biomolecular Study and Genetic Testing. Frederick Zenhausern[1], Jian Gu[1], Qihuo Wei[1], Robin Liu[1], Chia-Fu Chou[1] and Ghassan E. Jabbour[2]; [1]Applied NanoBioscience Center, Arizona State University, Tucson, Arizona; [2]Optical Sciences Center, Arizona State University, Tucson, Arizona.

Nanoimprinting Lithography (NIL) and Dip-pen Lithography are emerging patterning techniques for high-resolution and high-throughput fabrication of semiconductor and optoelectronic chips. Micro-contact pattern transfer techniques have been recently proven useful in cell growth and patterned protein antibodies surface engineering. By using similar non conventional micro/nanofabrication approaches to engineer well-defined high aspect nanostructures in confined environments, it is now possible to control molecular interactions at nanoscales for nucleic acids and proteins testing. We will report new designs of integrated clinical diagnostic platforms to assess likely response to therapy for complex diseases, and in particular for cancers. Applications to pathogens identification, forensic DNA fingerprinting, DNA mapping in nanochannels, near-field aperture fabrication for DNA and protein testing, and nanoparticle arrays fabrication for Raman and SERS spectroscopy at the single molecule level will also be reported. A major improvement is the capability of confining electromagnetic field gradients in patterned areas to be trapping sample DNA with capture probe DNA micro-beads with higher efficienciesand many folds of sample enrichment, transforming nucleic acid amplification protocol into a single step that can be combined with on-chip gene expression testing. The maturation of these nano-patterning techniques allow to generate designed geometries with required materials properties which exhibit high aspect ratios and high shaping accuracy of the nanostructures favorable to controlled surface energy and and molecular interactions. Some examples of nano-patterned DNA/proteins microarrays on

polymeric substrates revealed super-hydrophobic behaviour of nano-pillars which improves spot uniformity, fluorescence signal, while reducing spot size and increasing array density by several orders of magnitude beyond the current limitation. The fabrication of organic optical materials will also be enablers of displays and other flexible polymeric photonic devices that could be integrated into portable medical imagers or biosensors combining gene expression information. Hence the development of advanced nanoimprinting lithography technologies could impact significantly the areas of genomics, proteomics, drug discovery and emerging molecular clinical diagnostics.

9:00 AM *U6.2
The Special Industrial Application of Thermal Bubble Inkjet Technology. Je-Ping Hu, Opto-Electronics & Systems Labs; Printing Technology Division, Industrial Technology Research Institute, Hsinchu, Taiwan.

Inkjet technology is a promised technology for low cost, large area and well-controlled micro dispense. This presentation introduces the special industrial applications including LEP (Light Emitting Polymer), Color Filter, circuit board, high density bio Chip and high flow rate fuel injector. These special industrial applications strongly challenge the capability of inkjet method, because the working fluidic properties are generally with high viscous, corrosive and low surface tension. To overcome these problems, ITRI developed their self-designed inkjet platform and industrial inkjet head. Thermal bubble inkjet technology was first used to approach LEP printing process. The piezo-electric inkjet technology is an alternative inkjet method. In general, thermal bubble inkjet exhibits thermal degradation and ink incompatibility problem. However, the former has the advantages of low cost and simple control system comparing to the latter. This presentation reveals the feasibility of thermal bubble inkjet used on the LEP device including EL Logo, a 64x64 dot matrix device. In the bio chip application, we demonstrated the specified inkjet head with 200 kinds of fluid which provided high speed dispensed DNA arrayer named "Phalanx Jet Arrayer" technology. Also, the other key issue is the better film profile and printing quality which strongly affected by the substrate treatment and fluid properties. For better control film profile and inkjet process design, the inkjet dynamic simulation tool was developed. This presentation discusses about the limitation and the consideration of the inkjet process by this simulation tool.

9:30 AM *U6.3
Additive and Subtractive Jet-printing of TFT Backplanes for Flexible Displays and Image Sensors. Robert Street, Ana C. Arias, William S. Wong, Steve Ready, Kateri E. Paul, Michael Chabinye, Albert Salleo, Rene Lujan and Raj B. Apte; Palo Alto Research Center, Palo Alto, California.

Replacing conventional photolithography with simple printing technologies offers inexpensive fabrication of large area thin film transistor (TFT) backplanes, but presents numerous materials processing challenges. The combination of additive and subtractive jet-printing provides flexibility in the choice of materials, within a single printing process. We describe jet-printed fabrication of both amorphous silicon and polymer TFT backplanes on glass and flexible substrates, without using conventional photolithography. A-Si TFT arrays use a series of jet-printed wax mask for subtractive patterning of the TFT array. Once the wax mask is printed, the thin film of metal, dielectric or a-Si, is etched and the mask is removed prior to deposition of the next layer. Accurate registration of layers allows better than 75 dpi pixel resolution, and prototype 128x128 pixel arrays with have been demonstrated, including arrays on flexible substrates made with a low temperature a-Si process. These arrays are completed as image sensors by adding a high fill factor a-Si p-i-n photodiode. The TFT characteristics are excellent, and acquired images in both visible light and x-ray exposure will be presented. The polymer TFT arrays is fabricated using jet-printing for both subtractive and additive patterning. First, the subtractive wax mask digital lithography process is used to define the gate, and source/drain features of the array. Then, additive jet printing provided the patterned polymer deposition that is necessary to achieve semiconductor isolation between transistors in the array. The polythiophene polymer solution is jetted from a piezo-ink-jet head, and the devices exhibit TFT mobility of 0.1 cm^2/Vs, on/off ratios of 10^7, and low bias-stress. There is a high yield of TFTs and a reasonably narrow performance distribution across each array. The array process provides high performance display addressing, and the integration of display media to the backplane will be discussed.

10:30 AM *U6.4
Laser Printing of Micro-Power Sources. M. Ollinger[1], H. Kim[1], C. B. Arnold[2], T. E. Sutto[3] and A. Pique[1]; [1]Materials Science and Technology Division, Naval Research Laboratory, Washington, District of Columbia; [2]Dept of Mechanical and Aerospace Engineering, Naval Surface Warfare Center-Cahlgren Division, Bethesda, Maryland; [3]Dept of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

The trend for developing increasingly smaller and more autonomous micro-electronic devices has not yet been matched by power sources with correspondingly reduced volumes. An obvious solution would be to employ micro-power sources comprised of photovoltaics for harvesting power and microbatteries for storing it until it's needed. At NRL we are investigating the fabrication of these micro-power devices using a laser printing technique called laser direct-write. Since it is a rapid prototyping process, the size, geometry and configuration of an individual or an array of micro-power components can easily be changed to accommodate the requirements of a given system. Using this technique, we have fabricated micro-electrochemical power sources, such as primary Zn-Ag_2O and secondary Li-ion microbatteries, in planar and stacked configurations. Preliminary results show capacities over 200 mAhr and discharge currents of up to 1 mA for devices with mm^2 footprints weighing just a few milligrams. The same technique has also been used to produce dye-sensitized photoelectrochemical solar cells. Comparison to other micro-power source fabrication techniques will be discussed as well as implications for powering microdevice and microsensor systems. This work was supported by the Office of Naval Research.

11:00 AM *U6.5
Towards All Organic Electronic Components Circuits - From Diodes, Transistors, to Memory Device. Yang Yang, Department of Materials Science & Engineering, University of California-Los Angeles, Los Angeles, California.

Organic electronics are emerging as a strong field. In this presentation, I will summary recent progress done at UCLA which will eventually leads toward all organic (plastic) components circuits. We have invented high speed organic diode, high performance organic memory device, organic transistors, and printable circuits. By combing these components, it is possible to build electronic circuits contains all organic electronic components in the near future.