SYMPOSIUM U
Printing of Materials in Photonics, Electronics, and Bioinformatics

April 13 - 15, 2004

Chairs

Ghassan E. Jabbour
Optical Sciences Center
The University of Arizona
Tucson, AZ 85721
520-626-8324

James W. Stasiak
Hewlett-Packard Company
MS 321A
1000 NE Circle Blvd.
Corvallis, OR 97330
541-715-0917

John A. Rogers
Dept. of Materials Science
University of Illinois
1304 W. Green St.
Urbana, IL 61801
217-244-4979

Jie Zhang
Motorola Advanced Technology Center
Rm. 1014
1301 E. Algonquin Rd.
Schaumburg, IL 60196
847-538-6847

Christie R. Marrian
IBM Almaden Research Center
K13H/D1
650 Harry Rd.
San Jose, CA 95120
408-927-2416

* Invited paper
8:30 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-structured devices. In fact, these materials are already being used to fabricate commercial light-emitting displays having active organic layers of only several tens of nanometers 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 comb-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

Nanofabrication has three components: top-down, bottom-up, and interfacial (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 self 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 Mahon1, Neil Talbott1, Steve Yeoates1, Juergen Steiger2 and Stuart Speakman2; 1Avoca Research Centre, Aveca Ltd., Manchester, United Kingdom; 2Covion Organic Semiconductors GmbH, Frankfurt, Germany, Microdevice Science Ltd., Chelmsford, United Kingdom.

Drop-on-demand piezoelectric inkjet 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 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 CF4 and O2 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 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 Males, Steven K Volkman, Mark Chew, David Redinger, Brian Matus, Paul Chang, Ali Niknejad and Vivek Subramanian; Electrical Engineering and Computer Science, 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 limited to devices that are too long and/or too wide to be useful on a readable scale.
been inadequate for RFID applications. The two most widely printed organic semiconductors are polythiophene and P3T2; both have mobilities in the range of $10^{-3} \text{cm}^2/\text{V} \cdot \text{s}$ in the solid state, which is too low for RFID applications. Furthermore, there have been no studies on the AC performance of these devices. 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 $5 \times 10^{-3} \text{cm}^2/\text{V} \cdot \text{s}$ and $I_{ON}/I_{OFF}$ as high as 10$^4$. 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.

Printed 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 380 micron pixel size, using a regioregular polythiophene polymer semiconductor, and a method to fabricate polyaniline/TFT arrays using a 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-inject-jet head. The jetted polythiophene semiconductor exhibits TFT mobility of 0.1 \text{cm}^2/\text{V} \cdot \text{s}, ON/OFF ratios of 10$^{2}$, and minimal hysteresis. 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.

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 formed in such a way, that it minimizes aphosphor 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 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., BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$. BAM phosphor has a few problems to overcome for the application to PDP. For instance, a particularly brightness loss for phosphors in the initial diffusion stage after binder has burned out and little change of color coordinate of phosphor resulting from the burn out of the organic paste components. To overcome those problems, ethylcellulose, poly(butyl methacrylate), poly(n-butyl acrylate), poly(ethylene oxide), poly(methyl methacrylate), poly(ethyl vinyl acetate), poly(isobutyl methacrylate), and poly(ethylene oxide)/PEO carries its own oxygen enough to burn itself, it is possible to burn out the phosphor paste in N$_2$ atmosphere. The paste for PDP comprising a phosphor dispersed in an organic paste, that is, PEO retains at least about 95% 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 35% binder content in the paste yields a final product of less than 2% ash, and remaining ash content of less than 2ppm. In addition, PEO is soluble in many common solvents, such as water, benzene, alcohols, chloroform, ester, etc. The preferred paste composition, which maintained about 98% of phosphor brightness (relative to the unburnt powder, 10$^{-3}$ cm$^2$/Vs and IsoT2 of the blue PDP phosphor, BAM, has the following composition: 40 wt.% phosphor, 50 wt.% solvents, 0.5 wt.% PEO, and additives such as antioxidants, dispersant, plasticizer, and leveling agent of 0.5 wt.%. This type of phosphor paste can be printed to pattern nanostructures in an efficient manner to increase its current density.

SESSION U2: Soft Lithography
Tuesday Afternoon, April 13, 2004
Room 3002 (Moscone West)


Organic electronic systems offer the possibility of lightweight, flexible 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 printing, using printed or dry printed organic films, which are similar to the organic materials used in light emitting diodes at high process speed 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, Sang Hoon Lee, Hee-Yong Shin, Sung Min Woo, Eun-Kyung Ji, 1Department of Chemical & Biological Engineering, Korea University, Seoul, South Korea, 2Department of Chemical Engineering, Hanyang University, Seoul, South Korea.

Polydiacetylene-based vesicles are interesting materials in view of their 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 length of IT-electrons along diacetylenic backbones. Various binding events including viruses, toxins, glucose, and ionic interactions have been reported. 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 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 speed 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.
Because the masking is self-aligned, fluorescence microscopy image of Prodan in patterned PNIPAAm brushes compete with disordering forces due to ultrasonic agitation. They act as conducting sandwich immunnasogels in a combinatorial fashion on a planar surface with high-resolution and contrast using submicron-resolution quantities of samples and reagents, and on a time scale of a few minutes. These biopatterning methods in aqueous solution have the advantage of being easily scaled up. We demonstrate directed self-assembly of nanoparticles onto patterned structures. The resulting photoresist patterns are used by 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 saminopropyltrimethoxysilane and then the exposed spots were reacted with bromoisobutylisocyanate. The surface initiator ATRP of NIPAAm was carried out in methanol/water mixture using CuBr/pentamethyldiethylenetriamine (PMDETA) as the catalyst system, adjusting the concentration to about 100 nm. PNIPAAm brush thickness can be varied from a few nanometers up to about 50 nm. The chemical structure of the PNIPAAm brushes was confirmed by 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 DMP. 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 transferred into the thin 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.

Additive Contact Printing of Conductors for Thin Film Electronics. Yush-Lin Lee, Kwang Seok Lee and Kimberly C. Focht; Dept. of Chemical Engineering, University of Texas-Austin, Austin, Texas.

Developments in contact printing technologies have been fueled by the high costs associated with traditional methods. 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 polymers 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, development, and etching 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, hydrophobic regions. Conductive PANI patterns, with feature sizes as small as 20 microns, can be routinely produced using this technique.

In this presentation we will introduce a novel approach to additive contact printing of metal patterns. The method is presented here that employs programmable alignment patterns is developed. The resulting photoresist patterns are used by transfer radical polymerization of N-isopropylacrylamide and subsequently transferred into the thin-film electret by applying a voltage pulse. 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 masks 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 photore sist. 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 ultraviolet 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 a typical spot size of about 10 microns. Because the masking is self-aligned, the spots are uniformly positioned on top of the alignment marks with high-resolution and contrast using submicroliter quantities of liquids andDrexel 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 masks 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 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 ultraviolet 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 a typical spot size of about 10 microns. Because the masking is self-aligned, the spots are uniformly positioned on top of the alignment marks with sub-micron resolution. However, the lithographic applications of ferrofluid masks are not limited to just optical masking. Ferrofluid can be also be applied as a mask directly to the surface without the need for alignment-based syntheses, 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 extended to multiple layers of delicate biological materials like proteins and cells.

Additive Contact Printing of Conductors for Thin Film Electronics. Yush-Lin Lee, Kwang Seok Lee and Kimberly C. Focht; Dept. of Chemical Engineering, University of Texas-Austin, Austin, Texas.
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, anisotropic poly(amideamine) (PAMAM) dendrimers with positively charged end groups were used as the assembled species. First, conductive atomic force microscopy (AFM) tips were used as a 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
Salons N-9 (Marriott)

U3.1
Microcontact printing and selective atomic layer deposition. Mi-H. Park, K.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 self-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 micro lithography (DTM) is a new soft lithographic method for micro/nanopatterning. We have demonstrated micro/nanoscale 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 simple 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, Nishik D. Patel, Karen E. Legal and Diana D. Glave; 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 photo-etched surface relief formation as a molecular conveyor. Nobuyuki Zettu1,2, Takashi Ubukata2, Masahiko Haras3 and Takahiro Seki2; 1Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan; 2Frontier Research System, RIKEN, Wako, Japan; 3Nagoya 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 photoreactive 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). Sinaroidal 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 conveyor.

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 fabricated by two ways: 1) exposing the blend films to an interference pattern of p-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 (glove of mercury lamp) through a photomask. 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. We could obtain various patterns of poly(3-dodecylthiophene) 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 polymers inside the channels as highly oriented conducting polymers, whose electrical properties will also be described.

U3.6

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)-2×1 H surfaces [1]. A fiberglas 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 is that we will show the ability to deposit SWNTs onto UHV-deposited GAs(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 effects of changing different variables in the dry transfer process. STM will be also be used to determine the effects of using dry transfer under ambient conditions and its effect on the alignment of SWNTs.

remain suspended. The process is reversible by heating, fibronectin on the same polymer. Current results suggest that polymer fibrinogen and fibronectin on individual polymers. During the assay, fluorescence suggesting the specificity of the antibodies. Results for 90 minutes at 250 degrees C produced silver nanoparticles. The substrates, including polyimide. The inks were formulated from a 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 (PEG 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 dimethyldisulfide (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 left dry at room temperature and found to be stable under aqueous conditions. An immuno-fluorescence 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 be used to rapidly identify possible lead polymers for further investigation by using relatively small amounts of materials, including polymers, proteins and antibodies. (Supported by the New Jersey Center for Biomaterials and National Institute of Health (HL 66416 and P41 EB 000922-001))

Production of silver nanoparticles and subsequent formulation of an ink for use in DOD inkjet printing.

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 synthesized 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 10-50 nm, and they have been characterized by TEM, XRD, UV/vis, elemental analysis and TGA.

Laser Writing of Copper Lines in a Metal-Organic Precursor Film.

We describe the direct writing of copper lines with a digitally programmable technique. The copper lines are produced by the laser ablation of a metal-organic compound, copper hexamminetetraacetate. 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 thermolyses 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, the other is amorphous 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.
emitting polymers for OLEDs, and drug containing injectable microspheres for trans-dermal controlled release drug delivery among others. The lack of ink jet failure mechanisms for each of these device 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 materials 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 Strucutred Con Devices, Paul Calvert1, Yuko Yoshikawa1 and Ghasan Jabbour2; 1Textile Sciences, University of Massachusetts, Dartmouth, Dartmouth, Massachusetts; 2University of Arizona, Tucson, Arizona.

Inkjet printing is familiar as a method for forming 2-dimensional patterns. With a typical ink and substrate, a droplet jet has a diameter of 50-100 microns and a thickness of 100 nm. Much thicker layers can be formed by overlapping droplets 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 conductive 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 Smith1, Angela L Dearden2, Dong-Youn Shin3, Brian Derby3 and Paul O’Brien2; 1Manchester Materials Science Centre, UMIST, Manchester, United Kingdom; 2Department 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 requirements of a number of device designs. 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 conductive polymer and forming insoluble gels from self-assembling cationic and anionic polymers.

9:30 AM *U4.4
Inkjet patterning 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 performance triarylamine polymers were used as the semiconductor in the OFETs, offering increased mobility and stability. Using optimised source/drain 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 Moderegger1, Gennier Leising1, Harald Plank1, Stefan Gamenith2, Gernot Maurer1, Georg Gass1, Christoph Gademann1, Oliver Werner2 and Emil J W List2; 1Science & Technology Scientific, ATK AG, Leoben, Austria; 2Christian 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 etching-masks on unstructured metal sheets or ceramic wafers 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 maximize 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 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 resists based on novel material concepts.

11:45 AM *U4.7
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 nanostructures. Based on a conventional Atomic Force Microscope (AFM), 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 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.

11:50 AM U4.8
The Effect of Environmental Conditions on Dip-Pen Nanolithography of Mercaptobutanehexacarboxylic Acid. Ghassan Jabbour, Patrick J Smith1, Matt Leyden1, Chouk Tang1, Brandon Weeks1, James De Yoreo3 and Peter V. Schwartz1; 1Physics, Cal Poly, San Luis Obispo, California; 3Chemistry, Cal Poly, San Luis Obispo, California.

The direct patterning of mercaptobutanehexacarboxylic 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.

12:00 PM U4.9
Direct-Writing of Biological Materials Via Maskless Mesoscale Material Deposition (M3DTM) Technology, Gregory J. Marquez, Marcelino Essien, Bruce King and Michael J Renn; M3DT 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. 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 termed as 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 macromolecular 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 coaxial flow between the aerolized material and a sheath of inert gas used for aerodynamic focusing. Stock solutions containing biological materials such as functional...
catalytic peptides and enzymes, somatic extracellular matrix, immunoreactive and fluorescing proteins, or oligonucleotides have demonstrated functionality for 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 obtain for example due to denaturing. In addition, 3D printing requires a powder with good flowability, a controlled internal pore network and a channel diameter between 600 and 800 μm. This powder is processed in combination with different water based binder solution which are optimized in means of resorb ability 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 reached by modification of the powder properties. 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: Ghassem 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 Gao, 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 can be directly transferred to the resolution-limiting factors such as light diffraction or beam scattering that are often inherent with other more traditional approaches. The nanoimprint technique not only has the ability to pattern precise nanoscale features, it is also compatible with multiphoton material processing. Based on these characteristics, we have applied nanoimprint 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 nanochannel dimensions are fabricated by modifying the conventional NIL 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 thickness and the imprint 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 molecules. This method provides a simple and practical technique for low-cost fabrication of nanofluidic channels, which may serve as a useful tool for chemical analysis system in the nanoscale.

Further, the use of polymer materials for nanochannels enables us to exploit rich polymer chemistry in functionalizing the inner surface of the nanochannels. In addition, we will describe the applications 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 demonstrated post-process functionality and its new application for biochemical sensing.
Phase separation micro and nano molding (PSm/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 PSm/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 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 not deformed, free and exhibit a high uniformity, 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 PSm process, and therefore the boundaries evoked by the process are still unknown. PSm is an easy and cost effective process. A polymer solution is applied on a mould, and brought into contact with a miscible non-solvent solution for a separate in a polymer rich part and a polymer lean part. The polymer rich part solidifies and assembles 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 PSm in a similar process. Phase separation can yield a porous polymer structure, and therefore PSm enables the fabrication of porous microstructures. The possibility of tailored for catalytic and absorptive functionalities. 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 PSm is demonstrated. The structure originates from the controlled inclusion of air bubbles in the process, and does not require extra processing steps in the PSm process. PSm combines an easy and cost effective process with a broad range of materials, high reliability and new possibilities. PSm therefore complements the present spectrum of micro fabrication techniques well.
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 imaging devices combining diagnostic and therapeutic applications. Hence the development of advanced nanoimprint lithography techniques 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, Jen-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 54x54 dot matrix device. In the bio chip application, we demonstrated the fabricated thermal bubble inkjet head with 200 kinds of fluid which provided high speed dispensed DNA array 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

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 provides the patterned polymer deposition that is necessary to achieve semiconductor isolation between transistors in the array. The polyethylene polymer solution is jetted from a piezo-ink-jet head, and the devices exhibit TFT mobility of 0.1 cm²/Vs, on/off ratios of 10⁷, 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. Olinger², H. Kim¹, C. B. Arnold³, T. E. Sutto³ and A. Pique¹; ¹Materials Science and Technology Division, Naval Research Laboratory, Washington, D.C., District of Columbia; ²Dept of Mechanical and Aerospace Engineering, Naval Surface Warfare Center-Cahlgren Division, Bethesda, Maryland; ³Dept 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-Ag₂O 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 mm² 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 summarize 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 combining these components, it is possible to build electronic circuits contains all organic electronic components in the near future.