

SYMPOSIUM M

Flexible and Printed Electronics, Photonics, and Biomaterials

November 27 - December 1, 2005

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* Invited paper

TUTORIAL

FTM: Nanoimprint Technology and Printed Organic Thin-Film Transistors
Sunday, November 27, 2005
1:30 PM - 5:00 PM
Room 201 (Hynes)

Nanoimprint is an emerging lithographic technique that promises high-throughput patterning of nanostructures with simple equipment setups, and can achieve pattern resolutions beyond the limitations set by the light diffractions or beam scatterings in other conventional techniques. It can also directly imprint functional device structures using a variety of polymers. This tutorial will describe the basic principles and experimental details of the nanoimprint technology. It will also discuss some of the recent progress in this field, including several novel applications.

The second part of this tutorial will discuss the fabrication of organic thin-film transistors (OTFTs). The rapid development in this area has been fueled by the promise of low-cost fabrication, lightweight construction, mechanical flexibility and durability, as well as large-area coverage. The tutorial will cover (1) a brief introduction of the effect of the molecular structure and morphology of the organic semiconductors; and (2) recent progress in printing and patterning of OTFTs, such as inkjet, screen, and microcontact printing, and will focus on new patterning strategy by using the "tailored" adhesions as the patterning-driven force.

Instructors:

L. Jay Guo
University of Michigan

Yanchun Han
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SESSION M1: Nanopatterning and Nanoimprint
Chairs: Y. Chen and L. J. Guo
Monday Morning, November 28, 2005
Room 306 (Hynes)

8:00 AM *M1.1

6 nm Half-Pitch Nanoimprint Lithography and Applications in SRAMs, OTFTs, and Biochips. Stephen Chou¹, Michael D.

Austin¹, Nihua Li¹, Xiaogang Liang¹, Haixiong Ge^{1,2}, Zenli Fu¹, Keith Morton¹, Hua Tan², Wei Zhang² and Linshu Kong²;
¹Department of Electrical Engineering, Princeton University, Princeton, New Jersey; ²Nanonex Corporation, Monmouth Junction, New Jersey.

We report some recent developments in nanoimprint lithography (NIL) tools, masks, resists, and processes for fabrication of 6 nm half-pitch, 0.04 m^² (20 nm half-pitch) SRAM metal layers, OTFTs with 20 nm channel length and biochip for DNA analysis. First, to explore the ultimate resolution of NIL, we explored and developed novel molds of 6 nm half-pitch and various NIL resists, and then successfully transferred 6 nm half-pitch gratings on the mold into in NX-2010 uv-NIL resist using NX-2000 NIL tool (Fig. 1). The mold for the 6 nm half-pitch lines was fabricated by cleaving a GaAs/Al_{0.7}Ga_{0.3}As superlattice grown on GaAs with molecular beam epitaxy (MBE), and selectively etching the Al_{0.7}Ga_{0.3}As layers in hydrofluoric acid. Second, to test NIL capability of making complex patterns, we fabricated SRAM cell metal layer of the 0.04 m^² and 20 nm half-pitch using NIL (NX-2000 tool and NX-2010 resist) (Fig. 2). The mold was fabricated in silicon dioxide using 35 kV electron beam lithography with polystyrene as a negative resist and reactive ion etching. The imprint showed an excellent critical dimension (CD) control of 1.3 nm for one sigma (4 nm for 3-sigma). Third, to investigate NIL in fabrication of organic thin-film transistors (OTFTs), we fabricated OTFT with channel length as small as 20 nm (Fig. 3) and achieved significant current gain as the channel length become smaller. The molds for OTFTs were fabricated using EBL at Princeton NSL. Fourthly, we fabricated a broad range of biochips for DNA analysis. The NIL molds of these chips were fabricated using single or multiple NIL steps and mixed with other lithographies. Finally, we will present the results of ultra-thin resist layer thickness with a thickness control to 4 nm using NX-2000 NIL tool (single wafer imprinter) and NX-3000 (step-and-repeat imprinter).

8:30 AM *M1.2

The Use of Nanoimprint Lithography for Creation of Biomaterial Surfaces and Structures. Lars Montelius¹, Patrick Carlberg¹, Richard Bunk¹, Mark Sundberg², Jenny Rosengren², Ian

Nicholls², Sven Tagerud², Alf Mansson², Waldemar Hallstrom^{1,3}, Christelle Prinz¹, Fredrik Johansson^{3,1} and Martin Kanje³; ¹Physics Department, University of Lund, Lund, Sweden; ²Chemistry and Biomedical Sciences, University of Kalmar, Kalmar, Sweden; ³Cell and Organism Biology, University of Lund, Lund, Sweden.

Recent years have seen a large interest in the development of nanoimprint lithography (NIL), [1,2] opening new avenues for nanoscale research. Simultaneously, there is a growing trend in Nanoscience in general to apply nanotechnology in the life science area. Here, in this new cross-over science area the characteristics theme is the need to make many samples due to the necessity to investigate processes governed by the variability that is inherent to biological systems. Hence, the use of wafer scale nanoimprint lithography is very promising [2]. In this report, we will therefore address the use of advanced nanotechnology for the study of protein interactions. In particular we will report on two projects that we presently are working with in this area. The first one concerns the successful creation of a nano-traffic system employing motor proteins and the second one deals with fabrication of nanotextured surfaces for effective nerve cell guidance. In the first project we are studying the muscle proteins myosin and actin being responsible not only for the controlled muscle behavior in all living systems but also for the function of e.g. the internal cellular machinery. By forming nanochannels using the combination of nanostructured bi-layers of PMMA- and LOR-surfaces in combination with selective surface TMCS (trimethylchlorosilanes) functionalization of the exposed SiO₂ surface [3], we have achieved efficient immobilization of the myosin molecules, and hence we have managed to fabricate efficient tracks for guiding the movements of motor actin filaments [4]. In this report we will show various forms of transport structures such as rectifiers, injectors, roundabouts, crossings and components directing the flow of motor proteins with a control at the nanometer scale. Further, we will discuss about the potential for employing such a system for high-throughput drug screening. In the second project we have studied the interplay between nerve cells and nanostructured surfaces. The surfaces being investigated have had both grooves of various shapes and widths/pitches as well as nanopillars of varying dimensions. In this talk I will describe the effective guidance that we have obtained. Acknowledgement: This work is partly performed within the Nanometer Consortium at Lund University supported by the FP 6 projects NaPa and Nano2Life and by the Swedish Science Council, the Swedish Strategic Research Council and by the Swedish Agency for Innovation Systems. REFERENCES 1. S.Y. Chou, P.R. Krauss, P.J. Renstrom, Appl. Phys. Lett. 76 (1995) 3114. 2. Heidari B., Maximov I., and Montelius L. 2000, Nanoimprint lithography at the 6 in. wafer scale, J. Vac. Sci. Technol. B 18: 3557. 3. M. Sundberg et al. Analytical Biochemistry, 323 (2003) 127-138. 4. R. Bunk, J. Klinth, J. Rosengren, I.A. Nicholls, S. Tagerud, P. Omling, A. Mansson, L. Montelius, Towards a nano-traffic system powered by molecular motors, Microelectronic Engineering 67-68 (2003) 899-904

9:00 AM M1.3

Hot Embossing as a Dry Transfer Printing Process for Flexible Electronic Devices. Ashante' C. Allen, Erik Sundén, Andrew Cannon, William King and Samuel Graham; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The development of new manufacturing technologies is necessary for the creation of nanomaterial-based flexible electronic devices. The interest in 1-D nanomaterials for such electronics is due to their flexibility, high transport mobilities and unique optoelectronic and piezoelectric properties. However, the direct synthesis of these materials on polymer substrates is challenging due to potential processing incompatibilities. To circumvent this issue, a number of techniques have been developed to organize nanomaterials onto substrates such as solution based processing and dry transfer techniques. In general, dry transfer printing methods offer advantages as the need to address substrate-solvent incompatibility is mitigated. In this work, a dry transfer printing method based on hot embossing is presented. The method was demonstrated through the patterning of carbon nanotubes (CNTs) and ZnO nanowires on silicon and sapphire master stamps which were used to print on polymer substrates. The masters were utilized both as flat stamps or etched to create microtextured surfaces. Iron or gold catalyst was patterned on the stamps to direct the self-assembly of the nanostructures. The nanomaterials were embossed into the polymers near the glass transition temperature, resulting in the simultaneous transfer of the microtextured features and nanomaterial patterns with resistances between 1-9000 kΩ. Thus, the method shows the ability to directly print electrical components from nanomaterials into flexible substrates. Since carbon nanotubes possess a band gap which can lie between 0.1-1eV, experiments were performed to analyze the optical detection characteristics of the printed devices. Data revealed that the resistances of the carbon nanotube traces were very sensitive to ambient lighting as well as laser excitation at frequencies of 488 nm and 807 nm. Laser powers as low as 100 μW were detectable.

Additional demonstrations of the capability of these devices were performed through field emission testing. By coating the backside of the polymer substrate with gold and attaching electrodes to the front and back, an atmospheric plasma was created upon the application of a DC bias. Such field emission devices will have applications in a number of areas including flexible polymer field emission displays and ionized mass spectrometry for MEMS sensors. Additional characterization of the ZnO traces in the polymer substrates will be discussed, including investigation of their piezoelectric responses. In general, the fabrication technique is a scalable, low cost method for integrating nanomaterial patterns into flexible substrates to create electronic devices. Without loss of generality, this method is amenable to other semiconductor nanomaterials synthesized by the vapor liquid solid growth method. Techniques by which catalyst can be used to control the synthesis of dissimilar materials on the same masters will be discussed.

9:15 AM **M1.4**

Chemical Nanopatterning via Nanoimprint Lithography for Liquid Crystal Displays. Sunggook Park¹, Helmut Schiff²,

Celestino Padeste², Jens Gobrecht², Toralf Scharf³, Joachim Grupp⁴ and Naci Basturk⁴; ¹Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana; ²Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, Villigen PSI, Switzerland; ³Institute for Microtechnology, Neuchatel, Switzerland; ⁴ASULAB, Marin, Switzerland.

Nanoimprint lithography (NIL) is the next generation lithography for the fabrication of nanostructured surfaces with the potential of low-cost, mass production. As an easily accessible and flexible method, NIL opened new doors for interdisciplinary nanoscale research, particularly in the areas where two-dimensional nanopatterns are required, such as optoelectronics, photonics, and bioengineering. One potential application belonging to the abovementioned categories is liquid crystal (LC) displays. All the applications of LCs utilize the simple principle that LCs can easily be aligned by a proper treatment of the contact surfaces. While rubbing process is usually employed to produce linear gratings in the contact surfaces in the production of LC displays, a deliberate introduction of nanostructures allows creating more sophisticated surface alignment conditions and, thus, new functions of LCs interacting with the structures, which are keys for the next generation LC displays. The concept of using nanopatterns for achieving controllability and high functionality of LC cells has been suggested in a few studies. However, the systematic investigation has not been performed yet, mostly due to the lack of simple and reproducible methods to fabricate large area chemical nanopatterns. This can now be overcome thanks to the development of the NIL technology. In this presentation, we will report on the use of chemical patterns to align a nematic LC in LC cells. The chemical patterns at the micro- and nanometer scale down to 30 nm in feature size were fabricated by combining NIL, with subsequent reactive ion etching, chemical modification with a fluorinated silane in the gas phase, and lift-off. Simultaneous control over both polar and azimuthal orientation of LC is possible by using the chemical nanopatterns as LC alignment layers. The polar orientation depends on the ratio of the homeotropic/planar surface potential areas while the LC azimuthally orients along the direction of the silane patterns. The thermal transition behavior of LC on chemical patterns of appropriate chemistry and geometry gives a hint that the chemical patterns are a possible candidate to achieve bistability for the future LC display.

9:30 AM ***M1.5**

Spin-on UV and Thermal-Curable Siloxane Liquid Resist for Nanoimprint Application. Peng-Fei Fu¹, Xing Cheng², Carlos

Pina-Hernandez², Wayne Fung² and L. Jay Guo²; ¹Dow Corning Corporation, Midland, Michigan; ²Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

Nanoimprint lithography (NIL) promises high-throughput patterning of nanostructures with great precision. The rapid development of this technique in recent years has also stimulated the research for new materials that are better suited as nanoimprint resists. Because imprint lithography makes a conformal replica of surface relief patterns by mechanical embossing, the resist materials used in imprinting should be deformed easily under an applied pressure. The most commonly used materials in the original NIL schemes are thermal plastic polymers, which become viscous fluids when heated above their glass transition temperatures (T_g). However typically the viscosity of the heated polymers remains high and thus the imprinting process requires significant pressure. In addition, these thermal plastic resists normally have a high tendency to stick to the mold, which seriously affects the fidelity and quality of the pattern definition. Furthermore they do not offer the necessary etch resistance. Therefore a nanoimprint resist system with a combined mold release and etch resistance properties that allows a fast and precise nanopatterning is highly desired. We have developed a new UV-curable nanoimprint

resist based on cationic polymerization of silicone epoxies. Uniform film with thickness ranging from sub-50 nm to over 1 micron can be easily spin-coated by using a suitable under-coating layer on a substrate. Due to its very low viscosity, varies patterns of sizes from tens of micron to below 100 nm can be imprinted at room temperature using a pressure of less than 0.1 MPa. Compared to the free radical polymerization of acrylates, the silicone epoxies are insensitive to oxygen inhibition and have very low shrinkage, which relaxes the processing condition and increases the fidelity of the imprinted pattern. Lift-off is also possible by using an under-coating layer that can be dissolved in organic solvent. Those advantages, plus good dry etching resistance, low viscosity and low volatility, make such material an excellent resist for UV-assisted nanoimprint. We will also report the development of a fast thermal curable liquid resist that can be imprinted under a low pressure with high precision and throughput. In nanoimprinting, the liquid resist is first spin-coated on a silicon wafer, followed by imprinting with pressures in the range 100~300 psi (or lower) at room temperature, and crosslinking after being heated above 80°C within a minute. Due to the low surface tension of the patterned film ($\gamma = 19.8$ dynes/cm at 20 °C), the mold separation is quite easy. Importantly, the mold separation does not require cooling to room temperature. The Young's modulus of the nanoimprinted film can be adjusted easily by changing the ratio of polymer to crosslinker. The high efficiency and throughput of this new nanoimprint resist system would warrant a potentially viable process for industrial nanofabrication.

10:30 AM ***M1.6**

Nanoimprint lithography for 3D nanopatterning.

Clivia M. Sotomayor Torres, Marc Zelsmann, Nikolaos Kehagias and Claus Jeppessen; Tyndall National Institute, University College Cork, Cork, Ireland.

Nanoimprint lithography (NIL), with its apparent simplicity and resolution down to a few nanometers, has become a preferred technique for one-level nanopatterning of thin organic films, which themselves act as a mask for further nanofabrication steps, or which can be used as-printed thanks to the functionality of the thin film itself. We will review the use of NIL for optical passive device fabrication and will present our results on reversal NIL to realise 3D relief patterns using suitable polymers. Progress in the use of these patterns for molecular self-assembly will be discussed.

11:00 AM ***M1.7**

High aspect ratio pattern fabrication by nanoimprint and nano casting lithography. Yoshihiko Hirai, Physics and Electronics Eng., Osaka Pref.Univ., Sakai, Japan.

Nanoimprint lithography (NIL) is expected to fabricate nano optical devices because polymer pattern works itself as an optical element without any additional process. For advanced nano optical element such as quarter wave plate, high aspect ratio patterns are indispensable for optical pickup or ultra high speed optical/optical switches in optical information systems. To fabricate high aspect ratio patterns, we demonstrate advanced thermal NIL, where the process sequence and condition are optimized to avoid stress concentration. By the process optimization, a defect at the mold removing process is successfully released and we obtain fine patterns with 200nm in width and 2.1 micron in height. On the other hand, we propose nano casting method to fabricate fine patterns. A polymer is spin-coated on the mold and cast in the grooves of the mold. Then, the polymer is bonded to substrate and removes the mold. Using the casting method, 200nm half pitch pattern with 1.9 micron height is successfully transferred. This high aspect ratio pattern shows 1/5 wave shift against. Laser light in 633nm wave length.

11:30 AM **M1.8**

Directly Patternable Dielectric Materials for Step and Flash Imprint Lithography. Frank L. Palmieri¹, Jianjun Hao¹, Yukio

Nishimura¹, Colm Flannery², Michael D. Stewart^{1,3}, Andrew S. Chan¹, Bin Li¹, Soo Young¹, Brook Chao¹ and C. Grant Willson¹; ¹Chemical Engineering, University of Texas at Austin, Austin, Texas; ²Materials Reliability Division, NIST, Boulder, Colorado; ³Molecular Imprints, Inc., Austin, Texas.

The Back End of Line (BEOL) electrical connectivity in a modern integrated circuit (IC) may contain as many as ten levels of wiring and associated vias (connections between wiring levels). The dual damascene process used to generate these copper interconnects requires many difficult processing steps. BEOL processing using Step and Flash Imprint Lithography (SFIL) with a directly patternable dielectric material can dramatically reduce the number of processing steps. SFIL with a multi-level template can simultaneously generate both the via and the trench with a single alignment and lithography step. By directly patterning a dielectric material instead of a sacrificial resist material, many hardmask materials and pattern transfer processes are eliminated. This report concentrates on the

characterization of new, Directly Patternable Dielectrics (DPD's). Dielectric material requirements are both numerous and demanding. SFIL also requires properties not found in standard semiconductor dielectric materials. SFIL requires low viscosity monomers which undergo rapid photo-induced polymerization with minimal shrinkage. A set of materials that are compatible with SFIL processing has been examined for use as a dielectric material. Inorganic/organic hybrid materials derived from polyhedral oligomeric silsesquioxane (POSS) structures with various polymerizable organic pendant moieties show promise for this application. A two stage processing technique is used to control material properties of the DPD. Stage one utilizes the standard SFIL process to generate a patterned thin film. After pattern generation, the polymeric DPD film is heated to generate crosslinks and improve mechanical and thermal properties. The structure to function relationship of various POSS materials will be examined. Material properties of the precursor liquid such as viscosity, contact angle, and rate of polymerization are discussed. Properties of the UV cured films such as pattern resolution and elastic modulus, and properties of the fully cured resin such as thermal stability, dielectric constant, thermal shrinkage, elastic modulus, Poisson's ratio, CTE, and water sorption are discussed as well.

11:45 AM M1.9

Simulations for Process Design of Nanoembossing and Atomic Force Microscope Thermomechanical Nanoindentation.

Harry Dwight Rowland¹, William P. King¹, Amy C. Sun² and P. Randy Schunk²; ¹Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Multiphase Transport Processes, Sandia National Laboratories, Albuquerque, New Mexico.

Critical to transition of embossing-based nanomanufacturing from laboratory to commercial use is the ability to predict polymer flow during embossing. In practice, nanoimprint (NIL) embossing can result in incomplete filling or nonuniform residual layers due to lack of tools for predicting polymer flow. Predicting atomic force microscope (AFM) thermomechanical nanoindentation also requires understanding of polymer relaxation processes in thin films. This paper presents continuum models capturing polymer deformation at length scales less than polymer radius of gyration during AFM nanoindentation and simulations identifying critical geometries, materials properties, and process conditions that govern polymer flow during NIL embossing, thus allowing NIL design rules to be formulated. Finite-element simulations of polymer flow during NIL examine rectangular cavities embossing a Newtonian fluid under viscous-dominant conditions. Simulations vary mold geometry parameters of indenter width S , cavity width W , and cavity height h_c as well as initial polymer film thickness h_i for single cavities and non-uniform asymmetric cavities. Polymer deformation mode and cavity filling time can be predicted based on ratios of cavity height and width, indenter width, and polymer film thickness. Single peak deformation depends solely on W/h_i and always occurs when $W/h_i < 1$. Single peak, dual peak shear, and dual peak squeeze flow follow different fill time dependencies predicted by viscous flow theory of laminar flow between plates, Stokes flow, and squeeze flow. Squeeze flow occurs when $S/h_r > 1$, where h_r is the residual film thickness. By determining the proper flow mode based on mold geometry and polymer film thickness ratios, a characteristic NIL velocity V_{NIL} can be identified, allowing establishment of NIL embossing design rules based on NIL Capillary number Ca_{NIL} , directional flow ratio W/h_i , and polymer supply ratio S/h_r . Finite-element simulations of polymer flow during AFM nanoindentation examine a heated probe tip of radius 20 nm indenting a thin film of high molecular weight polymer. A Williams-Landau-Ferry-Carreau polymer viscosity model with bounds based on reptation and Rouse dynamics matches experimental measurements. High shear rates during nanoindentation thin the polymer and increase indent speed. Simulations vary polymer-tip and polymer-substrate slip, polymer-tip interface temperature, and thin film glass transition temperature to determine non-bulk material properties affecting tip velocity and polymer deformation profile. This paper simulates polymer deformation during nanoimprint embossing and AFM thermomechanical nanoindentation to develop design rules for embossing-based nanomanufacturing. This work reports the importance of shear-thinning effects in AFM nanoindentation and establishes design rules resolving phenomena reported in all previously published investigations of NIL embossing polymer flow.

SESSION M2: Patterning of Biomolecules
Chairs: Ashutosh Chilkoti and Lars Montelius
Monday Afternoon, November 28, 2005
Room 306 (Hynes)

1:30 PM *M2.1

Building with Macromolecules on Surfaces with Nanometer Precision. Ashutosh Chilkoti, Duke University, Durham, North Carolina.

I will present recent examples of work from my laboratory on the situ fabrication of nanoscale macromolecular structures of soft hydrated synthetic polymer brushes, stimulus responsive polypeptides and polynucleotides, with the goal of developing and ensemble of easy to use tools for bionanofabrication. In the first example, I will describe the fabrication of stimulus-responsive nanoscale arrays of a genetically engineered polypeptide by DPN that enables a few hundred-protein molecules to be captured from solution, displayed in a functionally active conformation at the surface, and then reversibly desorbed from the surface. In the second example, the in situ synthesis of nanometer thick brushes of an oligoethyleneglycol-functionalized polymer by surface-initiated polymerization will be described, and the extension of this methodology to the microscale by soft lithography and to the nanoscale by DPN. These nanometer thick polymer brushes show extraordinary resistance to protein adsorption and the adhesion of cells and provide a powerful platform to examine the interaction of cells with biochemical and topographical cues at length scales ranging from the nano-microscale. In more recent work, I will summarize recent results of nanoscale enzymatic manipulation of DNA, in which we have harnessed the catalytic power of enzymes at the surface at nanoscale dimensions. I will show how terminal deoxynucleotidyl transferase, which repetitively adds mononucleotides to the 3' end of a short DNA initiator, can be used to rapidly fabricate DNA nanostructures up to 120 nm high with lateral dimensions from 0.1 to 4 microns. These DNA nanostructures can direct the step-wise formation of composite molecular ensembles consisting of natural or unnatural nucleotides and serve as a structural component for more complicated two- or three-dimensional nanostructures by selectively docking other molecules along the z-direction with nanometer-level precision.

2:00 PM *M2.2

Patterning of Single DNA Molecules on Polymer Surface for Medical and Electronic Applications.

Jingjiao Guan¹ and L. James Lee^{1,2}; ¹Center for Affordable Nanoengineering of Polymer Biomedical Devices, The Ohio State University, Columbus, Ohio; ²Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio.

Patterning single DNA molecules is of great interest for genetic analysis and nanoelectronics. A number of methods have been developed to pattern single DNA molecules, but none of them is able to create well-defined array of stretched, oriented, and precisely positioned DNA molecules. We have developed methods to create such an array of single or multiple DNA molecules using topologically micropatterned polymer surface, from which the patterned DNA can be transferred onto other substrates to generate more complicated patterns. This technique has promise for producing DNA chips based on single DNA molecules, DNA-templated nanowire array, and multifunctional nanoparticles for gene delivery.

3:30 PM *M2.3

Light-Directed Synthesis of DNA Molecules.

Franco Cerrina, Electrical & Computer Engineering, University of Wisconsin, Madison, Wisconsin.

The direct synthesis of DNA constructs in the length of 2000-20,000 base pairs (bp) is at the root of a revolution in genetic engineering. As more and more genomes are decoded, and the function of the genes understood, there is the possibility of actually reprogramming some of the genetic material to achieve specific functions, from medicine to synthetic biology. The well-known base-by-base synthesis of DNA can be greatly enhanced by combinatorial techniques, whereby a large number of single-stranded sub-units (oligomers) are synthesized in parallel and later assembled in longer constructs. Using light-directed synthesis of the oligomers, hundred of thousands of different short sequences (40-70b) can be created in a few hours. After amplification, these sequences can be assembled in longer units in a hierarchical, multiple stages process. The final product – a synthetic gene – can then be used in a multiplicity of biological applications. We will review the state of the art of the base-by-base DNA synthesis, with particular emphasis on chip-based methods, and discuss the problem of the errors found in the sequence of synthetic DNA. Many applications require error-free DNA, and this can be guaranteed only by a sequencing operation of the final product. Typically, samples extracted from the final product are amplified and sequenced, to find the correct one – an expensive and time consuming process. The number of clones to be sequenced is a strong function of the error rate in the DNA synthesis, so that a rate of less than 1 error per 10,000 bp is necessary to produce a viable process for the synthesis of 2,000 bp genes. We have recently proposed several error-removal methods that can improve the purity of synthesized materials, and produce error-free output material. To achieve this goal it is necessary to combine optimized micro-fabrication techniques in the synthesis and purification of the oligomers, with biological and statistical methods for error removal. In the presentation we will focus on light-directed

synthesis, and error-removal solutions.

4:00 PM M2.4

Fabrication of Patterned Apatite by Electrophoretic Deposition. Seiji Yamaguchi, Takeshi Yabutsuka, Mitsuhiro Hibino and Takeshi Yao; Graduate School of Energy Science, Kyoto University, Kyoto City, Japan.

Formation of apatite pattern is considered to lead to development of various smart biomaterials. Advanced multifunctional biomaterials will be produced by a combination of bioaffinity of apatite with mechanical, electric, magnetic or optical properties of other materials. For example, a cellular biosensing system will be developed by a culture of cells on the apatite pattern. Also, biosensing devices can be developed by using adsorbability of apatite to biomolecules such as proteins. Usually, electrophoretic deposition (EPD) is applied only to electric conductive materials such as metals. Recently, we have found that when a porous insulating material is arranged between electrodes, particles can be migrated by force of electric field passing through the pores. Then we have considered that when a patterned mask that blocks electric field to pass through is set between electrodes, particles will be deposited regularly following the mask pattern. In this study, as the mask, a polytetrafluoroethylene (PTFE) board with holes of 100 μm in diameter or a layer of resist pattern with various minute patterns such as lines, dots and corners was used. A porous PTFE plate, 0.1 μm for average pore size, 68 % porosity, 25 mm in diameter and 0.07 mm in thickness was used as a substrate. Wollastonite is known for its high bioactivity and is often used as bioactive material for the purpose of forming apatite. Wollastonite particles about 3 μm in average diameter were deposited on the substrate following the mask pattern by EPD. It was observed that wollastonite particles were deposited transcribing the mask pattern just after the EPD operation. In the EPD operation, the electric field passed thorough the area that was not blocked by the mask, and consequently the wollastonite particles were deposited on the substrate so as to transcribe the mask pattern. Next, the substrate was soaked in a simulated body fluid (SBF) with inorganic ion concentrations (Na+ 142.0, K+ 7.5, Ca2+ 2.5, Mg2+ 1.5, HCO3- 4.2, Cl- 148.0, HPO42- 1.0, SO42- 0.5 mmol dm-3 pH=7.40) nearly equal to those of human blood plasma at 36.5 °C for 24 h. After soaking in SBF, apatite was induced on the wollastonite particles and replaced them, then apatite pattern was obtained. Generation of apatite was confirmed by XRD analysis. The distinct boundary between apatite-existing area and apatite-nonexistent area was verified by SEM/EDX observations. Apatite dot pattern about 250 μm in diameter was obtained when we used the PTFE board as the mask in the EPD operation, and, apatite line pattern about 100 μm was achieved for the minimum width when we employed the layer of resist pattern as the mask. This method is promising for production of multifunctional materials having bioaffinity.

4:15 PM M2.5

Biphase Ceramic Lattices for Bone Repair. Hongyi Yang¹,

Julian R. G. Evans¹, Shoufeng Yang¹, Xiaopeng Chi¹, Ian Thompson², Richard James Cook² and Paul Robinson²; ¹Materials Department, Queen Mary University of London, London, United Kingdom; ²GKT Dental Institute, Kings College, London, United Kingdom.

Porous biphase HA/TCP scaffolds providing osteoconduction and osteoinduction for bone repair were prepared by extrusion freeforming, a rapid prototyping method that allows both shape and a hierarchy of structure levels to be tailored by computer. Biphase ceramic pastes with a volatile solvent and binder were extruded through fine nozzles and solidified by evaporation such that filaments weld to the last layer of the lattice. In this way, multilayer 3D quasi-crystals were made and characterised such that the lattice spacing can be varied to provide large and small channels for vasculature and hard tissue development respectively, and the overall shape controlled. The organic content was removed before sintering. Characteristics of the sintered biphase ceramic scaffolds were studied.

SESSION M3: Poster Session: Nanopatterning and Nanomaterials

Monday Evening, November 28, 2005
8:00 PM

Exhibition Hall D (Hynes)

M3.1

A Novel Approach of Developing Hybrid Biomaterials: Two Photon Induced Polymerization of ORMOCERs for Drug Delivery, Tissue Engineering and Beyond. Anand Doraiswamy¹, R. J. Narayan¹, B. Chichkov², A. Ovsianikov², R. Houbertz³, R. Modi⁴ and D. B. Christey⁴; ¹Bioengineering Program, School of

Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Laser Zentrum Hannover, Hannover, Germany; ³Fraunhofer Institute for Silicate Research, Wurzberg, Germany; ⁴US Naval Research Laboratory, Washington, District of Columbia.

We introduce a novel approach of two-photon-induced polymerization or 2PP of hybrid materials for a wide range of biomedical applications. Organically modified ceramics or ORMOCERs are hybrid materials that have proportions of organic and inorganic units that can be modified to tailor the mechanical, optical, chemical and biological properties. Using this approach we have developed arrays of microneedles (a hybrid of hypodermic needles and transdermal patches) for painless and controlled drug-delivery. We have developed a variety of geometry of the microneedles for fracture and toughness studies. In this paper, we have also studied the biocompatibility of these materials using various cell-lines such as rat neuroblasts, mouse myoblasts, human osteoblasts. In a further step, we have developed Lego-like free-standing structures to mimic 3-dimensional multilayered scaffold structures. Each layer was developed with a different cell-line to develop a multicomponent bioactive system. We have demonstrated the potential of the 2PP process in developing high resolution, periodic, self-standing, biocompatible structures for a wide range of biomedical applications.

M3.2

DNA Directed Assembly of Colloidal Particles on Patterned Substrates for Sensors and Photonics. Paul V. Braun¹, Margaret H. S. Shyr¹, Daryl P. Wernet², Pierre Wiltzius^{1,3} and Yi Lu²; ¹Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; ³Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We have demonstrated the directed assembly of DNA functionalized colloidal particles onto substrates patterned with periodic structures through microcontact printing with complementary single-stranded DNA. The tethering of the colloidal particles to the surface is followed using laser diffraction, laser scanning confocal microscopy, and fluorescence optical microscopy. Through the use of a combinatorial in-vitro selection we have obtained DNzyme (DNA molecules that catalytic activities) that bind specific metal ions and catalyze the cleavage of DNA strands containing an RNA base. This DNA-based sensor motif is attached to either the colloidal particles or the substrate. In the presence of specific metal ions, the colloidal particles hybridize to or release from the substrate, and this process is followed through laser diffraction. The binding of the colloidal particles to the substrate can also be reversed by heating, melting the hybridized DNA strands.

M3.3

Patterning of Biomolecules/Materials Using PECVD Generated Surfaces. Joseph M. Slocik, Eric R. Beckel, Timothy J. Bunning, Hao Jiang and Rajesh R. Naik; Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB.

Currently, surface patterning of biomolecules/biomaterials involves techniques such as dip pen nanolithography, micromolding, and inkjet printing. These techniques are directed towards controlled deposition of materials, but are limited to the number and types of biomolecules that can be processed. Alternatively, plasma enhanced chemical vapor deposition (PECVD) provides an excellent generalized platform with a wealth of different substrate surface chemistries that can be utilized for the incorporation of a variety of biomolecules and other functional materials. These can include proteins, viruses, enzymes, peptides, and water soluble nanoparticles. Of interest are functionalized quantum dots, peptide encapsulated gold nanoparticles, and small biomimetic peptides. Herein, we utilized common coupling techniques for the patterning of quantum dots, gold nanoparticles, and peptides on PECVD generated surfaces; and as a result, create a biologically active surface for the biomimetic mineralization of inorganic materials.

M3.4

Stability of Some Non-Precious Dental Alloys in Artificial Saliva. Julia Claudia Mirza Rosca¹, Juan Rodriguez Castro¹, Daniel Mareci² and Delia Aelenei²; ¹Mechanical Engineering, Las Palmas de Gran Canaria University, Las Palmas de GC, Spain; ²Technical University Gh. Asachi, Iasi, Romania.

In recent years a number of new highly corrosion resistant alloys combining Nickel, Cobalt, Chromium and Molybdenum have been introduced as biomaterials. The aim of this study is to investigate the corrosion behaviour of two Nickel based alloys (Wiron NT and Wiroloy) and two Cobalt alloys (Vitallium and VeraPDI) in Carter-Brugirard AFNOR/NF (French Association of Normalization) artificial saliva [1]. The microstructures of the alloys were investigated by optical microscopy before immersion in artificial saliva. The

microhardness of all the alloys was also measured. Using the linear and cyclic polarization curves [2] and electrochemical impedance spectroscopy technique [3], the corrosion parameters were established. The corrosion potential, the Tafel slopes, the polarization resistance and the corrosion current density are measured from the linear potentiodynamic polarization curves. The transpassivation potential, the breakdown potential and the repassivation potential are obtained from the cyclic potentiodynamic polarization curves. The electrochemical impedance spectroscopy Bode-phase plots show two maxima and the equivalent circuit is consistent with the model of a two-layer structure for the passive film. The metallic surface after immersion was analysed with SEM. All the results obtained, regardless of the alloy type or the technique (microscopy, electrochemical, mechanical) show that the alloys exhibit a good corrosion resistance in artificial saliva. In extreme conditions (high potential) pitting corrosion appears to be specific for Wirrolloy while the other alloys show a generalised corrosion. References: [1] Grosgeat B., Reclaru L., Lissac M., Dalard F., *Biomaterials* 20, 993 (1999) [2] Kelly R.G., Schully J.R., Shoosmith D.W., *Electrochemical Techniques in Corrosion Science and Engineering*, Marcel Dekker Inc., (2003) [3] Rondelli G., Torricelli P., Fini M., Giardino R., *Biomaterials* 26, 739 (2004)

M3.5

Effects of Fluorides and Surface Treatment on Titanium and Titanium Alloys in Dentistry. Julia Claudia Mirza Rosca¹, Domingo Herrera Santana¹ and Heinz Sturm²; ¹Mechanical Engineering, Las Palmas de Gran Canaria University, Las Palmas de GC, Spain; ²Federal Institute of Materials Research, BAM VI 2901, Berlin, Germany.

Since hygiene products like toothpastes and prophylactic gels contain fluoride ions, in the dental environment the most aggressive ions for the protective oxide layer of titanium and titanium alloys are the fluoride ions. The aim of this paper was to investigate the effects of fluorides on the passive films of titanium and titanium alloys. In order to exhibit bioactivity, the titanium alloys must be previously subjected to a special surface treatment, involving changes in the passive film properties. In this paper, titanium and two titanium alloys were studied, Ti-5Al-4V and Ti-6Al-4Fe, with the composition presented in the Table 1. The alloys were soaked in 10M aqueous NaOH solution at 60°C for 24 hours and then were immersed for 3 months in Carter-Brugirard (French Association of Normalization) artificial saliva with addition of NaF 0.02 M. For comparison, samples with the same composition but without chemical treatment were immersed also in order to differentiate the treatment effects. Data about mechanical and electrochemical behaviour are presented. ESEM observations of the passive layer and EDX measurements were performed. EDX maps of elemental distribution were used to determine the oxide layer composition, the alloy morphology and to identify the contamination particles. The mechanical behaviour was determined using optical metallography, Vickers microhardness and tensile tests. The electrochemical behaviour of these films was determined in artificial saliva with fluoride additions, using the electrochemical impedance spectroscopy technique. It resulted that the tested oxide films presented passivation tendency and a very good stability, and no form of local corrosion was detected. The electrochemical behaviour of these films is described by an equivalent circuit with three time constants. The mechanical and EDX data confirm the presence of an outer porous passive layer with a high oxygen content and an inner compact and protective passive layer where Ti is the dominant element. EIS confirms the mechanical results. The results emphasised that the use of the surface treatment increase the passive layer resistance in the presence of fluoride ions. One of the main drawbacks of this treatment is that the samples were susceptible to contamination by bacteria taking into account that the artificial saliva is an ideal medium for bacterial growth if aseptic conditions are not ensured.

M3.6

Controlling the size, orientation, density and nucleation of calcium oxalate monohydrate crystals using self-assembled monolayers. Tania M. Cabrera, Leigh M. Friguglietti and Richard W. Gurney; Department of Chemistry, Simmons College, Boston, Massachusetts.

Calcium oxalate monohydrate (COM) is the main inorganic component of kidney stones. To understand which organic functional groups can promote COM nuclei formation, and how impurities interact with the different faces of the crystals, is to better understand kidney stone formation. Studies of the effect of impurities on the crystal growth of COM would be greatly facilitated if nuclei seed crystals of COM were templated on surfaces, whereby, the size, orientation, and density of the COM seed were controlled by the functionality of the templating surface. The nucleation effect of the organic functional group can also be determined directly by studying different templating agents. We adopted a route to crystal formation

using micropatterned, self-assembled monolayers (SAM) of alkanethiols on gold. The gold substrate was patterned with terminally functionalized alkanethiols having areas of different nucleating activity towards COM through microcontact printing. Micron-sized squares of carboxylic acid-terminated and hydroxyl-terminated alkanethiols were surrounded by a hydrophobic methyl terminated background. These patterns were tested for their ability to control COM nucleation and orientation on the polar-regions of the pattern and the results were documented using, differential interference contrast and scanning electron microscopies. We propose that this method can be extended to template crystal growth of COM from aqueous solutions, to further aid in the study of impurity interactions with growing calcium oxalate solutions and can also allow direct visualization of the different surfaces of a crystal positioned a priori without having to physically manipulate the microscopic crystal. Furthermore, research has shown that certain amino acids have a significant effect on the nucleation and growth of COM. To directly monitor the nucleating effects of amino acids on COM, we patterned key amino acids onto our crystal templating surfaces. Amino acids were immobilized on the surface through amide linkages to carboxyl terminated micropatterns, while the remaining regions in the pattern were functionalized with hydrophobic methyl terminated SAMs. These patterns are currently being tested for their ability to control COM nucleation and orientation on the polar-regions of the pattern. If the method proves successful one could imagine tailoring the amino acid composition of a surface to mimic protein surfaces determined to play an active role in kidney stone formation. We hypothesize that amino-acid, micropatterned SAM may play a role in elucidating COM crystallization phenomena on protein surfaces and these studies will have ramifications for potential application in the design of synthetic peptides for use in stone therapy.

M3.7

Method for the investigation of the relaxation time and viscosity of embossable films. Maud Foresti¹, Elin Sondergard¹, Etienne Barthel¹, Caroline Heitz¹ and Lena Saint Marcar¹; ¹Laboratoire du Surface du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain, Aubervilliers, France; ²Capteurs, Mesures, Controles, Saint-Gobain Recherche, Aubervilliers, France.

Viscosity and relaxation time are crucial physical parameters for development of resists for nanoimprinting. These parameters will control not only the embossing time but also the stability of the obtained profile after embossing. When the resist is a thermoplastic it is possible to characterise the bulk material and to some extent extrapolate the properties to a thin film. Such assumptions are clearly wrong when the resists are thin layers of more complex nature, like embossable sol-gels or reticulating polymers. In these systems the mechanical properties will be highly dependent on factors like the evaporation of the solvents and the amount of condensation or reticulation of the material. The bulk material and the thin film can therefore be of very different chemical nature and any valid mechanical characterisation has to be done directly on the embossable thin film system. Unfortunately there is currently no simple characterisation method allowing for quantitative mechanical measurements on fairly fluid thin films. We present an original optical characterisation method, based on diffraction from an embossed structure, which allows us to follow the evolution of the mechanical properties of a thin film. The variation of the intensity of the diffraction peaks is related to the relaxation of the profile of the pattern. Real time measurements of the relaxation profile of UV embossable thin films will be presented.

M3.8

Directed Assembly of Nanomaterials on Topographically Patterned Substrates Using Inbuilt Fringing Fields. Chad R. Barry and Heiko O. Jacobs; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

We report on a new printing approach to deposit nanomaterials onto desired areas on nanostructured thin films. The nanostructured thin films act as templates to direct the assembly process. The approach makes use of local electrostatic fringing fields to direct the assembly of charged nanomaterials from the gas phase. The fringing fields occur as a result of the different charging characteristics and work functions of the materials involved. In the first demonstration we use a topographically patterned PMMA thin film on top of a silicon substrate to create localized fringing fields with 30 nm lateral confinement. The results show that inbuilt potentials between different materials are sufficiently large to direct the deposition of nanomaterials. A gas phase assembly process has been used to deposit silicon and metallic nanoparticles into the topographically patterned areas. The strength and lateral dimensions of the inbuilt potential has been characterized using scanning probe based methods. The fringing fields were confined to 30 nm sized areas and exceeded 1 MV/m

M3.9

Dynamic all-optical tuning of transverse resonant cavity modes in photonic bandgap fibers and applications for tunable dispersion compensation. Gilles Benoit^{1,2}, Ken Kuriki^{1,2}, Jean-Francois Viens^{1,2}, John D. Joannopoulos³ and Yoel Fink^{1,2}; ¹DMSE, MIT, Cambridge, Massachusetts; ²Research Laboratory of Electronics, MIT, Cambridge, Massachusetts; ³Physics Department, MIT, Cambridge, Massachusetts.

Fibers with multiple radial alternating submicron layers of high index amorphous semiconductors and low index polymers have recently been shown to exhibit optical cavity modes for transverse illumination. We previously demonstrated the precise placement and thickness control of the defect layer leading to optical cavity quality factors of 35. Here we introduce an additional degree of freedom associated with our system namely the ability to independently control the composition of the optical defect layer. Specifically, we report on the fabrication of all optical tunable fibers with an optical cavity layer consisting of a highly photorefractive chalcogenide glass. We demonstrate a 2 nm optically induced reversible shift of a cavity resonant mode at 1.5 microns with quality factor of 225 under transverse illumination at 514 nm. Dynamic all optical tuning is reported at frequencies up to 400 Hz. Experimental results are compared with simulations based on the amplitude and kinetics of the transient photodarkening effect characterized in situ in thin films by combined transmission and ellipsometry measurements. These results present significant opportunities for device fabrication such as tunable dispersion compensators on very long length scales. We present preliminary group delay dispersion measurements and demonstrate pulse compression at telecommunication wavelengths in a transmission fiber containing a cavity layer induced Gires-Tournois interferometer.

M3.10

Ruthenium(II) Complexes and Polymers: Potential Materials for Applications in Solar Cells. Veronica Marin^{1,2}, Elisabeth Holder^{1,2}, Martijn M. Wienk^{2,3}, Dmitry Kozodaev^{1,2} and Ulrich S. Schubert^{1,2}; ¹Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands; ²Dutch Polymer Institute (DPI), Eindhoven, Netherlands; ³Laboratory of Molecular Materials and Nanosystems, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands.

Silicon-based photovoltaic devices are still the workhorses in the field. Due to the high production costs, alternative solar cells for commercial applications are in focus. Transition-metal complexes with low lying excited states such as e.g. ruthenium(II) are finding increasing use as photosensitizers.[1] Two distinct approaches can be considered when ruthenium(II) polypyridyl complexes are employed: bulk heterojunction solar cells (BHSCs) and dye-sensitized solar cell (DSSC) devices. Ruthenium(II) trispyridyl complexes can successfully act as p-type materials since they display suitable photophysical, photochemical and electrochemical properties.[1] The metal-to-ligand charge-transfer (MLCT) and ligand-centered excited states of these complexes are fairly long lived to contribute to electron transfer processes in the donor-acceptor systems (e.g. with n-type materials such as viologen or fullerene derivatives) in p-n type BHSCs.[2] To ensure straightforward processing of the materials by spincoating or inkjet printing, the metal complexes are covalently linked to a polymer backbone (aggregation is prevented and the physical features of the complexes are maintained).[3] The ruthenium bispyridyl complexes with polymeric tails may be potential candidates for the fabrication of quasi-solid state DSSCs. Although DSSCs shows superior energy conversion compared to the present p-n heterojunction devices, their commercial application is still limited due to drawbacks like degradation of the dye or leakage of the liquid electrolyte. For that reason, solid-state versions of DSSCs are aimed. Current state of the art quasi-solid-state DSSCs based on polymer gel electrolyte reach an efficiency of >6% in full sunlight.[4] Recently, Kim et al. reported successful results on the fabrication of a quasi-solid-state dye-sensitized solar cell based on a hydrogen-bonded poly(ethylene glycol) electrolyte (PEO).[5,6] Motivated by this development our initiative envisages combination of two features in one material: solid electrolyte and solar-to-current conversion, thus the synthesis of bispyridyl ruthenium (II) complexes with polymeric tails and anchoring groups. [1] A. S. Polo, M. K. Itokazu, N. Y. M. Iha, *Coord. Chem. Rev.*, 2004, 248, 1343. [2] D. M. Guldi, M. Maggini, N. Martin, M. Prato, *Carbon*, 2000, 38, 1615. [3] E. Holder, M. A. R. Meier, V. Marin, U. S. Schubert, *J. Polym. Sci. Part A: Polym. Chem.*, 2003, 41, 3954. [4] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Graetzel, *Nature Materials*, 2003, 2, 402. [5] G. Katsaras, T. Stergiopoulos, I. M. Arabatzis, K. G. Papadokostaki, P. Falaras, *J. Photochem. Photobiol. A: Chemistry*, 2002, 149, 191; Y. J. Kim, J. H. Kim, M.-S. Kang, M. J. Lee, J. Won, J. C. Lee, Y. S. Kang, *Adv. Mater.*, 2005, 16, 1753. [6] V. Marin, E. Holder, M. A. R.; Meier, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* 2004, 25, 793.

M3.11

Synthesis and Electrical Behavior of Silver Nanoparticles Stabilized with Binary Capping Molecules. In-Keun Shim, Kwi Jong Lee and Jae Woo Joung; Central R&D Institute, Samsung Electro-Mechanics, Suwon-Si, kyungki-do, South Korea.

Silver nanoparticles have been used frequently as a conductor in printed electronics due to their low sintering temperature and high conductivity. We have tried to find the effect of interaction between the silver nanocrystal and capping molecule on electrical behavior. In this study, we chose schematically two types of capping molecules with different interaction force to silver nanocrystal in spite of same chain length. Monodispersed silver nanocrystals with 9 nm were prepared from thermolysis of binary silver-surfactant complexes without size selection process. The silver nanoparticles stabilized with binary capping molecules were characterized through X-ray diffraction, UV-Visible spectra, Fourier transform infrared, transmission electron micrograph and elemental analysis. Furthermore, sintering and electrical behaviors with the ratio of two different capping molecules having different interaction force with silver nanocrystals were investigated.

M3.12

Photoresist-free Lithographic Deposition of Amorphous Titanium Oxide Films from a Photosensitive Titanium Complex. Xin Zhang and Ross H. Hill; Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada.

Crack-free amorphous titanium oxide films were photochemically deposited on silicon substrates from titanium (IV) 2-ethylhexanoato n-butoxide. Photosensitive titanium (IV) complexes with improved photosensitivity and thermal stability were prepared from titanium (IV) alkoxides by ligand exchange reaction. Synthesis, composition, and thermal stability of the titanium (IV) complexes were investigated by Fourier transform infrared spectroscopy, nuclear magnetic resonance, microanalysis, and thermal gravimetric analysis. Among the prepared photosensitive titanium (IV) complexes, titanium (IV) 2-ethylhexanoato n-butoxide was determined to be the best precursor to photochemically deposit uniform and continuous titanium oxide films. The photochemistry of the precursor films from titanium (IV) 2-ethylhexanoato n-butoxide was studied by Fourier transform infrared, UV-vis and mass spectroscopy. A mechanism is proposed to explain the photochemical decomposition of titanium (IV) 2-ethylhexanoato n-butoxide. Product films that resulted from photolysis of the precursor films were found to be amorphous, as indicated by X-ray diffraction and transmission electron microscopy. The product films consist of titanium oxide with no detectable carbon contamination, as evidenced by Auger electron spectroscopy. Upon annealing at 500 degree Celsius in air, the amorphous titanium oxide films were converted to anatase. Patterned titanium oxide films, with a feature size of 1 micron or less, were obtained by applying direct photolithography or direct electron-beam writing lithography to the precursor films, without use of a photoresist.

M3.13

Gold nanotube membranes with tunable tube diameter and their applications. Woo Lee, Hong Jin Fan, Sung Kyun Lee, Steffen Richter, Sven Matthias, Marin Alexe, Roland Scholz, Margit Zacharias, Dietrich Hesse, Kornelius Nielsch and Ulrich Goesele; Max Planck Institute of Microstructure Physics, Halle, Germany.

One advantage of shadow mask techniques over conventional photoresist-based nanopatterning is a resist-free process. The process has a low risk of cross-contamination or structural failure in nanopatterning, apart from simplicity and speed in the surface nanostructuring process. In this contribution, we present a simple and widely accessible method for fabricating perfectly ordered arrays of Au nanotubes in the form of membranes, which can be used as shadow masks for the fabrication of nanodot arrays with a perfect arrangement on a cm² scale. Our nanofabrication method involves the electrodeposition of metals to replicate a master pattern structure of nanoporous anodic aluminum oxide (AAO) or macroporous silicon membrane. By taking advantage of the unique capability for controlling the pore diameter of AAO templates, we fabricated structurally well-defined metal nanotube membranes with different aperture sizes (80 nm - 300 nm). On the other hand, control over the shape and 2-D arrangement of metal nanotubes could be achieved by using patterned silicon substrates as replication masters. The fabricated nanotube membranes have been successfully used as shadow masks not only in sputter deposition of metals and ferroelectric materials to generate 2-D arrays of nanodots with tunable dot size, but also in reactive ion-beam etching (RIE) to transfer the pattern of the masks to various substrates. In addition, large-scale growth of 2-D perfect hexagonal arrays of ZnO nanorods will also be demonstrated by combining the vapor-liquid-solid (VLS) growth process and the present mask technique to define the location of catalytic Au nanodots. The fabricated metal nanotube membranes

exhibited interesting optical transmission properties depending on the tube diameters. Optical properties of the metal nanotube membranes having sub-wavelength scale apertures will be discussed. Financial support from the German Federal Ministry for Education and Research (BMBF, Project No. 03N8701) is greatly acknowledged.

M3.14

Abstract Withdrawn

M3.15

Abstract Withdrawn

M3.16

Synthesis and Characterization of Nanowire based Anisotropic Conductors. Mahnaz El-Kouedi¹, Emile Charles Sykes², Aja Andreu¹ and Kasra Daneshvar³; ¹Chemistry, UNC-Charlotte, Charlotte, North Carolina; ²Center for Optics and Optical Communications, UNC-Charlotte, Charlotte, North Carolina; ³Electrical and Computer Engineering, UNC-Charlotte, Charlotte, North Carolina.

We investigate the potential of commercially available porous templates to be used for the fabrication of functional anisotropic conductive films. Galvanostatic deposition into porous polycarbonate membranes was utilized to fabricate arrays consisting of 200 nm diameter nanowires. A tape-lift off procedure was used to completely remove any residual metal from both sides of the polymer membrane to form an anisotropic conductive film. The ten micron thick film has roughly three hundred million nanowires per square centimeter, and it shows almost zero electrical resistance perpendicular to the surface while appearing completely open to circuits between any points on the surface. The preparation of the film, and characterization using SEM, AFM and resistance measurements are presented.

M3.17

A Large Scale Synthesis of Silver Nano Particle in Aqueous Phase. Young Ah Song, Taehoon Kim and Sung Il Oh; Manufacturing Engineering Team, Samsung Electro-Mechanics, Suwon, Gyunggi-Do, South Korea.

The most widely used methods of silver nano particles in a aqueous phase are chemical reduction of silver salts by reducing agents such as sodium and potassium borohydrides. However this method usually known as its production of relatively larger size of particles, 20~30 nm above, due to be stabilized by high molecular weight agent (PVP, amphiphilic polymer etc.) and a few solid loading contents that amount only to 10-5 ~ 10-3M. In this study, we successfully synthesized a 10 nm size of silver nano particle in high solid concentration of 10-2M. By stabilizing with a strong capping thiol ligand of mercaptosuccinic acid (MSA), the growth rate of nucleation of silver atoms could be hindered. However, in an aqueous phase, a H₂O molecule could combine with either two carbonyl groups in the MSA molecule through a hydrogen bonding interaction and make connections with either silver particle. To prevent agglomeration and precipitation of silver nano particles, we used another agent to hinder hydrogen bonding and could obtain stable silver nano particle colloid solution.

M3.18

Vibrational Coupling in Conjugated π Systems in Relation to Optimization of Fluorescence Yield through Phonon Confinement. Luke Andrew O'Neill^{1,3}, Hugh James Byrne^{1,3}, Patrick Lynch^{1,2} and Mary McNamara^{1,2}; ¹Focas Research Institute, D.I.T., Dublin, Ireland; ²Chemistry, Focas Research Institute, D.I.T., Dublin, Ireland; ³Physics, Focas Research Institute, D.I.T., Dublin, Ireland.

A series of π conjugated systems were studied by absorption and photoluminescence spectroscopy. As is common for these systems, a linear relationship between the positioning of the absorption and photoluminescence maxima plotted against inverse conjugation length is observed. The relationships are in good agreement with the simple particle in a box method, one of the earliest descriptions of the properties of one-dimensional organic molecules. In addition to the electronic transition energies, it was observed that the Stokes shift also exhibited a well-defined relationship with increasing conjugation length, implying a correlation between the electron-vibrational coupling and chain length. This correlation is further examined using Raman spectroscopy, whereby the integrated Raman scattering is seen to behave superlinearly with chain length. There is a clear indication that the vibrational activity and thus nonradiative decay processes are controllable through molecular structure. The correlations between the Stokes energies and the vibrational structure are also observed in a selection of PPV based polymers and a clear trend of increasing luminescence efficiency with decreasing vibrational activity and Stokes shift is observable. The implications of such structure property relationships in terms of materials design are discussed.

M3.19

Fully Mass Printed Integrated Circuits. Florian Doetz¹, Ingolf Hennig¹, Peter Eckerle¹, Arved C. Huebler^{2,4}, Heiko Kempa², Howard E. Katz⁵, Matthias Bartzsch², Nicole Brandt², Uta Fuegmann², Subramanian Vaidyanathan³, Jimmy Granzstrom³, Sen Liu³, Tino Zillger², Georg Schmidt², Elsa Reichmanis³, Thomas Weber¹, Frauke Richter¹, Thomas Fischer², Ulrich Hahn²; ¹BASF AG, Ludwigshafen, Germany; ²Institute for Print and Media Technology, Chemnitz University of Technology, Chemnitz, Germany; ³Lucent Technologies Bell Labs, Murray Hill, New Jersey; ⁴Printed Systems GmbH, Chemnitz, Germany; ⁵Johns Hopkins University, Baltimore, Maryland.

Additive mass printing of functional electronic materials is considered to provide a powerful path to low-cost manufacturing of integrated transistor circuits. Such a high-speed approach requires successive in-line capable solution deposition of each layer on flexible substrates. Typical strategies reported include printing techniques such as screen and pad printing or ink jet. However, to be useful in mass production the final process must allow high throughput rates and high resolution. Therefore, offset and gravure printing represent attractive deposition techniques since they are commonly used for the production of newspapers and packaging with printing speeds ranging from 2 to 15 m/s. Meeting printing requirements (formulation and rheology of inks, adhesion) and device performance is a key challenge for an efficient production process. We report the first fully mass printed ring oscillator consisting of 7 inverter stages proving the logic capability of each top gate organic field effect transistor (FET). The substrate used was a commercially available, corona treated PET foil, the source and drain electrodes were made of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS), which was re-formulated to make it offset-printable. As the active semiconducting layer we used commercially available poly(9,9-dioctyl-fluorene-co-bithiophene) (F8T2) which was deposited by a carefully adjusted gravure printing process resulting in high quality, structured layers. For the gate dielectric, we chose a double layer structure of a low k (low permittivity) and a high k material (high permittivity). The low k material is a hydrogenated copolymer of butadiene and styrene formulated in long chain alkanes, especially designed to be processable by gravure printing into very thin and smooth, structured layers. As high-k material we used a re-formulation of a commercially available, printable BaTiO₃-suspension, flexo printed on top of the low k layer. Finally, the gate electrodes were made by flexo printing a silver ink. The channel length of the FET was L = 0.1 mm, the channel width W = 30 mm and W = 6 mm for the load and driver transistors, respectively. When a supply voltage V_{DD} of 40 V is applied, the ring oscillator started oscillating, the frequency increasing with VDD up to 3.9 Hz at 80 V. The mobility of a single FET was 4 x 10⁻³ with an on/off ratio of 2300. Further work is focusing on optimization of the process to enable the manufacturing of RFID tags and flexible backplanes for displays.

SESSION M4: Emerging Patterning Techniques

Chair: L. J. Guo

Tuesday Morning, November 29, 2005

Room 306 (Hynes)

8:00 AM *M4.1

Nanoscale Electric Lithography. Yong Chen, Mechanical Eng, UCLA, Los Angeles, California.

In previous research, scanning probe microscopy (SPM) has been used to generate nanoscale patterns by electrochemical reaction between the probe and a resist. Although this technique can reach sub-10 nm resolution, it can not be used for mass production due to its slow speed. A new nanoscale lithographic technique: nanoscale electric lithography (NEL) is demonstrated. In NEL, nanoscale patterns a mask are transferred to a resist layer on a substrate by an electrochemical process in which the resist is configured by the electric field generated between the mask patterns and the substrate. The basic NEL process is simple and straightforward. A layer of resist is spin-coated onto a substrate, and then a mask with conductive metal patterns that are separated by insulating materials is pressed down toward the resist. After the top electrode is brought into contact with the resist, an electric field is applied between the top and bottom electrodes. The resist residing under the mask conductive patterns will be configured due to an electrochemical reaction (e.g. by solvents). After the mask is removed, the resist in the exposed areas can be developed selectively from the substrate by further chemical process. We have demonstrated that the NEL can have a sub-10 nm resolution, high manufacturing rate, and scale-up capability. By using specific dynamic masks, the NEL can also be used to fabricate on-demand patterns.

8:30 AM *M4.2

The Physics and Limits of Femtosecond Laser Micromachining. Alan J. Hunt,¹ Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; ²Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, Michigan.

Damage produced by optical breakdown becomes very precise for pulse durations less than a picosecond; while nanosecond laser ablation results in an uncertainty of 10-20% shot to shot, femtosecond ablation is repeatable to 1% or less. This precision is particularly evident near the critical breakdown threshold intensity, thus enabling the application of optics at critical intensity (OCI) for reproducible laser machining of sub-diffraction limit features on surfaces. We have recently demonstrated precision OCI machining even at the nanoscale by producing surface features on the order of 10 nm on a wide variety of materials. This competes with the resolution of e-beam lithography, but is more straightforward and less material-specific. The production of nanoscale features raises fundamental questions about the mechanism of OCI optical breakdown. Foremost from the viewpoint of practical applications and theory are the ultimate physical limits in respect to size, wavelength, and material. Applying OCI nanomachining we can produce regular features that are more than an order of magnitude smaller than the wavelength of the light that produced them. This indicates that optical breakdown is critically dependent on a material property that exhibits little spatial variability down to the nanoscale. We argue that material damage occurs only after all valence electrons are ionized, thus the valence electron density provides the requisite homogenous material property, and constitutes a material-dependent limit on feature size and reproducibility. Although the physics of optical breakdown plays a central role in establishing the limits of micro or nanomachining, in practice machining is often limited by a less subtle difficulty: the ultimate destination of ablated materials. Ablated materials may be redeposited at or near the site of breakdown, creating unintended structures or debris at the machining site. We have investigated using unusual long-lived bubbles that are produced during machining as a mechanism to extrude fluid entrained debris. During higher-energy microscale machining, bubbles can diminish the accuracy due to unintended damage associated with their violent collapse, but we find a low energy regime exists in which highly damped and surprising long-lived microbubbles gently extrude debris. These results demonstrate the efficacy of OCI nanomachining for creating submicron surface features, and channels in arbitrary 3D patterns in transparent dielectric materials. We have also used the same method to machine solid 3D objects such as cones, spheres, and cantilevers. OCI nanomachining of analytical devices in hard materials enables rapid "art to part" construction of micro and nanofluidic devices, with potential to dramatically accelerate development of micro-TAS applications such as integrated HPLC devices, micro scale sensors, and integrated nanopores for patch-clamp studies of cells.

9:00 AM M4.3

The Direct Nanoscale Deposition of Molecular Electronic Materials with Thermal Dip Pen Nanolithography.

Paul E. Sheehan¹, Minchul Yang¹, Arnaldo R. Laracuenta¹, Brent A. Nelson², William P. King² and Lloyd J. Whitman¹; ¹Chemistry, Naval Research Laboratory, Washington, District of Columbia; ²Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

We have developed a new technique, called thermal Dip Pen Nanolithography (tDPN), where a heated atomic force microscope cantilever controls the deposition of a solid "ink." The heated cantilever becomes a nanoscale "soldering iron" or "glue gun" which has been successfully used to deposit semiconductors, insulators, and metals. tDPN has several demonstrated advantages over conventional DPN. First, control over writing is much greater—deposition may be turned on or off and the deposition rate changed without breaking contact with the surface. Secondly, imaging with a cool tip does not appear to contaminate the surface, thereby allowing in situ confirmation of the deposited pattern. Thirdly, because the ink is solid at room temperature, the deposits can be highly three-dimensional. Finally, tDPN expands the range of useable inks. One material that is easily deposited by tDPN but which is challenging by other means is poly(3-dodecylthiophene), or PDDT. PDDT is a conducting polymer that shows great promise as an active component in organic electronic devices. Using tDPN, well-ordered PDDT nanostructures have been deposited on silicon oxide and gold surfaces with layer-by-layer thickness control. By adjusting the tip heating power and the writing speed, we can vary the polymer thickness from a single monolayer (~2.6 nm) to tens of monolayers with lateral dimensions below 100 nm. Unlike conventional DPN inks, this low vapor pressure polymer may be deposited in UHV, thereby allowing integration with CMOS processing. With the recent demonstration of metallic indium deposition by tDPN, we now have all the requisite elements for the direct deposition of electronic circuitry by DPN.

9:15 AM M4.4

Non-Lithographic Subtractive Micropatterning of Thin Crystal Films and Bulk Micro-Machining via Hydrogel Stamping. Stoyan K. Smoukov, Christopher J. Campbell, Kyle J. M. Bishop and Bartosz Grzybowski; Chemical & Biological Engineering Dept., Northwestern University, Evanston, Illinois.

Anisotropic Solid Microetching (ASOMIC) – a subtractive printing process we have developed – uses hydrogel stamps patterned in bas relief to create patterns and devices of various functional thin metal, metal oxide, and crystalline semiconducting films. The stamps are soaked in a solution of a desired reagent(s) to deliver this reagent(s) onto, and remove products from a solid substrate. ASOMIC is a 1-step alternative to traditional lithographic patterning procedures (involving 5 or more steps); deep bulk etching of glass and metals produces microlens arrays, micromolding, and microfluidics applications. ASOMIC and the more general Wet Stamping (WETS) method overcome many limitations of soft-lithographic techniques, e.g. reagents can penetrate into and modify the bulk of the substrate. Besides etching, control over reaction geometries and fluxes allows doping and reactive patterning on the micrometer and even hundreds of nanometers scales to produce diffraction gratings, optical elements, and microfluidic devices. We have recently extended the process to 1-step etching of curvilinear depth profiles. Several applications in deep etching of materials will be discussed in detail. 1-step etching of functional device prototypes is will also be highlighted.

10:00 AM *M4.5

Rigiflex Lithography: Nano-Patterning and Printing.

Hong H. Lee, Dongchul Suh, Dahl-Young Khang, Hyunsik Yoon, Young Park and Joon Kim; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We introduce rigiflex lithography as opposed to hard and soft lithographies. The lithography is based on a rigiflex mold that is rigid enough for high resolution as with a hard mold for imprinting but is flexible enough to mimic a soft mold for soft lithography that allows for an intimate contact over large area. This rigiflex lithography is demonstrated for the transfer of metal nanostructures and the patterning by capillary force. When the lithography is applied to imprinting, a reduction by orders of magnitude in the pressure needed is realized. Continuous printing is also made possible.

10:30 AM *M4.6

Coulomb-Force Directed Assembly and Transfer of

Nanomaterials. Chad R. Barry¹, Aaron M. Welle¹, Thomas J. Hatch², Uwe Kortshagen², Stephen A. Campbell¹ and Heiko O. Jacobs^{1,2}; ¹Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota; ²Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota.

This talk will review recent results in the use of long-range electrostatic forces to direct the assembly of nanomaterials. Concepts will be presented to adjust and program coulomb forces locally and globally. Local patterns are used to direct self-assembly of nanomaterials onto charged surface areas (receptors) with 40 nm resolution. We report on a gas-phase process that uses a transparent particle assembly module to direct and monitor the assembly of nanoparticles from the gas phase as well as a new electro spraying system to print organic and inorganic materials from polar solutions. First patterns of bio-molecules will be presented. A computer model will be discussed to analyze and the deposition process. Currently, the Coulomb force directed assembly of sub 10 nm sized proteins, 10 - 100 nm sized metal, 40 nm sized silicon nanocubes, and 30 nm - 3000 nm sized carbon nanoparticles has been accomplished. The application to nanoparticle devices and first results on a nanoparticle transistor will be discussed.

11:00 AM M4.7

Direct-Write Assembly of 3-D Micro-Periodic Silicon

Structures. Gregory Gratson¹, Floren Garcia-Santamaria¹, Mingjie Xu¹, Virginie Lousse², Paul V. Braun¹, Shanhui Fan² and Jennifer A. Lewis¹; ¹University of Illinois, Urbana, Illinois; ²Stanford University, Palo Alto, California.

We have developed a novel approach for patterning 3D micro-periodic structures via direct-write assembly (DWA). Central to our approach is the creation of a concentrated polyelectrolyte ink that flows through fine deposition nozzles and then "sets" almost instantaneously to facilitate shape retention of the as-patterned structures. By combining direct-write assembly and chemical vapor deposition, we demonstrate the fabrication of 3D silicon structures with micron-sized features. First, polymer woodpile structures are created by direct writing a polyelectrolyte ink. These structures are then coated using a room temperature silica CVD method followed by silicon CVD at elevated temperatures to produce 3D hollow-woodpile and inverse woodpile

structures. The optical properties of the resulting structures are measured after each processing step to identify the effects of their geometry and material composition, and a comparison to theoretical predictions is made. These 3D silicon structures could find potential application as photonic crystals, low-cost MEMS, or microfluidic networks for heat dissipation or biological applications.

11:15 AM M4.8

Optical-Maskless Lithography for Fast, Flexible Patterning of Complex Geometries at the Nanoscale. Rajesh Menon^{1,2},

Michael Walsh², David Chao¹, Amil Patel¹ and Henry I. Smith^{1,2};
¹MIT, Cambridge, Massachusetts; ²LumArray Inc., Somerville, Massachusetts.

The primary mode of imparting spatial information in the nanoscale is lithography. Although several variants of lithography are used in manufacturing, they almost always share the use of a patterned photomask, whose demagnified image is recorded in a photoresist layer on a substrate. In order to print patterns close to the diffraction limit imposed by the illuminating wavelength and the imaging optics, a large variety of resolution-enhancement techniques and illumination techniques are employed. As a result of these techniques, the geometries of printable patterns are highly constrained, for example to periodic lines (gates in transistors) and "Manhattan" geometries. These constraints ensure that the designs are overly conservative, and experimentation is restrained, since the price of first-time failure can be extremely high. The case we described here is for the semiconductor industry. For all applications outside the realm of conventional CMOS, there is a large variety of fields that require patterning of very complex geometries. Various forms of nanoimprint and soft lithographies have been used for such applications. These techniques involve the use of a pre-patterned template. Here, we present a form of optical-maskless lithography that can achieve the highest resolution for patterns of all geometries, and may also be used to pattern templates for other lithographies. In Zone-Plate-Array Lithography (ZPAL), an array of high-numerical-aperture zone plates is used to create an array of tightly focused spots on the photoresist-coated surface of a substrate. The array of zone plates is illuminated by an array of pixels in a spatial-light modulator (SLM). The substrate is scanned on a high-precision stage, while the pixels in the SLM are modulated to achieve grayscale intensities in the focused spots. Thereby, patterns of arbitrary geometries may be written in a "dot-matrix" fashion. Since a large number of zone plates (over 1000) is used, the overall writing process is massively parallel, and fast. Each spot is formed by the interference of coherent illumination ("focusing") by the zone plate. The final pattern is formed by the incoherent addition of such spots over time. Thus, the spatial resolution is only dependent on the pattern density and not on the pattern geometry itself (as in the case of periodic patterns in partially-coherent imaging). By accurately positioning the spots, and controlling the grayscale intensity in each spot, ZPAL can achieve linewidth control that is a small fraction of the linewidth itself. For example, using 5 bits of grayscale, and a spot-to-spot placement of 75nm, the linewidth control can be 2.4nm. This enables the patterning of curved and non-Manhattan geometries with high pattern fidelity. In this presentation, we will describe the alpha-prototype system at MIT, and the commercialization effort underway at LumArray Inc. We will also illustrate a number of novel devices being fabricated using ZPAL.

11:30 AM M4.9

Novel Methods for the Direct Fabrication and Packaging of MEMS Devices using Sacrificial Polymers. Yueming Hua and Clifford L. Henderson; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

A wide array of MEMS based devices have been designed and fabricated which are capable of accomplishing a variety of mechanical, electrical, and optical tasks. However, one major limitation that is hindering more widespread adoption of MEMS devices is the difficulty in developing low cost and easily integrated packaging technologies. Over the past several years we have developed a variety of thermally sacrificial polymer materials and processing methods that can be used to build MEMS and microfluidic devices and which are compatible with conventional microelectronics fabrication techniques. Recently we have extended these methods by developing new cross-linkable versions of our photodefinable sacrificial polymers that can be used like a conventional photoresist to mold and plate-up MEMS structures. Furthermore, these polymers can continue to be layered on top of the MEMS devices and finally overcoated with a protective organic or inorganic capping layer. When the device build-up and encapsulation is completed, the entire device can be heated to the decomposition temperature of the sacrificial polymer which vaporizes cleanly to produce gaseous byproducts, thus leaving behind a fully released and encapsulated MEMS device. This paper will present an update on our materials and methods developed for such applications.

SESSION M5: Printed OLEDs, Displays
Chair: Ghassan Jabbour
Tuesday Afternoon, November 29, 2005
Room 306 (Hynes)

1:30 PM *M5.1

Inkjet Printed Backplanes for Displays: Polymer Based Self-Encapsulated TFTs. Ana Claudia Arias, Fred Endicott and Robert Street; Palo Alto Research Center, Palo Alto, California.

Polymeric materials have created interest in the application of document printing technologies to the fabrication of transistor arrays. These materials are easily processed from solution providing the potential of a vacuum free fabrication process. We use inkjet printing as the only patterning technique on the fabrication of display backplanes and we integrate conventional conducting and dielectric materials processed at low temperatures with a polymeric semiconductor. The encapsulation of polymeric electronic devices is very challenging since most of materials available and used for encapsulation require process steps that involve high temperatures or solvents that may damage the polymeric semiconductor. Here we study the environmental stability of two polythiophene derivatives, P3HT and PQT-12, used to fabricate thin film transistors (TFTs). The polymer films were self encapsulated by depositing the semiconductor blended with an insulating polymer from solution. The morphology of the phase separated film was controlled so that the insulator material segregates to the top surface encapsulating the underlying semiconductor. Bottom gate TFT were fabricated with blends of semiconducting and insulating polymers at different concentrations and mobilities as high as 0.05 cm²/Vs were obtained. TFT devices were fabricated in air and showed stable sub-threshold voltages up to 21 days in air. This self-encapsulating process is compatible with inkjet printing and allowed the fabrication of 128x128 pixels (more than 16000 TFTs) array for display backplanes. The self-encapsulating process also improves the integration of printed TFT backplanes with display media. We show that pixel design benefits from the registration accuracy of jet-printing and that the electrical performance is suitable for addressing capacitive media displays.

2:00 PM M5.2

Laser-Assisted Patterning of Conjugated Polymer Light Emitting Diodes. David George Lidzey¹, Alastair Buckley², Monika

Voigt³, Carsten Giebeler², Karl Boehlen⁴, Jeff Wright², Phil Rumsby⁴ and Jim Fieret⁴; ¹Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom; ²MicroEmissive Displays Ltd., Edinburgh, United Kingdom; ³Department of Physics, Imperial College of Science, Technology and Medicine, London, United Kingdom; ⁴Exitech Ltd., Oxford, United Kingdom.

We have developed a patterning procedure based on laser-ablation in combination with the use of water-soluble sacrificial-resists that we use to pixelate different light emitting polymers (LEPs) on a surface, creating a simple array of light-emitting diodes (LEDs). In our technique, LEP films are selectively removed from a surface using pulses from a 248 nm excimer laser to form a set of LED pixels. The surface is then coated by a resist polymer that is soluble in a range of solvents that are orthogonal to those used to process the LEPs. The structure is re-ablated to define the eventual location of the next set of pixels and a second LEP is coated onto the surface. This second LEP can be deposited without removing pixels patterned in previous step as they are 'protected' by the resist overcoat. The structure is washed in water which removes the resist and unwanted LEPs, resulting in the creation of a second set of LEP pixels. This conceptually simple technique permits a sequence of different LEPs to be patterned at high resolution. Importantly, we present control experiments that demonstrate that there are no adverse effects arising from the combination of conjugated polymers with sacrificial resists. Furthermore, we show that the laser can be used to selectively remove a conjugated polymer from a PEDOT:PSS surface without causing any appreciable damaging to its electronic functionality. Our process has been designed such that the functional LEPs that we deposit are never directly exposed to the laser-radiation that is used to define their location. As we demonstrate, this largely eliminates any possible photo-induced oxidation. The strength of our patterning process is that it is not material specific and we are thus able to pattern pure, state-of-the-art materials. Our patterning process is capable of high spatial resolution, with structures having a characteristic length-scale of 10 micrometers achieved. We use our process to pattern red, green and blue emitting LED pixels side-by-side on a common substrate. We note that laser processing is already recognized as a highly versatile and accurate manufacturing process, which in many cases can be used to can define feature sizes that are only limited by optical-diffraction. Laser-machining can also be used to pattern moving substrates, permitting large-areas to be exposed at speed. Our process could therefore be scaled-up into a high-volume manufacturing environment. It could also be used to pattern polymers that have a chemical,

biochemical or opto-mechanical response, which could allow the direct integration of electronic and functional polymeric materials together to create new types of miniaturized chemical sensors and micro-machines.

2:15 PM M5.3

Organic-Inorganic Nanocomposite Material Synthesis and Properties. YuanQiao Rao, Samuel Chen and Tomohiro Ishikawa; Research Labs, Eastman Kodak Co, Rochester, New York.

This paper focuses on our effort of developing novel oxide-polymer nanocomposite materials. A new approach, in situ nanocomposite, was proposed and realized to overcome the challenge in the make of nanocomposites. In this in situ nanocomposite synthesis, the oxide nanophase is formed in the present of polymer matrix. Several different classes of nanocomposite materials are then made. It is shown that this approach yields novel nanocomposite materials with controlled optical properties such as refractive index, birefringence, chromatic dispersion and birefringence dispersion. The materials can also render functions such as UV absorption, improved mechanical properties such as stiffness, strength and hardness; improved thermal/thermal mechanical properties, such as dimensional stability and improved barrier properties to oxygen and moisture vapor.

3:30 PM *M5.4

Roll-to-Roll Manufacturing Technologies for Flexible Device Applications. Harri Kopola, VTT Electronics, Oulu, Finland.

Roll-to-roll fabrication of electrical, optical and optoelectrical structures and functional elements on the web will be described. Based on the realized components the potential of the roll-to-roll printing techniques for the volume-scale active device fabrication will be demonstrated.

4:00 PM M5.5

Modification of Metal-laminated Plastic Foils for Flexible Displays. Furong Zhu, Li-Wei Tan, Kian Soo Ong and Xiao-Tao Hao; OESC, Institute of Materials Research and Engineering, Singapore, Singapore.

An aluminum-laminated polyethylene terephthalate (Al-PET) is used as the substrate for flexible organic light-emitting devices (OLEDs). The efficient flexible electroluminescent devices have a top-emitting OLED architecture. An acrylic layer is formed on the Al-PET surface to improve the surface morphology and also the adhesion between the substrate and the anode. Poly(styrene sulfonate)-doped poly(3,4-ethylene dioxathiophene) was used as hole transporting layer. The light-emitting polymer used is a phenyl-substituted poly(p-phenylenevinylene). Bilayer anodes of Ag/CF_x and Ag/indium-tin-oxide and a semitransparent top cathode were used for the flexible polymer OLEDs. For a flexible polymer OLED with a 110-nm-thick light-emitting polymer, it exhibited a luminous efficiency of 4.56 cd/A at an operating voltage of 7.5V. The aluminum layer in the flexible substrate serves as a barrier to minimize the permeation of oxygen and moisture to the OLEDs. The robustness of this substrate is also very good. The top-emitting electroluminescent devices on Al-PET foil can be bent to a substantial degree without breaking.

4:15 PM M5.6

Low Frequency Noise Measurement and Analysis in Organic Light Emitting Diode. Lin Ke, Xin Yue Zhao and Soo Jin Chua; OESC, Institute of Materials Research & Engineering, Singapore, Singapore.

Low frequency noise characteristics of organic light-emitting diodes are investigated. Device conductive noise and noise from photodiode current which is related to fluctuation of the luminescence from organic Light Emitting Diodes (OLEDs) are measured. There have been several publications dealing with low frequency noise in both semiconductor materials and devices. However, there are very few studies on low frequency noise of OLEDs. First, two noise components were found in device low frequency conductive noise records: 1/f Gaussian noise from device bulk materials and an excessive frequency related part of noise related to device interfaces or defects and traps. 1/f noise is said to be related to carrier mobility. Degradation, especially photo-oxidation of the electroluminescence polymer is a possible reason to affect carrier mobility. Excessive part of noise is believed to be related to the carrier numbers which the fluctuation could be from the interface deterioration and defects and traps generation and furnish. Second, The luminance-time behaviors of organic light emitting device (OLED) was measured using photodiode and the low frequency noise-time from photodiode current is also measured and investigated. Square impulses noises were observed in time domain. The square impulse is believed to be related to carrier number sudden change in the device. It shows that two dominant mechanisms take turns to govern the photonics noise levels. Degradation process pictures are given out to describe the

corresponding noise change. This photonics noise observation is a direct reflection of polymer intrinsic degradation. Over the past months of experiment on the OLED device noise study, there are some new discoveries and we firmly believe this new discoveries coupled with the new results can greatly contribute the understanding of OLED degradation mechanism. With this submission of our findings on the research, we trust that your esteem materials research society (MRS) will find this information valuable. Thus, at this juncture, we seek to apply for an oral presentation on this research for this fall of 2005.

4:30 PM M5.7

Preparation and Properties of Reinforced Silicone Resin Films: A New Class of High Temperature, Lightweight, Flexible Substrates. Bizhong Zhu, Carl Fairbank, Nicole Anderson, Dimitris E. Katsoulis and Herschel Reese; Advanced Technologies and Ventures Business R&D, Dow Corning Corp, Midland, Michigan.

For a variety of applications including high power density thin film solar cells, a polymeric substrate with temperature capability exceeding that of polyimide is highly desired. No polymer films currently available on the market meet this and other requirements such as optical performance and durability under long term radiation of a relevant wavelength range. Owing to their already oxidized backbone bonds (SiOSi) and a higher bond energy of Si-O than C-C, highly crosslinked silicone polymers offer better thermal and radiation resistance than most other polymers. But their mechanical properties are less than satisfactory and films made from these polymers traditionally are not widely used as high temperature substrates. This paper will discuss several reinforcing approaches to mechanically strengthen free standing films prepared from these polymers without or with minimum compromise on the optical properties of the films. Many reinforced films have been prepared. The mechanical, optical, thermal, thermo-mechanical, electrical, and other physical properties of the films have been investigated. The properties of continuous process made films suitable for roll-to-roll processing have also been studied. These flexible films generally have very high strength and high modulus, although the strain to failure is relatively limited. Depending on the composition the optical transmission in the visible wavelength range can be as high as >90%. Surface properties can be engineered to suite specific applications. The temperature capability of the films, measured by an extended exposure to a certain temperature without observable dimensional change, mechanical cracking, and discoloration, ranges from 300 to 600 °C depending on the choice of resin compositions. Preliminary experiments show that useful devices can be fabricated on them through ultrahigh temperature processes.

SESSION M6: Poster Session: Light Emitting and
Other Photonic Devices
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

M6.1

Fabrication and Characteristics of Organic Light Emitting Diodes and Photo Detectors Using Printable Silver Nanoparticles as an Electrode. Yutaka Ohmori, Hideki Maki, Zenken Kin and Hirotake Kajii; Center for Advanced Science and Innovation, Osaka University, Suita, Osaka, Japan.

Polymer based light emitting diodes (PLED) and organic photo detectors (OPD) have been investigated utilizing silver (Ag) nanoparticles as a cathode by wet process. A printable polymer of poly(3-hexylthiophene) (PAT6) has been employed as an active layer fabricated by spin coating onto an ITO anode. As a cathode, Ag nanoparticles were employed and casted onto an active layer. The formation of the electrode was done heated upto 210 C, since we found that the Ag nanoparticles can be formed by wet processing onto the organic layer with an amorphous carbon nitride (a-C:N) buffer layer. The buffer layer act as a barrier layer to prevent Ag nanoparticles from penetrating into the organic layer. The a-C:N layer was formed by a damage free sputtering system, whose layer thickness was 10 nm. The PAT6 device shows a red light emission at 700 nm in the forward bias condition as a PLED, whereas in the reverse bias, it shows a photo-response by illumination of a red or a blue light as an OPD. The results demonstrate the realization of a PLED and an OPD fabricated by wet process utilizing Ag nanoparticles as an electrode.

M6.2

A High-Resolution Photolithographic Patterning Method for Organic Thin Films and Its Application to the Fabrication of Flexible Polymer Optoelectronic Devices. Jingsong Huang¹, Xuhua Wang¹, Oliver Hofmann², Andrew J. de Mello², John C. de Mello² and Donal D. C. Bradley¹; ¹Physics Department, Imperial College London, London, United Kingdom; ²Department of

Chemistry, Imperial College London, London, United Kingdom.

There is considerable interest in patterning technologies that allow well-defined geometric features to be produced in organic thin film structures at micron resolution, reproducibly and at low cost. These techniques are of particular interest for electronic, optoelectronic and photonic applications based on organic semiconductors, where the ability to create densely packed regular arrays of components is important for many applications, including displays, imaging, communications and sensors. Patterning procedures that are compatible with flexible plastic substrates are especially attractive, since they permit the use of roll-to-roll manufacturing techniques. We have recently patented a new, inexpensive, simple and reproducible lithographic patterning technique for organic thin films. The procedure allows for the creation of intricate in-plane geometric features at near-micron resolution on a range of substrates without causing discernible degradation of the properties of the patterned material. This technique is very well suited to pattern a conducting polymer layer on a flexible plastic substrate to form a device contact replacement for ITO. Here, we report, for illustration, patterning of the well known conducting polymer PEDOT:PSS on a PET substrate. We demonstrate the effectiveness of the approach by fabricating flexible polymer light emitting diodes and photovoltaic devices. The light emitting diodes show very promising properties: peak power efficiency and current efficiency of 13.7 lm/W and 8.8 cd/A, respectively; 2V turn-on voltage and a maximum luminance greater than 7300 cd/m², characteristics that are acceptable for flat panel display applications. The flexible polymer photovoltaic devices show a similarly impressive performance with external quantum efficiencies of 50% that are comparable to conventional devices with ITO anodes. These results confirm that our new patterning method is well suited to the fabrication of high quality polymer optoelectronic devices on flexible substrates.

M6.3

Nanoimprinted Semi-Transparent Metal Anode for OLED Applications. Myung-Gyu Kang, Xing Cheng and L. Jay Guo; EECS, The University of Michigan, Ann Arbor, Michigan.

Organic light emitting devices (OLED) are promising for solid state lighting and display applications. In traditional OLED devices, transparent indium tin oxide (ITO) is the predominant choice for the anode material. However, the discovery of enhanced transmission in relatively thick nanostructured noble metal film[1] has motivated us to explore its potential application as a new type of anode for OLED. Using semi-transparent metal (e.g. Au) structure as anode could provide several advantages over conventional ITO: (1) it can potentially prolong OLED lifetime because for devices using ITO anode indium and oxygen can migrate from ITO to organic semiconductor causing device degradation:[2] (1) Certain metal (e.g. Au) has higher work function which can better facilitate hole injection; (3) it is possible to fabricate top-emitting devices; and (4) one can potentially exploit metal-dielectric-metal microcavity and surface plasmon resonances to modify device spectrum and efficiency. In this work, we present a scheme to fabricate nanoscale perforated gold film by nanoimprint lithography that exhibits semi-transparent property. We also evaluate its potential as OLED anode. The semi-transparent gold structure consists of periodically perforated holes or gratings of various periodicities. The grid pattern for nanoimprinting was either directly written by electron beam lithography or by nanoimprinting twice using a grating mold, followed by reactive ion etching to create Si molds. The nanoscale grating or grid pattern is imprinted into a polymer thin film such as polystyrene, and then transferred into a thin metal film such as Au by metallization and lift-off in acetone. Transmission through such nanostructured metal film can be as high as 80%, while for a non-patterned metal film with the same thickness it is 10% or less. A polymer light-emitting diode is then fabricated using the periodically perforated metal film as the anode. After UV-ozone cleaning of the patterned substrate surface, thin layers of PEDOT:PSS and emissive polymer are spin-coated on the nanostructured metal surface followed by a vacuum baking. Finally, thermal evaporation of Ca/Al cathode bilayer through a shadow-mask completes the device fabrication. The device showed bright light emission upon electrical biasing. The device characteristics are similar to those made with ITO anode. Work on making top emitting OLED devices using such nanostructured semi-transparent metal film is currently underway.

* Currently with Purdue University. [1] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, P. A. Wolff, *Nature* 1998, 391, 667. [2] M. P. de Jong, D. P. L. Simons, M. A. Reijme, L. J. van IJendoorn, A. W. Denier van der Gon, M. J. A. de Voigt, H. H. Brongersma, R. W. Gymer, *Synth. Met.* 2000, 110, 1.

M6.4

Inkjet printing of polymers and nanoparticles.

Daan Wouters^{1,2}, Berend-Jan de Gans^{1,2}, Jolke Perelaer^{1,2} and Ulrich S. Schubert^{1,2}; ¹Macromolecular Chemistry and Nanoscience,

Eindhoven University of Technology, Eindhoven, Netherlands; ²Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

A solvent droplet inkjet printed on top of a polymer layer may leave a hole in this layer by dissolution of the polymer and subsequent redeposition at the contact line. This is a consequence of the coffee-ring effect. The hole size does not depend strongly on the choice of solvent. The hole diameter increases with the number of droplets N printed at a spot as $N^{1/3}$. Matter can be printed inside the holes in a second printing round. This demonstrates the possibility to use inkjet printing of holes for the formation of microarrays. Crystals of monodisperse colloidal particles are considered promising candidates for photonic bandgap materials. For the integration of such materials in a photonic circuit a technique is required that allows deposition of well-defined quantities of dispersion at a well-defined location, such as inkjet printing. It will be shown that inkjet printing of well-dispersed latex particles of several hundreds of nanometers in size is feasible. Depending on the choice of substrate ring-like or dot-like deposits form with a high degree of crystallinity. Printing techniques, such as inkjet printing, are interesting alternatives to conventional photolithography for the production of low-cost electronics. A typical application is inkjet printing of conductive tracks, using inks based on noble metal nanoparticles. A sintering step is needed to render the tracks conductive. The use of nanoparticles reduces the sintering temperature due to the large fraction of surface atoms. We will demonstrate the possibility to print tracks of silver nanoparticles on various types of thermoplastic substrates and sintering these to obtain a finite conductivity.

M6.5

Electrically Conductive Carbon Nanotube Doped Polymer Inks. John A. DeFranks^{1,3}, Brian D. Koberlein¹, Ryne P. Raffaele¹ and William J. Grande^{2,1}; ¹Nanopower Research Labs, Rochester Institute of Technology, Rochester, New York; ²Ohmcraft Inc., Honeyoye Falls, New York; ³Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York.

The deposition of highly conductive traces, typically metal, generally requires vacuum metallization processes that often result in increased substrate temperature. While these methods are suitable for some applications, many polymeric substrates are far too sensitive for such means of conductive trace deposition. In addition, many applications involving polymeric substrates require conductive lines that are able to bend and flex without experiencing microfracture or large spikes in resistivity. To this end, the incorporation of single-walled carbon nanotubes (SWNTs) into a silver microparticle / polyester based ink is being investigated. This is expected to produce a composite with increased tensile and flexural strength and a tunable composite conductivity, and obviates the necessity of vacuum deposition techniques. The dispersion of SWNTs in the composite ink was characterized through both thermal and microscopic analysis, and the electrical conductivity was measured as a function of SWNT % w/w doping in the composite ink. A direct-write, stylus method of deposition was demonstrated using MicroPen[®] technology (Ohmcraft Inc.). The thermal and structural integrity of composite ink lines deposited on polyethylene terephthalate were also analyzed. The controlled deposition of electrically conductive inks using SWNTs offers the opportunity to develop robust conductive traces will aid in the advancement of polymer electronics.

M6.6

Organic-inorganic optical composites for MicropenTM Direct-write. Jingjing Sun, E. Koray Akdogan, Lisa C. Klein and Ahmad Safari; Materials Science and Engr., Rutgers University, Piscataway, New Jersey.

MicropenTM Direct-write is a novel CAD-based 2-D fabrication technique, which is able to deposit patterns on a substrate through the use of a fully automated precision dispensing system. Although this technique has been widely applied to fabricate ceramic or polymeric electronics, its potential for photonic devices has not been fully exploited. The successful use of the MicropenTM relies on developing suitable feedstock materials that possess the right chemistry, rheology, surface tension, and stability. Our work was based on polymethylmethacrylate (PMMA)/SiO₂ composites, perfluorocyclobutyl (PFCB) polymer, and PFCB/SiO₂ composites. Those were developed and studied for their suitability as feedstock to fabricate passive and active optical waveguides. First, the PMMA/SiO₂ was synthesized by the polymerization of TEOS in the presence of PMMA through the sol-gel process. The sols of PMMA:TEOS=80:20(wt.%) were used for its high optical transparency. N,N-dimethyl (DMAc) was the co-solvent instead of the normal solvent (tetrahydrofuran, THF). Because the high boiling point solvents was found a critical factor in MicropenTM deposition to avoid quick drying at the pen tip and to better control the viscosity. The patterns of one and multi-layer lines were successfully

deposited with the height up to 20 μ m and width up to 140 μ m. SEM revealed another interesting phenomenon of the disc shaped SiO₂ particles in matrix, probably due to fast solvent evaporation during deposition. We also studied a commercial PFCB polymer because of its superb optical transparency in the 800~1600nm window in contrast to PMMA. This is because the substitution of fluorine in lieu of hydrogen, thus the vibrational absorption band falling outside of the 800~1600nm window. After writing, the patterns were cured at 200°C for 2h under controlled atmosphere. The variation of line dimension as a function of writing parameters was extensively studied. For instance, both the width and height decreased with increasing writing speed (WS). In regards to PFCB/SiO₂ composites, we have optimized the materials synthesis for MicropenTM by studying the effects of organic-inorganic ratio, and a 80:20 ratio (wt.%) was found the best. Also, toluene was found the best co-solvent to avoid the phase separation between the organic-inorganic moieties. In addition, silica-based nonequilibrium processed nanoparticles containing up to 1 wt.% Er³⁺ were doped into the PFCB and PFCB/SiO₂ for active waveguides. The emissions at 1550nm were observed for both systems. Notably, the SiO₂ induced in the composites was helpful to prevent the agglomeration of nanoparticles compared with that in pure PFCB. We will also present the patterns based on the composites with/without the nanoparticles.

M6.7

Sol-Gel Inks for Direct-Write Assembly of 3-D Micro-periodic Titania Structures. Eric B. Duoss¹, Mariusz Twardowski¹ and Jennifer A. Lewis^{1,2}; ¹Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

3-D micro-periodic titania structures have been patterned by direct-write assembly (DWA) for use as photonic crystals. Central to our approach is the creation of a concentrated sol-gel based ink that flows through a fine deposition nozzle as a continuous filament, and then rapidly solidifies to maintain its shape even as it spans gaps in the underlying layer(s). Face-centered tetragonal woodpile structures have been fabricated and thermally annealed to remove the organic phase. The resulting 3-D structures are comprised of TiO₂ (anatase), and exhibit a corresponding increase in their refractive index from 1.6 to 2.5. Preliminary optical measurements have been performed using a modified FTIR spectrometer on both as-patterned and annealed structures. Current efforts are underway to extend this approach to finer feature sizes (< 1 μ m) and create 3-D photonic bandgap materials at commercially relevant wavelengths.

M6.8

Paste Inks for Electrically and Mechanically Interconnecting Flexible RF Device Components. Saurabh Nanavati¹, Samali Datta¹, Dustin Vaselaar¹, Nathan Schuler¹, Rob Sailer¹, Aaron Reinholz¹, David Wells², Dean Webster³ and Douglas L. Schulz¹; ¹Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota; ²Industrial and Manufacturing Engineering, North Dakota State University, Fargo, North Dakota; ³Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota.

Radio-frequency identification (RFID) is a system that utilizes a single chip computer and an antenna to collect and communicate information. Emerging markets enabled by RFID (e.g., inventory tracking) are providing the need for advanced manufacturing routes to materials including conductors for use as interconnects and antenna. While Ag- and C-based systems are actively being engineered by major industrial entities for low-cost and high-throughput manufacture with acceptable performance at radio frequencies, there are niche opportunities that might be realized by alternative production formats. Towards this end, NDSU has developed a Ag-based zero-VOC paste ink system that remains tack-free and thermoplastic after UV curing. This novel formulation was designed to allow high speed printing (e.g., via a rotary screen printer) of a conductor layer onto a web-based substrate followed by a UV treatment to render the composite tack-free and amenable to being rolled up. The residual thermoplasticity is targeted to allow a secondary component to be electrically and mechanically bonded to the web in a subsequent processing step. In this paper, an overview of the chemical formulation of the paste ink will be presented. Cure times of less than 15 seconds were typically observed when using a UV lamp of intensity 40 mW/cm². Experimental parameters utilized with a Milara semiautomatic screen printer will be correlated to print quality parameters such as percent bleed. Electrical performance of the printed features were assayed by standard DC methods to give sheet resistances of 3.6 ohm/sq for UV-cured film and 1.4 ohm/sq after UV cure and thermal treatment at 100 C in air. Preliminary AC impedance characterization of a microstrip transmission line prepared using an NDSU paste ink gave 0.52 ohm/sq and 0.63 ohm/sq at 900 MHz and 2.45 GHz, respectively, after UV cure with impedance

decreasing slightly to 0.13 ohm/sq and 0.26 ohm/sq after an additional thermal treatment at 100 C in air. Scanning electron microscopy data will be used to illustrate morphological development of the composites. The effects of hot pressing and accelerated lifetime testing upon both electrical performance and microstructural development will be presented. In general, NDSU formulations provide slightly superior electrical performance compared to commercially-available UV-curable paste inks with the added advantage of remnant thermoplasticity.

M6.9

Polymer Blends with Applications in Photonics: Analyzed by Conducting Tip Atomic Force Microscopy. Elisabeth Holder^{1,2}, Dmitry Kozodaev^{1,2}, Martijn M. Wienk^{2,3}, Veronica Marin^{1,2} and Ulrich S. Schubert^{1,2}; ¹Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands; ²Dutch Polymer Institute (DPI), Eindhoven, Netherlands; ³Laboratory of Molecular Materials and Nanosystems, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands.

Functional polymer systems are in the focus for many potential applications in plastic electronics. A very attractive point is the multifunctional active layer fulfilling all necessary requirements in just one layer. In bulk heterojunction solar cells (BHSCs)[1] the active polymer layer combines all functions such as light absorption through the donor, exciplex formation, electron transfer to the acceptor, excitones formation and charge separation, followed by the charge transport through the active layer to the respective counter electrodes of such a donor-acceptor BHSC. Therefore, the complete construction of a polymer BHSC can be simpler than that of small molecule donor-acceptor solar cells. Wet-chemistry fabrication processes (spincoating and printing techniques) are used for applying polymers. They are giving access to cover also larger areas, which becomes important for cost-effective industrial production processes. The donor-acceptor couple in the BHSC described herein consists of a ruthenium(II) complex (donor) covalently linked to a poly(methyl methacrylate (PMMA)[2] backbone and a PC60BM (acceptor).[3] On the other hand, the phase separation and resulting morphology is crucial to obtain working polymer solar cell devices. The charge transport through such a single active layer consisting of a polymer blend will only work if there are no isolated areas. Also the donor and the acceptor need to be connected to respective counter electrodes to obtain the desired solar energy. To obtain information of both the morphology of the films and the electrical behavior of the active layer after illumination conductive tip atomic force microscopy (c-AFM, TiN coated tip) serves as an optimal characterization and analysis tool. With our materials this approach lead to similar results as received with standard solar cell devices monitoring (the electrical response of the full area of the conductive layer). The I/V characteristics were found to be in the same range. However, some deviations were observed and can be ascribed to a slightly different measurement set-up (inert atmosphere, illumination source, etc.). In this presentation c-AFM is applied to characterize the morphology of conductivity blends on a nanoscopic level. This information might be used to complement the information obtained by standard device fabrication and characterization methods. Furthermore, it is less time consuming and cost intensive than usual device preparation methods. Therefore, the described method may find use as a pre-screening tool for novel materials. [1] M.M. Wienk, J.M. Kroon, W.J.H. Verhees, J. Knol, J.C. Hummelen, P.A. van Hal, R.A.J. Janssen, *Angew. Chem. Int. Ed.*, 2003, 42, 3371. [2] E. Holder, M.A.R. Meier, V. Marin, U.S. Schubert, *J. Polym. Sci. Part A: Pol. Chem.*, 2003, 41, 3954. [3] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, *J. Org. Chem.*, 1995, 60, 532.

M6.10

Interfacial Roughness in 1D Photonic Crystals: Quantification and Physical Model of Decreased Optical Response.

Karlene Rosera Maskaly¹, W. Craig Carter¹, Richard D. Averitt² and James L. Maxwell²; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Los Alamos National Laboratory, Los Alamos, New Mexico.

The well-known and technologically useful properties of one-dimensional photonic crystals (1DPCs), in particular the presence of tunable optical band gaps for certain wavelength ranges and polarizations, are based on theoretical crystal models of perfect structures. However, the actual fabrication of 1DPCs will inevitably introduce interfacial roughness and other defects that were not treated in the models. Thus, the aim of this study seeks to answer three questions: (1) how tolerant are the optical properties of 1DPCs to imperfections such as interfacial roughness; (2) what parameters/design conditions can be modified to improve tolerances; and (3) what is the physical reason behind the change in reflectivity of the imperfect structures? The first two questions have been answered by simulating the optical response of several 1DPC configurations with varying degrees of interfacial roughness using a two-dimensional

finite-difference time-domain (FDTD) code. We have found that the normal reflectivity of a roughened photonic crystal at the center of the band gap can decrease by more than 25% in some cases. However, this decreased optical performance can be mitigated by either increasing the number of bilayers in the structure or increasing the index contrast between the two constitutive materials in the 1DPC. The third question above has been addressed by applying the homogenization approximation to the same imperfect structures, which produced results that are equivalent to the FDTD results. This suggests that the primary role of the roughness features is to grade the refractive index profile at each interface in the crystal, rather than diffusely scattering the incident light. Consequently, this also implies that the amount of incoherent reflected power from the roughened structures is small compared to the total amount of reflected power, even for extremely rough structures. This conclusion has been verified by extracting the amount of incoherent reflected power directly from the FDTD results, further strengthening the claims we put forth here.

M6.11

Fabrication of three-dimensional photonic crystals with aperiodic features using multi-beam holography and two photon polymerization. V. Raman¹, A. Brzezinski¹, S. A. Pruzinsky¹, P. V. Braun^{2,1} and P. Wiltzius^{2,1,3}; ¹Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois; ²Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana-Champaign, Urbana, Illinois; ³Department of Physics, University of Illinois, Urbana-Champaign, Urbana, Illinois.

Holographic lithography is an attractive technique for the fabrication of large area, defect-free, three-dimensional photonic crystals. Various FCC based structures were formed in the photoresist SU-8, through concurrent exposure with 4 non-coplanar coherent beams of laser radiation. The dimensions of the fabricated structures closely matched those predicted by full intensity calculations for the beam parameters used. Prisms were employed prior to entry into the photoresist to yield the appropriate beam orientations for definition of FCC crystals. Aperiodic features were written within the crystals by using two-photon polymerization, directly into the undeveloped photoresist, thereby eliminating the need for any infilling step. In addition, the optical properties of the crystal were investigated via spectroscopy.

M6.12

Comparative Analysis of a One Dimensional Metal Dielectric Photonic with a Dielectric Photonic Crystal. Miguel Angel Basurto¹, Jose Javier Sanchez-Mondragon², Daniel May-arriola³, J. Jesus Escobedo-Alatorre¹ and Alvaro Zamudio-Lara¹; ¹CIICAP, Universidad Autonoma del Estado de Morelos, Cuernavaca, Morelos, Mexico; ²Optica, INAOE, Tonantzintla, Puebla, Mexico; ³Optica, CREOL & FPCE, Orlando, Florida.

We discuss a one Dimensional Metal- Dielectric Photonic Crystals created by inserting ultra thin metallic layers between the dielectrics of a regular Photonic Crystal. We discuss the new band structure taking as a reference the underlying Dielectric Photonic Crystal and corresponding Metallic Photonic Crystal. In particular, we characterize the new metallic band gap that arise by the metal presence in two particular cases: keeping the periodicity of the Dielectric PC and by introducing new periodicities. that sep the periodicity of the PC as well as other that introduce new periodicities. We demonstrate that the changes introduced goes well beyond the perturbative corrections introduced by the metallic presence; in particular we discuss the properties of the new ultrathin metallic band gaps, that arise before the predominance of the metallic features. Work supported by CONACyT, Mexico, under grant 45667 and ALFA Project IPECA

M6.13

Bistability, Chirping and Switching in a Lineal-Nonlinear Photonic Crystal. Jose Javier Sanchez-Mondragon¹, J. Jesus Escobedo-Alatorre², Margarita Tecpoyotl-Torres², Romeo Selvas Aguilar³, Ismael Torres-Gomez³ and A. Martinez-Rios³; ¹Optica, INAOE, Tonantzintla, Puebla, Mexico; ²Optica, CIICAP, Cuernavaca, Morelos, Mexico; ³Optica, CIO, Leon, Guanajuato, Mexico.

Bistability, Chirping and Switching have been shown in a Stack, the simplest model of the fully Nonlinear One Dimensional Photonic Crystals. These features have also demonstrated for the fully nonlinear Cylindrical fiber and the microsphere. However, those features do not occur in the fully linear cases, and there is hardly any information in the intermediate case, when only one of the dielectrics is linear or nonlinear. We present a comparative numerical analysis with the corresponding fully nonlinear PC and the linear PC. Work supported by CONACyT, Mexico, under grant 45667 and ALFA Project IPECA.

M6.14

Preparation of PVP-Protected Silver Nanoparticle for

Conductive Patterns. Hyejin Cho¹, Kwi Jong Lee¹, Sung Il Oh² and Jaewoo Joung¹; ¹Central R&D Institute, Samsung Electro-Mechanics Co.,LTD, Suwon, Gyunggi-Do, South Korea; ²Manufacturing Engineering Team, Samsung Electro-Mechanics Co.,LTD, Suwon, Gyunggi-Do, South Korea.

Recently metal nanoparticles have received considerable attention due to their applications to bio, optics and electronics. This study was attended to demonstrate synthesis of silver nanoparticles stabilized with polymer and their applicability to printed electronics. First, the silver nanoparticles were synthesized by reduction of silver nitrate in aqueous solution by N,N-dimethyl formamide in the presence of polyvinyl pyrrolidone (PVP) as a stabilizer and showed average size of 50 nm at molar ratio of PVP to silver below 8. The silver nanoparticles were redispersed in ethylene glycol at 25 wt% and then were printed on various substrates. The printed silver patterns were cured in the temperature range between 100 and 300 °C and showed low specific resistance (< 10 μohm-cm) even at low sintering temperature below 250 °C.

M6.15

Sintering Behavior and Electrical Property of Printed Conductive Line with Silver Nano Particles. Jaewoo Joung, Young Ah Song and Sung Il Oh; Central R&D Center, Samsung Electro-Mechanics, Suwon, Gyunggi, South Korea.

Silver nano particles are being widely used in electronic parts. The conductive line of electronic parts required high electrical conductivity and low sintering temperature. We have developed new suspension solutions consist of two-different-size-distributed silver nano particles. In this study, we synthesized 5 to 20 nm and 70 to 150 nm of particles in aqueous phase, which were stabilized with MSA and PVP relatively. After mixing and dispersing each 2-different sized particle by using another dispersant. We formulated suspension solutions with various contents. We was make fine printed conductive line by a micro dispenser and then was sintered at 200 to 250 C for 30 to 60 minutes in air. We have found that small size particles have unique sintering property by SEM analysis. As a result, we could obtain 3 times higher electrical conductivity of 7.0 x 10⁻⁶ ohm.cm than single size-distributed particles with sintered 200 C.

M6.16

Bioactive Surfaces on Titanium and Some of its Alloys for Orthopaedic Implants. Agustin Santana Lopez¹, Julia Claudia Mirza Rosca¹, Heinz Sturm², Paula Drob³ and Ecaterina Vasilescu³; ¹Mechanical Engineering, Las Palmas de Gran Canaria University, Las Palmas de GC, Spain; ²Federal Institute of Materials Research, BAM VI 2901, Berlin, Germany; ³Institute of Physical Chemistry "I.G.Murgulescu", Bucharest, Romania.

Titanium and its alloys are largely used because of their good biocompatibility, superior mechanical strength and high corrosion resistance. But the artificial materials implanted are, generally, encapsulated by a fibrous tissue isolating them from the surrounding bone. Recently, it was demonstrated that the alkali treatment of the titanium implants produce spontaneously bond to living bone. In this study, following alkali treatment, a dense bone-like apatite layer is formed on titanium and Ti-5Al-4V in simulated body fluid (SBF). Further studies have shown that the release of Al ions from the well known Ti-6Al-4V produces potential neurological disorders. Different alloys were primarily developed in response to concerns of these health problems and one of them is Ti-5Al-4V. Optical, microhardness and electrochemical impedance spectroscopy determinations were made on Ti and Ti-5Al-4V before and after the alkali treatment. The ESEM technique was used to observe the evolution of the surface appearance in the SBF: it results that the first nuclei appeared after 3 days of immersion; once the first nuclei had appeared, the growth of the apatite layer was very rapid. The nature of the deposited layer on the metallic surface is characterised by EDX. The observed Ca/P atomic ratio was 1.65 which is equal to that of bone apatite. This means that bone-like apatite had formed on the surface of both materials.

SESSION M7: Printed OTFTs

Chair: Arokia Nathan

Wednesday Morning, November 30, 2005

Room 306 (Hynes)

8:00 AM *M7.1

Printed Integrated Electronic and Electrochemical Systems on Paper. Magnus Berggren¹, Lars-Olov Hennerdal³, David Nilsson¹, Anurak Sawadtee³, Robert Forchheimer² and Nathaniel Robinson¹; ¹ITN, Linköping University, Norrköping, Sweden; ²ISY, Linköping University, Linköping, Sweden; ³Acree AB, Norrköping, Sweden.

Integrated electronic systems built up from the combination of printed organic insulators, semi-conductors, conductors and electrolytes for electronic labels and intelligent packaging are reported. Printed batteries power these labels, touch buttons and electrochromic displays provide for communication and electrochemical transistor systems offer simple computing. A more in-depth description will be devoted to logic and analogue circuit design for electrochemical transistors and a review of the printing steps needed to achieve these all-integrated circuits on paper labels. The electrochemical transistors utilized function in equivalence to a p-type depletion mode FET-transistor, which then require a non-conventional approach in designing digital circuits. Printing electro-active organic polymers, new opportunities arise from a patterning point of view. We describe a novel subtractive patterning technique for coatings of PEDOT:PSS on paper based on electrochemical over-oxidation. This patterning technique has successfully been implemented in a traditional rotary screen-printing station. In addition, we report results from flexo-printed conducting polymers on paper. Printing speeds beyond 50 m/min have been achieved.

8:30 AM *M7.2

Novel Contacts for Flexible Electronics: Amorphous TCO's and Direct Write Metals and Polymers. David S. Ginley¹, Alex Miedaner¹, Lee Smith², Andrew Leenher², John Perkins¹, Tanya Kaydanova¹, Maikel Van Hest¹, Ruben Collins², Sean Shaheen¹, Matthew Taylor², Dana Olson², Matthew Dabney¹ and Calvin Curtis¹; ¹Process Technology and Advanced Concepts, NREL, Golden, Colorado; ²Colorado School of Mines, Golden, Colorado.

There is an increasing interest in developing flexible and non-planar electronics on a variety of low temperature substrates including plastics, glass and flexible foils. To be able to build circuits on these substrates requires contacts that can be processed at low temperature (<200°C) and ideally in a non-contact fashion. We have been developing new approaches to contacts specifically addressing these needs. These include amorphous transparent conducting oxides (TCOs) based on In-Zn-O that can go down at room temperature with electrical and optical properties similar to InSnO (>3000 ohm⁻¹cm⁻¹) but much smoother and with stability in air to nearly 600°C. We have also investigated ink-based approaches for direct write contacts by inkjet for metals and polymers. In metals we have developed inks for Ag, Cu and Ni that produce on decomposition near vacuum quality metallizations (i.e. for Ag 5 x 10⁵ S/cm) for polymers we have focused on PEDOT/PSS where we have observed conductivities as high as 120 S/cm for ink jet printed films subsequently treated with DMSO or ethylene glycol. The inkjet printable contacts are suitable for a wide variety of applications and can be deposited in a non-contact approach with high materials utilization and no additional patterning. These contacts point the way towards new atmospheric based processing specifically suited to flexible and 3D electronics. This work was supported by the DOE through the NCPV and by DARPA under the OPV program.

9:00 AM M7.3

Room-temperature deposited high-k gate dielectrics for low-voltage flexible electronics. Il-Doo Kim^{1,3}, YongWoo Choi^{1,2}, Akintunde I. Akinwande² and Harry L. Tuller¹; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Microsystems Technology Laboratory (MTL), Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Transistors using organic semiconductors (OTFTs) have received intensive interest for applications requiring low cost, large area coverage, and especially flexibility. Such applications include digital logic devices, electronic paper and books, wearable electronics, and flexible large area display. Recently, gate insulators for OTFTs have received increasing attention because OTFTs switching voltages can be reduced by either using high-K gate dielectrics or ultrathin dielectric layers. Generally, high operating voltage results in high power consumption, a potential critical barrier for portable, battery-powered applications. Thus, some combination of higher permittivity gate dielectric and reduced dielectric thickness is desired to achieve lower voltage operation. However, the use of ultra-thin gate insulators leads to significant manufacturing problems (pinholes, significant leakage current, and low manufacturing yields) due to the surface roughness of polymers which may be of the order of the thickness of the insulators. Therefore, flexible polymer substrates, often characterized by rough surfaces (RMS roughness ~ 3 nm), would benefit from the use of high K dielectrics because high electric fields could be achieved using thicker films (~ 200 nm) without need to increase operating voltage. As new candidates, we developed pyrochlore structured Bi_{1.5}Zn_{1.0}Nb_{1.5}O₇ (BZN) and various acceptor doped (Ba,Sr)TiO₃ thin films deposited at room temperature providing the requisite high dielectric constant coupled with excellent

leakage current characteristics, while remaining compatible with the processing requirements of flexible OTFTs. Here we report the successful fabrication of low voltage (< 5 V) organic transistors using a 200 nm thick gate oxides by an all room temperature process. The introduction of an extremely thin organic and inorganic films between high-K gate oxide dielectric and the pentacene semiconductor markedly shifts the threshold voltage, making it possible to fabricate both enhancement (E) and depletion (D) TFTs. Based on these results, it becomes possible to demonstrate the ability to co-fabricate a number of key OTFT-based circuit elements on flexible substrates.

9:15 AM M7.4

Ultra-Thin Crosslinked Polymeric Gate Insulators for Organic Field-Effect Transistors. Optimization via Polymer and Crosslinker Design. Myung-Han Yoon, Hyuk-Jin Choi, He Yan, Antonio Facchetti and Tobin J. Marks; Chemistry, Northwestern University, Evanston, Illinois.

Organic Field-Effect Transistors (OFETs) based on molecular and polymeric semiconductors need substantial performance and processibility improvement for utilization in commercial devices. Furthermore, OFETs typically operates at very high voltages and exhibit shift of key device parameters upon continuous operation. We report here our latest results on a new crosslinked polymeric gate insulator family exhibiting high capacitance and excellent insulating properties. Furthermore, these dielectrics are compatible with a variety of p- and n-type organic semiconductors allowing fabrication of complementary circuits. The corresponding devices perform at exceptionally low operating voltages (~1 V) with minimal shift of operational parameters. Finally, we will present our latest results on the optimization of these dielectric materials via design/synthesis of new polymeric and crosslinking building blocks. This study provides a new evidence of the fundamental importance of an optimized organic dielectric layer, besides the organic semiconductor, to strengthen OFETs performance and meet the market expectations.

10:00 AM M7.5

Nanotransfer Printing as a Method for Fabricating Organic and Carbon Nanotube Thin-Film Transistors on Flexible Substrates. Daniel Hines^{2,1}, Sergey Mezheny^{2,1}, Michaela Breban^{2,1}, Vinod Sangwan^{2,1}, Ellen Williams^{2,1}, Vince Ballarotto¹, Gokhan Esen² and Michael Fuhrer²; ¹Laboratory for Physical Sciences, University of Maryland, College Park, Maryland; ²Department of Physics, University of Maryland, College Park, Maryland.

Nanotransfer printing has been developed as a method for fabricating high quality organic based devices onto flexible substrates. This is a non-lithographic process for the sequential assembly of device components such that an entire device can be fabricated without exposure to incompatible processes. As a demonstration of nanotransfer printing we have assembled a gold (Au) gate electrode, a poly(methyl methacrylate) (PMMA) dielectric layer, Au source/drain (S/D) electrodes and three semiconductor films from different materials classes onto a polyethylene terephthalate (PET) substrate. The three semiconductor materials are pentacene (Pn) from the small-molecule class, poly (3-hexylthiophene) (P3HT) from the polymeric class and carbon nanotube mats (CNT) from the macromolecule class and have all resulted in active thin-film transistor devices.[1] The details of the transfer printing method using Au electrodes and a PMMA dielectric layer as model components will be presented. The use of other dielectric layers such as polyvinyl phenol (PVP) with also be discussed. [1]. D. R. Hines et al., Appl. Phys. Lett. 86, 163101 (2005). * Work supported by the Laboratory for Physical Sciences.

10:15 AM M7.6

Micron-scale Organic Thin Film Transistors with PEDOT Electrodes Patterned by Polymer Inking. Dawen Li and L. Jay Guo; Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan.

We report a simple, low-cost, and parallel fabrication of pentacene organic thin-film transistors (OTFTs) with conductive polymer PEDOT electrodes that are patterned by a special "polymer inking and stamping" technique. In this technique, a PDMS stamp with source/drain electrode patterns was first made by casting and curing PDMS against a Si Master. Conductive polymer PEDOT was spin-coated on the PDMS stamp. Next the PEDOT coated stamp was placed on Si/SiO₂ substrate or deposited pentacene film without additional force, and the PEDOT on top of the stamp protrusion regions were in conformal contact with the substrate. Subsequently the PDMS stamp was removed and PEDOT patterns were left on the substrate having identical dimensions as the source/drain patterns on the stamp. We found that success of pattern transfer depends on both substrate surface and PEDOT solution, and pattern transfer took place when a certain amount of glycerol was added into PEDOT

aqueous solution. OTFT channel length of $2\mu\text{m}$ for both top contact (TC) and bottom contact (BC) configurations has been achieved. During the pattern transfer for TC device, pentacene at the active device region can also be defined simultaneously due to adherence of pentacene material that surrounds source/drain pads to the PDMS stamp. This naturally created the device-to-device isolation, without additional pentacene patterning steps. Electrical characteristics of TC pentacene TFTs with PEDOT electrodes is superior than those with gold electrodes. This is due to a lower energy barrier between the PEDOT and pentacene. Field-effect mobility and on/off current ratio in saturation regime as large as $0.7\text{cm}^2/\text{Vs}$ and on the order of 10^6 were obtained. On the other hand the electrical performance of BC pentacene TFTs with PEDOT electrodes is very similar to OTFTs with Ti/Au electrodes. This is because for BC OTFT configuration, interface morphology between the electrode and the pentacene deposited on top limits the carrier injection efficiency. We have quantified that the contact resistance (R_c) of TC OTFTs with PEDOT electrodes is an order of magnitude smaller than those with gold electrodes. Further more, for TC pentacene TFTs with PEDOT electrodes, R_c has the same order of magnitude as channel resistance (R_{ch}) per micron meter. Electrical performance can be further improved by reducing channel length. While R_c of BC OTFTs is in about two orders of magnitude greater than R_{ch} , scaling down channel length will not effectively improve OTFTs performance. Reduction of R_c is the only way for further improvement of OTFTs electrical performance. The PEDOT source/drain patterning by this new polymer inking and stamping technique not only provides much higher resolution than the thermally evaporated gold electrodes via shadow mask, but also is much more cost effective. This technique can be potentially developed as a rapid, reel-to-reel patterning technology for conductive polymers.

10:30 AM M7.7

Monolayer Formation in Oligothiophene Based OTFTs.

Paul Chang¹, Amanda R. Murphy², Jean M. J. Frechet² and Vivek Subramanian¹; ¹Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, California; ²Department of Chemistry, University of California, Berkeley, California.

Recent work has shown oligothiophenes deposited via inkjet printing can undergo a thermolysis driven reorganization that results in films a single monolayer thick between adjacent source and drain electrodes. This work studies the mechanisms behind such film formation, including the surface mobility of deposited molecules and the effects of substrate surface energy. Oligothiophenes of different size are studied in order to better examine the kinetic tradeoffs in observed the surface rearrangement. Molecules are verified to have a preferential affinity for gold surfaces and the ability to diffuse >5 um over the surface. Under specific processing conditions and electrode configurations, resulting films using particular oligothiophenes are seen to form single-monolayer films in OTFTs with channels up to 10 um long. Compared to aggregated, thicker film devices, monolayer devices films show significantly reduced trapping behavior, resulting in improved performance and consistent low bias behavior. Overall, for printed monolayer devices, field-effect mobilities of $>0.1\text{cm}^2/\text{Vs}$ are measured, with peak inverse subthreshold slopes $<200\text{mV}/\text{dec}$.

10:45 AM M7.8

Organic Thin Film Transistors from Uniaxially Aligned Films of Hexa-peri-hexabenzocoronenes (HBCs).

Jason Christopher Pinto¹, Richard Friend¹, Henning Sirringhaus¹, Wojciech Pisula², Tadeusz Pakula² and Klaus Mullen²; ¹Optoelectronics Group, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; ²Max Planck Institute for Polymer Research, Mainz, Germany.

Recent interest in polymeric systems for optoelectronics has been motivated by the many advantages polymers offer over traditional inorganic semiconductors. Ease of processing through room temperature solution deposition is one of these key advantages. This makes polymer electronics potentially inexpensive and compatible with flexible substrates. Polymeric semiconductors, however, suffer from a lack of long-range order which is thought to be the major cause of low mobility in polymer thin film transistors (TFTs). Discotic liquid crystals (DLCs) present an alternative approach to flexible organic electronics. Conjugated core DLCs are disc shaped molecules that have the ability to self-organize into columnar aggregates. The self-organization of these molecules produces a highly ordered system where columns form efficient pathways for charge transport. These pathways can be exploited for high mobility field-effect transistors (FETs) if the columns lie in plane with the transistor channel and span the source and drain contacts. We report here the use of a novel deposition method called zone casting to fabricate uniaxially aligned films of hexa-peri-hexabenzocoronene derivatives. These films were used to fabricate field-effect transistors that demonstrated the highest observed charge-carrier mobility for these materials. These devices also showed high mobility anisotropy when devices made parallel and

perpendicular to the coating direction were compared. The temperature dependence of charge transport in these films was investigated for insight into the prevalent mode of carrier transport parallel and orthogonal to the column direction. We also performed spectroscopic studies on these highly aligned materials.

11:00 AM M7.9

Fused thiophene semiconducting polymers for OFETs:

Solutions to high mobility and stability. Steven Tierney, Clare Bailey, Kristijonas Genevicius, Martin Heeney, Iain MacDonald, Ruth Rawcliffe, Richard Simms, David Sparrowe, Maxim Shkunov, Weimin Zhang and Iain McCulloch; Merck Chemicals Ltd., Southampton, United Kingdom.

The emergence of organic field-effect transistors (OFETs) for incorporation into lightweight flexible electronic devices has generated interest in the development of solution-processable organic semiconductors. Novel semiconducting polymers containing thieno[3,2-b]thiophene and thieno[2,3-b]thiophene moieties were prepared via a fast highly reproducible microwave-assisted reaction. These polymers were solution-processed to form the active semiconducting element of an OFET. Processing parameters including surface treatment, annealing temperature, and device architecture were optimised in order to maximise thin-film morphology and charge transport in the polymers. Field-effect mobilities higher than $0.1\text{cm}^2/\text{Vs}$ are reported for thieno[3,2-b]thiophene co-polymers and thieno[2,3-b]thiophene co-polymers. Excellent air-stability is also reported for thieno[2,3-b]thiophene co-polymers in an OFET.

11:15 AM M7.10

Non-Volatile Memory Effect of Ferroelectric Field-Effect

Transistors based on a Printed Polypeptide Film. Sei Uemura¹,

Manabu Yoshida¹, Toshihide Kamata¹, Masahiko Kojima², Takeshi Kondo² and Takeshi Kawai²; ¹AIST, Tsukuba, Ibaraki, Japan; ²Department of Industrial Chemistry, Tokyo University of Science, Shinjuku, Tokyo, Japan.

Biomaterial is one of the most attractive materials for the printed devices due to its solubility and unique dielectric properties. Polypeptide is one of the typical biomaterials with unique dielectric phenomena, thus it can be a good candidate for the component of printed devices. It has been known that some kind of polypeptide shows a ferroelectric phase due to its rigid rod-like structure. In this study, we have examined to prepare a printed thin film of the poly (γ -methyl-L-glutamate) (PMLG), and investigated its film structure and ferroelectric behaviors. In the printed thin film, PMLG showed a rod-like α -helix structure. Its molecular axis was oriented to the parallel direction to the substrate surface. A ferroelectric field-effect transistor (FeFET) was prepared by using the printed PMLG thin film as a dielectric layer. Large hysteresis was observed in the I-V characteristics of the FeFETs. The bistable states could be obtained. The obtained bistable states were very stable more than 10 days without any applied voltages. Then, it can be expected to be used as a non-volatile memory. Such phenomena were dependent on the molecular weight of PMLG. While the thin film of PMLG with large molecular weight (M.w. $>60,000$) does not show the bistable state, that with small molecular weight (M.w. $<30,000$) showed large hysteresis in the I-V characteristics. A.c and d.c. current-voltage properties, spectroscopic measurements and morphology observation revealed that the observed phenomenon was dependent on the motion of main-chain and side-chain dipoles. In the case of high molecular weight PMLG, the aggregation of the PMLG and change of the morphology was observed by applying voltage. However, in the case of the low molecular weight PMLG, such a drastic molecular motion was not occurred but dipole motion could be observed. Furthermore, we have also observed that the driving voltage was dependent on the concentration of the dipole in the dielectric layer. From these results, we have proposed that the memory effect is causable by the motion of the main-chain rather than the side-chain without morphological change.

11:30 AM M7.11

Organic Field-Effect Transistors with Suppressed DC

Bias-stress Degradations. Tsuyoshi Sekitani¹, Shingo Iba¹, Yusaku

Kato¹, Yoshiaki Noguchi¹, Takayasu Sakurai² and Takao Someya¹; ¹Quantum-Phase Electronics Center, The University of Tokyo, Tokyo, Japan; ²Center for Collaborative Research, The University of Tokyo, Tokyo, Japan.

We report our observation that the DC bias stress-induced degradations of organic field-effect transistors (FETs) can be suppressed drastically by postannealing effects. Heat-resistant pentacene FETs were manufactured on polyimide films with polyimide gate dielectric layers and annealed at 140 degree Celsius for 12 h in a nitrogen environment. When DC biases of V_{DS} and $V_{GS} = -40\text{V}$ are continuously applied to these FETs for 11 h, the change of source-drain currents is as small as $3 \pm 1\%$ and the threshold voltage

(V_{th}) shift is less than 0.4 V. Heat-resistant organic FETs were fabricated on a 75- μm -thick polyimide film with a polyimide gate dielectric layer. First, a gate electrode was formed by thermal evaporation of 5-nm-thick Cr and 100-nm-thick Au through a shadow mask. A 600-nm-thick polyimide gate dielectric layer was then prepared by spin coating and a 50-nm-thick pentacene layer was deposited through the same thermal evaporation. A 60-nm-thick Au layer was deposited using a shadow mask to form the drain and source electrodes. The nominal channel length and width of organic FETs were 100 μm and 1 mm, respectively. Finally, the base film with transistors was uniformly coated by a 6- μm -thick poly-chloro-para-xylylene (parylene) layer. Both the annealing experiment and the electric measurements were performed in a light-shielding nitrogen environment with less than 1 ppm oxygen and moisture. After the postannealing process, the mobility was enhanced from 0.3 to 0.4 cm^2/Vs and the on/off ratio was improved from 10^3 to 10^6 , where V_{th} was shifted from -4 V to -6 V. Furthermore, the annealed FETs showed no significant changes even after applying continuous DC voltage biases of V_{DS} and $V_{GS} = -40$ V for 11 h; in other words, the degradations of the source-drain currents associated with the DC bias stress-induced drifts of V_{th} were suppressed by as little as $3 \pm 1\%$. We would like to emphasize here that the manufacturing of heat-resistant organic FETs is crucial for annealing the device at 140 degree Celsius for 12 h without cracking or chemical decomposition. Polyimide is used as the base and gate dielectric layers, both of which have almost identical coefficients of thermal expansion, thereby realizing an excellent heat-resistance up to 160 degree Celsius. Suppression of DC bias stress-induced degradation can be ascribed to the elimination of the deep-trapping site by high-temperature annealing. The present study provides a promising method to stabilize transistor characteristics such as mobility, V_{th} , and I_{DS} under continuous DC bias stress, which is crucial in order to realize reliable and sophisticated integrated circuits comprising organic transistors. This study is partially supported by IT Program, MEXT, MPHPT, and NEDO.

11:45 AM M7.12

High performance vertical-type organic transistors using a metal base structure. Ken-ichi Nakayama, Shin-ya Fujimoto and Masaaki Yokoyama; Graduate School of Engineering, Osaka University, Osaka, Japan.

The vertical-type organic transistor is a promising device structure that can make the channel length much shorter, leading to low voltage operation and high frequency response. So far, some vertical transistors have been reported, for example, an organic triode device and a static induction transistor. However, these devices need complicated processes to fabricate the third controlling electrode, such as a self-assembled polymer network or a fine-pitch striped pattern. In this letter, we report a very high performance vertical transistor having a simple layered structure composed of organic/metal/organic layers. This device could modulate a sheet current between the emitter and collector by a voltage applied to the thin metal base inserted. The device was fabricated by vacuum deposition. The first organic layer of perylenetetracarboxylic derivatives (Me-PTC) was deposited on an ITO of a collector electrode. The base electrode of aluminum was deposited with a thickness of 20nm. The second organic layer of C60 and the emitter electrode of Ag were deposited. Without the base voltage (V_b), the small collector current (I_c) was observed on applying the collector voltage ($V_c = 5\text{V}$). However, application of V_b markedly increased the collector current, which finally exceeded 300 mA cm^{-2} for only 3 V of V_b . The value of the ON/OFF ratio was around 100, rather high for vertical-type transistors. In addition, the value of current amplification factor (hFE) reached as high as 180. This indicated that the change in the output current was much larger than that of the input current, which means that current amplification occurred like bipolar transistors. There are two requirements to observe a large amplification using the simple semiconductor/metal/semiconductor structure. One is the thickness of the base electrode. The thickness more than 40 nm makes the device a simple series connection of two organic films. The other is the used material. So far, the best performance was obtained for the combination of C60 as an emitter and Me-PTC as a collector. The other electron transporting materials show small or no amplification. The mechanism of the current amplification is not clear, but we consider that the key should be the coverage of the base aluminum electrode, that is, whether the thin base electrode covered the organic film surface fully or covered it partially like a mesh electrode. In the latter case, the triode mechanism can be valid to explain the modulation. On the other hand, if the base electrode covered the surface fully (we guess that may be true), some other mechanisms for electrons passing in the electrode would be needed. Now, we are investigating the electrode structure using various microscopic techniques.

1:30 PM *M8.1

Inkjet Printing of Functional Polymers and Nanoparticles.

Ulrich S. Schubert, Berend-Jan Gans, Emine Tekin, Jolke Perelaer, Antje van den Berg and Elisabeth Holder; Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, Eindhoven, Netherlands.

The inkjet processing of functional polymers and nanoparticles represents a major goal in the current research activities, both in fundamental science as well as in industry. In order to understand the printing physics, detailed studies of the printing behavior of different polymer containing inks were performed. The printability of a polymer containing ink is impeded by the formation of elastic filaments. The lifetime of the filaments increases strongly with molecular weight and concentration of the polymer. Analysis of the elongation of the filaments proves that filament formation is related to a coil-stretch formation of the macromolecules. Subsequently, the preparation of defined dots and films was investigated varying different solvents, solvent mixtures, nozzle temperatures, substrates and substrate temperatures. Besides different non-conductive polymers, also PPV derivatives, phosphorescent iridium complex containing polymers and others were utilized. Moreover, also the printability of nanoparticles, silver nanopaste, ITO dispersions and others was investigated in order to obtain semi-conductive, electroluminescent or conductive dots, antennas, tracks or films. The xy dimensions were varied from 50 micrometer to several millimetres; the thickness from 50 nm to multiple micrometers. The substrates were varied from glass, ITO, polyimide, polyester to polycarbonate. Besides the investigation of the printing process by a stroboscope camera system, also the drop impact was directly visualized and investigated. Finally, the printed dots, tracks, antennas and films were characterized by optical profilometer, confocal microscope as well as SPM and investigated regarding there properties. Finally, crystals of monodisperse colloidal particles were printed at a well-defined location. Selected publications: B.-J. de Gans, E. Kazancioglu, W. Meyer, U.S. Schubert, *Macromol. Rapid Commun.* 2004, 25, 292-296; B.-J. de Gans, P. Duineveld, U.S. Schubert, *Adv. Mater.* 2004, 16, 203-213; B.-J. de Gans, U.S. Schubert, *Langmuir* 2004, 20, 7789-7793; E. Tekin, B.-J. de Gans, U.S. Schubert, *J. Mater. Chem.* 2004, 14, 2627-2632; E. Tekin, E. Holder, V. Marin, B.-J. de Gans, U.S. Schubert, *Macromol. Rapid Commun.* 2005, 26, 293-297; B.-J. de Gans, L. Xue, U.S. Agarwal, U.S. Schubert, *Macromol. Rapid Commun.* 2005, 26, 310-314.

2:00 PM *M8.2

Enabling Desktop Inkjet Printers as a Tool to Pattern Conductive Polymers. Yuka Yoshioka¹ and Ghassan E. Jabbour²;

¹Flexible Display Center, Arizona State University, Tempe, Arizona; ²Chemical and Materials Engineering, Arizona State University, Tempe, Arizona.

We will discuss how to use desktop inkjet printers as tools to pattern and control the sheet resistivity of a conductive polymers on any substrate ranging from glass to paper. The adequate choice and preparation of the ink and the control of the deposition (printing) variables will be presented. Examples of several applications that benefit from this approach will be highlighted.

3:30 PM *M8.3

Inkjet Printing for Flexible Electronics and Smart Textiles.

Paul Calvert, Amit Sawhney and Aminesh Agrawal; Textile Sciences, University of Massachusetts, Dartmouth, North Dartmouth, Massachusetts.

Inkjet printing can be used to deposit electronic materials such as conducting polymers and metals. The printing of uniform PEDOT films onto hard surfaces, the printing of silver lines and piezoresistive sensors onto textiles and the printing of active optical layers onto textiles will be discussed. In many cases when building complex structures, it will be desirable to print a receptor layer and then print the active materials into this. Hence it is of interest to explore printing into gels and porous substrates.

4:00 PM M8.4

Inkjet Printing of Polyimide Precursors and its Application to Organic Field-Effect Transistors. Yoshiaki Noguchi¹, Tsuyoshi

Sekitani¹, Yusaku Kato¹, Shingo Iba¹, Takayasu Sakurai² and Takao Someya¹; ¹School of Engineering, The University of Tokyo, Tokyo, Japan; ²Center for Collaborative Research, The University of Tokyo, Tokyo, Japan.

Employing an inkjet printing machine, heat-resistant polyimide gate dielectric layers are patterned on plastic films and exploited to

manufacture high-quality pentacene field-effect transistors (FETs). The measured mobility of pentacene FETs with inkjet polyimide is $0.2 \text{ cm}^2/\text{Vs}$. The on/off ratio exceeds 10^6 , showing that leakage current through inkjet polyimide is sufficiently low. The surface smoothness of inkjet-printed polyimide layers characterized by AFM is comparable to that of spin coated polyimide films (RMS=0.22 nm). A high-purity polyimide precursor (Kemitite CT4112, Kyocera Chemical) was patterned by an inkjet printer (IJP-1, Ricoh Printing Systems) with a stainless steel inkjet head (GEN3E1), which is driven by multilayered piezoelectricity and equipped with 96 linear array nozzles. A solution containing polyimide precursors was diluted by N-Methyl-2-pyrrolidone (NMP) so that its viscosity could be the vendor's recommended value (11 mPa-s). Before manufacturing organic transistors, various kinds of dot and line polyimide patterns were printed on 75- μm -thick polyimide films coated by a 50-nm-thick Au layer. The samples were cured at 180°C for 1 hour in the nitrogen environment. We have controlled the discharge-voltage (30-40V) of the inkjet head. The minimum diameter of dots was $120 \mu\text{m}$ without surface treatment, showing feasibility of inkjet patterning of polyimide at high spatial resolution of 200dpi. The variation in diameter was less than $\pm 5\%$ for measured 100 dots. The surface of the inkjet-patterned polyimide layer was characterized by AFM. Its smoothness is comparable to that of spin coating (RMS=0.22 nm). Pentacene FETs were fabricated with inkjet-printed polyimide gate dielectric layer. A gate electrode consisting of 5-nm-thick Cr and 50-nm-thick Au layers was evaporated through a shadow mask on the same polyimide film. A polyimide gate dielectric layer was prepared by inkjet, whose thickness was 510 nm after curing process. A 50-nm-thick pentacene was deposited by thermal evaporation. Finally, source and drain electrodes were formed by thermal evaporation of 50-nm-thick Au through a shadow mask. The channel length and width of organic FETs are $100 \mu\text{m}$ and $500 \mu\text{m}$, respectively. The mobility was $0.2 \text{ cm}^2/\text{Vs}$ in the saturation regime and the on/off current ratio was above 10^6 . Compared with spin coating, the present inkjet printing of polyimide is compatible with a roll-to-roll process and does not require additional patterning process for via interconnection, thus it is potentially ultra low in manufacturing cost. Although the present precursor-type polyimide was dissolved in an NMP-based solution harm to bonding segment, we have demonstrated that the newly developed inkjet head, which is assembled with minimum use of bonding segment, can realize inkjet patterning of high-quality precursor-type polyimide suitable for organic FETs. This study is partially supported by IT Program, MEXT, MPHPT, and NEDO.

4:15 PM M8.5

Organic FET Grown by Direct Printing of Pentacene Channel and Metal Contacts Using a Molecular Jet Printer.

Jianglong Chen¹, Valerie Leblanc¹, Annie Wang¹, Marc A. Baldo¹, Paul J. Benning², Martin A. Schmidt¹, David M. Schut² and Vladimir Bulovic¹; ¹Microelectronics Technology Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; ², Hewlett-Packard Company, Corvallis, Oregon.

We recently demonstrated Molecular Jet (MoJet) printing technique for high-resolution patterning (up to 800 dpi, $30\mu\text{m}$ features) of organic semiconductors and metals, and we applied the technique to printing patterned molecular organic LEDs. In contrast to the ink-jet printing of solutions, the MoJet technique employs a solvent-free additive deposition. Compared to shadow mask evaporative processing, the MoJet technique is potentially scalable to fabrication on large area substrates. We now demonstrate that with the MoJet technique organic semiconductor pentacene and metal silver can also be directly printed, solvent-free and mask-free, to define a channel, a source, and a drain of an organic field effect transistor (OFET). To modulate organic and metal vapor flux, we fabricated an electrostatically actuated MEMS printhead with a $30\mu\text{m}$ by $120 \mu\text{m}$ aperture and a microshutter. Deep reactive ion etching was used to pattern both the through-wafer aperture and the freestanding comb-drive structure. An operating voltage of less than 100V DC is required to actuate the comb-drive which closes the microshutter and obstructs the aperture, modulating the deposition flux. Using the MoJet printhead we print an OFET inside a high vacuum chamber (5×10^{-6} Torr) by sequentially printing silver and pentacene on top of a thermally grown silicon oxide thin film. OFET channel length down to $5\mu\text{m}$ is achieved. We will present the grain morphology of printed pentacene channel and silver films as well as the electrical characteristics of the printed devices.

4:30 PM M8.6

Inkjet Printed Inorganic Channel Materials for Thin Film Transistors.

Yu-Jen Chang, Doo-Hyoung Lee and Chih-Hung Chang; Chemical Engineering, Oregon State University, Corvallis, Oregon.

Low cost integrated circuits will enable many new applications for our daily life. Amorphous silicon (a-Si) is the current material of choice for low-cost thin-film transistors (TFTs) that are widely used as switching devices in active-matrix liquid-crystal displays. Organic

(molecular crystals or polymeric) semiconductors with advantages of flexibility and potential low-cost processing are major candidates. Another promising but less explored approach is to use high performance inorganic materials for the active devices. Inorganic compound semiconductors have advantages of high carrier mobility and excellent long-term stability. We are exploring this concept by fabricating inorganic thin film transistors via inkjet printing processes. Simple and low cost chemical precursors for a variety of metal oxide semiconductors that is suitable for inkjet printing were developed in our labs. Using these precursors, we have successfully fabricated working thin film transistors with inkjet patterned channel layers in a metal insulator semiconductor field effect transistor structure. The mobility values of these devices were higher than $5 \text{ cm}^2/\text{Vs}$. The success of inkjet printable inorganic semiconductors opens a new avenue for fabricating low-cost high-performance devices via inkjet printing.

4:45 PM M8.7

A novel high-Q printed inductor technology for RFID applications.

David Redinger and Vivek Subramanian; EECS, University of California, Berkeley, Berkeley, California.

Deposition of low-resistance materials is crucial to the fabrication of high-quality inductors necessary for power coupling in low-frequency RFID tags. There is great interest in using printing to realize these inductors since it lowers the cost of the tag; unfortunately, to date, printed technologies have not provided the requisite low resistance conductors required for high-Q inductors. Therefore, most low-frequency tags today are realized using conventional etch or cut-based techniques, which are more expensive. Copper is an ideal material for use in low-cost circuits due to its high conductivity and relative abundance. Here, we demonstrate a novel high-quality inductor technology based on the use of ink-jet printed nanoparticles as an initial pattern, followed by subsequent electroless plating to deposit copper, resulting in extremely low resistance. This leads to a significant improvement (10-20X) in inductor quality factor over printed nanoparticles alone. Finally, therefore, performance levels required for inductively coupled RFID are realized via a low-cost printing technology. Several metals catalyze the electroless plating of copper. Gold or silver nanoparticles catalyze the electroless plating reaction when deposited with adequate concentration. The seed layer consisted of oleic acid-encapsulated silver nanoparticles in dihydroterpineol solvent, along with a palladium organometallic adhesion promoter. Using inkjet-printing, a seed pattern was printed onto conventional DuPont Melinex substrates, and annealed to drive off the nanoparticle encapsulant. The plating solution consisted of CuSO_4 , EDTA complexing agent, RE-610 surfactant, pyridine accelerant, paraformaldehyde reducing agent, and DI water. The pH was adjusted to 13.2 using potassium hydroxide. The bath was kept at 60°C and aerated during the deposition. Line height increases linearly with plating time until a point where the plating solution becomes unstable, which happens after approximately two hours. Copper lines $3.5 \mu\text{m}$ thick are reliably grown, giving a sheet resistance as low as $7.5 \text{ m}\Omega/\text{square}$. At low frequencies series resistance determines inductor quality, and therefore sheet resistance of the metal layer is a very important metric. Conductivity of the deposited copper was as high as 73 percent of bulk copper. A $3.2 \mu\text{H}$ inductor was fabricated that had a series resistance of 12.4Ω , giving a quality factor of 21.3 at 13.56 MHz. This is expected to be more than adequate for RFID applications. Therefore, this process represents an important step towards the fabrication of low-cost RFID systems.

SESSION M9: Poster Session: Printed TFTs and Circuits

Wednesday Evening, November 30, 2005

8:00 PM

Exhibition Hall D (Hynes)

M9.1

Using a Flexographic Printer for Organic Field Effect Transistors.

Henrik G. O. Sandberg and Tapio Makela; Polymer Electronics, VTT Information Technology, Espoo, Finland.

Field effect transistors (FETs) are key elements in printed electronic applications. Electronics are expanding into new fields where cost of manufacture is critical, which has led to the development of new methods for preparing devices. Such application areas are for example simple devices used in packages and other "throw away" products where embedded electronics can give additional value. In this work flexible organic FETs are studied, where the flexographic (flexo) printing method is used for manufacture of polymer elements in the device. The main component geometry used in this study is the thin film transistor and the flexographic printing method is used primarily for manufacture of semiconductor and dielectric layers using solutions of regioregular poly(3-hexylthiophene) and polyhydroxystyrene,

respectively. The use of flexographic printing methods for doublelayer polymer structures are investigated and the devices are characterized in various stages of manufacture. The electrode layers are initially made from metal thin films using standard methods, or by using a flexo printed etching mask, as the resolution and printing quality of high conductivity polymers using the flexo printing method is not as such ideal for the desired transistor channel dimensions/geometry. The gate electrode is made using inkjet or flexo for conducting polymer electrodes or by metal evaporation. The flexographic printing method is chosen as it allows for low-cost fabrication using organic material in solution and the process is easily scaled for high volumes.

M9.2

n-Type Organic Field Effect Transistor Prepared by Supramolecular Nanotransfer Printing.

Christian Albertus Nijhuis^{1,2}, Jurjen Maat^{1,2}, Maria Peter¹, Marcel Wuesthof^{1,2}, Cora Salm^{1,2}, Jurriaan Schmitz^{1,2}, Bernard Boukamp^{1,2}, Wilfred van der Wiel^{1,2}, Bart Jan Ravoo^{1,2}, Jurriaan Huskens^{1,2} and David N. Reinhoudt^{1,2}; ¹Universite of Twente, Enschede, Overijssel, Netherlands; ²MESA+ Institute for Nanotechnology, Enschede, Overijssel, Netherlands.

Organic field effect transistors (OFETs) can have applications in identification tags, smart cards, and display drivers, but n-type semiconducting organic molecules are still relatively rare. Moreover, the preparation of organic electronic devices by conventional lithography requires expensive and elaborated equipment and/or high temperatures and wet chemicals which may cause degradation of the relatively fragile organic molecules. For these reasons, the development of other fabrication techniques is of current interest. Printing techniques circumvent many of the limitations of conventional patterning techniques, and only low cost tools are required. Especially nanotransfer printing is interesting for device fabrication, since a thin metal film is transferred from the stamp to the substrate.¹ Most examples rely on the formation of covalent bonds between the metal film and the substrate resulting in an effective metal transfer. In our group self-assembled monolayers (SAMs) of β -cyclodextrin (β CD) on gold and on glass have been extensively studied.^{2,3} The surface confined β -cyclodextrin moieties retain the ability to form host-guest complexes with different molecules from solution. Redox-active ferrocenyl (Fc) functionalized PPI dendrimers constitute a particularly interesting class of polyfunctional guest molecules that can be placed onto these molecular printboards. These molecules form stable assemblies at β CD SAMs owing to the formation of multiple specific host-guest interactions with the host surface.⁴ A β CD SAM was formed at thin Au films that were thermally deposited at PDMS stamps. Placing these functionalized PDMS stamps in conformal contact with a monolayer of the ferrocene dendrimers at a β CD SAM resulted in an effective transfer of the Au from the PDMS stamp to the substrate. The effective transfer is caused by the formation of multiple host-guest interactions of Fc-endgroups with the β CD SAM at the stamp. Nanotransfer printing at heavily p-doped Si wafers with 50 nm SiO₂ on which β CD SAMs were prepared, resulted in three-terminal devices with two Au top electrodes and the p-doped Si substrate as a gate. The organic FETs showed n-type semiconducting behavior due to the redox-active ferrocene endgroups. The potential at which the FET switches to the conducting state is very close to the redox potential of the Fc-units and devices fabricated with redox-inactive adamantyl-functionalized dendrimers showed no FET behavior. References 1. Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* 2002, 81, 562. 2. Beulen, M.J.W.; Bügler, J.; Lammerink, B.; Geurts, F.A.J.; Biemond, E. M. E. F.; Leerdam, K. G. C.; Van Veggel, F. C. J. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *Langmuir*, 1998, 14, 6424. 3. Onclin, S.; Mulder, A.; Huskens, J.; Ravoo, B. J.; Reinhoudt, D. N. *Langmuir*, 20, 2004, 5460. 4. Nijhuis, C.A.; Huskens, J.; Reinhoudt, D.N. *J. Am. Chem. Soc.* 2004, 126, 12266.

M9.3

Printed Nanocomposite Dielectric Gate Insulator for Organic Field Effect Transistors.

Amjad S. Rasul^{1,2}, Jie Zhang¹, Dan Gamota¹ and Christos Takoudis²; ¹Motorola Labs, Motorola Inc., Schaumburg, Illinois; ²Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois.

Printed high capacitance nanocomposite dielectric material was demonstrated as a gate insulator for organic field effect transistors (OFETs). A nanocomposite consisting of cross-linked Propylene Glycol Methyl Ether Acetate and Barium Titanate (BTO) nanoparticles was developed and utilized as the gate insulator. The high permittivity ($k=35$), bimodal nanocomposite utilized had two different filler particle sizes; 200 nm. and 1000 nm. diameter particles. Due to the nanosize of the BTO particles, they disperse well in the organic solvent, which makes it possible to use solution-processable methods, such as printing to fabricate the devices. Bottom contact OFETs were demonstrated using a combination of pad printing and spray coating technologies. An aluminum coated Mylar film was used

as the flexible gate substrate. An amorphous organic semiconductor was utilized as the active layer to evaluate the dielectric properties of room temperature, solution-processed OFET devices. The use of an amorphous semiconductor material enabled a more consistent nanocomposite gate insulator evaluation since morphology effect can be largely neglected. It was demonstrated that OFETs with the nanocomposite dielectric layer have higher field-induced current than that of conventional devices due to the high dielectric constant of the gate insulator.

M9.4

Solvent annealing improves thin-film transistor performance of an anthradithiophene organic semiconductor.

Kimberly Dickey¹, John Anthony² and Yueh-Lin (Lynn) Loo¹;

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The development of organic semiconductors is driven by the promise of low-cost device applications. The success of reducing fabrication costs and creating low-cost devices hinges on the ability to deposit and pattern the organic semiconductor material from solution, a relatively inexpensive deposition method, as compared to thermal evaporation. To date, several solution-processable organic semiconductors have been developed. Devices built with these materials, however, tend to exhibit carrier mobilities that are several orders of magnitude lower than thermally evaporated pentacene, the quintessential organic semiconductor with an average mobility of the order of 1cm²/V-sec. One solution-processable organic semiconductor we have studied is triethylsilyl anthradithiophene (TES ADT), an anthradithiophene molecule that has been functionalized with bulky side groups to promote π -stacking and solution solubility. We have fabricated thin-film transistors on silicon substrates with spun-cast TES ADT thin films. The hole mobility of the spun-cast TES ADT transistors is significantly lower (0.005cm²/V-sec) than thermally evaporated anthradithiophene thin films (0.1 cm²/V-sec). Annealing the spun-cast TES ADT thin film over a pool of toluene for a mere two minutes, however, significantly improves the device performance. Specifically, the current-voltage characteristics of these annealed devices exhibit significantly reduced hysteresis, increased hole mobility of several orders of magnitude (0.2cm²/V-s), and increased on-currents (100 fold). Annealing TES ADT thin films with dichloroethane produces similar effects, but annealing with other solvents, such as hexanes and acetone, does not result in any significant improvement over unannealed films. The marked improvement in device performance can be directly correlated with structural changes and macroscopic morphological transformations that are traceable by near edge x-ray absorption fine structure spectroscopy and atomic force microscopy, respectively.

M9.5

Contact resistance in asymmetric pentacene thin-film transistors with polyaniline and gold electrodes.

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The performance of organic thin-film transistors (TFTs) is frequently limited by contact resistance at the organic semiconductor and metal interface. Such contact resistance results in pronounced non-linear current-voltage (I-V) characteristics in the linear regime. We have recently fabricated bottom-contact pentacene TFTs with polyaniline (PANI) electrodes that function as effectively as TFTs with gold electrodes. Specifically, the saturation characteristics (hole mobility, on/off ratios, etc.) of PANI devices are comparable to those of gold devices. In the linear regime, however, PANI devices do not exhibit the typical non-linear "hooking" behavior that is characteristic of bottom-contact gold devices. We attribute this observation to reduced contact resistance in the PANI devices. To quantify the contact resistance at the pentacene/gold and the pentacene/PANI interfaces, we have fabricated asymmetric pentacene TFTs with one PANI and one gold electrode. The asymmetric electrode configuration allows us to compare the two interfaces with the same pentacene channel. We have conducted surface potential measurements on these devices using Kelvin probe force microscopy (KPFM). KPFM simultaneously provides the surface topography and the surface potential distribution of pentacene TFTs during operation. Using this technique, we have been able to separate the potential drop at each interface. The contact resistance at these interfaces can then be quantified by normalizing the potential drop by the respective drain current. The asymmetric devices were tested in two configurations: PANI source/gold drain then PANI drain/gold source to characterize the nature of charge injection and drawing at each contact. Our results reveal a large potential drop at the gold/pentacene interface whether

the gold contact functioned as the source or the drain electrode. In sharp contrast, the potential drop at the PANI/pentacene interface is negligible; this is consistent with our previous I-V characteristics and indicates that PANI provides significantly better contact with pentacene for both charge injection and drawing, as opposed to gold.

M9.6

Fabrication of low-molecular weight molecule material films by using a cocktail spin coat technique. Takuya Kambayashi, Hitoshi Wada, Takehiko Mori, Hideo Takezoe and Ken Ishikawa; Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan.

Organic semiconductors have some advantages, such as flexibility, variety, and easiness of fabrication, over inorganic ones. Easiness means that organic thin films can be fabricated in lower temperature than inorganic ones can. Organic thin films are able to be fabricated by wet processes such as a spin coat and a drop cast technique. So, organic materials are promising candidates for future devices, i.e., organic transistors and organic light emitting diodes. Usually, films of low-molecular weight molecules (LMWM) are fabricated by a vacuum evaporation technique as inorganic films are. The vacuum evaporation technique needs high vacuum condition, so this technique needs high cost and it is difficult to fabricate films with large area using this technique. While, the spin coat technique does not need high vacuum; moreover it is easy to fabricate films with large area. This technique has been generally used for polymer materials. Fabrication of LMWM films by using this technique is difficult, since the viscosity of LMWM solutions are too low for spin coating. If we can fabricate LMWM films by spin coating, fabrication process of organic devices would be easier and simpler. One organic material and a kind of solvent are usually used in the conventional spin coat technique. Uniform polymer films are fabricated by conventional spin coating. Recently, we developed the conventional spin coat technique into a new spin coat technique which we named it a cocktail spin coat technique. In cocktail spin coating, we first prepare the solution which contains a few kinds of organic materials and solvents. And then we fabricate organic films from the solution. Using the cocktail spin coat technique, we can fabricate functional films, such as LMWM films and films having graded structure. In this work, we will demonstrate the fabrication of dibenzotetrathiafulvalene (DBTTF) films by using the cocktail spin coat technique. These films were composed of large crystalline domains with $\sim 10 \mu\text{m}$. We used poly (3-hexylthiophene) (P3HT) and DBTTF as source materials. First, we prepared two kinds of chloroform solutions (solution A, B); solution A, B were the P3HT solution (0.25 wt %) and DBTTF solution (0.5wt %), respectively. Using the cocktail of solution A and B, we fabricated films by spin coating (3000rpm/20sec). Obtained films were observed by AFM and XRD. I-V characteristics of films were measured by four-probe method. All experiments and analysis were done under air. The mixing ratio of the solution B being under 30%, conductivity of films were quite low. This low conductivity results from the nature of P3HT. High conductive films obtained in the mixing ratio of the solution B from 30 to 80%. We could observe that DBTTF domains contacted with each other in AFM images of samples. Conductivity decreased as the mixing ratio exceeded 90%. In this case, films showed island morphology in AFM images.

M9.7

Fabrication of Organic Static Induction Transistors Using Colloidal Lithography. Takaaki Hiroi¹, Kiyoshi Fujimoto², Masakazu Nakamura¹ and Kazuhiro Kudo¹; ¹Electronics and Mechanical Engineering, Chiba University, Chiba, Japan; ²Japan Chemical Innovation Institute, Chiba, Japan.

To improve the electrical characteristics of organic static induction transistors (SITs) [1], fabrication of nano-scale structures in the horizontal direction is strongly desired without introducing an electrical damage to functional organic materials. The size of the fine lateral structure must be in the same length scale as the thickness of an organic semiconductor film which corresponds to channel length of the vertical type transistors. We have therefore developed novel fabrication techniques for the organic SITs [2, 3] using 'colloidal lithography' [4]. The preparation procedure developed in this work is as follows: First, positively charged colloidal particles as a deposition mask were adsorbed on a glass surface via electrostatic self-assembly. The particle monolayer film with no aggregation could be formed by optimizing adsorption and drying conditions. Second, a drain electrode, a bottom CuPc layer, and a Schottky gate electrode were deposited successively on the particle-adsorbed glass substrate. Third, the particles were removed using an adhesive tape. Thus, a large number of nano-pores were formed without destroying the films. Then a top CuPc layer and a top source electrode were deposited on the nano-porous layers. Details of the optimization of the particle adsorption process and device characteristics will be presented. This work was supported in part by NEDO's "Nanotechnology Materials Program Rewritable Paper Project" based on funds provided by METI

and administered by JCII, and by Grant-in Aid for Scientific Research (No. 15686014) from Ministry of Education, Culture, Sports, Science and Technology. [1] K. Kudo et al., *Synth. Metals* 111 - 112 (2000) 11. [2] N. Hirashima et al., *Proc. Int. Symp. on Super-Functionality Organic Devices*, IPAP Conference Series 6 (2005), in press. [3] Joseph M.C. et al., 2003 MRS Fall Meeting (Boston, USA), K10.57. [4] P. Hanarp et al., *Colloids Surf. A* 214 (2003) 23.

M9.8

Significant Controllability of Threshold Voltage ($\Delta V_{th}/\Delta V_{top} \sim 0.85$) of Pentacene Field-effect Transistors with Double-gate Structures. Shingo Iba¹, Tsuyoshi Sekitani¹, Yusaku Kato¹, Takayasu Sakurai² and Takao Someya¹; ¹Quantum-Phase Electronics Center, School of Engineering, The University of Tokyo, Tokyo, Japan; ²Center for Collaborative Research, The University of Tokyo, Tokyo, Japan.

We have unambiguously controlled threshold voltage of flexible pentacene field-effect transistors (FETs) with novel double gate structures, where the top- and bottom-gate electrodes can independently apply voltage biases to channel layers [1-3]. The threshold voltage (V_{th}) is shifted systematically by as much as -26 V when the voltage bias of the top-gate electrode (V_{top}) is varied by +40 V. The value of slope ($\Delta V_{th}/\Delta V_{top}$) is equal to the ratio of areal capacitances of top and bottom gate dielectric layers. We have compared an FET with top-gate electrodes that cover the entire channel layers as well as source and drain electrodes and an FET with top gate that covers only a part of channel layers and found that top-gate bias mainly affects the channel part rather than the contact part. A 620-nm-thick polyimide gate dielectric layer (5.4 nF/cm²) is formed on a 75- μm -thick polyimide film coated by a 50-nm-thick Au layer as gate. The channel layer is a 50-nm-thick pentacene. 50-nm-thick Au drain and source electrodes are evaporated through a shadow mask. The channel length L and width W are 100 μm and 1 mm, respectively. The transistors are uniformly coated by a 600-nm-thick parylene layer (4.5 nF/cm²). Finally, a 150-nm-thick Au layer is deposited to form top-gate electrodes. In one of the devices, source-drain electrodes and channels are completely covered by a 300x1000 μm^2 top-gate electrode, while other structures with narrower width of top gate electrodes are also investigated. The device characteristics were measured in the ambient air. When the top-gate electrode is in the floating state, the DC characteristics in the saturation regime demonstrated mobility of 0.2 cm²/Vs and ON/OFF ratio of 10⁶. The characteristics were measured at V_{top} of -60V to +60V, and characteristics in the linear regime showed systematic changes. The change in V_{th} is very small when V_{top} is varied from -60 V to +20 V, but V_{th} decreases from -17 V to -43 V when V_{top} is varied from +20 V to +60 V. The value of slope ($\Delta V_{th}/\Delta V_{top}$) is 0.85, which is equal to the ratio of areal capacitances of polyimide and parylene insulation layers[4]. Such a large slope becomes possible in organic transistors with careful optimization of structural parameters, although similar structures have been investigated recently both in silicon and organic transistors [1-4]. We also examined FET with identical structures except the size of top-gate electrode, which is 80x1000 μm^2 square covering only channel. There were no significant differences between those two FETs, indicating that top-gate bias mainly affects the channel part rather than the source-drain electrode part. This study is partially supported by IT Program, MEXT, MPHPT, and NEDO. [1]Flora Li, *etal.* 2005 MRS Spring, I9.3, (2005). [2]R. Coehoorn, *etal.* 2005 MRS Spring, I9.7, (2005). [3]G. H. Gelinck, *etal.* SID, 3.1, (2005). [4]J.-P. Colinge, *Silicon-on-insulator technology*, Chap. 5. (Kluwer Academic Publishers)

M9.9

Investigation into the DOS of States within Organic Semiconductors. David Donaghy¹, Naser Sedghi¹, Munira Raja¹, Sam Badriya², Simon Higgins² and William Eccleston¹; ¹Electrical Engineering, University of Liverpool, Liverpool, United Kingdom; ²Chemistry, University of Liverpool, Liverpool, United Kingdom.

It has been generally accepted that charge transport in organic disordered semiconductors occurs via variable range hopping or multiple trapping among localized states. The density of states (DOS) in these materials is commonly believed to be described by a Gaussian distribution of energy sites [1] but there has been a wide range of papers published where the density of states has been assumed to be an exponential distribution [2-5]. The value of s controls the width of the DOS while the Fermi energy level, E_F , specifies the range of energy levels on the DOS curve that the majority of the carrier concentration, $n(E)$, are situated in. The abstract examines the trends in $n(E)$ and also the error from substituting a DOS with an exponential function. It should be remembered that the total current in a polymer device is primarily equal to the product of the carrier concentration, $n(E)$ and the hopping rate. As the rate of increase in the gradient of the DOS decreases with energy and as the rate of decrease in the gradient of the Fermi-dirac function is constant with energy the carrier concentration should reach a peak at some energy

level, Entmax. However, the latter is only correct if the increase gradient of the DOS is greater than that of the Fermi-Dirac function, i.e. dependent on the position of the Fermi-level in relation to the peak in the DOS. If this is the case then $n(E)$ will reach a maximum at an energy equal to Entmax that is proportional to σ^2/kT . The width of the distribution of the carrier concentration with energy f was found to be linearly proportional to σ . If it is assumed that the only energy states above EF are responsible for the current conduction (since those below EF are all occupied and therefore do not take part in the hopping process) then only $n(E)$ above EF is of any interest. Depending on the value of EF the $n(E)$ is either a Gaussian distribution ($EF_{min} < \sigma^2/kT$), a part of a Gaussian distribution or one half of a Gaussian distribution ($EF_{max} > \sigma^2/2kT$). The point of inflexion for the DOS is equal to σ . For $\sigma < 2kT$ and $EF > EF_{max}$ the carriers reside in localized states above the point of inflexion. In this region the DOS is not exponential. The carrier concentration was plotted against EF for various values of σ . The carrier concentration is exponentially proportional to EF for EF below EF_{min} . Above this value the carrier concentration becomes relatively linear with EF and after EF_{max} the concentration saturates before decreasing. The explanation for charge transport within a TFT polymer device should become clearer when the concentration is multiplied by the hopping rate which is the next part of this study. Ref: [1] R. Schmechel, Phys. Rev. B, 66, 235206 [2] D. Monroe, Phut. Rev. Lett 14th Jan 1985, p146. [3] S. Boranovskii, et al, J. Non-Cryst. Solids, 198-200, 222. [4] M. Visser, M. Matters, Phys. Rev B, Vol. 57, No. 20, p57. [5] S. Boranovskii et al, J. Non-Cryst. Solids, 190, p. 283.

M9.10

Screening Studies of Metal Chalcogenocarboxylates as Potential Precursors for Printed Chalcogenide Electronic Materials. Douglas L. Schulz, Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota.

Metal-organic ink systems targeted for low-temperature, atmospheric-pressure deposition of metal chalcogenide electronic materials are described. The approach was designed to allow direct write of active electronic components (i.e., diodes, transistors) for application as field effect transistors and x-ray detectors. The inks were comprised of metal chalcogenocarboxylates in non-aqueous solvents where the metal-organic was envisioned to transform at low-temperature (i.e., < 350 C) into a targeted chalcogenide phase with concomitant evolution of volatile byproducts. The synthetic route to five cadmium selenocarboxylates, four cadmium tellurocarboxylates and four zinc tellurocarboxylates will be described. Thermogravimetric analysis of these complexes indicates appreciable vapor pressure at ambient pressure, however, a complete transformation of the metal-organic complexes into volatile bis(acyl)chalcogenide plus the targeted metal chalcogenide was not observed for all complexes. While one purified cadmium selenocarboxylate complex exhibited the anticipated mass loss, thin films of CdSe produced from this precursor did not exhibit a field effect perhaps as a consequence of the use of non-optimum source and drain electrodes (i.e., Al). More recent results that utilize this chemistry will be presented as available.

M9.11

Mechanical Properties of Thin Films of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDT/PSS). Udo Lang and Juerg Dual; Center of Mechanics, ETH Zurich, Zurich, Switzerland.

In recent years there have been vast efforts to establish organic electronic devices. A key property of such devices is the possibility to fabricate them on flexible substrates. As the layers are mechanically stressed during bending, the knowledge of mechanical properties of the materials used will become very important. At the Center of Mechanics at ETH Zuerich a tensile test set-up had already been established and applied to experiments on silicon [1] and on thin copper foils [2]. It is based on a moveable z-stage to which the specimen is glued. The other end of the specimen is glued to a weight. This weight stands on a balance and is being pulled on vertically during testing. By measuring the reduction of weight the force acting on the specimen can be calculated with a resolution of $10e-5$ N. The dimensions of the specimens are measured using a UBM laser profilometer with a resolution of up to 100nm. The strain is determined by a least-square-template matching algorithm with a resolution of $10e-4$ [1]. BAYTRON P (PEDOT/PSS) was chosen for the experiments due to its widespread applications [3, 4, 5]. The fabrication of the specimens started off with pipetting 10ml of Baytron on a 3" polystyrol (PS) petri dish and then letting it air dry. After 24 hours a homogeneous layer of approx. 20microns was obtained. It could then be easily peeled off the substrate. Afterwards 150nm thick gold lines were evaporated on as markers for strain measurement. Finally the specimens were laser cut. The tensile tests showed two important results: PEDOT/PSS embrittles when exposed to UV radiation for a longer period of time and it exhibits a strong

dependence of its mechanical properties on relative humidity. The higher the relative humidity was, the lower was Young's modulus and tensile strength. This might be explained by the hygroscopic nature of PEDOT/PSS films. Actual values for Young's Modulus were in a range from 2 to 2.7GPa and for the tensile strength in a range from 20 to about 44 MPa. Additional preliminary experiments showed a Poisson's ratio of 0.36 for brittle behavior after exposure to UV radiation and of 0.44 for ductile behavior at higher relative humidities. References: 1. Mazza, E. et al., "Light optical deformation measurements in microbars with nanometer resolution", Microsystem Technologies 2 (2): 83-91 1996. 2. Simons, G. et al., "Investigating Size Effects on Mechanical Properties: Preliminary Work and Results for Thin Copper Foils", Materialsweek 2001, Munich, OCT 2001. 3. Elschner, A. et al., "PEDT/PSS for efficient hole-injection in hybrid organic light-emitting diodes", Synthetic Metals 111: 139-143 JUN 1 2000. 4. Ouyang, J. Y. et al., "High-performance, Flexible Polymer Light-Emitting Diodes Fabricated by a Continuous Polymer Coating Process", Advanced Materials 14 (12): 915-918 JUN 18 2002. 5. Stutzmann, N. et al., "Self-Aligned, Vertical-Channel, Polymer Field-Effect Transistors", Science 299 (5614): 1881-1884 Mar 21 2003.

M9.12

Processing, Morphology and Physical Properties of Functionalized Pentacenes. Jihua Chen¹, Sankar Subramanian⁴, John E. Anthony⁴ and David C. Martin^{1,2,3}, ¹Macromolecular Sci Eng, University of Michigan, Ann Arbor, Michigan; ²Materials Sci Eng, University of Michigan, Ann Arbor, Michigan; ³Biomedical Eng, University of Michigan, Ann Arbor, Michigan; ⁴Chemistry, University of Kentucky, Lexington, Kentucky.

We are investigating the variations in microstructure and physical properties of a family of functionalized pentacenes of interest for making organic electronic devices such as thin film transistors. These pentacenes have been modified with alkyl acetylene or alkyl silyl groups with systematic variations in the alkyl spacer length. This modification disrupts the herringbone packing seen in neat pentacene, promoting face-to-face arrangements between the acene rings and providing for solubility in a variety of convenient solvents. Thin films can be readily formed by solution casting from toluene and other organic solvents. We have investigated the structure and properties of the functionalized pentacenes using hot stage optical microscopy, differential scanning calorimetry, transmission electron microscopy, and electron diffraction. The materials show regular variations in their thermal behavior and macroscopic properties as the chemistry of the side-group substituent changes.

M9.13

Oligothiophene Semiconductors and Crosslinked Polymeric Dielectric Materials. A Synergetic Combination for High Performance Organic Thin-Film Transistors. Antonio Facchetti, Sara DiBenedetto, Joseph Letizia, Myung-Han Yoon, Hyuk-Jin Choi and Tobin J. Marks; Northwestern University, Evanston, Illinois.

The design and synthesis of new oligothiophenes functionalized with a variety of phenacyl, alkylcarbonyl, and perfluoroalkylcarbonyl is presented. These semiconducting materials exhibit low-lying LUMOs which allows efficient electron injection/transport. Field-effect transistors fabricated by conventional methods exhibit electron mobilities as high as $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for vapor-deposited film and $0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for solution cast films with current modulation of 10^5 . Furthermore, these materials perform optimally when integrated with a new crosslinked polymeric dielectric family developed by our group. These dielectric layers are fabricated via spin-coating of a polymer-crosslinker mixture, exhibit very low leakage currents ($J < 10^{-8} \text{ A/cm}^2$), very high breakdown fields ($> 3 \text{ MV/cm}$), and are fully compatible with both electron- and hole transporting materials allowing fabrication of complementary circuits.

M9.14

Comparing the Morphological and Electrical Properties of Spincoated and Inkjet Printed Films of Opto-electronically Active Iridium(III) Complexes using AFM Techniques. Elisabeth Holder^{1,2}, Dmitry Kozodaev^{1,2}, Emine Tekin^{1,2}, Veronica Marin^{1,2}, Bas G. G. Lohmeijer¹, Michael A. R. Meier^{1,2} and Ulrich S. Schubert^{1,2}; ¹Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; ²Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

The tuning and controlling the architectures of macromolecules is an important goal to determine materials structure-property relationship. Very recently, we have introduced metal-ligand complexes modified with supramolecular linkers giving rise to a metallo-supramolecular materials [1-3] that can be selectively complexed with a wide range of transition metal precursor complexes. This approach allows the construction of smart materials with tunable morphological and electrical properties. Moreover, the electrochemical and photochemical

properties of the utilized complexes can be engineered by choosing the appropriate ligands, metal ions and counterions. Iridium(III) complexes are popular for potential applications mainly in device and display technology but they may find also use in molecular electronics as well as in sensing technology.[4,5] Desired are phosphorescent emitters that favorably have high quantum yields and show lifetimes in the region of several microseconds. Furthermore, they need to be easy to process and do not aggregate. The chosen deposition methods as well as the conditions have also a strong influence on the film morphology and the obtained device performance. It was found that spincoated films display different morphologies compared to morphologies of inkjet printed films.[6] To analyze these differences atomic force microscopy (AFM) and conductive tip atomic force microscopy (c-AFM) was found to be a strong and complementary analysis tool. AFM is useful to obtain morphological and electrical information on a nanometer scale giving also raise on information regarding the structure-property relationship. Titanium nitride (TiN) coated tips worked best to achieve the desired information about the electrical performance (I/V characteristics) of the respective metallo-supramolecular films. This presentation highlights in detail the role of the deposition method for charged iridium(III) complexes. Optical features of the materials are briefly summarized. The processing properties using spincoating and inkjet printing are described and evaluated. The different morphology of the obtained films is shown comparing the two wet-processing methodologies (spincoating and inkjet printing) with respect to the resulting film quality and electrical conductivity using c-AFM. [1] E. Holder, V. Marin, M.A.R. Meier, U.S. Schubert, *Macromol. Rapid Commun.* 2004, 25, 1491. [2] E. Holder, V. Marin, A. Alexeev, U.S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* 2005, 43, 2765. [3] B.G.G. Lohmeijer, U.S. Schubert, *J. Polym. Sci. Part A: Polym. Chem.* 2003, 41, 1413. [4] E. Holder, V. Marin, D. Kozodaev, M.A.R. Meier, B.G.G. Lohmeijer, U.S. Schubert, *Macromol. Chem. Phys.* 2005, 206, 989. [5] E. Holder, B.M.W. Langeveld, U.S. Schubert, *Adv. Mater.* 2005, 17, 1109. [6] E. Tekin, E. Holder, V. Marin, B.-J. de Gans, U.S. Schubert *Macromol. Rapid Commun.* 2005, 26, 293.

M9.15

High-Speed GaAs Transistors and Circuits on Plastics.
Yugang Sun and John A. Rogers; Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

This presentation introduces a novel process for fabricating bendable GaAs transistors and circuits with high speed response on low-cost plastic substrates. In a typical process, arrayed micro/nanowires of GaAs, one of the most important semiconductor materials with high carrier mobility, have been fabricated through a 'top-down' process including both traditional photolithography and wet chemical etching. The aligned GaAs wires with organization similar to the layout defined by lithography can be transferred to unconventional flexible substrates (e.g., plastics, paper, etc.) using a 'dry transfer printing' technique, which requires elastomeric PDMS stamps as transfer elements. The GaAs wires on plastics can serve as unique channel materials for building metal-semiconductor field-effect transistors (MESFETs), which have the essentially same performance as wafer-based MESFETs. For example, MESFETs with channel length of 50 microns and gate length of 2 microns exhibit high-speed response as high as 1.55 GHz. A series of typical circuits elements are also demonstrated by integrating GaAs MESFETs with specific parameters. Mechanical characterization of the resultant devices and circuits on plastic substrates reveals that they can withstand surface strain of ~1% without substantial degradation of performance. The results indicate promise for the applications of the devices and circuits in consumer and military electronics systems.

M9.16

Ladder Oligo(*para*-aniline)s for Electronic Applications: Design, Synthesis, and Characterization. Salem Wakim^{1,2}, Nicolas Drolet^{1,2}, Ye Tao² and Mario Leclerc^{1,2}; ¹Department of Chemistry, Laval University, Quebec city, Quebec, Canada; ²Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada.

Organic field-effect transistors have received a great attention over the last 10 years because of their potential applications in low-cost fabrication devices. However, novel electroactive molecules are still required to solve important remaining problems which are: stability and processability together with good charge transport properties. One interesting approach is the development of ladder-type π -conjugated oligomers which show coplanar structure and favorable packing geometry together with improved stability and processability. Starting from this point, we have developed a new class of semiconductor organic materials from phenyl-capped ladder oligo(*p*-aniline) derivatives. The syntheses of these soluble ladder oligo(*p*-aniline) derivatives will be presented. The relationship between the chemical structure of these oligomers and their optical

and electrochemical properties, as well as their performances as active material in a field-effect transistor configuration will be also discussed.

M9.17

Studies of Printing and Electric Properties of conductive patterns Printed with Ag nanoparticles. Sung Il Oh¹, Kwi Jong Lee², Tae Hoon Kim² and Sung Nam Cho²; ¹Manufacturing Engineering Team, Samsung Electro-Mechanics, Suwon, Gyunggi-Do, South Korea; ²Central R&D Center, Samsung Electro-Mechanics, Suwon, Gyunggi-Do, South Korea.

Recently, in response to the request of low cost manufacturing process for electronic industry, printing technologies have been arousing many interests. Printing technologies, especially direct writing, when it is utilized to make certain patterns, conductive paths, complicated electrodes etc., can eliminate high cost photolithographic process. Printing technologies, however to be applied to electronic industry featured as downsizing and high performance, should satisfy high printing quality and good electric properties. In this study, our group studied the features of printing quality and electric property of conductive patterns printed with Ag nanoparticles. To proceed this study, we synthesized Ag nanoparticles with various particle sizes and formulated pastes dispersed in different kinds of solvents for printing on polyimide substrate. We could find out that dispersion media and sintering process affected printing quality and electric conductivity. By controlling the type of dispersion media, solid contents and sintering temperature, we could obtain a fine conductive line width of 100 μ m as well as a high conductivity of $9.0 \times 10^{-6} \Omega$ cm.

M9.18

Facile Synthesis of Silver Nanoparticles by Thermal Decomposition Method Useful for Metal Nano Ink.
Youngil Lee, In Keun Shim, Kwi Jong Lee and Jae Woo Joung; R&D Center, Samsung Electro-Mechanics, Suwon, Gyunggi-Do, South Korea.

Ag powders having a very fine and uniformly distributed sizes are desirable in many fields of industrial applications. One such example would be as the major constituent of conductive inks and pastes for various electronic components. In this study, Ag nanoparticles with narrow particle size distribution was simply synthesized by thermal decomposition of various Ag-alkanoate(laurate, myristate, oleate)complex, which was prepared by a reaction with AgNO₃ and sodium alkanoate in water solution. The resulting alkanoate stabilized Ag nanoparticles were produced by controlling the temperature and time. Transmission electron microscopic images of the particles showed a 2-dimensional assembly of the particles with a diameter 3~8nm according to a kind of alkanoate. Also Ag thin film spin cast from metal nano ink prepared by alkanoate stabilized Ag nanoparticles showed good electrical conductivity.

M9.19

Low Temperature Fabrication of Al₂O₃ on Cu for Embedded Capacitors. Jun hee Bae, SooHyun Lyoo, Sung Taek Lim, Hyun ju Jin, Hyung-dong Kang and Yul gyo Chung; Central R&D Institute, Samsung Electro-mechanics, Suwon, Gyunggi-Do, South Korea.

Today's electronic devices require increasing functionality and speed to meet the consumer demands and consequently need more and more passives along with powerful actives. The conventional surface mounting technique therefore faces the circumstance that the number of passives limits the size of the printed circuit board (PCB) and thus of the devices. One measure to handle this drawback is using the spaces below the surface to embed passives into the PCB. However, the process temperature limited up to 250 C due to the use of polymeric basis is still the main obstacle in the build-up of embedded passives. We prepared Al₂O₃ thin film capacitors using atomic layer deposition (ALD) at temperatures below 200 C. We used copper clad laminate (CCL) as a substrate, the material which serves as a substrate in the real fabrication process. The thickness of Al₂O₃ films was varied 50 to 100 nm. We monitored the film structures using TEM and showed the electrical properties of the dielectric films in dependence on both film and electrode structures. We measured the capacitance density of nearly 1 nF/mm². Al₂O₃ films show an excellent leakage behavior and will be one of the best candidates for the embedded capacitor application. *Corresponding author: hyungdong.kang@samsung.com

M9.20

Organic field effect transistors using metal complexes.
Tomohiro Taguchi, Hiroshi Wada, Takuya Kambayashi, Bunpei Noda, Masanao Goto, Takehiko Mori, Ken Ishikawa and Hideo Takezoe; Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan.

Recently organic field-effect transistors (OFETs) have attracted a great deal of attention [1]. In particular, development of good N-type

materials is imperative because both P and N-type semiconductors are necessary to construct low power complementary circuits [2]. However, N-type organic semiconductors which work in air are very few. In this respect, we have explored OFETs using metal complexes because a wide range of reduction potentials is known in metal complexes, and stable anionic compounds are easily accessible. Bis(4-methyl-1,2-phenylenediamino) nickel [Ni(mpa)₂] [3] and bis(dithiobenzyl) nickel [Ni(tb)₂] [4] were investigated. The oxidation potential of [Ni(mpa)₂] to a monocation (1+) was observed at 0.00 V vs Ag/AgCl. Whereas the reduction potential of [Ni(tb)₂] to a monoanion (1-) was reported to be +0.12 V [5]. The former value corresponds to the location of the HOMO level to be 4.44 eV, and the later value indicates that the LUMO level of [Ni(tb)₂] is 4.32 eV [6]. Therefore, [Ni(mpa)₂] is expected to work as a P-type semiconductor, while [Ni(tb)₂] works as an N-type semiconductor. Bottom contact-type OFETs were fabricated on n⁺⁺-Si substrates with thermally grown SiO₂. Au (work function: 5.1eV) was used as source and drain electrodes for the [Ni(mpa)₂] transistor, whereas Al (work function: 4.1eV) was used for the [Ni(tb)₂] transistor. Organic semiconductors were thermally evaporated on the substrates. Transistor characteristics were measured by Keithley 4200-SCS semiconductor parameter analyzer. After thermal evaporation of the metal complexes, the substrates were once taken out from the evaporation chamber and transferred to a measurement chamber. Then field effect mobilities in air and under vacuum were compared. [Ni(mpa)₂] showed P-type transistor characteristics with $\sim 10^{-4}$ cm²/Vs in air, and $\sim 10^{-5}$ cm²/Vs (on/off ratio, 10⁴) under the vacuum of 5.0×10⁻⁶ Torr. By contrast, [Ni(tb)₂] exhibited N-type characteristics with $\sim 10^{-6}$ cm²/Vs even in air, and the mobility increased to $\sim 10^{-5}$ cm²/Vs with the on/off ratio of 10² under vacuum. The present work demonstrates that some metal complexes, which are easily reduced to form stable monoanions, are good candidates of N-type organic semiconductors used in OFETs. [1] a) B. Crone et al., *Appl. Phys. Lett.* **78**, 2229 (2001). b) C. D. Dimitrakopoulos et al., *Adv. Mater.* **14**, 99 (2002). c) A. Kraft, *Chem. Phys. Chem.* **2**, 163 (2001). [2] B. Crone et al., *Technical Digest – International Electron Devices Meeting* 115 (1999) [3] S. H. Kim et al., *Dyes and Pigments*, **8**, 381 (1987). [4] G. N. Shrauzer et al., *J. Am. Chem. Soc.* **87**, 1483 (1963). [5] J. A. McCleverty, *Prog. Inorg. Chem.* **10**, 49 (1968). [6] Hong Meng et al., *Chem. Matter.* **15**, 1778 (2003).

SESSION M10: Soft Lithography and PDMS Applications

Chair: John A. Rogers
Thursday Morning, December 1, 2005
Room 306 (Hynes)

8:00 AM *M10.1

Optics and Microfluidics. George Whitesides¹, Dmitri Vezenov¹, Brian Mayers¹, Richard Conroy², Daniel Wolfe¹, Mara Prentiss², Piotr Garstecki¹ and Sindy Tang¹, ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Department of Physics, Harvard University, Cambridge, Massachusetts.

The combination of “light” and “microsystems” provides many opportunities for new types of devices and capabilities. This talk will focus on three subjects in fluidic optical devices: i) liquid core/liquid cladding optical systems; ii) spectrally dispersed optical detectors for microfluidics; and iii) optical diffraction from flowing lattices of bubbles.

8:30 AM *M10.2

A New Roadmap: Macro and High Performance Devices via Printing. Ralph Nuzzo, Materials Research Laboratory, University of Illinois, Urbana, Illinois.

The emergence of new forms and applications of electronics presents both opportunities and challenges for developing new approaches to materials patterning. This talk will explore these issues in the context of recent advances made in Soft-Lithography and materials assembly, methods that allow the removal of design rule constraints for devices that are intrinsic to patterning protocols based on photolithography. New forms of materials for applications in electronics, processes for integrating them in complex functional arrays, and the development of a new model for fabrication based on both bottom-up and top-down approaches to large area patterning will be discussed.

9:00 AM M10.3

Rate-controlled Transfer Printing of Solid Objects. Matthew Meitl¹ and John A. Rogers^{1,2}, ¹Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana,

Illinois; ²Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

In the context of printing materials with a rubber stamp, specific chemical interactions or nonspecific forces usually govern the transfer of inks. When the ink takes on solid character, the rate-dependent adhesive nature of the rubber stamp arises as another factor that can facilitate or impede transfer. This talk will demonstrate that the stamping rate, or the speed at which a stamp separates from a substrate, can control the stamp's ability to grab and release small solid objects. This phenomenon can be exploited to transfer arrays of micro objects between substrates without surface treatments or conformable glues and generate microstructured hybrid materials systems for optoelectronics, photonics, non-planar applications, and more. Examples of materials printed by this new rate-dependent stamping strategy will include silicon, III-V materials, silica microspheres, mica, graphite, and biological objects.

9:15 AM M10.4

Patterned Flat Stamps and Catalytically Active Stamps for Improved Microcontact Printing. Jurriaan Huskens,

¹Supramolecular Chemistry & Technology, University of Twente, MESA, Enschede, Netherlands; ²Strategic Research Orientation “Nanofabrication”, University of Twente, MESA+, Enschede, Netherlands.

Microcontact printing (mCP) is a versatile technique for the creation of patterned surfaces [1]. It commonly employs flexible, elastomeric relief stamps to transfer an ink (e.g. a thiol) onto a surface (e.g. a gold-coated substrate) thus forming a patterned self-assembled monolayer (SAM). Patterns of different thiols can be created using self-assembly of a second thiol from solution, or the printed patterns can be used directly as etch resists allowing the structuring of the underlying substrate itself. Resolution of mCP is typically around 200 nm, diffusion of the ink during the printing stage and deformation of the elastomeric stamp features being the main limiting factors. Diffusion can be limited when heavy inks are used, such as high-molecular-weight thioethers, proteins, or nanoparticles. Stamp deformation can be controlled to some extent by using stiffer stamp materials and hybrid stamps. The present study will show radical solutions to both problems. The first is the complete elimination of diffusion as an underlying principle of mCP. We have shown recently that nanoparticles can be coated with catalytically active acid groups to hydrolyze protecting silyl ether groups on a homogeneous SAM when transferred onto this SAM by mCP [2]. This has led to patterned SAMs with an edge resolution below 100 nm. Based on this catalytic principle, we will show that oxidized [3] and catalyst-functionalized PDMS stamps can catalytically cleave the same silyl ether groups of these SAMs in an ink-free mCP process, thus removing all possible ink diffusion. The stamp feature deformation problem is eliminated by the use of patterned flat stamps [4]. It is shown that patterned oxidation of flat PDMS, followed by functionalization with silanes can lead to chemico-physical barriers for ink transfer on the stamp surface, rather than the commonly applied void barriers present in relief stamps. This allows high resolution mCP and the use of inks that cannot be applied in regular mCP. [1] Xia, Y. N.; Whitesides, G. M. *Angew. Chem. Int. Ed.* **1998**, *37*, 551-575; Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J.-P.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. *IBM J. Res. Dev.* **2001**, *45*, 697-719. [2] Li, X.-M.; Paraschiv, V.; Huskens, J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2003**, *125*, 4279-4284. [3] Li, X.-M.; Peter, M.; Huskens, J.; Reinhoudt, D. N. *Nano Lett.* **2003**, *3*, 1449-1453. [4] Sharpe, R. B. A.; Burdinski, D.; Huskens, J.; Zandvliet, H. J. W.; Reinhoudt, D. N.; Poelsema, B. *J. Am. Chem. Soc.* **2005**, *127*, in press.

9:30 AM *M10.5

Charge Transport at Organic-Organic Heterointerfaces.

Henning Sirringhaus, Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Polymer transistors offer new opportunities for the controlled manufacturing of active electronic circuits by a combination of solution processing and direct printing. We will review current understanding of their device physics with a particular emphasis on understanding the electronic structure of the interface between the organic semiconductor and the gate dielectric. Recent advances towards realizing ambipolar organic transistors through control of interface electronic structure will be presented. This has enabled realization of ambipolar light-emitting field-effect transistors, in which the position of the recombination zone can be moved to any position along the transistor channel by varying the applied gate, and source-drain voltages. We will also review recent progress towards manufacturing of organic transistor circuits by high-resolution printing techniques.

10:30 AM *M10.6

Silicone for Advanced Lithography. Anne Shim¹, John Rogers² and Ralph Nuzzo²; ¹Dow Corning Corporation, Midland, Michigan; ²University of Illinois, Urbana-Champaign, Illinois.

Silicones are commonly used for a group of advanced lithography techniques termed soft lithography and nanoimprint lithography. Soft lithography can again be subdivided into techniques such as micromolding, microcontact printing and replica molding. The silicone material used in the process is enabling for all of these soft lithographic techniques. Dow Corning desires to participate in the emerging soft lithographic industry by supplying value added materials to enable the process and the final device. To that end, Dow Corning has established an Advanced Lithography project. This presentation will discuss utilization of silicones to meet the emerging needs of the advanced lithographic industry.

11:00 AM M10.7

The origin of large elastic stretchability of thin gold films on elastomeric substrates. Stephanie Perichon Lacour¹, Donald Chan¹, Sigurd Wagner¹, Teng Li² and Zhigang Suo²; ¹Electrical Engineering, Princeton University, Princeton, New Jersey; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Thin gold films patterned on soft elastomeric substrates produce highly stretchable conductors. These can be used as interconnects in elastic electronic circuits. Such circuits typically will be stretched and relaxed reversibly. We studied the microstructure and electrical resistance of 25nm thick gold films on elastomeric silicone substrates during cyclic mechanical loading. Our films on silicone consists of a contiguous gold network that contains micron scale cracks. The metal network is well bonded to the silicone substrate. The cracks render the gold film particularly stretchable and make the electrical resistance change reversibly during cyclic mechanical loading. We observed the morphology of the gold conductors prior to, during, and after mechanical stretching using scanning electron microscopy (SEM). 2cm long samples were elongated in a mechano-electrical tensile test apparatus to a strain $\epsilon_{max} = 32\%$ with strain increments varying from 1, 4, 8, 16 to 32%. All samples remained electrically conducting. The electrical resistance at ϵ_{max} increases when the strain is raised in large strain increments. A conductor was cycled 100 times to $\epsilon_{max} = 32\%$ in strain increments of 8%. The variation in electrical resistance correlated with the mechanical cycles. The minimum and maximum values of the electrical resistance, at 0% and 32% strain respectively, remained essentially constant over the 100 cycles. During the first stretching cycle, several neighboring micro-cracks merged to form $\sim 5-10\mu m$ long scratches running perpendicularly to the stretching direction. In situ SEM during the second cycle and after 100 cycles revealed almost no further development of the gold microstructure. The metallic film appears to behave similarly to an accordion upon stretching and relaxation, and deforms only elastically. Most of the elongation is then accommodated by the out-of-plane deflection and opening of the micro-cracks. Our observations suggest that highly stretchable electrical conductors for elastic electronic surfaces can be designed of a variety of metals.

11:15 AM M10.8

Design Aspects of Multi-user 3D Displays using Deformable Lenticulars. Mostafa El-Ashry and Henry Daniel Young; Dept. of Mech. and Mat. Eng., Wright State University, Dayton, Ohio.

A new optical technique to accurately steer the light beams to demonstrate a virtual 3D picture for multi-users is presented. This technique utilizes a deformable lenticular, fabricated from transparent silicone elastomer-polydimethylsiloxane (PDMS), placed directly on the LCD display. Different designs were explored where the elastomer is deformed in a curved manner. The curved surface steers the beam in different directions depending on the radius of the curvature and the position of the light beam. Stress induced birefringence, time response, mechanical properties and the effect of fatigue on the optical properties for various compositions of the PDMS lenticulars are investigated. This novel approach opens up the possibility of designing and manufacturing of new type of 3D lenticular based displays.