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, and 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, as well as focus on new patterning strategy by using the “tailored” adhesions as the patterning-driven force.

Instructors:
L. Jay Guo
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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 Joules1, Michael D. Austin1, Nihan Li1, Xiaogang Li1, Haixiong Ge1, Zenfu Fu1, Keith Morton2, Hua Tao3, Wei Zhang2, and Linshu Kong2
1Department of Electrical Engineering, Princeton University, Princeton, New Jersey; 2Nanoxon Corporation, Mountom 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 μm Cu-pair (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 the transferred 6 nm half-pitch gratings on the mold into in NX-2000 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/Al0.5Ga0.7As layers on hydrofluoric acid. Second, to test NIL capability of making complex patterns, we fabricated SRAM cell metal layer of the 0.04 μm Cu-pair (20 nm half-pitch) (Fig. 2). The mold was fabricated in silicon dioxide using 35 kV electron beam lithography with polyisoprene as a negative resist and reactive ion etching. The imprint showed an excellent circular standard (CD) control of 1.3 nm, and wafer yield of 100%. 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 Carlsberg2, Richard Bunk1, Mark Sundberg2, Jenny Rosengren2, Ian Nichols2, Sven Tagedu2, Alf Mansson2, Waldemar Hallstrom1,3, Christelle Prinz1, Fredrik Johansson1,3, and Martin Kauje1,2
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), 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 area of science the challenge 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. 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 are currently working with in this area. The first one concerns the successful creation of a nano-scale system employing 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 (trimethylchlorosilane) functionalization of the exposed SiO2 surface, 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 present various forms of transport structures such as microarrays, injectors, roundabous, crossings and components directing the flow of motor proteins with a control at the nanometer scale. Further, we will discuss about the potential for using such a system for high-throughput drug screening. In the second project we have studied the interplay between nerve cells and nanotextured surfaces. The surfaces being investigated have 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 Swedish 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. 70 (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: 5557. M. Sundberg et al. Analytical Biochemistry, 323 (2003) 127-134. R. Bunk, J. Kluth, J. Rosengren, I.A. Nichols, S. Tagedu, 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 integration in 1-D nanomaterials such as electronic components into flexible, high transport mobilities and unique optoelectronic and piezoelectric properties. However, the direct synthesis of these materials on polymer substrates is challenging due 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 they avoid address substrate-to-substrate incompatibility. 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 nanomaterials. The nanomaterials were embedded into the polymers near the glass transition temperature, resulting in the simultaneous transfer of the microtextured features and nanomaterial patterns with resistances between 1-5000 kΩ. Thus, the method shows the ability to directly lithographically printed electronic components from nanomaterials onto polymer 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 film with gold and applying a voltage 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 ionic mass analyzers for MEMS sensor arrays. Further 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 nanomaterials into flexible 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 catalysts can be used to control the synthesis of disimilar materials on the same masters will be discussed.

9:15 AM *M1.4 Chemical Nanopatterning via Nanoimprint Lithography for Liquid Crystal Displays, Sungsoon Park1, Helmut Schift2, Celestino Padoce2, Jens Gobrecht2, Toralf Scharf2, Joachim Grupp2 and Naci Basturk3,1 Mechanical 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 possibilities for interdisciplinary nanomaterials research, particularly in the areas where two-dimensional nanomaterials are required, such as optoelectronics, photonics, and bioengineering. One potential application belonging to the abovementioned categories is liquid crystal aligned 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 with structures, which are keys for the next generation LC displays. The concept of using nanoparticles for achieving a high functionality is a promising technology that 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 nanomaterials. 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 nanoparticles as LC alignment structures. The alignment of the LC polar orientation depends on the ratio of the hexagonal/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 size of the chemical pattern indicates a good 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 Lithography, 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 nanoscale features that precision in the past was not possible. 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 temperature. However typically due to the viscosity of the heated polymers remains high and thus the imprinting process requires significant force. 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 standard printing technique. The simplicity and characteristic 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 nanomaterials into flexible 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 catalysts can be used to control the synthesis of disimilar materials on the same masters will be discussed.

10:30 AM *M1.6 Nanoimprint Lithography for 3D Nanopatterning, Cheil Jometalohmgro Torres, Marc Zelmann, Nikolas Kehagias and Clas Jeppesen, 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 reversable 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., Sakaai, 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/thermal switching in optical information systems. To realize 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 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 bowed 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. Palmeri1, Jinjuan Hao1, Yukio Nishikawa2, Colin Flannery3, Michael D. Strojwas3, Andrew S. Chan1, Bin Li2, Soo Young2, Bruce Chao3 and C. Grant Wilsson1, 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 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 fabrication cost and 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, although not forming homogeneous 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 the fabrication of nanoscale arrays. These 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 the polymer, the second one of the POSS SFIL parallelizes 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 cured resin such as elastic constant, thermal shrinkage, elastic modulus, Poisson’s ratio, CTE, and water sorption are discussed as well.

11:45 AM M1.9
Harry Dwight Rendall1, William P. King1, Amy C. Sun2 and P. Randy Schunk2, *1Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2Materials & 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 polymer flow during NIL examine rectangular cavities embossing a Newtonian fluid under viscous-dominated conditions. Simulations vary mold geometry parameters of indenter width $W$, cavity width $W$, and cavity height $h$, as well as initial polymer film thickness $h$, 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 $W/h$, and always occurs when $W/h < 1$. 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 $W/h > 1$, where it is independent of $W/h$. By determining the proper flow mode based on mold geometry and polymer film thickness ratios, a characteristic NIL velocity $V_{NCL}$ can be identified, allowing establishment of NIL embossing design rules based on NIL critical number $CN_{NCL}$, dimensional flow ratio $W/h$, and polymer supply ratio $s/h$. 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-Landas-Ferry-Carruto 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.

I will present recent examples of work from my laboratory on the situ fabrication of nanoscale structures of novel synthetic polymer brushes, stimulus responsive polypeptides and nucleic acids, with the goal of developing and assembling of use tools for bionanofabrication. In the first example, I will describe the fabrication of stimulus responsive polypeptide brush by DPN that can be used to capture surface-initiated polymerization will be described, and the extension of this methodology to the microscale by soft lithography and the nanoscale by DPN. These nanometer thick polymer brushes show extraordinary resistance to protein adsorption and the attachment and provide a powerful platform to examine the interaction of cells with biochemical and topographical cues at length scales ranging from the nanoscale to microscale. In the second example, I will use 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 assemblies 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.
Jinghao Guan1 and L. James Lee1, 2. *1Center for Affordable Nanoeengineering of Polymer Biomedical Devices, The Ohio State University, Columbus, Ohio; 2Center for Affordable Nanoeengineering of Polymer Bioelectronic Devices and Biomedical 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 2000-20000 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 (oligonucleotides) are synthesized in parallel and later assembled in longer constructs. Using light-directed synthesis of the oligomers, hundred of thousands of different short sequences (40-70 bp) can be created in a few hours. After amplification, these sequences can be assembled in longer units in a hierarchical, multi-stage process. The final product – a synthetic DNA – 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 accuracy of errors found in the sequence of synthetic DNA. Many of the 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 transfection, and purification of the oligomers, with biological and statistical methods for error removal. In the presentation we will focus on light-directed
M3.4 Fabrication of Patterned Apatite by Electrophoretic Deposition. Seiji Yamaguchi, Takeshi Yabutsuka, Mitsuhiro Hibino and Takeshi Yos; 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 bioactivity 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 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, 20 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– = 180.0, HPO42- = 7.0, SO42– = 0.5 mmol dm–3; pH = 7.0) 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 over 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.

M3.5 Biphasic Ceramic Lattices for Bone Repair. Hongyi Yang1, Julian R. G. Evans2, Shoufeng Yang3, Xiaopeng Chi4, Ian Thompson5, Richard James Cook6 and Paul Robinson7; 1Materials Department, Queen Mary University of London, London, United Kingdom; 2GKT Dental Institute, Kings College, London, United Kingdom.

Porous biphasic 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. Biphasic 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 vasculization and hard tissue development respectively, and the overall shape controlled. The organic content was removed before sintering. Characteristics of the sintered biphasic ceramic scaffolds were studied.
microhardness of all the alloys was also measured. Using the linear and cyclic polarization curves [2] and electrochemical impedance spectroscopy measurements, the corrosion mechanisms 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, where the passive film adherent to the underlying substrate (high potential) pitting corrosion appears to be specific for Wiroloy while the other alloys show a generalised corrosion. References: [1] Grosgeot B., Reclaú L., Lisser M., Dalarad F., Biomaterials 20, 933 (1999). [2] García J.R., Alcalde J.L., Rojo J.W., Bioelectrochemistry 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 Roza1, Domingo Herrera Santana2 and Heinz Stumm3. Mechanical 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 purpose 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 for Non-Standard) 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 fluorides 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 behavior 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.


Calcium oxide monohydrate (COM) is the main inorganic component of dental plaque. To understand how organic functional groups can promote COM nuclei formation, and how impurities interact with the different faces of the crystals, it is better to 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 is determined by directly dosing 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 topographically functionalized areas of SAMs. The patterns were used to control the 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 microscopes. We propose that this method can be utilized to create 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 apically without having to manipulate the microscope. Further 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 acid molecules on W.S., Rondelli, G., Torricelli, P., Fini, M., Giardino, R., Biomaterials 26, 739 (2004)

M3.7 Method for the investigation of the relaxation time and viscosity of embossable films. Maud Forest1, Elin Sonderegår1, Etienne Barthel2, Caroline Heitz2 and Lena Saint Marcay2. 1Laboratoire du Surface du Verre et Interfaces, UMR 125. CNRS/Saint-Gobain, Aubervilliers, France; 2L’optique, 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 resist is 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 been done directly on the embossable thin film system. Unfortunately there is currently no single characterisation method allowing for quantitative mechanical measurements on fairly 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 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 charging regions inside the topography. 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 silver and metallic nanoparticles into the topside areas. The strength and lateral dimensions of the inbuilt potential has been characterized using scanning probe based methods. The fringing fields were confined to 50 nm sized areas and exceeded 1 MV/m

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Fibers with multiple radial alternating submicron layers of high index amorphous silicon oxynitride and low index germanium oxide have 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 the new degree of freedom provided by the geometry of the 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 high photon density of states (DOS). This type of all optical fiber demonstrated a 2 nm optically induced reversible shift of a cavity resonant mode at 1.55 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 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 Marin1,2, Elisabeth Holder1,2, Martijn M. Wienk2,3, Dmitry Kozodoev1,2 and Ulrich S. Schubert1,2; 1Institute of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), Eindhoven University of Technology (TU/e), Eindhoven, Netherlands; 3Institute of Molecular Materials and NanoEsystems, 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 photocatalysts. [1] Two distinct approaches can be considered when ruthenium(II) poly(pyridyl) complexes are employed: bulk heterojunction solar cells (BHSCs) and dye-sensitized solar cell (DSSC) devices. Ruthenium(II) tripyridyl complexes can successfully act as p-type materials since they display suitable photophysical, photochemical and electrochemical properties. [2] The metal-to-ligand charge-transfer (MLCT) and ligand-centered excited states of these complexes are known to have led to a large variety of electronic and optical properties 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, ruthenium(II) complexes with a flexible polymer backbone (aggregation is prevented and the physical features of the complex are maintained). [3] The ruthenium bispyridyl complexes with polymeric tails may be potential candidates for the fabrication of rapid prototyping. Although DSSCs show 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 this 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 >5% in full sunlight. [4] Recently, Kim et al. reported successful results on the fabrication of a quasi-solid-state solar cell. [5] A 12 cm2 device with a ruthenium(II) bispyridyl complex as donor material showed an efficiency of 1.2% (2.6% with the ruthenium(II) complex). [6] This development is motivated by the fact that the material can be readily adapted to form thin films and is not sensitive to humidity. [7] This work is supported by the Dutch Polymer Institute (DPI) and the Dutch Ministry of Education, Culture and Science (OCW). The authors thank C. J. J. Janssen and P. E. M. Meijer for their contributions to this work.

M3.11 Synthesis and Electrical Behavior of Silver Nanoparticles Stabilized with Bina2-4. Chi Jin, Jong Lee and Jae Woo Joung; Central R&D Institute, Samsung Electro-Mechanics, Suwon-Si, Kyungki-do, South Korea.

Silver nanoparticles have been frequently used 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 dichloromethane (DCM) as a solvent and a successful synthesis of silver nanoparticles stabilized with binary capping molecules was characterized through X-ray diffraction, UV-Visible spectra, Fourier transform infrared, transmission electron micrograph and elemental analysis. Furthermore, sintering and electrical behavior 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. Photoactive titanium (IV) complexes with increased 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, X-ray 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 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 presented to explain the photodecomposition of titanium (IV) 2-ethylhexanoato n-butoxide. Product results 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.


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. By using a homogenous polyelectrolyte solution and an 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 size and 2-D arrangement of metal nanotubes could be achieved by using patterned silicon substrates as replication masters. The fabricated nanotube membranes not only in sputter deposition of metals and ferroelectric materials to generate 2-D arrays of nanodots with tunable dot size, but also in photolithography 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 photoelectrochemical techniques with the localized 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 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


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, Gyeonggi-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, amorphophilic polymer etc.) and a few solid loading contents that amount only to 10-5~10-3 M. 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 mercaptoauric 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 agglomeraion 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, 2, 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 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 yield 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 Doeta1, Ingolf Hennig1, Peter Eckerle1, Arved C. Huelber2,2, Heiko Kempa1,1, Howard E. Katz2, Matthias Bartzsch2, Njole Brandt2, Uta Fuegmann2, Subramanian Vaidyanaathan2, Jimmy Granstrom2, Sen Liu2, Tino Zöllner1, Georg Schmidt2, Elisa Reichnann3, Thomas Weber1,1, Franke Richter2, Thomas Fischer3, Ulrich Hahn4, BASF 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 throughputs and high resolution. Therefore, offset and graving 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 production oriented offset printing approach, integrating the necessary logic capabilities 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(3,4-ethylenedioxythiophene-co-bithiophene) (P3TF2) which was deposited by a carefully adjusted graving 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 graving 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 VDD ≥ 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 10⁻² cm²/Vs 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 Patternning 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 's' 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 solvolysis). After the mask is removed, the resist in 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.
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 when optical breakdown is used in 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 using the features of the order of 100 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 requires fundamental questions about the mechanism of OCI optical breakdown. Foremost from the viewpoint of practical applications and theory are the ultimate physical limits in 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 setting the limits of material 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 high-energy microscale machining, bubbles can diminish the accuracy due to unintended damage associated with the 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 structures 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 Dip Pen Nanolithography
Paul E. Sheehan1, Minchul Yang1, Arnaudo R. Laracuente1, Brent A. Nelson2, William P. King2, and Lloyd J. Whitman2
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 affect the surface, thereby allowing in situ confirmation of the deposition 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 but which has been traditionally poly(3-dodecyl thiophene), 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 the surface of gold and silicon, enabling 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 UV, 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 Silicon Films and Micro-Machining via Hydrogel Stamping
Stoyan K. Smoukov, Christopher J. Campbell, Kyle J. M. Bishop and Bartosz Gryzbiowski; 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 polymer materials. Patterns are etched into the surface 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) of 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 the substrate. Besides etching, control over reaction geometries and fluxes allows doping 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.

10:15 AM M4.5
Rigiflex Lithography: Nano-Patterning and Printing
Hong H. Lee, Dongchul Suh, Dahl-Yeong Khang, Hyunskil 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
Couomb-force Directed Assembly and Transfer of Nanomaterials
Chad R. Barry1, Aaron M. Welle1, Thomas J. Hatch2, Uwe Kortshagen1, Stephen A. Campbell3 and Heiko O. Jacobs4,5; 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 control nanomaterials 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 phase that uses a transparent polymer 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 polymer 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 Louise2, Paul V. Braun1, Shauhe 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 silicon CVD method and etched by wet chemical methods to produce 3D hollow-woodpile and inverse woodpile structures.
structures. The optical properties of the resulting structures are measured after each processing step to identify the effects of their geometry, and make 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 Menon1,2,
Michael Walsh2, David Chao1, Amir Patel1 and Henry J. Smith1,2
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 photosensitive 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 and repeatable 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 lithography 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 photosensitive 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. In this presentation, we will discuss the methods by new cross-linkable photopolymers materials and processing methods that can be used to make MEMS and microfluidic devices and which are compatible with conventional microelectronics fabrication techniques. Recently we have developed a variety of the above-photopolymer material 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 processing methods by developing new cross-linkable versions of our photodefined sacrificial polymers that can be used like a conventional photosensitive droplets to mold and plate-up MEMS structures. Furthermore, these polymers continue to be layered on top of the MEMS device, 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 the desired profile without leaving behind, thus releasing 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. Anna Claudia Ares, Friedric Eidscott and Robert Street; Palo Alto Research Center, Palo Alto, California.

Polymeric materials have created interest in the application of 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 polyurethane derivatives, P3HT and PQT-12, used to fabricate thin film transistors (TFTs).

The polymer films were self-encapsulated by depositing the semiconductor blend and 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. Both P3HT and PQT-12 are compatible with inkjet printing and allowed the fabrication of 100x100 pixels (more than 16000 TFTs) array for display backplanes. The self-encapsulating process also improves the integration of printed TFT backplanes with display technology. We show that the performance 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, Alistair Buckley2, Monika Voigt2, Carsten Giebeles2, Karl Boeslheim2, Jeff Wright3, Phil Readman2 and Jim Frieret2
1Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom; 2MicroEmisive 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 conjunction with the use of water-soluble sacrificial-resists that we use to pixelete 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. 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-abstracted to define the eventual location of the next set of sites. This re-abstracted and a second LEP is coated onto the surface of the LEP. The 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 polymer and resist. Furthermore, we show that the laser can be used selectively remove a conjugated polymer from a PEDOT:PSS surface without causing any appreciable damaging the 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 define feature sizes that are only limited by optical-diffraction. Laser-ablation machining can also be used to pattern microchannels, potentially 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 polymer materials together to create new types of miniaturized chemical sensors and micro-machines.

2:15 PM M5.3

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. Its shown that this approach yields novel nanocomposite materials with controlled optical properties such as refractive index, birefringence, chromatic dispersion and birefringence dispersion. The nanocomposites 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 Kopela, 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 know how of the potential of the roll-to-roll printing techniques for the volume-scale active device fabrication will be demonstrated.

4:00 PM M5.5

An aluminium-laminated polyethylene terephthalate (AI-PET) is used as the substrate for flexible organic light-emitting devices (OLEDs). The efficient light-emission devices have a half-wavelength OLED architecture. An acrylic layer is formed on the AI-PET surface to improve the surface morphology and also the adhesion between the substrate and the anode. Poly(styrene sulphonate)-doped poly(3,4-ethylenedioxythiophene) was used as hole transporting layer. The light-emitting polymer used is a phenyl-substituted poly(p-phenylenevinylene). Bilayer anodes of Ag/CFx 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 aluminium 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-embedding electroluminescent devices on Al-PET foil can be bent to a substantial degree without breaking.

4:15 PM M5.6

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 semiconducting thin films 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 luminescence-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 that control it govern the photodiode 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 microscopes 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 esteemed 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

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 (SiO(Si) 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 detectable 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 in 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 Printatable Silver Nanoparticles as an Electrode. Yuko Okuno, 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) (P3T6) 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-CN) buffer layer. The buffer layer acts as a barrier layer to prevent Ag nanoparticles from penetrating into the organic layer. The a-CN layer was formed by a damage free sputtering system, whose layer thickness was 10 nm. The P3T6 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
High-Resolution Photolithographic Patternning 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 Donald D. C. Bradley1; 1Physics Department, Imperial College London, London, United Kingdom; 2Department of
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. One advantage of organic thin films is 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 the creation of intricate planar 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 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 as anode.

These results confirm that our new patterning method is well suited to the fabrication of high quality polymer optoelectronic devices on flexible substrates.


Organic light emitting devices (OLEDs) are promising for solid state lighting and display applications. In traditional OLED devices, transparent indium tin oxide (ITO) is the predominantly used material for the anode. However, the discovery of enhanced transmission in relatively thick nanostructured noble metal films has motivated the exploration of potential applications as a new type of anode for OLEDs. 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 devices using ITO anode indium and oxygen can migrate from ITO to organic semiconductor causing device degradation; (2) 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 resonance to non-destructively monitor and control the current.

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 metal structure consists of periodically perforated holes or gratings of various periodicities. The grid pattern for nanoimprint was either directly written by electron beam lithography or by nanoimprint 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 metal thin film and spin coating of a photosensitive polymer, the subsequent positive photoresist is spin-coated and then baked in a vacuum oven. Finally, the photoresist is patterned using a shadow mask and the device is fabricated using conventional photolithography.

M6.4 Inkjet printing of polymers and nanoparticles.

Dana Wenders, 1,3 Bercend-Jan de Gans, 1 Jolke Perelée, 1,2 and Ulrich S. Schubert 1,2

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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 capillary effect. The hole diameter 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. 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 sinter these to obtain a finite conductivity.


The deposition of highly conductive traces, typically metal, generally requires vacuum metallisation 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 microcracking or delamination 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, stylos method of deposition was demonstrated using MicroPen® technology (Ohmcraft Inc.). The thermal and structural integrity of composite ink lines deposited on polycarbonate terminals were also analyzed. Controlled deposition of electrically conductive inks using SWNTs offers the opportunity to develop robust conductive traces that will aid in the advancement of polymer electronics.


Micropen7TM 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 dot-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 Micropen7TM relies on developing suitable feedstocks 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. These 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 from the sol-gel process. The sols of PMMA/TEOS=80/20 (wt. %) were used for (a) their high 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 Micropen7TM deposition to avoid quick drying at the pen tip and to better control the viscosity. The patents of micropen and multi-layer lines were successfully
deposited with the height up to 20 μm and width up to 140 μm. SEM revealed another interesting phenomenon of the disc shaped SiO₂ particles in its shape mainly due to dielectric freezing. We also studied a commercial FFCB polymer because of its superb optical transparency in the 800–1600 nm window in contrast to FMMAs. This is because the substitution of fluorine in lieu of hydrogen, thus the vibrational absorption band falling outside of the 800–1600 nm window. After writing, the patterns were cured at 200°C for 2 h under controlled atmosphere. The variation of line dimension as a function of writing parameters was extensively studied. In our work, the width decreased with increasing writing speed (WS). In regards to FFCB/SiO₂ composites, we have optimized the materials synthesis for Micropen 3,4 by studying the effects of organic-inorganic ratio, and a 50:20 ratio (wt%) was found to be 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 FFCB/SiO₂ for active waveguides. The transmission at 1550 nm were observed for both systems. Notably, the SiO₂ induced in the composites was helpful in preventing the agglomeration of nanoparticles compared with that in pure FFCB. 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. Duong1, Marian Twardowski1 and Jennifer A. Lewis1,2,3
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 fabrication of a conformal 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 (anastase), 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 to confirm the prepared and annealed structures. Current efforts are underway to extend this approach to finer feature sizes (< 1 μm) 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 Naravat1, Samali Datta1, Dustin Vaseela1, Nathan Schuler2, Rob Salter3, Aaron Reinholz1, David Wells2, Dean Webster3 and Douglas L. Schultz1,2
1Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota; 2Industrial and Manufacturing Engineering, NDSU, 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 achieve high electrical conductivity (e.g., via a carbon-filled 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 300 mW/cm². Electrical and interfacial parameters utilized with a Milura semiautomatic screen printer will be correlated to print quality parameters such as percent bleed. Electrical performance of the printed features were assessed by standard DC methods to give sheet resistance. In addition, 1.4 Ω/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 Ω/sq and 0.63 Ω/sq at 900 MHz and 2.45 GHz, respectively, after UV cure with impedance decreasing slightly to 0.13 Ω/sq and 0.26 Ω/sq after an additional thermal treatment at 100°C in air. Scanning electron microscopy data will be used to illustrate the morphology 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 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 Holder1,2,3, Dmitriy Kozyrev1,2,3, Martijn M. Wierink1,2,3, Verónica Marin1,2,3 and Ulrich Schubert1,2,3
1Technology Center of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), Eindhoven, Netherlands; 3Labatory 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 electronic plastics. A very attractive point is the multifunctional active layer fulfilling all necessary requirements in just one layer. In bulk heterojunction solar cells (BHSCs) the active polymer layer combines all functions such as light absorption through the donor, exciplex formation, electron transfer to the acceptor, excitons 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 polymer BHSCs can be smaller than that of classical donor-acceptor solar cells. Wet-chemistry fabrication procedures (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, Ti 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 conductive polymer blends on a nanoscopic level. This information can 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 screening tool for novel materials. [1] M.M. Wierink, 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 B: Polym. Phys., 2010, 48, 2461. [3] J.C. Hummelen, B.W. Knight, F. LePeq, F. Wudl, J. Yao, C.L. Wilkins, J. Org. Chem., 1995, 60, 532.

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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 such structures is not perfect through a fabrication process that 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 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 calculating the optical response of several 1DPCs 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 that has been applied is 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 that is affected 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 aeroponic features using multi-beam holography and two photon polymerization.** Brin Suwan Mastra1, Raiko Zareno1, Christian Selvaggi2, A. S. P. T. Prinz5, P. V. Braun2, and P. Wiltzius2,1,3,4. 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, two-dimensional photonic crystals. Various FCC based structures were formed in the photoreist 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 photoreist to yield the appropriate beam orientations for definition of FCC crystals. Aeroponic features were written within the crystals by using two-photon polymerization, directly into the undeveloped photoreist, thereby eliminating the need for any infilling step. In addition, the optical properties of the crystals were investigated via spectroscopy.

**M6.12**

**Comparative Analysis of a One Dimensional Metal Dielectric Photonic with a Dielectric Photonic Crystal.** Miguel Angel Basurto1,1, Jose Javier Sanchez-Mondragon2, Daniel May-arrioja3,4, Jesus Escobedo-Alatorce4,5, and A. Martinez-Hitos1. 1Optica, INAOE, Tonantzintla, Puebla, Mexico; 2Optica, CICAp, Cuernavaca, Morelos, Mexico; 3Optica, CICAp, Cuernavaca, Morelos, Mexico; 4Optica, INAOE, Tonantzintla, Puebla, Mexico; 5Optica, CREOL & FPC, Orlando, Florida, USA.

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 advantage of 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**

**Biselasticity, Chirping and Switching in a Linear-Nolinear Photonic Crystal.** Jose Javier Sanchez-Mondragon1,2, Jesus Escobedo-Alatorce3, Margarita Tecpoyotl-Torres4, Romeo Solvas Aguilar1,5, Samuel Torres-Gomez2, and A. Martinez-Hitos3. 1Optica, INAOE, Tonantzintla, Puebla, Mexico; 2Optica, CICAp, Cuernavaca, Morelos, Mexico; 3Optica, CICAp, Cuernavaca, Morelos, Mexico; 4Optica, CICAp, Cuernavaca, Morelos, Mexico; 5Optica, CICAp, Cuernavaca, Morelos, Mexico.

Biselasticity, 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 planar case, 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 Lee2, Sung Il Oh1 and Jaewool Joung1. 1School of Material Science and Engineering, Postech, Pohang, Korea; 2School of Physics, Sungkyunkwan University, Suwon, 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 ohm-cm) even at low sintering temperature below 250 °C.

**M6.15**

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

Silver nano particles are being widely used in electronic parts. The current line of electronic part can be affected by the printing 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 another dispersant. We formulated suspension solutions with various contents. We make fine printed conductive line by a micro dispenser and then each 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**

**Biodegradable Surfaces on Titanium and Some of its Alloys for Orthopaedic Implants.** Agustin Sanchez Lopez1, Julia Claudia Mirza Rosca1, Heinz Sturm2, Paula Drob3 and Ecartera Vasilescu4. 1Mechanical Engineering, Engineering University, Paris, France; 2Medical Institute of Materials Research, BAM, 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 spurs of bone wanted 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 OTTs**

**Chair:** Arokia Nathan

**Wednesday Morning, November 30, 2005**

**Room 306 (Hynes)**

8:00 AM - 8:30 AM: Printed Integrated Electronic and Electrochemical Systems on Paper, Magnus Berggren1, Lars-Olov Henndal2, David Nilsson1, Anurak Sawadee3, Robert Forchheimer2 and Nathaniel Robinson1.

1ITN, Linkoping University, Norrkoping, Sweden; 2ISY, Linkoping University, Linkoping, Sweden; 3Acreo AB, Norrkoping, Sweden.
Integrated electronic systems built up from the combination of printed organic insulators, semi-conductors, conductors and electrolytes for electronic lab-on-chip and microfluidic devices built on paper. 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 the design of a high analog circuit design. The electron transportation and a review of the printing steps needed to achieve these all-integrated circuits on paper labels. The electrochemical transistors utilized in function in equivalence to a p-type depletion mode FET-transistors which also 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 high-voltage electrophoretic deposition. This novel patterning technique has successfully been implemented in a traditional rotary screen-printing station. In addition, we report results from flexo-printing 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 Miedaner2, Lee Smith3, Andrew Leenher2, John Perkins2, Tanya Kuydanova1, Maikel Van Hest1, Rubin Collins2, Sean Shaheen1, Matthew Taylor2, Dana Olson3, Matthew Danbury2, 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 based on the low temperature deposition of thin films of conducting plastics, glass and flexible foils. To be able to build circuits on these substrates requires contacts that can be processes at low temperature (<200°C) and ideally in a non-contact fashion. We have been developing novel contacts to specifically address 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-cm1) but much more high resistivity, and with stability 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 deposition near vacuum quality metalizations (i.e. for Ag 5 x 106 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 utilization and no additional patterning. These contacts point the way towards new organic-based processing specifically suited to flexible and 3D electronics. This work was supported by the DOE through the NCPV and DARPA under the OPV program.

9:00 AM M7.3 Room-temperature deposited high-k gate dielectrics for low-voltage flexible electronics. Si-Doob Kim1,3, YongWoo Choi1,2, Akintunde I. Akinwande2 and Harry L. Tuller1, 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Microsystems Technology Laboratory (MIST); 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 extensive 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 using high-k dielectrics or ultra-thin gate 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, which is 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 applied (thick substrates need to increase operating voltage. As new candidates, we developed pyrochlore structured Bi2.5Sr2.5O6 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 (<5V) organic transistors using a 200 nm thick oxide gates 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 possible 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.


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 semiconductor allowing fabrication of complementary circuits. The corresponding devices perform at exceptionally low operating voltages (~1V) 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, beside 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 Hines1,2, Sergey Mezhnev2,1, Michaela Breban4,3, Vinod Sangwan2,1, Ellen Williams2,1, Vince Ballarott2,1, Gokhan Esen1,9 and Michael Fuhrer1,9, 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 lithography-free 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 200 mm silicon wafer that is then coated with a thin evaporated 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 nanomaterial class and have all resulted in high performance 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.


We report a simple, low-cost, and parallel fabrication of pentacene organic thin-film transistors (OTFTs) with coarse-patterned 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 across 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. Subsequently, when 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 2µm for both top contact (TC) and bottom contact (BC) configurations has been achieved. During the patterning for TC device, the pentacene region can also be defined simultaneously due to adherence of pentacene material that surrounds source/drain pads to the PEDOT 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 to 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 are 25 cm²/V·s and 1.0 x 10⁶, respectively, on the same area of 1 x 10⁶ cm². These 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 (Rc) of TC OTFTs with PEDOT electrodes is an order of magnitude smaller than those with gold electrodes. Therefore, for both TC and BC PEDOT electrodes, Rc has the same order of magnitude as channel resistance (Rch) per micron meter. Electrical performance can be further improved by reducing channel length. While Rc of BC OTFTs is in about two orders of magnitude greater than Rch, scaling down channel length will not effectively improve OTFTs performance. Reduction of Rc is therefore the key for further improvement of OTFTs performance. We have also found that the 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 conducting polymers. 10:30 AM M7.7 Monolayer Formation in Oligothiophene Based OTFTs. Paul Chang¹, Amanda R. Murphy², Jean M. J. Frechet² and Vivek Subramanian¹;¹ Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, California; ²Department of Chemistry, University of California, Berkeley, California. Recent work has shown oligothiophene deposited via inkjet printing can undergo a thermosly driven reorientation that results in films a single monolayer thick between adjacent source and drain electrodes. This work studies the mechanisms behind such film formation, i.e., 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 surface to diffuse >5  um over the surface. Under specific processing conditions and electrode configurations, resulting films using particular oligothiophenes are seen to form nearly one/four/five layers in TFTs with channels up to 10 um long. Compared to aggregated, thicker film devices, monolayer devices show significantly reduced trapping behavior, resulting in improved performance and consistent low bias behavior. Overall, for printed electronics, field-effect transistors with 10% Vth are measured, with peak inverse subthreshold slopes <200 mV/dec. 10:45 AM M7.8 Organic Thin Film Transistors from Uniaxially Aligned Films of Hexa-peri-hexabenzenoterpenes (HBCTs). Jason Christopher Plato¹, Richard Friend¹, Henning Sirringhaus¹, Wojciech Pisula², Tadeusz Pakula³ and Klaus Mueller²;¹ Optoelectronics 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 polymers inexpensive and easily deposited on 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). Discrete 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 can act as charge transport pathways. 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 device fabricated novel device fabricated by casting uniaxially aligned films of hexa-peri-hexabenzenoterpenic 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, Kristjónas Genevićus, Martin Heeney, Iain MacDonald, Ruth Rawcliffe, Richard Sirtsin, David Sparrow, Maxin Skuknov, 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 thiieno[2,3-b]thiophene and thiieno[2,3-b]thiophene 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 cm²/V·s are reported for thiieno[2,3-b]thiophene co-polymers and thiieno[2,3-b]thiophene co-polymers. Excellent air-stability is also reported for thiieno[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 Polyamide Film. Sei Uemura¹, Manabu Yoshida¹, Toshihide Kamata¹, Masahiko Kojima¹, Takeshi Kondo² and Takeshi Kawai³;¹ AIST, Tsukuba, Ibaraki, Japan; ²Department of Industrial Chemistry, Tokyo University of Science, Shinjuku, Tokyo, Japan. Polypolyamide is one of the most attractive materials for the printed device due to its solubility and unique dielectric properties. Polypolyamide 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 polypolyamide shows ferroelectric phase transition in 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-phase 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 FeFET. 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 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, spectroscope measurement and morphology analysis revealed that the observed phenomenon was dependent on the transition of main-chain and side-chain dipole. 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 caused 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. Tazuyoshi Seki¹, Shingo Ib¹, Yusaku Kató¹, Yoshiaki Noguchi¹, Takayasu Sakurai¹ and Takao Someya¹;¹ Quantum-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 VDS and VDS = -40 V are continuously applied to these FETs for 11 h, the change of source-drain currents is as small as 3 ± 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. The gate electrode was formed by thermal evaporation of 5-μm-thick Cr and 100-μm-thick Au through a shadow mask. A 600-μm-thick polyimide gate dielectric layer was then prepared by spin coating and a 50-μm-thick pentacene layer was deposited through the same thermal evaporation. A 60-μm-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 coated by a 6-μm-thick poly-chloro-paraxyylene (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 nitrogen. After the annealing process, the mobility was enhanced from 0.3 to 0.4 cm²/Vs and the on/off ratio was improved from 10² to 10⁵, 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} = -4 cm²/Vs and V_{DS} = -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 ± 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 100 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_{DSS} 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, MITI, 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 triode was fabricated by vacuum deposition. The first organic layer of perylenetetracarboxylic derivatives (Me-PDC) was deposited on an ITO of a collector electrode. The base electrode of aluminum was deposited with a thickness of 20 nm. The second organic layer of C60 and the emitter electrode of Ag were deposited. Without the base voltage (Vb), the small collector current (Ic) was observed on applying the collector voltage (Vc = 5 V). However, application of Vb markedly increased the collector current, which finally exceeded -300 μA/cm² for only 3 Vb. The value of the ON/OFF ratio was around 10⁵, 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/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 electronic properties of materials show strong effects 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 electrode, that is, whether the thin base electrode covered the organic film surface fully or covered it partially. 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 mechanism for the current passing in the electrolyte would be needed. Now, we are investigating the electrode structure using various microscopic techniques.
manufacture high-quality pentacene field-effect transistors (FETs). The measured mobility of pentacene FETs with inkjet polyimide is 0.2 cm²/V·s, which is comparable to that of spin coated polyimide films (RMS=0.22 nm). A high-purity precursor (Kemitite CT412, Chemical) was patterned by an inkjet printer (UP-1, Ricoh Printing Systems) with a stainless steel inkjet head (GEN3E1), which is driven by multilayered piezo-electricity 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 gold thick polyimide layers patterned by 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 nm without surface contamination. The feasibility of inkjet patterned polyimide at high spatial resolution of 200dpi. The variation in diameter was less than ±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 patterned by thermal evaporation of 50-nm-thick Al through a shadow mask. The channel length and width of organic FETs are 100 μm and 500 μm, respectively. The mobility was 0.2 cm²/V·s in the saturation regime and the on/off current ratio was above 10⁶. Compared with spin coating, the present inkjet printing of polyimide is considerably faster than a 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 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-thick polyimide suitable for organic FETs. This structure 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, Valérie Leblanc1, Annie Wang1, Marc A. Baldo2, Paul J. Benning2, Martin A. Schmidt2, David M. Schur3 and Vladimir Bulovic1, 1Microelectronics Technology Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2, Hewlett-Packard Company, Corvallis, Oregon.

We recently demonstrated Molecular Jet (MJet) printing technique for high-resolution patterning (up to 800 dpi, 30μm features) of organic semiconductors and metals, and we applied the technique to printing patterned molecular LCDs. In contrast to the ink-jet printing of solutions, the MJet technique employs a solvent-free additive deposition process to modulate shadow mask evaporation process, the MJet technique is potentially scalable to fabrication on large area substrates. We now demonstrate that with the MJet 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 30μm by 120 μm 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 additive deposition flux. Using the MJet printhead we print an OFET inside a high vacuum chamber (5×10⁻¹¹Torr) by sequentially printing silver and pentacene on top of a thermally grown silicon oxide thin film. OFET channel length down to 5μm is achievable. We will present the gain 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-Hyoun 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. Anomalous showing that both10° and 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 (TFTs) using inkjet processes. Simple and low cost chemical precursors for a variety of metal oxide semiconductors that is suitable for inkjet printing were developed in our lab. 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 cm²/V·s. The success of inkjet printable inorganic semiconductors opens up the possibility 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, high Q inductors. Thus, in this study, we demonstrate a novel high-quality inductor technology based on the use of ink-jet printed nanoparticles as an initial pattern, followed by subsequent electrophoresis plating to deposit copper, resulting in excellent low loss and relatively high Q, each 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 electrolss plating reaction when deposited with adequate concentration. The seed layer consisted of oleic acid-capped silver nanoparticles in dialkylimine solvent, along with a palladium organic 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 CuSO4, EDTA complexing agent, RE-610 surfactant, pyridine accelerator, 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 μm thick are reliably grown, giving a sheet resistance as low as 7.5 mΩ/square. At high frequencies, this 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 μm inductor was fabricated that had a series RLC of 260 Ω, giving a quality factor of 21.3 at 13.56 MHz. This is expected to be improved further, giving it an acceptable for RFID applications. Therefore, this process represents an important step towards the fabrication of low-cost RFID systems.
respectively. The use of flexographic printing methods for doublelayer polymer structures are investigated and the devices are characterized in a vacuum. The materials 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 suitable for high complexity microfluidic applications. 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 scalable for high volumes.

M9.2 n-Type Organic Field Effect Transistors Preparing for Supramolecular Nanotransistor Printing

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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 elaborate 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 represent an alternative to 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. The simplicity and reliability of the process relies on the formation of metallic bonds between the metal film and the substrate resulting in an effective metal transfer. In our group self-assembled monolayers (SAMs) of β-cyclodextrin (βCD) on gold and on glass have been extensively studied. The surface confined β-cyclodextrin moieties retain the ability to form host-guest complexes with different molecules from solution. Redox-active ferrocenyl (Fc) functionalized PDI dimertrixes constitute a particularly interesting class of polyfunctional guest molecules that can be bonded onto the βCD SAMs. These molecules form stable assemblies at βCD SAMs owing to the formation of multiple specific host-guest interactions with the host surface. A βCD 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 dimertrixs at a βCD 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 βCD SAM at the stamp. Nanotransfer printing at heavily p-doped Si wafers with 50 nm SiO2 on which βCD SAMs were prepared, resulted in three-terminal devices with two Au top electrodes and one p-doped Si substrate as a gate. The resulting 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 with the bare aduanantyl-functionalized dimertrixs showed a FET behavior. References: 1. Luo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. Appl. Phys. Lett. 2002, 81, 1621-2. Beulen, M. J. W.; Büger, J.; Lammerink, B.; Geurts, F. A. J.; Biemond, E. M. E. F.; Leerdom, 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.; Husken, J.; Ravoo, B. J.; Reinhoudt, D. N. Langmuir, 2004, 20, 5400. 4. Nijhuis, C.A.; Husken, J.; Reinhoudt, D. N. J. Am. Chem. Soc. 2004, 126, 12966.

M9.3 Printed Nanocomposite Dielectric Gate Insulator for Organic Field Effect Transistors

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Printed high capacitance nanocomposite dielectric material was demonstrated as a gate insulator for organic field effect transistors (OFETs). A nanocomposite consisting of cross-linked Polypropylene Glycol Molecular Weight 1000 (P1000) and Bismaleimide Triazine (BTX) nanoparticles was developed and utilized as the gate insulator. The high permittivity (κ=35), bimodal nanocomposite utilized had two different filler particle sizes: 200 nm and 1000 nm, diameter particles. Due to the nazoize 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, solvothermally treated BTO nanocomposite devices. The capacitance 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) Lo1. 1Chemical Engineering, University of Texas at Austin, Austin, Texas; 2Chemistry, University of Kentucky, Lexington, Kentucky.

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, low-power devices hinges on the ability to deposit 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 improved solubility and solution self-assembly. We have fabricated thin-film transistors on silicon substrates with spincast TES ADT thin films. The hole mobilities of the spin-cast TES ADT transistors is significantly lower (0.005cm²/V·sec) than thermally evaporated anthradithiophene thick films (0.1cm²/V·sec). Annealing the spin-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·sec), and increased on-currents (100 fold). Annealing TES ADT thin films with dichloroethane produces similar effects, but annealing with other solvents, such as hexane, has not shown 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 ratio, 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 observed 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 at the gate. 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 negligibly small. This result suggests that P3HT is an ideal EOT material for high-speed organic electronics and indicates that PANI provides significantly better contact with pentacene for both charge injection and drawing, as opposed to gold.


Organic semiconductors have some advantages, such as flexibility, variety, and easiness of fabrication, over inorganic ones. But, 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 coat technique. So, organic materials have been promising candidates for future device materials. 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 polymers films are fabricated by conventional spin coating. Recently, we developed the conventional spin coat technique into a new spin coat technique which we call 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 as an LMWM films and films having graded structure. In this work, we will demonstrate the fabrication of dibenzotetrathiafulvalene (DITTF) films by using the cocktail spin coat technique. These films were composed of large crystalline domains with -10 nm. We used poly (3-hexylthiophene) (P3HT) and DITTF 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 DITTF solution (0.5 wt %), 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% of 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 solutions from 30 to 90%. We could observe that DITTF 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 Nakamura2,1,1,1 Electronic Devices and Materials, 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 organic semiconductor 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 development of colloidal lithography 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 optimization of this condition.[5] 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 holes were formed in the substrate. 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 by NEDO-Mexico Technology Material Program Start-Up Project Paper based on funds provided by METI and administered by JICJ, and by Grant-in Aid for Scientific Research (No. 15560014) from Ministry of Education, Culture, Sports, Science and Technology, [1] R. Kudo et al. Synth. Met. 111 - 112 (2000) 11. [2] N. Hiroshika 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), K10.37. [4] R. Hanap et al., Collids Surf. A 214 (2003) 23.

M9.8 Significant Controllability of Threshold Voltage (ΔVth) ~ 0.85) of Pentacene Field-effect Transistors with Double-gate Structures. Shingo Ihb1, Tsuyoshi Sekitani1, Yusaku Kato1, Takayasu Sakurai2 and Takao Soneya1; 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 electric fields can independently apply voltage biases to channel layers [1-3]. The threshold voltage (Vth) is shifted systematically by as much as -26 V when the voltage bias of the top-gate electrode (Vtop) is varied by +40 V. The value of the difference in the threshold voltage (ΔVth) of ~0.85 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. The 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-nm-thick polyimide film coated by a 50-nm-thick Au layer as the gate. The channel layer is a 50-nm-thick pentacene. 50-nm-thick Au drain and source electrodes are evaporated through a mask. The channel length L and width W are 100 μm and 1 mm, respectively. The transistors are uniformly coated by a 620-nm-thick parylene layer (4.1 nF/cm²). Finally, 50-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 μm² top-gate electrode, while other devices 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 depend on the ON/OFF ratio of 106. The characteristics were measured at Vtop of +60V to +60V, and characteristics in the linear regime showed systematic changes. The change in Vth is very small when Vtop is varied from +60 V to +20 V, but Vth decreases from -17 V to -43 V when Vtop is varied from +20 V to +60 V. The value of the difference in the threshold voltage (ΔVth) with Vtop of +60V 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 800x800 μm² square covering entire channel layer. 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, NEDO and NEDO. [1]T. Ih, et al. J. Appl. Phys. Lett. 83 (2003); [2]R. Coehoorn, et al. 2005 MRS Spring, B17.9 (2005). [3] C. H. Gelinck, et al. SID, 31.1, (2004). [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 Donogh1,2, Naesderg1,3, Muniira Rahma1,3, Sun Badriya4, 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. There are multiple trapping among localized states. The density of states (DOS) in organic materials is commonly believed to be described by a Gaussian distribution of energy sites [1] but there has been a wide range of parameterization where the density of states is described by an exponential distribution [2-3]. The value of the exponent in the Gaussian distribution, \( n(E) \), is related to the characteristic energy level of the system. In the case of organic semiconductors, the DOS is characterized by an exponential function. It is important that the total current in a polymer device is primarily equal to the product of the carrier concentration, \( n(E) \) and the hopping rate. 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, Extmax. However, the latter is only correct if the increase gradient of the DOS is greater than that of the Fermi-Dirac function, i.e., if the gain of the DOS is 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 Extmax that is proportional to $\sigma^2/kT$. The width of the distribution of the carrier concentration with energy factors was found to be in proportion to $\sigma^2$. All 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. Dependence of Extmax on EF is a Gaussian distribution (EFmin to $\alpha^2/2kT$), a part of a Gaussian distribution or one half of a Gaussian distribution (EFmax to $\sigma^2/kT$). The point of inflexion in the DOS is equal to $\sigma$ for $\sigma^2/kT > EF > Extmax$. The carrier concentration is exponentially proportional to EF for EF below EFmin. Above this value the carrier concentration becomes constant with EF and after Extmax 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. Schmichel, Phys. Rev. B, 66, 235206 [2] D. Monroe, Phut. Rev. Lett. 14 Jan 1985, p146. [3] S. Borovskii et al., J. Non-Cryst. Solids, 198-200, 222. [4] M. Vissaenu, M. Matters, Phys. Rev B, Vol. 57, No. 20, p57. [5] S. Borovskii et al., J. Non-Cryst. Solids, 190, p 283.

M0.10 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, atmosphere-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 applications in 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 conversion enhanced by the use of volatiles in a 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 possibly 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.

M0.11 Mechanical Properties of Thin Films of Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate)(PEDOT/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 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]. For those measurements on a movable sample, 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 0.1 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 (PES/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 2-3 hours the metal-organic thin films were 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 has a modulus as high as 2 cm$^2$ V$^{-1}$ s$^{-1}$ for vapor-deposited film and 0.25 cm$^2$ V$^{-1}$ 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$^{-9}$ A/cm$^2$), very high breakdown fields (> 5 MV/cm), and are fully compatible with both electron- and hole transporting materials allowing fabrication of complementary circuits.

M0.12 Processing, Morphological and Physical Properties of Functionalized Pentacene. Jiang Chen1, Sankar Subramanian1, John E. Anthony2 and David C. Martin1,2,3; 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 pentacene of interest for making organic electronic devices such as thin film transistors. These pentacenes have been modified with alkyl acrylate or alkyl silyle grafted 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 high stage optical microscopy, differential scanning calorimetry, transmission electron microscopy, and electron diffraction. These results show the variations in their thermal behavior and macroscopic properties as the chemistry of the side-group substituent changes.


The design and synthesis of new oligothiophenes functionalized with a variety of phenacyl, alky carbonyl, 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 on-off mobilities as high as 2 cm$^2$ V$^{-1}$ s$^{-1}$ for vapor-deposited film and 0.25 cm$^2$ V$^{-1}$ 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$^{-9}$ A/cm$^2$), very high breakdown fields (> 5 MV/cm), and are fully compatible with both electron- and hole transporting materials allowing fabrication of complementary circuits.
properties of the utilized complexes can be engineered by choosing the appropriate ligands, metal ions and counterions. Iridium(III) complexes are of great interest 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 those 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 and the UV 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, J. Polym. Sci. Part A: Polym. Chem. 2005, 43, 2765.[2] B.G.G. Lohmeier, 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. Lohmeier, U.S. Schubert, Macromol. Chem. Phys. 2005, 206, 989.[5] E. Holder, T. Uehara, U.S. Schubert, J. 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.
Yuguang 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, arrays of the polymer/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 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.

M9.16 Ladder Oligo(para-aniline)s for Electronic Applications: Design, Synthesis, and Characterization. Salem Bakri,
Nicolas Drole, and Marisa I. Zanisi; Department of Chemistry, Laval University, Quebec city, Quebec, Canada; Institute 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 some 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 of the microg molecules, leading to improved stability and processability. Starting from this point, we have developed a new class of semiconducting organic materials from phenyl-capped ladder oligo(p-aniline) derivatives. The synthesis of these soluble ladder oligo(p-aniline)s will be presented. The relationship between the chemical structure of these oligomers and their optical and chemical 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 Oh1,2, Kwi Jong Lee2, Tae Hoon Kim1 and Sung Nam Cho3; 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 electronic devices etc., can eliminate the expensive steps of photolithography. Printing technologies, however to be applied to electronic industry featured as downsizing and high performance, should satisfy high printing quality and good electronic properties. In this study, our group studied the features of printing quality and electronic properties 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 µm as well as a high conductivity of 9.0 x 10-5 cm.

M9.18 Facile Synthesis of Silver Nanoparticles by Thermal Decomposition Method Useful for Metal Nano Ink.
Youngil Lee, In Keun Shin, Kwi Jong Lee and Jae Woo Jung; 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 work, we used Ag nanocrystals with narrow particle size distribution was simply synthesized by thermal decomposition of various Ag-alkanolate(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 nano particles showed good electrical conductivity.


Today's electronic devices require increasing functionality and speed to meet the consumer demand. Consequently, new more and more logistics along with powerful active. The conventional surface mounting technique therefore face the circumstance that the number of passes 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 measured the film thickness by BET and 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, Bumpei Noda, Masamune 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-2-
phenylenediamino)-Ni(N-methyl-2-butylnitrile)nickel [Ni(tba)2] [4] were investigated. The oxidation potential of Ni(npa)2 to a monocation (+1) was observed at 0.00 V vs Ag/AgCl. Whereas the reduction potential of Ni(tba)2 to a monoaon (-1) was reported to be +0.72 V vs Ag/AgCl. The former value is much closer to the location of the HOMO level to be 4.44 eV, and the later value indicates that the LUMO level of Ni(tba)2 is 4.32 eV [6]. Therefore, [Ni(npa)2] is expected to work as a p-type semiconductor, while [Ni(tba)2] works as an N-type semiconductor. Bottom contact-type OFETs were fabricated on n+-Si substrates with thermally grown SiO2. Au (work function: 5.1 eV) was used as source and drain electrodes for the [Ni(npa)2] transistor, whereas Al (work function: 4.1 eV) was used for the [Ni(tba)2] transistor. Organic semiconductor films 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(npa)2] showed P-type transistor characteristics with ~10-5 cm2/Vs in air, and ~10-3 cm2/Vs (on/off ratio, 10) under the vacuum of 5.0×10-5 Torr. By contrast, [Ni(tba)2] exhibited N-type characteristics with ~10-5 cm2/Vs even in air, and the mobility increased to ~10-4 cm2/Vs with the on/off ratio of 105 under vacuum. The present work demonstrates that some metal complexes, which are easily reduced to form stable monoaons, are good candidates of N-type organic semiconductors used in OFETs. [1] a) B. Crane et al., Appl. Phys. Lett. 78, 2229 (2001). b) C. D. Dimitrakopoulos et al., Adv. Mater. 14, 99 (2002). c) A. Kraft, ChemPhysChem 2, 163 (2001). [2] B. Crane et al., Technical Digest of the International Electron Devices Meeting 115 (1999) [3] S. H. Kim et al., Dyes and Pigments, 38, 1 (1997). [4] G. N. Shrauzer et al., J. Am. Chem. Soc. 87, 1483 (1965). [5] J. A. McCleverty, Prog. Inorg. Chem. 10, 49 (1968). [6] H. Meng et al., Chem. Mater. 16, 1778 (2003).

SESSION M10: Soft Lithography and PDMs

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

8:00 AM *M10.1
Optics and Microfluidics. White Whitesides1, Dmitri Veenova2, Brian Myers,1 Richard Conroy2, Daniel Wolfe1, Mara Prentiss2, Piotr Garstecki1 and Shuxing 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 simpler optical detectors for microfluidics; and iii) optical diffraction from flowing layers of bubbles.

8:30 AM *M10.2

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 Mehl1 and John A. Rogers1,2; 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 usually inhibits the transfer 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 Huskins1, Supramolecular 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 flexes elastic, elastomer 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-assembling 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 thiocarbamates, proteins, or nanoparticles. Stamp deformation can be controlled to some extent by using stiff mCP 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 chemicochemical barriers for ink diffusion 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; [2] Baldo, M. A.; Bernards, A.; Bhattacharyya, E.; Kisielowski, C.; Juncer, 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; [3] Li, X.-M.; Parashiv, V.; Huskins, J.; Reinhoudt, D. N. Am. Chem. Soc. 2003, 125, 4279-4284; [4] Mehl, X. M.; Peter, N.; Huskins, J.; Reinhoudt, D. N. Nano Lett. 2003, 3, 1449-1453; [4] Sharpe, R. B. A.; Burdinski, D.; Huskins, J.; Zandvliet, H. J. W.; Reinhoudt, D. N.; Poelhema, 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 fabrication of electronic circuits by a combination of solution processing and direct printing. We will review our 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-source-drain voltages. We will also review recent progress towards manufacturing of organic transistor circuits by high-resolution printing techniques.
Silicone for Advanced Lithography. Anne Shim¹, John Rogers²
and Ralph Nuzzo³; 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 Suo³; 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 mechno-electrical
tensile test apparatus to a strain $\varepsilon_{\text{max}} = 32\%$ with strain increments
varying from 1, 4, 8, 16 to 32%. All samples remained electrically
conducting. The electrical resistance at $\varepsilon_{\text{max}}$ increases when the
strain is raised in large strain increments. A conductor was cycled 100
times to $\varepsilon_{\text{max}} = 32\%$ 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 $\sim 2-10\mu m$ 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.