

# Thursday Morning, October 23, 2008

## Nanomanufacturing Focus Topic

Room: 309 - Session NM+EM+PS+NS+NC-ThM

### Printable Lithography and Processing

Moderator: D. Janes, Purdue University

8:00am **NM+EM+PS+NS+NC-ThM1 Techniques for Three Dimensional and Molecular Scale Nanofabrication**, *J. Rogers, D. Shir*, University of Illinois, Urbana-Champaign **INVITED**

Progress in nanoscience and technology relies critically on the ability to build structures with nanometer dimensions. This talk describes unconventional lithographic methods based on (i) advanced forms of soft nanoimprint lithography for 2D patterning with resolution that extends to molecular (~1 nm) length scales, and (ii) conformable phase mask optics for single step formation of fully three dimensional (3D) nanostructures. The first method relies on optimized polymers for molds and mold materials that, together, enable lithographic fidelity at the ~1-2 nm scale, as demonstrated by the replication of relief structures defined by individual single walled carbon nanotubes with diameters down to ~0.7 nm. The use of this method to form alignment layers for liquid crystal devices illustrates a realistic application and a simple example of the broader notion of molded molecular structures for chemical and biological surface recognition. The second method exploits an unusual class of optical element – an elastomeric, sub-wavelength phase mask – in a contact mode exposure geometry to generate 3D structures in photopolymers and other materials in a single patterning step. Aspects such as the self-imaging, Talbot effect optics of this approach, its capabilities for creating periodic, aperiodic and quasi-crystalline 3D nanostructures and selected applications in microfluidics, laser fusion targets and photonic crystals will be discussed. This work was supported by the NSF and the Department of Energy.

8:40am **NM+EM+PS+NS+NC-ThM3 Preparation of 25-nm-spaced PdAu Metal Electrodes on Silicon by Direct Nanotransfer Printing**, *S. Strobel, S. Harrer, G. Penso-Blanco, G. Scarpa, G. Abstreiter, P. Lugli*, Technische Universität München, Germany, *M. Tornow*, Technische Universität Braunschweig, Germany

Nanometer scale metallic contacts which can be directly deposited on planar substrates are of growing importance in view of future applications involving the integration of molecular electronics with current silicon technology. Here, a method which may provide well defined nanogap electrodes of predetermined spacing in a reproducible manner, without the need of sequential direct writing techniques, would be highly advantageous. We present a novel technique using direct high-resolution metal nanotransfer printing and demonstrate its capability to fabricate nanogap electrodes of predetermined spacing on a solid substrate such as silicon. The one-step transfer process is economical, simple and fast, and preserves the mold for manifold transfer. Using molecular beam epitaxy (MBE) a sandwich-like structure is grown with monolayer precision, comprising few nanometer thick GaAs layers embedded in AlGaAs. This structure is cleaved atomically flat perpendicular to the <110> crystallographic direction. Subsequently, the exposed GaAs layers are wet chemically etched thereby generating a 3D grating structure with nanometer-resolution at their edges. This structure serves as mold for nanotransfer printing: By coating the grating surface with a metallic thin film of PdAu/Ti (7/5 nm) and pressing the mold against a Si/SiO<sub>2</sub> substrate the patterned PdAu/Ti sandwich structure is directly transferred onto the surface. This one-step process does not require any flexible buffer layer or additional organic adhesion promoters. We report on a series of successful transfer experiments using different multi-line molds with varying aspect ratios and linewidths down to below 10 nm. In particular, we demonstrate electrically functional PdAu metal electrode pairs with separations down to 25 nm, featuring lead resistances of the order of kΩ and gap isolation in excess of 50 GΩ up to 2 Volts.

9:00am **NM+EM+PS+NS+NC-ThM4 Adhesion Enhancement using Plasma Processing in the Printing of Carbon-based and Organic Flexible Electronics**, *D.R. Hines*, University of Maryland, *V.W. Ballarotto, C. Hull*, Laboratory for Physical Sciences, *G.S. Oehrlein, D.Y. Lee*, University of Maryland, *C.M. Stafford, C.L. Soles, E.K. Lin, J. Liu, J.-Y. Chung*, National Institute of Standards and Technology, *S.G. Walton, E.H. Lock*, US Naval Research Laboratory

High quality organic & carbon-based thin-film transistors (TFT) have been successfully fabricated onto plastic substrates using transfer printing. With this printing process, each device component (conducting electrodes, polymer dielectric layer and semiconductor layer) was printed using only

pressure and temperature, eliminating all chemical processing on the plastic device substrates. Pentacene (Pn), poly(3-hexylthiophene) (P3HT), carbon nanotube mats (CNTM) and graphene TFTs were all fabricated on polyethylene terephthalate (PET) substrates. Bottom gate, bottom source/drain devices yielded mobilities of 0.237 cm<sup>2</sup>/Vs for Pn and 0.04 cm<sup>2</sup>/Vs for P3HT. Bottom-gate CNTM TFTs exhibited p-type behavior, mobilities of 13.7 cm<sup>2</sup>/Vs, on/off ratio of 10<sup>3</sup> and minimal hysteresis. Top-gate graphene TFTs exhibited mobilities of 1.0x10<sup>4</sup> cm<sup>2</sup>/Vs for holes and 4x10<sup>3</sup> cm<sup>2</sup>/Vs for electrons. The organic TFT devices were fabricated using a variety of polymer dielectric layers including poly(hydroxystyrene) (PHS), polystyrene (PS), polycarbonate (PC) and poly(methylmethacrylate) (PMMA). The resulting TFTs showed little variation in mobility, but strong variation in threshold voltage for different dielectric layers. The transfer printing process relies primarily on differential adhesion for the assembly of both patterned and unpatterned films onto a common flexible, plastic substrate. It is a simple and robust process that is compatible with a wide range of materials. Plasma processing techniques are being adapted to control the surface energy of polymer and plastic surfaces in order to increase adhesion forces at the interface between polymer dielectric layers and plastic substrates. The printability and surface characterization of plasma treated polymer/plastic surfaces will be discussed. One goal of this work is to enable the incorporation of many different dielectric materials (including 10 test polymer dielectric films) and substrate materials (including 11 test plastic substrate sheets) into the fabrication of flexible electronics. This work partially supported by the Office of Naval Research and the Laboratory for Physical Sciences. \*E.H. Lock, NRC/NRL Postdoctoral Research Associate.

9:20am **NM+EM+PS+NS+NC-ThM5 Fabrication of Microarrays with Nanoscale Chemical Contrast by Nanoimprint-Assisted Lift-Off**, *A. Ruiz*, JRC, European Commission, *C.A. Mills*, Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *A. Valsesia*, JRC, European Commission, *E. Martinez*, Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *P. Colpo*, JRC, European Commission, *J. Samitier*, Inst. for Bioeng. of Catalonia, Barcelona Sci. Park, *F. Rossi*, JRC, European Commission

The fabrication of ordered microstructures of colloidal crystals is increasingly attracting interest due to their potential applications as sensing, optical and photonic band-gap materials. Depending on the application (i.e. chemical or biochemical sensors, photonic chips), specific microstructured configurations of the colloidal crystal are needed. Most of the methodologies reported so far for the production of colloidal crystals are based on the directed self-assembly of micro or nanospheres, in which patterning and formation take place simultaneously in a template created beforehand, normally by the modification of the surface chemical or topographic properties. However, methods for patterning the colloidal film after it has been formed are scarce. The interest in such methods lies in the fact that they allow fine control over the microstructure of the colloidal film by selective removal of a single layer of close-packed nanospheres. Recent top-down approaches to the micropatterning of nano-beads are based on soft lithography lift-off processes using PDMS stamps. Removal of nano-beads strongly adhering to the substrate is however hard to realize and limitations related to the PDMS structural properties, i.e. deformation, appear. Normally, the beads have to be loosely attached so that bead transfer or removal is not inhibited. In this work, a new soft-lithographic method for micro-patterning nano-bead arrays, based on structured poly(methyl methacrylate) (PMMA) and using a nanoimprinter apparatus, is described. The properties of the PMMA, with respect to hardness and flexibility, are promising for resolving sub-micron patterns of nanoparticles. The use of the nanoimprinter allows careful control of the temperature and pressure during the contact-stripping operation; this ensures accurate removal of nanoparticles over large areas even when they are strongly attached to the substrate. Patterns of polystyrene nano-beads in several micro-scale configurations have been obtained using beads of different diameters (100 ~ 500 nm) and with different levels of adherence to the substrate. The micropatterning of nanobeads thus achieved has been then used to create surfaces with nanoscale chemical contrast inside the micro-patterns. Having structured regions separated by flat, unstructured regions is advantageous for many applications, such as sensing platforms for parallel detection or cell culture platforms for examining cell-surface interactions at the nanoscale.

9:40am **NM+EM+PS+NS+NC-ThM6 Inkless Deposition of Microparticles by Electrostatic Acceleration for Materials Processing.** *I. Eu, L. Musinski, T. Liu, University of Michigan, D. Morris, ElectroDynamic Applications, Inc., J.M. Millunchick, B. Gilchrist, A.D. Gallimore, University of Michigan*

We have developed a particle accelerator that electro-statically charges nanometer- to micron-sized conductive particles that are then accelerated through grids with bias voltages up to roughly 10kV, allowing for the deposition of particles without using a carrier solution or "ink". By carefully controlling the energy of the particles, various regimes of materials processing may be achieved. For example, high energy high mass particles are expected to etch a substrate, while decreasing either the mass or velocity will result in deposition of the particles. A prototype device has been fabricated based on transporting the particles to and through an ultrafine "sieve" via back pressure and acoustic and/or mechanical vibration. The pressure and vibration moves the particles through the sieve apertures, allowing for electrostatic acceleration of the particles one at a time for maximum impulse. The experimental data shows a roughly Gaussian distribution of 50 micron Ag-coated glass spheres extracted at a mean electric field of about 1.9 MV/m with a standard deviation of approximately 0.4 MV/m. The data agrees well with the analytical model for required extraction fields determined using calculated Van der Waal's forces and a Lipschitz constant of 0.6 eV. The variance likely attributable to electrode surface roughness and manufacturing imperfections in particle shape. Initial feasibility tests have been conducted in which this system has been used to impact aluminum spheres of size 5-20 microns on glass slides. Scanning Electron Micrographs show that at a charging field of approximately 1.3 MV/m and an acceleration voltage of roughly 10kV, the glass slides are uniformly coated with individually isolated Al particles. The particle isolation and deposition control implies the potential for very high vertical and horizontal resolution in target applications. Now that the proof of concept has been established, we are scaling down the technology so that submicron particles may be deposited, with the long-term goal to deposit individual particles on the order of tens of nanometers.

10:40am **NM+EM+PS+NS+NC-ThM9 Plasma-Lithography Interactions for Advanced CMOS Manufacturing (45nm and Beyond).** *K. Kumar, International Business Machines* **INVITED**

The advent of 45nm saw the introduction of immersion lithography with up to 1.20 NA exposure conditions. The need for higher fidelity lithography printing gave rise to new resist, which in turn necessitated closer interactions with the plasma etch conditions. An overall synergistic model between litho and plasma etch was crucial for overall pattern fidelity. With the near horizons of the lithographic tooling window being limited to 1.35NA, and with EUV looking distant for prime time use, more emphasis is being placed on plasma etch pattern transfer for overall patterning fidelity. Added to scenario, is increased complexity in the form of "Double Expose Double Etch" which has helped increase the overall fidelity and density in the printing of the final structures in 32nm. In order to accomplish these tasks, engineering tools were developed or modified, that methodically studied the interactions between lithography and plasma etch. Strategy and results from Lithography - Plasma Etch interaction will be presented.

11:20am **NM+EM+PS+NS+NC-ThM11 Etching Development and Characterization for a Novel Nano-Imprint Lithography Technology.** *J. Chiaroni, Y. Le Cunff, C. Charpin, Minatec/Cea-Leti, France, M.P. Clement, St Microelect., France, H. Denis, Minatec/Cea-Leti, France, G. Medico, M.L. Villani, St Microelect., France, N. Rochat, A. Fanton, L. Lachal, P. Brianceau, S. Barnola, F. Perrin, E. Vermande, P. Lavios, Minatec/Cea-Leti, France, N. Khusnatdinov, D. Labrake, Molecular Imprint Inc., J.P. Gouy, Minatec/Cea-Leti, France, P. Gubbini, Molecular Imprint Inc.*

Nano-Imprint Lithography (NIL) is one of the most promising candidates (ITRS road map 2007) to address the 32 nm node and below thanks to a high resolution capability (templates are manufactured with E-Beam Lithography), a compatibility with CMOS technology and a lower COO as a simpler technology. The method is based on stamping out patterns on a specific polymer and then transferring into the underneath materials. SFIL/R® is an innovative NIL technology proposed by Molecular Imprint Inc, which uses a stack of three materials: 1. TranSpinTM for initial planarization; 2. MonoMatTM in which pattern is printed; 3. SilSpinTM which planarizes MonoMatTM material. Then, two specific dry etching processes are required to generate the polymer mask: 1. Imprint features opening (SilSpinTM dry etch back with stop on MonoMatTM); 2. Polymers mask opening (TranSpinTM and MonoMatTM dry etching with high selectivity on SilSpinTM Hard Mask and CD control). One of the main challenges is to obtain a good etching selectivity between these three materials which are polymer based and very similar one to the other. SilSpinTM characterization has been performed with XPS and SIMS

analysis in order to determine etching orientation. According to these results, imprint features opening was achieved with fluorinated chemistry (CHF<sub>3</sub>/O<sub>2</sub>/Ar) and Polymer mask opening with HBr/O<sub>2</sub> or Cl<sub>2</sub>/O<sub>2</sub> based chemistry. Study of plasma impact on SilSpinTM with XPS and FTIR analysis has shown a clear impact of chlorine due to its higher efficiency to break SilSpinTM characteristic bonding. So, HBr/O<sub>2</sub> plasma has been preferred to perform the polymer mask opening. A Design Of Experiments was achieved with HBr/O<sub>2</sub> based chemistry in order to determine the most effective input parameters and get the optimized selectivities. By adjusting HBr/O<sub>2</sub> ratio and bias power, a selectivity of seven was obtained between SilSpinTM and pure organic materials, which is consider as high enough. Then, Vias and Lines applications were studied with cross section SEM and CD bias measurement. This work has been carried out within the frame of European program MEDEA+ 2T305 "«Fantastic»".

11:40am **NM+EM+PS+NS+NC-ThM12 Influence of Polymer Structure on Dry Etch Behavior of Resists in Soft Lithography.** *R.L. Bruce, F. Weinhoeck, S. Engelmann, T.C. Lin, R. Phaneuf, G.S. Oehrlein, University of Maryland, College Park, B. Long, G. Willson, University of Texas, Austin, D.G. Nest, J.J. Vegh, D.B. Graves, University of California, Berkeley, A. Alizadeh, GE Global Research Center*

For the realization of sub-10 nm resolution, soft lithography alternatives to conventional photolithography are being considered. In soft lithography, the imprint material is used for pattern definition and also as a mask for pattern transfer into underlying layers. For successful nanoscale pattern transfer, a rational design of polymer resists and an atomistic understanding of plasma-polymer interactions are required. In this study, the effect of different species of the plasma (ions, UV, neutrals) on model polymers with distinct chemical structure (styrene-, acrylate-, methacrylate-, and vinylpyridine-based) was investigated. Model polymers were exposed to Ar and C<sub>4</sub>F<sub>8</sub>/Ar plasmas. Modification of the polymer surface was characterized using in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy (AFM). The effect of crosslinking and chain scission reactions, as well as oxygen containing functional groups, is considered. Mechanisms of plasma-polymer interactions for the different polymer structures are proposed. Finally, select polymers (poly(styrene), poly( $\alpha$ -methylstyrene), and poly(4-vinylpyridine)) were used as imprint materials, patterned, and plasma processed. The top and sidewall profiles and morphologies were examined by AFM and secondary electron microscopy before and after exposure. The importance of polymer structure and plasma species on pattern transfer in soft lithography is discussed.

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