

# Wednesday Morning, October 22, 2008

## Nanomanufacturing Focus Topic

Room: 309 - Session NM+MS+NS+NC-WeM

### Beyond CMOS

Moderator: A. Diebold, University at Albany

8:00am **NM+MS+NS+NC-WeM1 Excitronics: Excitonic Circuits for post-CMOS Electronics.** *J.-U. Lee*, University of Albany **INVITED**

In this talk, I will describe the properties of excitons in one-dimensional semiconductors that make them attractive as a post-CMOS state variable. The essential properties needed for any new state variable are: creation, transport and detection. These properties will be described for excitons created within single-walled carbon nanotube p-n diodes, one of the most fundamental of all electronic devices. The p-n diodes are formed along individual nanotubes and can show ideal diode behavior, the theoretical limit of performance for any diode. I will describe their dc, optical and the interplay between transport and optical properties. As an optical detector, these diodes are extremely sensitive and are able to probe the complete excited states of SWNTs, including the lowest exciton transition and the continuum. Based on these results, we extract properties that are meaningful for electronic applications, including exciton binding energy, transport, and optical cross section. This work was supported by the NRI/INDEX program and the University at Albany.

8:40am **NM+MS+NS+NC-WeM3 Magnetism in Mn Ion Implanted Si.** *C. Awo-Affouda*, Naval Research Laboratory, *M. Bolduc*, Tekna Plasma Systems, Inc., *V.P. LaBella*, University at Albany-SUNY **INVITED**

Magnetic semiconductors hold great potential to produced spin based devices with increased functionality and performance. Making Si ferromagnetic via ion implantation of Mn will aid in integrating such devices with conventional semiconductor manufacturing. Although observations room temperature ferromagnetic phases in Mn-doped Si have been reported by several groups, the origin of the ferromagnetism remains elusive.<sup>1-3</sup> We investigate the influence of annealing on the lattice disorder and dopant distribution of Mn ion implanted Si samples. These depth profiles reveal a strong influence of annealing temperatures on the magnetization of the samples. Specifically, above 800°C a drastic drop in the Si lattice disorder is observed which is coincident with a decrease in magnetization. Furthermore the correlation of the structural and magnetic properties suggests that the magnetization of the samples originates from Mn atoms located in the least damaged implanted region.<sup>4</sup> Finally, analysis of the magnetization of the samples reveals the presence of superparamagnetic phases magnetically active at low temperatures.

<sup>1</sup> Bolduc et al., Phys. Rev. B, 71, p.033302 (2005)

<sup>2</sup> Yoon et al., J. Magn. Magn. Mater./331, p.693

<sup>3</sup> Kwon et al. Solid State Commun., 136, p. 257 (2005)

<sup>4</sup> Awo-Affouda et al. J. Vac. Sci. Tech. A, 25, p. 976 (2007).

9:20am **NM+MS+NS+NC-WeM5 Graphene Electronic Devices.** *A. MacDonald*, *S.K. Banerjee*, *L.F. Register*, *M. Gilbert*, *J.-J. Su*, *R. Bistrizter*, *H. Min*, University of Texas at Austin **INVITED**

Graphene is an atomically two-dimensional material which is described by ultra-relativistic quantum mechanics. I will review progress toward graphene-based electronic devices based on both conventional ideas and on the properties of novel broken symmetry states which might be realized when two graphene layers are separated by a nm scale dielectric barrier. The absence of a mass (a gap) in ultra-relativistic quantum mechanics presents a challenge in adopting conventional device physics to this material. I will discuss progress in inducing gaps by making narrow graphene ribbons or by places graphene bilayers in external electric fields. The broken symmetry which might be realized in systems with two separated graphene layers is one in which phase coherence is established spontaneously between separate layers. These states are counterflow superfluids in which current can flow in opposite directions in the two layers without dissipation. I will discuss some ideas for electronic devices based on the properties of these unusual superfluids.

10:40am **NM+MS+NS+NC-WeM9 Intrinsic and Extrinsic Limits of Charge Carrier Mobility in Graphene.** *M.S. Fuhrer*, University of Maryland **INVITED**

Graphene, a single atom-thick sheet of graphite, is a zero-gap semiconductor with an unusual linear dispersion relation (analogous to the Dirac equation for massless relativistic particles) and a density of states that vanishes at a singular point. Due to the high conductivity and charge carrier mobility, graphene is being considered for a number of applications ranging

from transparent, conducting thin films to high-speed electronics. Here I will discuss experiments performed on atomically-clean graphene on SiO<sub>2</sub><sup>1</sup> in ultra-high vacuum to determine the intrinsic and extrinsic limits of mobility in graphene,<sup>2,3</sup> which point out both the promise of the material as well as the technological challenges that lie ahead in realizing better graphene samples. Intrinsic scattering by the acoustic phonons of graphene<sup>3</sup> limits the room-temperature mobility to 200,000 cm<sup>2</sup>/Vs at a carrier density of 10<sup>12</sup> cm<sup>-2</sup>, higher than any known material. However, conduction in current graphene samples is limited almost entirely by extrinsic scattering due to charged impurities in the substrate<sup>2</sup> and substrate polar optical phonons<sup>3</sup> currently, pointing out the importance of substrate engineering for improving graphene devices.<sup>4</sup> I will discuss the implications for the future of graphene technologies in terms of the manufacturing methods for large-area graphene currently being explored, such as solution processing methods, chemical vapor deposition, and epitaxial growth on metals and insulators.

<sup>1</sup> "Atomic Structure of Graphene on SiO<sub>2</sub>," Masa Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, Nano Letters 7, 1643 (2007).

<sup>2</sup> "Charged Impurity Scattering in Graphene," J. H. Chen, C. Jang, M. S. Fuhrer, E. D. Williams, and M. Ishigami, Nature Physics 4, 377 (2008).

<sup>3</sup> "Intrinsic and Extrinsic Performance Limits of Graphene Devices on SiO<sub>2</sub>," J. H. Chen, C. Jang, S. Xiao, M. Ishigami, M. S. Fuhrer, Nature Nanotechnology 3, 206 (2008).

<sup>4</sup> "Printed Graphene Circuits," Jian-Hao Chen, Masa Ishigami, Chaun Jang, Daniel R. Hines, Michael S. Fuhrer, and Ellen D. Williams, Advanced Materials 19, 3623 (2007).

11:20am **NM+MS+NS+NC-WeM11 Tunneling Conductance of Molecular Wires.** *E. Prodan*, Yeshiva University

Tunneling transport through long, insulating molecular chains is characterized by the exponential decay law  $g = g_c e^{-\beta N}$ , where N is the number of monomers. In the modern formulation of the tunneling transport, is determined from the complex band structure of the isolated molecular chain, a procedure that extends far beyond the limitations of simple models that approximate electron tunneling in molecular devices using square potential barriers. However, until recently, an analytic expression for the contact conductance  $g_c$  was missing. In the first part of the talk, I will review a newly formulated theory of tunneling transport in long molecular wires. This theory provides a rigorous way of computing the exponential decay constant and gives  $g_c$  as an overlap integral between three well defined and physically relevant quantities: the spectral density of the device at the Fermi level, the potential perturbation of the metallic contacts on the molecular chain, and the evanescent electron waves traversing the molecular chain.<sup>1</sup> The formalism will be exemplified on molecular devices made of alkyl<sup>2</sup> and phenyl chains linked to gold wires via amine groups. If the time allows, I will present the extension of the theory to the spin dependent transport, in particular to the problem of tunneling magneto-resistance.

<sup>1</sup>E. Prodan and R. Car, DC Conductance of Molecular Wires, Phys. Rev. B 76, 115102 (2007).

<sup>2</sup>E. Prodan and R. Car, Tunneling conductance of amine linked alkyl chains, Nano Letters (in press).

# Wednesday Afternoon, October 22, 2008

## Nanomanufacturing Focus Topic

Room: 309 - Session NM+PS+AS-WeA

### Nanomanufacturing I: Plasma Processing and Materials

Moderator: R.M. Martin, IBM T.J. Watson Research Center

1:40pm **NM+PS+AS-WeA1 Silicon Nanocrystal Inks: Plasma Processing as a Route to Solution-Processed Silicon Films, U.R. Kortshagen, R. Cram, D. Rowe, X.-D. Pi, University of Minnesota**  
**INVITED**

Colloidal nanocrystals are studied for a wide spectrum of applications from more efficient quantum dot solar cells to printed electronics. While significant advances have been made with chalcogenide semiconductors, similar progress with silicon has been hampered for a long time by the lack of efficient synthesis approaches. However, silicon has the undoubted advantage of being non-toxic, environmentally benign, abundant and cheap. This talk describes a plasma synthesis approach for the efficient synthesis of silicon nanocrystals. Silicon crystals are synthesized in a flow through plasma reactor on time-scales of a few ms. The residence time of the silicon crystals can be used to tailor the nanocrystal size. Dopants can be introduced into the crystals and changes in the photoluminescence properties as well as surface etching studies allow to deduce the dopant location within the nanocrystal. The nanocrystal surfaces can be functionalized with organic ligands that impart solubility to the nanocrystals. By making silicon nanocrystals soluble in organic solvents, inks of doped silicon crystals can be formed that can be used to prepare silicon nanocrystal films through solution processes such as drop coating, spin coating, or ink-jet printing. Laser annealing is used to produce conducting films from the colloidal nanocrystal precursors. Structural and electrical properties of the films are determined with a wide array of characterization techniques. Properties and potential applications of these materials will be discussed.<sup>1</sup>

<sup>1</sup>This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. Partial support is acknowledged by NSF grant DMI-0556163, and by Center for Nanostructure Applications at the University of Minnesota.

2:20pm **NM+PS+AS-WeA3 Vertically Aligned Si Nanostructure Arrays formed using SF<sub>6</sub>/O<sub>2</sub> Plasma, C. Yang, S.H. Ryu, Y.D. Lim, W.J. Yoo, Sungkyunkwan University, Korea**

Arrays of high aspect ratio (>10:1) vertically aligned Si nanostructure were formed in an inductively coupled plasma (ICP) reactor using SF<sub>6</sub>/O<sub>2</sub> plasma without any masks at noncryogenic temperature. Mean diameter of the nanostructure arrays is about 100 nm and the mean height is up to 4.77 μm. These nanostructure arrays can be fabricated for large area (>100 cm<sup>2</sup>). The formation of the nanostructure arrays are studied as a function of time, bias RF-power and O<sub>2</sub>/SF<sub>6</sub> ratio. The processing condition of the SF<sub>6</sub>/O<sub>2</sub> plasma is known to markedly affect the preparation of the nanostructure arrays. O<sub>2</sub>/SF<sub>6</sub> ratio determines the formation of the nanostructure arrays. The nanostructure arrays only could be fabricated when the O<sub>2</sub> content is not too low or too high, the range is 0.5 < O<sub>2</sub>/SF<sub>6</sub> < 2.5. Two types of the nanostructure arrays formed because of the different bias RF-power, one is nanohole arrays and another is the nanopillar arrays. The formation of the nanostructure is hole when the bias power is 10 W, but the diameter is only 420 nm after etching 150 s. If the bias power increased to 30 W, the nanopillar arrays appear, the mean height is up to 4.77 μm after etching 150s. The etching time is also important for the nanostructure arrays. After etching about 40s, the nanostructure arrays appear abruptly and become longer and longer. But very long time etching has destroyed the nanostructure arrays. The mechanism of the plasma etching for fabricating the nanostructure arrays has been investigated using OES, XPS and SEM analyses. From the analyses, the properties of the plasma and the formed passivation layer are mainly reasons for the fabrication of the nanostructure arrays. The best condition to fabricate a high aspect ratio vertically aligned Si nanostructure arrays is suggested.

2:40pm **NM+PS+AS-WeA4 Structured Growth of Silver Nanoparticles Within a Hydrocarbon Matrix, E. Körner, J.F. Lübben, G. Fortunato, D. Hegemann, EMPA, Switzerland**

Low pressure plasma processes enable an extensive variety of surface adjustments for medical applications or technical textiles. Specifically, a modular plasma vacuum chamber provides the base for highly flexible and tailor-made coating technology. Different modification strategies, e.g. activation, etching, plasma polymerization or metallization by sputtering can be used separately or combined with each other. This work presents the

combination of plasma polymerization and etching with a co-sputtering process which leads to the formation of a nanoporous polymer matrix with embedded metal nanoparticles. A capacitively coupled radiofrequency power input and an asymmetric reactor geometry allow the production of such multifunctional coatings within a one-step process. The hydrocarbon matrix is built-up by using ethylene (C<sub>2</sub>H<sub>4</sub>) as a monomer gas. In addition, carbon dioxide (CO<sub>2</sub>) or ammonia (NH<sub>3</sub>) is used as the reactive gas, to structure the matrix and add functional groups to the a-C:H network. The deposition rate and the functionality of the coatings are adjusted by the ratio of reactive gas to monomer. With increasing the ratio of reactive gas the functionality of the matrix increases at the expense of the deposition rate. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode. The growth, distribution and formation of Ag particles are analyzed carefully under different conditions with respect to the gas mixture. The films are investigated with atomic force microscopy and scanning electron microscopy after different growth steps. It can be seen that the particles are more embedded in the matrix for higher film thicknesses and lower reactive gas ratios. Additionally, X-ray photoelectron spectroscopy analyses are performed to evaluate the surface chemistry and Ag surface concentration. For bulk measurements, the overall Ag content is measured with inductively coupled plasma optical emission spectrometry. Target covering or oxidation can decrease the Ag deposition rate and has to be taken into account in determining the optimal plasma conditions. In contrast to magnetron sputtering the Ag particles appear to be bigger with RF sputtering, which could provide a Ag reservoir with a slower release and a better long-term antibacterial effect. This is important for the application of the films as antibacterial coatings, where an optimal antibacterial efficiency for a minimal amount of Ag is desirable.

3:00pm **NM+PS+AS-WeA5 Photoluminescence Brightening from Freestanding Single-Walled Carbon Nanotube Bundles Prepared by Diffusion Plasma CVD, R. Hatakeyama, T. Kato, Tohoku University, Japan**

The optical property of single-walled carbon nanotubes (SWNTs) has been the subject of intense interest in recent years, since the discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs. Because it was believed that the debundle of SWNTs was the inevitable process to capture the PL signal from SWNTs, the bundle forming SWNTs were, in most cases, treated as by-products or impurities causing a spectrum broadening and shifting, and hence their optical features, especially the PL, have not attracted a great deal of attentions so far. Very recently, the PL from bundled SWNTs in an aqueous solution has been reported. Since the PL from bundled SWNTs includes outstanding advantages such as an exemption from a complicated debundle process and easy manipulation, it can be expected that the SWNT-bundle engineering has a great potential for the nanotube-based PL device fabrication. From an industrial point of view, the application of nanotube-PL to the well-organized present semiconductor technology is an inevitable factor, i.e., the establishment of bright PL emission from a solid-state material is considered to be a still remained fundamental problem. In this study we report unique PL features obtained from as-grown vertically-, and individually-freestanding SWNTs prepared by a diffusion-plasma chemical vapor deposition method.<sup>1</sup> The intensity of PL is clearly observed to increase through the morphology transition from isolated to thin-bundled of the freestanding SWNTs.<sup>2</sup> Based on the precise spectrum analysis and equation-based estimation of the PL time trace, the origin of the PL brightening is consistently explained in terms of the exciton energy transfer through the tube bundles. The PL brightening is also revealed to obviously depend on SWNT diameters. Only the small-diameter rich sample can realize the PL brightening, which can be interpreted to be due to the different concentration of metallic SWNTs causing a PL quenching. Since it appears to be possible to fabricate brightly illuminating nanotubes on various kinds of substrates, the bundle engineering with freestanding nanotubes is expected to be a potential candidate for realizing the nanotube-based PL device fabrication.

<sup>1</sup>T. Kato and R. Hatakeyama, Appl. Phys. Lett., 92 (2008) 031502.

<sup>2</sup>T. Kato and R. Hatakeyama, J. Am. Chem. Soc., accepted.

4:00pm **NM+PS+AS-WeA8 Practical Considerations for Implementation of Nanomaterials in Aerospace, K.D. Humfeld, The Boeing Company**  
**INVITED**

4:40pm **NM+PS+AS-WeA10 Large-Scale Production and Metrology of Vertically Aligned Carbon Nanotube Films, L. Dai, K. Bosnick, National Research Council Canada**

We have successfully produced carbon nanotube (CNT) films (25-50 wafers per load) on a large scale in a commercial Tystar chemical vapor deposition (LPCVD) system. Electron microscopy studies indicate that the CNT films

are consisted of densely packed and vertically aligned multi-walled CNTs. A series of catalysts and growth conditions are tested systematically to synthesize high quality CNTs by varying the catalytic metal compounds and the CVD parameters. Both Fe films and ternary metal Cr/Ni/Fe films have been found favorable for the growth of aligned CNT films. To assess the as-grown vertically aligned CNT films, we are developing a general metrology which contains various analytical techniques to qualify the CNT film morphology, size, chirality, homogeneity, purity, dispersion, etc. This metrology uses some of the measurement equipments that are broadly used for material characterizations, including scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, profilometry, contact angle measurement and thermo gravimetric analysis (TGA). The metrology will facilitate quality control and process optimization necessary for industry applications of CNT films.

**5:00pm NM+PS+AS-WeA11 Linewidth Measurements on sub-20 nm HSQ/Graphene Nanostructures, J.J. Peterson, Intel Corporation, M.A. Rodriguez, V. Tileli, University at Albany-SUNY, M. Sprinkle, C. Berger, W.A. de Heer, Georgia Institute of Technology**

Although linewidth measurements of patterned graphene nanoribbons using the high resolution (HR) scanning electron microscope (SEM) have been reported in the literature,<sup>1</sup> it is known that such measurements are generally destructive to the structures which are being measured. Furthermore, due to the destructiveness of the measurement, the critical dimensions may be changing even as the measurement is being made. For this reason, the atomic force microscope (AFM) and scanning probe microscope (SPM)<sup>2</sup> has become an accepted method of linewidth measurement for graphene or hydrogen silsesquioxane (HSQ) on graphene structures, but this methodology is not scaleable to a manufacturing environment. For this reason, it is desired that a more manufacturable method of linewidth measurement may be developed for measurement of critical dimensions of graphene nanostructures. In this talk, we compare linewidth measurements sub-20 nm HSQ/graphene structures using the HR SEM and environmental-SEM (E-SEM) and report that E-SEM measurements will support the necessary resolution to enable linewidth measurements of graphene nanostructures without the damage associated with typical HR scanning electron microscopes. Furthermore, we make a comparison of linewidth measurements using both the SPM and E-SEM and discuss each respective method's advantages and disadvantages.

**5:20pm NM+PS+AS-WeA12 Size Distributions and Agglomeration Effects in FePtAu Nanoparticles, V.V. Krishnamurthy, Oak Ridge National Laboratory, Z. Jia, D. Reed, M. Mandal, G.J. Mankey, J.W. Harrell, D.E. Nikles, The University of Alabama, L. Porcar, NIST Center for Neutron Research**

We have investigated the effect of thermal treatment on the microstructure and positional ordering of chemically synthesized  $(\text{Fe}_{49}\text{Pt}_{51})_{88}\text{Au}_{12}$  nanoparticles using small angle neutron scattering (SANS). The as made FePtAu particles have an average diameter of 3 nm. Thin films of nanoparticles were prepared by spincoating the dispersion of FePtAu nanoparticle on Si wafers. The samples were annealed for 30 minutes in a flowing nitrogen atmosphere in order to promote FCC-L1<sub>0</sub> phase transformation. The annealing temperature of the samples was varied from 300 °C to 550 °C in steps of 50 °C. The crystal structure and the lattice constant of the samples have been determined by x-ray diffraction. The magnetization hysteresis has been measured in a vibrating sample magnetometer. SANS measurements were performed at room temperature with an incident neutron wavelength of 6 Å using the 30 m NG3 SANS instrument at NIST. The scattering vector magnitude (q) dependence of the SANS intensity, I(q) shows strong dependence on the sample annealing temperature. The q dependence of the SANS intensity in the range of 0.2 to 3 nm<sup>-1</sup> could be fitted by modeling the nanoparticles as polydisperse spheres with Schultz distribution for the diameters and a hard sphere interaction between the particles. In this q range, the agglomerates are assumed to be polydisperse spheres. The results indicate that significant agglomeration occurs in all the samples. The average size of the agglomerates is found to increase from 18 nm at 300 °C to 53 nm at 550 °C. The data also seem to indicate the sintering of particles in the temperature range of 500-550 °C. These results will be compared with the particle size distributions in off-situ annealed  $\text{Fe}_{49}\text{Pt}_{51}$  nanoparticles and in-situ annealed  $(\text{Fe}_{49}\text{Pt}_{51})_{88}\text{Au}_{12}$  nanoparticles.

# 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 Lipshitz 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.

# Thursday Afternoon, October 23, 2008

## Nanomanufacturing Focus Topic

Room: 309 - Session NM+MS+NS+NC-ThA

## Nanomanufacturing II: Nanostructures

Moderator: J. Murday, University of Southern California

2:00pm **NM+MS+NS+NC-ThA1 Superionic Electrochemical Patterning of Metallic Nanostructures**, *P.M. Ferreira, N.X. Fang, K. Hsu, K. Jacob, A. Kumar, P. Schultz*, University of Illinois, Urbana **INVITED**

Nanoscale metallic nanostructures find widespread and critical application in many micro and nanoscale technologies. Processes such as electrochemical and electro-discharge machining lack the fine control to obtain sub-micron resolution. As a result, such structures are generally fabricated using indirect patterning techniques, resulting expensive, lengthy multi-step manufacturing operations. In this presentation, we introduce a new means of directly patterning metal films into metallic nanostructures. The process, Solid-State Superionic Stamping (S4), uses a patterned solid-electrolytic stamp or mold to directly create metallic nano- and microstructures through electrochemical anodic dissolution. As a result, it requires very small mechanical forces and no contaminating liquids, and is capable of producing structures with nanoscale precision over large areas. This presentation will discuss the mechanism that underpins the process; characterize its capabilities in creating silver and copper nanostructures; discuss the fabrication of stamps, and some applications that such a process enables. The presentation will conclude with a description of the process technology under development and directions for future research.<sup>1</sup>

<sup>1</sup> This research was supported by NSF through the Center for Chemical-Electrical-Mechanical Manufacturing Systems (Nano-CEMMS) under Grant DMI-0312862, the Office of Naval Research under grant N00173-07-G013 and the University of Illinois through the Grainger Foundation grant. We are grateful that part of this work was carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-ER45439.

2:40pm **NM+MS+NS+NC-ThA3 Designing Semiconductor Nanocrystals for Optoelectronic and Biological Applications**, *M. Bawendi*, Massachusetts Institute of Technology **INVITED**

Semiconductor nanocrystals, aka quantum dots, have become the prototypical material for the emergence of new properties when dimensions are reduced to the nanometer range. The size dependent properties of excitons and multiexcitons in quantum dots, coupled with a material that can be engineered and processed from solution, has led to potential applications in fields that include emissive displays, solar energy conversion, and biological and biomedical fluorescence imaging. A fundamental understanding of exciton processes is critical for any of these applications to become realized. The design and synthesis of well characterized materials is obviously key, not only of the functional inorganic particle itself, but also the ligand shell that protects it and couples it chemically to molecules and matrices of interest. This talk will review some of the chemistry and photophysics of quantum dots and then explore the fundamental properties and challenges behind broadly applying quantum dots as light emitters and light absorbers in devices and for biological imaging.

3:20pm **NM+MS+NS+NC-ThA5 Controlled Assembly and Nanoscale Doping of Semiconductor Quantum Dots Using Focused Ion Beams**, *J.F. Graham, C.D. Kell*, University of Virginia, *J.L. Gray*, University of Pittsburgh, *J.A. Floro, S.A. Wolf*, University of Virginia, *L. Bischoff*, Research Center Dresden-Rossendorf Inc., Germany, *R. Hull*, University of Virginia and Rensselaer Polytechnic Institute

Self-assembled semiconductor quantum dots are a candidate for use in potential nanoelectronic device architectures such as quantum cellular automata and magnetic spin exchange switches. It is possible to grow quantum dots (QDs) with relatively uniform size-distributions using heteroepitaxial techniques, but in order to apply QDs in such nanoelectronic devices they must also be spatially ordered into patterns of varying complexity. In addition, the QDs must possess the magnetic or electronic properties required for device operation. We have previously demonstrated the use of Ga<sup>+</sup> focused ion beam (FIB) templating of Si surfaces prior to growth in order to fabricate patterns of Ge(Si) QDs of any desired complexity. Our current work employs a mass-selecting FIB with liquid metal alloy ion sources, enabling the generation of a wide range of separated species in focused beams, to template QD structures and electrically or magnetically dope them at a dot-by-dot level for nanoelectronic device applications. Ions can be selected according to isotope mass and charge state by using a mass-selecting Wien filter.

Suitable alloy sources then provide the ability to template a Si substrate with electrically non-invasive ions (i.e. Si or Ge) and implant dopant ions for electronic or magnetic activation (e.g. with B or Mn), with resolution of < 50nm and doses down to a few ions per dot. Key technical issues we are addressing include i) the attainable limits of spatial resolution and the dot-by-dot implantation dose, ii) comparisons between Ga and Si ion templated growth, iii) physical alignment between a templating ion beam and a dopant implantation ion beam and iv) procedures for eliminating unwanted exposure of adjacent areas of the sample to implantation ions.

4:00pm **NM+MS+NS+NC-ThA7 Semiconductor Nanowires: From Materials Science to Device Physics**, *L. Samuelson*, Lund University, Sweden **INVITED**

In the general trend towards the use of self-assembly for realization of ultra-small devices on the 10nm-scale, semiconductor nanowires (NWs) have emerged as one of the most interesting candidates. In this talk I will describe different materials science aspects of NW growth, with a focus on III-V NWs grown epitaxially on a single-crystalline substrate as a top-down guided bottom-up growth of NWs. I will present recent progress in studies of structural properties of such NWs, including the importance and control of the stacking sequence of subsequent layers in NWs. I will then describe the controlled formation of axial and radial heterostructures, which is of great importance for the use of NWs for basic physics studies as well as for applications in electronics and photonics. As examples of recent physics studies of NWs I will describe transport via single and multiple quantum dots and optical studies of excitonic recombination in single quantum dots in NWs. Finally, I will give an update on the progress in realizing electronic as well as photonic devices using NWs, and will here primarily present progress in technology and performance of wrap-gate field-effect transistors. I time allows I will conclude with some visions for where I think NW-based science and technology may be heading in the future.

4:40pm **NM+MS+NS+NC-ThA9 Surface Plasmon Enhanced Photoluminescence from Noble Metal/CdS Hybrid Semiconductor Nanowires**, *W. Luo, S.C. Kung, W.V. Veer, R.M. Penner, J.C. Hemminger*, University of California, Irvine

Surface plasmon enhanced techniques provide promising methods to improve the light emission efficiency of semiconductor materials. In this talk, we present the growth of noble metal/CdS hybrid semiconductor nanowires, and the plasmon-enhanced photoluminescence from these nanowires. In our previous studies, we demonstrated the straightforward fabrication of ordered linear arrays of spherical silver nanoparticles with gaps between the individual nanoparticles of less than 10 nm on highly oriented pyrolytic graphite (HOPG) surfaces using physical vapor deposition (PVD) under controlled experimental conditions. These silver nanoparticle arrays were capable of supporting very strong surface plasmon resonances, which was demonstrated by our polarized surface enhanced Raman scattering experiments. In this presentation, we describe experiments where following the PVD growth of Ag or Au nanoparticle arrays on HOPG surfaces, we electrochemically deposit cadmium around these nanoparticle arrays to form hybrid nanowires as thin as 50-60 nm in width. Further annealing of these hybrid nanowires in H<sub>2</sub>S at temperatures of 300-320°C enables the formation of CdS nanowires around the Ag or Au nanoparticle cores. Using this combined PVD/electrochemistry/chemical modification approach we have been able to generate ordered 2-D arrays of hybrid semiconductor nanowires that are as small as 100 nm in diameter and 100s of microns in length. Under light illumination, the surface plasmon supported by the Ag or Au nanoparticle cores enhances the photoluminescence of the outer CdS nanowires.

5:00pm **NM+MS+NS+NC-ThA10 Metal Oxide Nanowires by Near Field Electrospinning**, *M. Rinaldi, F. Ruggieri*, University of L'Aquila, Italy, *L. Lozzi*, CNISM and University of L'Aquila, Italy, *S. Santucci*, CNR-INFN and University of L'Aquila, Italy

The growth of metal oxide nanowire is an important challenge for the realization of nanostructured devices, as for example highly sensitive gas sensors.<sup>1</sup> A very easy method to deposit metal oxides is the electrospinning.<sup>2</sup> This simple and low cost technique allows the growth of very thin nanofibers, whose diameter can be varied from 50 nm to about 1 μm. It is based on the effect of an electric field on a charged liquid (polymer or solution) ejected from a nozzle. The charged jet is accelerated by the electric field, dries and is deposited onto a grounded substrate, forming nanofibers. Generally the nozzle-substrate distance is about 10-15 cm and the applied voltage is about 10-15 kV. Unfortunately this method does not allow easily the growth of well ordered nanofibers. In the present study TiO<sub>2</sub> nanofibers were electrospun with a novel approach of electrospinning called NFES (Near-Field Electrospinning), in which the tip-substrate

distance is strongly reduced to few millimetres, decreasing also the applied bias voltage to few hundreds of volts.<sup>3</sup> Significant advancement in collecting aligned electrospun nanofibers has been made with this improved technique that complements conventional electrospinning by providing the feasibility of controllable deposition for sub-100-nm nanofabrication. Well aligned TiO<sub>2</sub> nanofibers were grown onto a silicon dioxide substrate. These nanofibers were up to several millimetres long with a diameter of about 200-400 nm. The scanning electron microscopy showed the presence of microcrystallites, whose crystalline nature was confirmed by X-ray diffraction measurements after a thermal process, also used for removing the polymer. The chemical composition was investigated by X-ray photoemission spectroscopy showing that the nanofibers are composed by stoichiometric TiO<sub>2</sub> crystallites.

<sup>1</sup> S. Piperno, M. Passacantando, S. Santucci, L. Lozzi, S. La Rosa, *J. Appl. Phys.*, vol. 101, (2007) 124504.

<sup>2</sup> W.E. Teo and S. Ramakrishna, *Nanotechnology*, vol. 17, (2006) R89.

<sup>3</sup> D. Sun, C. Chang, S. Li, and L. Lin, *Nanoletters*, vol 6, (2006), p. 839.

**5:20pm NM+MS+NS+NC-ThA11 Luminescent Rare-Earth Doped Metal Oxide Nanostructures, Y. Mao, J. Dorman, J.P. Chang, University of California at Los Angeles**

Advanced luminescent materials have practical applications in nearly all devices involving the artificial production of light and considerable research has been carried out to synthesize new luminescent materials. Their luminescent properties have been shown to be dependent on the size and morphology of the crystallites, hence materials with dimensions in the nanometer regime emerges as promising materials. These attributes make them viably applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent work on the fabrication of rare-earth doped metal oxide nanostructures, including Er:Y<sub>2</sub>O<sub>3</sub> nanotubes (NTs) and nanoparticles (NPs) and Er:La<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> NPs, by hydrothermal and molten-salt syntheses.<sup>1,2</sup> The formation of nanostructures were probed in-situ by time-resolved synchrotron x-ray diffraction and absorption spectroscopy to delineate the process-structure-property relations. The as-synthesized nanostructures were further characterized by electron microscopy and various spectroscopy<sup>3</sup> to be single crystalline, with well controlled size distributions around 100-400 nm in outer diameter and 2-5 μm in length for Er:Y<sub>2</sub>O<sub>3</sub> NTs, around 80 nm in diameter for Er:Y<sub>2</sub>O<sub>3</sub> NPs, and around 15 nm in diameter for Er: La<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> NPs. The erbium coordination number and local bonding environment were shown to dictate the measured photoluminescent characteristics, including photoluminescence and cathodoluminescence. Specifically, these 0-100% erbium-doped oxide nanostructures have sharp and well-resolved photoluminescent behavior in the near-infrared region, outstanding green and red upconversion emissions, and excellent cathodoluminescent properties. These properties make these nanostructures promising for applications in display, bioanalysis and telecommunications.

<sup>1</sup>Mao, et al. Synthesis and luminescence properties of erbium-doped Y<sub>2</sub>O<sub>3</sub> nanotubes, *J. Phys. Chem. C*, 112, 2278 (2008).

<sup>2</sup> Mao, et al. Molten salt synthesis of highly luminescent erbium-doped yttrium oxide nanoparticles, submitted (2008).

<sup>3</sup> Mao, et al. Correlation between luminescent properties and local coordination environment for erbium dopant in yttrium oxide nanotubes, *J. Appl. Phys.* in press (2008).

## Nanomanufacturing Focus Topic

Room: Hall D - Session NM-ThP

## Nanomanufacturing Poster Session

**NM-ThP1 Nanoscale Release Effect of Antisticking Layer for Nanoimprint Resin Characterized by Scanning Probe Microscopy.** *M. Okada*, University of Hyogo, Japan, *M. Iwasa*, SII Nanotechnology Inc., *K. Nakamatsu*, *K. Kanda*, *Y. Haruyama*, *S. Matsui*, University of Hyogo, Japan  
Nanoimprint lithography (NIL) has a capability to fabricate nanostructure devices with a high-throughput and a low cost. Nanoimprint lithography molds are coated with an antisticking layer so that they do not come in contact with the adhesion of replication materials. Friction and adsorption occurs between the nanostructure mold and nanoimprint resin during demolding. Measuring the nanoscale frictional force and adsorptivity between the antisticking layer and resin is therefore important. In this paper, we measured the nanoscale frictional force and adsorptivity between a cantilever and nanoimprint resin by scanning probe microscopy (SPM) using Si cantilevers with and without antisticking layer. We used a self-assembled monolayer (SAM) consisting of a silane-coupling agent with fluoropolymer (OPTOOL DSX: Daikin industries) as an antisticking layer. The thermoplastic resin (PMMA; OEER 1000: TOKYO OHKA KOGYO Co.) and the photosensitive resin (PAK-01: Toyo Gosei Co.) were also used. In the SPM measurement using Si cantilever, results were obtained between the Si and NIL resin. On the other hand, the measurement results between the antisticking layer and resin were obtained by SPM using the cantilever with an antisticking layer. The frictional force of PMMA and PAK-01 measured using the cantilever with an antisticking layer are respectively 0.7 and 0.6 times lower than those using the cantilever without the antisticking layer. The adsorptivity of PMMA and PAK-01 measured by SPM using the cantilever with an antisticking layer are 0.4 and 0.6 times lower than those using the cantilever without the antisticking layer. These results show that SPM measurement using the cantilever with and without antisticking layers can be applied to evaluate the nanoscale release effect between an antisticking layer and nanoimprint resins.

**NM-ThP2 Ultrasonic Nanoimprint on Engineering Plastics.** *H. Mekaru*, *M. Takahashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

We have developed a new ultrasonic nanoimprint technology that is superior to the current thermal and UV nanoimprint technologies. In this method an ultrasonic vibration is impressed in the direction of loading force during a molding operation at room temperature. Our nanoimprint system employed a magnetostriction actuator capable of generating ultrasonic vibration with frequencies and amplitudes ranging from DC to 30 kHz, and from 0 to  $\pm 30 \mu\text{m}$  respectively. Here an electroformed-Ni mold consisting of dot and line/space patterns with a minimum width of 500 nm was employed to endure the mechanical stress by the ultrasonic vibration. The mold was mounted onto the ultrasonic generator with a photoresist. We report on the results of ultrasonic nanoimprinting on various engineering plastics. At first, several optimized imprinting conditions were investigated by using polyethylene terephthalate (PET,  $T_g = 75^\circ\text{C}$ ) with a comparatively low glass transition temperature ( $T_g$ ) in engineering plastics. When the frequency of the ultrasonic vibration was varied in steps of 0.1 - 10 kHz, and the amplitude in steps of 0.5 - 3  $\mu\text{m}$ , the height of the imprinted pattern was found to rise with the increase in the frequency and the amplitude. In this case, a rubber sheet serving as a buffer was interposed between the thermoplastic sheet and the bottom loading stage to keep the contact force of mold patterns on the thermoplastic uniform. By employing four kinds of rubbers the hardness of the buffer material was changed to 32, 57, 80, and 90°. When the low repulsion rubber sheet in the hardness of 57° was used without ultrasonic vibration, the height of the imprinted pattern reached a maximum. However, in the presence the ultrasonic vibration the optimized buffer material was a sheet of urethane in the hardness of 90°. Then under those same molding conditions, polycarbonates (PC,  $T_g = 150^\circ\text{C}$ ) and polymethyl methacrylates (PMMA,  $T_g = 105^\circ\text{C}$ ) were successfully imprinted and the pattern was observed by SEM; although in the absence of the ultrasonic vibration it was not possible to mold. The heights of the imprinted pattern were measured to be 1  $\mu\text{m}$  in PET, 750 nm in PMMA, and 370 nm in PC. The assisting effect of the ultrasonic vibration was found to be inversely proportional to  $T_g$ . Therefore, it is inferred that the thermoplastic was softened locally with the frictional heat generated by the ultrasonic vibration.

**NM-ThP3 Atomic Layer Etching of Cl-Adsorbed GaAs by Using a Low-Angle Forward Reflected Ne Neutral Beam.** *W.S. Lim*, *J.B. Park*, *G.Y. Yeom*, Sungkyunkwan University, Korea

GaAs compound-based semiconductors are currently investigated for various devices such as high efficiency solar-cell, high mobility electronic devices, optical devices, etc. due to direct band structure, high electron mobility, high operating temperature range, etc. For the processing of gallium arsenide (GaAs), conventional dry etching processes such as chlorine-based inductively-coupled plasma (ICP) are used but they tend to cause physical damage on the surface due to the irradiation of high energy ions during the etching, and which results in the degradation of the devices. Therefore, the removal of surface damage during the processing is essential and, among the various dry etching processes, atomic layer etching (ALET) has been studied to realize atomic scale etch-rate controllability of GaAs without physically damaging the surface of GaAs. In this study, the characteristics of ALET for (100)/(111) GaAs have been investigated as functions of  $\text{Cl}_2$  pressure during the adsorption stage and Ne neutral beam irradiation dose during the desorption stage. By using the Ne neutral beam dose and the  $\text{Cl}_2$  pressure higher than the critical values of  $3.03 \times 10^{16}$  atoms/cm<sup>2</sup>·cycle and 0.4 mTorr, respectively, one monolayer etching condition of 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs could be obtained through the adsorption of one monolayer of  $\text{Cl}_2$  during the adsorption stage and desorption of all of the chlorides formed on the surface by the sufficient Ne neutral beam irradiation. At the monolayer etching conditions, the surface roughness was the lowest and was similar to that of as-received GaAs. Therefore, the use of ALET condition enabled us to control the etch depth with an atomic-scale precision without damaging the surface physically or chemically.

**NM-ThP4 Fabrication of a Highly-Oriented Line Structure on an Aluminum Surface and the Nanoscale Patterning on the Nanoscale Structure using Highly-Functional Molecules.** *Y. Watanabe*, *H. Kato*, *S. Takemura*, *H. Watanabe*, *K. Hayakawa*, *S. Kimura*, *D. Okumura*, *T. Sugiyama*, *T. Hiramatsu*, *N. Nanba*, *O. Nishikawa*, Kanto Gakuin University, Japan, *M. Taniguchi*, Kanazawa Institute of Technology, Japan

The surface of an Al plate was treated with a combination of chemical and electrochemical processes. Chemical treatment with acetone and successive electrochemical process were performed on the aluminum surface. Dynamic force microscopy (DFM) measurements after the chemical treatment demonstrated that a fibril-like structure with random widths in the same orientation was initially formed. The successive electrochemical process made the initial fiber-like structure more ordered and finer. The anodization successfully created a nanoscale highly-oriented line structure on an Al surface. The distance between the oriented lines was estimated as 30-40 nm. Furthermore, the present work intended to make an organic-inorganic nanoscale pattern using this nanoscale structure. Copper phthalocyanine (CuPc), fullerene C60, and polyaniline were selected in fabrication of functional nanoscale patterning. CuPc and C60 molecules were deposited on the highly-oriented line-structure on an aluminum surface. A toluene droplet containing CuPc molecules was cast on the Al plate and extended on the surface. CuPc deposition on the Al surface was made by evaporation of toluene. Cross section analysis of the DFM measurements clarified that each row line was filled with CuPc molecules because the line structure was clearly observed after the deposition. The depth of the row line became shallow and in some area the row width became narrower after the CuPc deposition. X-ray photoemission spectroscopy (XPS) measurements clarified that N 1s and Cu 2p lines appeared, which also supports the CuPc deposition on the nanoscale structure creating a nanoscale organic line pattern. The spectral profile difference of Al 2p pre- and after CuPc deposition suggested the molecular-surface interaction. Furthermore, the fabrication of a polyaniline nanowire along the row channel of the highly-oriented line structure was performed. A droplet of HCl solution containing aniline molecules was cast and extended on the nano-structured Al plate. Successively, a droplet containing APS was put and extended on the surface. DFM and XPS clarified that aniline molecules were polymerized in the channel. X-ray photoemission spectroscopy (XPS) and Fourier transform spectroscopy measurements supported the polymerization of the nanowire. This work was supported by High-Tech Research Center Project aided by MEXT.

**NM-ThP5 Fabrication and Photoluminescent Properties of Nanostructured Al Surfaces Topped by Polythiophene Film and Copper Phthalocyanine.** *H. Kato, S. Takemura, A. Ishii, Y. Takarai, H. Kobe, Y. Watanabe, T. Hiramatsu, N. Nanba,* Kanto Gakuin University, Japan

Nanostructures such as linked-crater structure and highly-oriented line structure were fabricated on an Al surface by combination process of chemical and electrochemical treatments. Conducting polymer polythiophene nanofilm growth on the nanostructured Al surface was conducted by an electrochemical synthetic method. Copper phthalocyanine (CuPc) doping in the nanofilm was conducted by a diffusion method. Photoluminescent properties of the nanostructured Al surfaces and the surfaces topped by the nanofilm and CuPc were investigated. A nanoscale linked crater structure was fabricated on an Al surface by treatment with Semi Clean in order to create crater-shaped erosion on the surface as an initial structure. The successive electrochemical anodization in H<sub>2</sub>SO<sub>4</sub> solution created a nanoscale finer linked-crater structure on the surface. The crater size was estimated as 80-150 nm in diameter. Dynamic force microscopy (DFM) measurements clarified that small pores with 9 nm in diameter were created in each crater. Regarding the highly-oriented line structure, the anodization process applied to the original fiber-like surface structure on the Al plate. The anodization fabricated the finer line structure on the Al surface. The line distance was estimated as 40 nm. In the case of polythiophene film growth on the linked-crater structure, nanofilm was grown along the crater structure and the secondary structure remained demonstrated by DFM. Photoluminescence measurements on the linked-crater structure showed that five emission peaks appeared while no emission peaks were observed in the case of the original Al surface. Photoluminescence measurements on the polythiophene nanofilm on the linked-crater structure showed that the five emission peaks clearly appeared. The emission wavelengths were shifted. Furthermore, the photoluminescence measurement on the nanofilm doped with CuPc showed that the five emission peaks were enhanced. The photoluminescence measurements clarified that the nanostructured Al surface and the surface topped by nanofilm and CuPc molecules showed the characteristic emission properties for creation of functional hybrid materials. This work was supported by High-Tech Research Center Project aided by MEXT.

**NM-ThP6 Synthesis of Various Shaped Pt and FePt Nanoparticles.** *N. Shukla, M.M. Nigra, M. Bartel, T. Nuhfer, A.J. Gellman,* Carnegie Mellon University

We report the synthesis and self-assembly of controlled shapes and sizes of Pt nanoparticles using a high pressure synthesis technique. Our work suggests that solvent plays an important role in tailoring the shapes of Pt nanoparticles. Solvents can impact the synthesis because their boiling points dictate reaction trend and they also play a role as surfactants. Using various types of solvents under high pressure we have been able to synthesize Pt spheres, nanocubes and hexagons. 3D shapes of these nanoparticles are characterized using angle resolved high resolution TEM imaging. In addition, we report one step synthesis of core shell structures of cubic Pt nanoparticles. In this synthesis cubic Pt nanoparticles are the core and hexagonally shaped iron oxide/Fe is the shell. The most interesting part of this synthesis is that the shape of the core particles and shell is different. In most cases the core shells are either spherical or they acquire the shape of the nanoparticles. In this work we have achieved formation of cubic Pt nanoparticles with well hexagonal shaped iron oxide. These types of multiphase nanoparticles can have interesting applications in catalysis

**NM-ThP7 Analytical Model for Geometrical Characteristics Control of Laser Sintered Surfaces.** *Y. Ioannou, K. Polychronopoulou, C.C. Doumanidis,* University of Cyprus

Selective laser sintering (SLS) is an additive rapid manufacturing technique where high-power laser is used to fuse small particles into a specified 3-dimensional geometry. The goal of this work was to develop an analytical model for the SLS manufacturing processes, in order to control the geometrical characteristics of the sintered areas when iron/copper (Fe/Cu) powder alloy is used on a flat substrate. Powder particles are subject to melting by the laser energy and form a liquid globule, which solidifies as the laser beam spot moves on the substrate. The model is based on a system of lumped energy and mass balances, and the temperature field is computed via Green's function formulations by convolution of impulsive heat inputs at specific times and locations. The Green's function is dependent on the material conductive properties, substrate geometry, and boundary conditions. In considering the generated surface tensions due to powder melting, an approximation of the sintered area geometry after solidification of the material is performed via fluid dynamic equilibrium theory. Independent process parameters considered to govern the intensity of energy delivered to the powder material include laser power, beam spot size, beam velocity, hatch spacing and scan line length. Computational

simulations are calibrated via and validated against experimentally fabricated SLS samples with simple deposition geometries.

**NM-ThP8 Low Damage Etching of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> by using Halogen-Based Neutral Beams.** *S.-K. Kang,* Sungkyun Advanced Institute of Nano Technology (SAINT), Korea, *B.J. Park, S.W. Kim, T.H. Min,* Sungkyunkwan University, Korea, *G.Y. Yeom,* Sungkyun Advanced Institute of Nano Technology (SAINT), Korea

Phase-change random access memory (PRAM) has made a prominent progress in memory performance and has brought a bright prospect for the next generation nonvolatile memory technologies due to its excellent advantages. One of the chalcogenide-based phase-change materials that have been paid attention for nanoscale nonvolatile memories is Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) which has advantageous properties such as high-speed phase transformation and high degree of read-write cyclability without any compositional change between different phases. Ge-Sb-Te based materials are known to be formed by halogenations easily and apt to be damaged when exposed to plasma in the etch process. In this work, we present X-ray photoelectron spectroscopy (XPS) data obtained from the surface of blank GST and etched GST features after etching in the halogen inductively coupled plasmas (ICP) such as CF<sub>4</sub>, Cl<sub>2</sub> and HBr to investigate the extent of halogenation damage. And we also investigated surface damage of the GST etched by halogen-based neutral beam to compare with ICP process. Recently, the neutral beam etching (NBE) method is used by several researchers to avoid the charge-related damage. The damage related to charging can be eliminated because, compared to the conventional reactive ion etching, no ions participate in the etch process. Our neutral beam was formed using a low angle forward reflection of a parallel ion beam obtained by an ion gun. The XPS compositional depth profiling for the blank GST and the topological XPS analysis for the patterned GST were investigated after etching in the ICP and the NBE system to prove less damage process condition. In the etching of GST in halogen-based ICP and NBE system, the spectra of Ge, Sb and Te are shifted to higher binding energy region with different extents for different halogen-based plasmas. It indicates that GST film received different extent of damage for the halogen-based plasmas. Significantly, we could observe the less changes of GST-degradation when the NBE was applied to etch the GST.

**NM-ThP9 Templated Self-Assembling Conducting Polymers as a Substrate for Nanoscale Design.** *M.V. Lee, J.P. Hill, K. Ariga,* National Institute for Materials Science, Japan

Various strategies are being utilized to revolutionize nanoscale fabrication. A method based on a series of novel conductive polymers is demonstrated. Several functional groups can be incorporated into structures produced to affect both self-assembly and properties of the resulting polymer structures. Three dimensional structures for sensing and biological applications are envisioned.

**NM-ThP10 Plasma Treatment of PE Powder - From Laboratory Experiments to Production Plant.** *P. Spatenka, J. Hladik,* Technical University of Liberec, Czech Republic, *J. Pichal,* Czech Technical University of Prague

Plasma modification of powder has recently attracted much interest because of new perspectives of the interfacial properties supervision. Plasma modified powder was used as a filler for composite materials or for production of components using roto-molding technique. Parts sintered from the plasma modified polyethylene powder preserved high surface tension, which allowed e.g. direct painting or adhesive bonding without any additional pretreatment. Plasma modification also significantly enhanced adhesion of the polymer to the substrate. Various methods for powder treatment have been reported for low-pressure plasma treatment of powder including fluidized bed or reactors with mechanical stirring. Based on laboratory experiments and analysis of various treatment methods we proposed a concept for industrial scale production of plasma-modified powder. The principle of the industrial-scale reactor will be presented. Production capacity and cost estimation will be also presented. Partial support of the projects KAN101120701 and MSM 4674788501 and GACR 106/08/1665 is greatly acknowledged.

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