

## Thin Film

Room: B4 - Session TF-WeM

## Nanostructuring Thin Films I

Moderator: A.V. Melechko, North Carolina State University

8:00am **TF-WeM1 Growth of Thin Films of Nanomeshes on Solid Surfaces through Self-Assembly**, *F. Tao, S. Bernasek*, Princeton University

The growth of homogeneous 2-D multi-component ordered thin films has attracted surprising interest because they may offer the multiple functions of organic materials and the flexibility in fine-tuning the chemical, physical and mechanical properties for desirable needs in a wide spectrum of technological areas. Controllable molecular self-assembly on solid surfaces is a promising approach to the design of such thin films. Coadsorbed monolayers of 5-octadecyloxyisophthalic acid (5OIA) and octanoic acid and of 5OIA and terephthalic acid were fabricated on highly-ordered pyrolytic graphite (HOPG). The atomically-resolved morphology of these self-assembled monolayers was investigated using high-resolution scanning tunneling microscopy (STM). 5OIA coadsorbs with terephthalic acid via a hydrogen-bonding network, forming ordered domains made of alternating 5OIA and terephthalic acid lamellae. In the coadsorption of 5OIA with octanoic acid, 5OIA and octanoic acid alternately pack at the molecular level in each lamella, forming a homogeneous two-component crystal. Due to the different chain-lengths of the two components, a nano-hole with a size of  $13.5 \text{ \AA} \times 8.5 \text{ \AA} \times 1.8 \text{ \AA}$  is formed in each lattice unit, producing homogeneous nano-meshes. The size of nano-hole in the meshes is tunable by using alkyl chain of either of the two components with different length. This coadsorbed molecule-by-molecule self-assembly is the first demonstration of an approach to fabricating multi-component 2-D crystalline thin films at the molecular level. It suggests a new strategy to precisely and controllably grow homogeneous nano-structured composite thin films.

8:20am **TF-WeM2 Nanometer-Scale Direct-Write 3D-Patterning using Probes**, *A.W. Knoll, D. Pires, U. Drechsler*, IBM Zurich Research Laboratory, Switzerland, *J.L. Hedrick*, IBM Almaden Research Center, *M. Despont, U.T. Duerig*, IBM Zurich Research Laboratory, Switzerland

Progress in nanotechnology is intimately linked to the existence of high quality methods for producing nanoscale objects and patterns at surfaces. Scanning probe technologies are intrinsically capable of addressing real space with atomic resolution and have been used to fabricate nano-scale devices with exceptional quality. However, high resolution patterning in combination with sufficient throughput remains challenging. We have discovered that organic molecular glasses can be reproducibly removed at the micro-second time scale with nanometer scale precision using heated probes, which opens up new perspectives for nanopatterning.

In our experiments, a thin film of molecular glass with a thickness of 10-100 nm is deposited on a substrate by spin-coating or evaporation. The material is locally desorbed by heating the tip to 300-500 °C and applying a mechanical force of 50-100 nN for a duration of 5  $\mu$ s, leaving behind a well defined void. By laterally displacing the probe and repeating the process, any arbitrary pattern can be written whereby the resolution of the process is determined by the apex dimensions of the probe.

Material removal can be cumulated thereby enabling the fabrication of three-dimensional structures. A replica of the Matterhorn was fabricated by consecutive removal of molecular glass layers. The almost perfect conformal reproduction of the original proves that the final structure is a linear superposition of well defined single patterning steps.

The created two and three-dimensional structures were transferred into silicon substrates using standard RIE technology. Additionally, to enhance the aspect ratio, a three layer transfer process has been developed. It enables vertical amplification of the written structures by a factor of 50 without significant loss of lateral resolution.

Using this new technology, one is able to fabricate complex three-dimensionally textured substrates, e.g. for the guided and directed assembly of shape-matching objects. The technique also offers a competitive alternative in terms of resolution and speed to high-resolution electron beam lithography.

8:40am **TF-WeM3 Subwavelength Patterning of Organic Monolayers Via Nonlinear Laser Processing with fs-laser Pulses**, *N.O. Hartmann, S. Franzka, M. Mathieu*, University of Duisburg-Essen, Germany, *J. Koch, B.N. Chichkov*, Laser Zentrum Hannover, Germany, *A. Ostendorf*, Ruhr-Universität Bochum, Germany

In the last decade, surface processing with ultra-short laser pulses has emerged as a powerful tool for nanofabrication. Here, fs-laser patterning of self-assembled organic monolayers offers a variety of particularly promising perspectives. The ultrathin nature of these coatings allows for single pulse processing and hence ensures short processing times. It also allows for well-defined irradiation and burr-free patterning of the coating and avoids bubble and particle formation. All off which are problems usually encountered in fs-laser processing. Moreover, varying the chemical structure of the monolayer provides a means to tailor cross sections, incubation effects and resist properties and to enable chemical nanopatterning. Surprisingly, despite these promising perspectives, fs-laser processing of organic monolayers still is largely unexplored. In a recent study we investigated fs-laser patterning of alkylsiloxane monolayers on quartz glass substrates at  $\lambda=800$  nm and pulse lengths below 30 fs [1]. Selective decomposition of the coating with single laser pulses at subwavelength resolution can be carried out over a wide range of fluences from 4.2 down to 3.1 J/cm<sup>2</sup>. In particular, at a 1/e laser spot diameter of 1.8  $\mu$ m, structures with a width down to 250 nm and below were fabricated. Very similar results were also obtained from multiple pulse patterning experiments suggesting that incubation effects are negligible. Hence precise fabrication of complex patterns appears feasible. This opens up a facile route towards laser fabrication of transparent templates with chemical structures down into the sub 100 nm regime. Such templates represent promising platforms for biotechnological applications, e. g. biosensor arrays. Processing at higher fluences, also provides a facile route towards combined chemical/topographic structures, e. g. for microfluidic applications. With a band gap of 9 eV, quartz glass, of course, represents an ideal platform for nonlinear fs-laser processing via multiphoton absorption processes. Further results, though, demonstrate that fs-laser processing also allows for subwavelength patterning of organic monolayers on thin gold films. A general account on recent achievements in nonlinear laser patterning of organic monolayers via multiphoton absorption and photothermal processes is given.

[1] N. Hartmann, S. Franzka, J. Koch, A. Ostendorf und B. N. Chichkov, Appl. Phys. Lett. 92 (2008) 223111.

9:00am **TF-WeM4 Alloy Destabilization Behavior of Cu-Ni Thin Films on Si during Solid State Dewetting**, *S. Seshabhattar*, North Carolina State University, *P.D. Rack, R. Pearce*, University of Tennessee, *D.K. Hensley, M. Fuentes-Cabrera, J.D. Fowlkes*, Oak Ridge National Laboratory, *M.L. Simpson*, Oak Ridge National Laboratory and University of Tennessee, *A.V. Melechko*, North Carolina State University

Synthesis of nanoparticles research witnessed a remarkable headway with techniques spanning a wide range of materials and offering good control over particle shape and size. Top-down approaches have become successful in achieving controlled positioning of nanoparticles in pre-defined templates. A self-assembly method, however, is highly desirable because of its simplicity and compatibility with heterogeneous integration processes. Thin elemental or multicomponent films can be destabilized into self assembled arrays of nanoparticles. We will discuss how heating of ultrathin films can be a powerful but simple tool to fabricate functional nanostructures. Thin metal films on inert substrates are generally unstable, with their free energy resembling that of a spinodal system. Such films can spontaneously evolve into predictable morphologies with defined length scales. This process has been extensively used to prepare arrays of catalytic nanoparticles on Si surfaces for growth of vertically aligned carbon nanofibers. In this work we report on the behavior of Cu-Ni alloy thin films during solid state dewetting. The segregation of Cu-Ni alloy thin films during solid state destabilization on Si is in contrast to behavior expected from isomorphous system. Thin films of Cu-Ni and Ti-Cu-Ni were formed on Si and subjected to annealing temperatures from 300 °C - 700°C. Scanning Electron Microscopy(SEM) micrographs of these films revealed the formation of Cu-rich clusters on the surface prior to complete dewetting of the film in the range of temperatures much lower than dewetting of Ni film. The size and density of the Cu-rich regions increased with the increase in annealing temperatures. With increase in temperature the shape of these regions developed from irregular to cubical. The evolution of the alloy composition studied with Energy-Dispersive X-ray spectroscopy(EDX) mapping on both Si and Si covered with a Ti diffusion barrier will be presented. The solid state dewetting will be compared to laser processed

films, that is, dewetting in a fluidic transport regime rather than diffusive transport regime.

This work was sponsored by the Materials Sciences and Engineering program of the DOE Office of Science.

9:20am **TF-WeM5 Electrical, Optical and Structural Studies of Shallow Buried Au-PMMA Composite Films formed by Very Low Energy Ion Implantation**, *F.S. Teixeira, M.C. Salvadori, M. Cattani*, University of Sao Paulo, Brazil, *I.G. Brown*, Lawrence Berkeley National Laboratory

We describe our electrical, optical and structural studies of sub-nanometer composite films formed using a pulsed cathodic arc plasma gun to implant 49 eV gold ions into PMMA (polymethylmethacrylate) thin films (~ 50 nm thick). Electrical resistance measurements *in situ* as a function of implantation dose (up to  $2 \times 10^{16}$  atoms/cm<sup>2</sup>) show a conductivity increase that is well described by the percolation theory power law  $\sigma/\sigma_0 \approx (x - x_c)^t$ , where  $\sigma/\sigma_0$  is the measured metal/insulator composite conductivity ratio,  $x$  is the normalized concentration of the conducting phase atoms,  $x_c$  is the normalized critical concentration (percolation threshold) below which the composite has zero conductivity, and  $t$  is the critical exponent. For our Au/PMMA composite we found  $\sigma/\sigma_0 \approx (x - 0.4)^{1.65}$ , where  $x_c$  corresponds to a critical dose  $\phi_c = 1.0 \times 10^{16}$  atoms/cm<sup>2</sup>. We point out that the low energy implantation used here does not create any target vacancies or carbonization, which can occur for incident ion energy greater than about 100 eV, and thus that the electronic transport properties of the composite formed here are due only to the gold phase embedded in the original polymer. TEM (Transmission Electron Microscopy) images reveal that the gold phase is a shallow-buried sub-10 nm layer consisting of a distribution of nanoclusters (diameters  $\approx 2$  nm – 5 nm for implantation dose  $\phi < \phi_c$ ), spontaneously aggregated from the implanted gold ions, evolving to larger clusters as the dose increases. The computer simulation software TRIDYN, a dynamic version of the widely used TRIM (Transport and Range of Ions in Matter) that is more suitable when compositional changes are induced by the implantation itself as is the case here, gave very good predictions for the intermixed layer width and ion range, both with values lower than 10 nm. UV-Vis optical spectroscopy (ultraviolet to visible wavelength range) of the samples showed localized plasmon surface resonance effects from gold nanoparticles. SAXS (Small Angle X-ray Scattering) analysis was used to study the fractal character of the growth dynamics, the correlation lengths, and the size of agglomerates and elementary clusters. We related SAXS and UV-Vis data to percolation electrical behaviour. Note that the entire material is composed of a sequence, from substrate to surface, of PMMA thin film, shallow-buried composite film of nanoclusters, and an ultra thin film of unaltered polymer. These three layers can be electron beam lithographed at the same time, a highly desirable feature for application of the material for organic electronics/photonics.

9:40am **TF-WeM6 Preparation and Microstructure of Silver Nanoparticles Embedded into a Fluorocarbon Matrix Prepared by RF and DC Sputtering**, *D.G. Vásquez Mazzoti, A.F. Talledo Coronado*, Universidad Nacional de Ingeniería, Peru, *C. Benndorf*, University of Hamburg, Germany

Composite materials consisting of metal nanoparticles embedded in transparent dielectric materials are interesting materials due the size effects induced by the nanoparticles. We report about the preparation of fluorocarbon thin films with embedded silver nanoparticles and their characterization with UV-VIS spectroscopy, XPS (X-ray induced photoelectron spectroscopy), IR (infrared spectroscopy) and HRTEM (high resolution transmission electron microscopy). Further, the surface free energy was determined from contact angle measurements using different liquids. The metal-dielectric nanocomposites with a layered structure were prepared by switching alternatively the substrates (glass or stainless steel) from an RF powered Teflon target towards an Ag target powered by DC. The high resolution XPS spectra from the C 1s region displayed four peaks (on stainless steel substrates) with positions of 284.5, 286.5, 288.6 and 290.7 eV, related to C-H<sub>x</sub>, C-F, C-F<sub>2</sub> and C-F<sub>3</sub> bonds, respectively. For comparison, we measured the XPS spectrum from a Teflon surface (after scratching the surface). From this surface, the carbon 1 s region was dominated by two peaks, located at 284.6 (C-H<sub>x</sub>) and 289.0 eV (C-F<sub>2</sub>). The different composition of the sputtered films is due to the plasma process, which produces fragments like F, CF, CF<sub>2</sub> and CF<sub>3</sub> radicals and ions. The incorporated Ag nanoparticles gave only weak XPS signals from the Ag 3d doublet around 368 - 374 eV. UV-VIS spectra, measured in the range of 300 - 800 nm in transmission, showed with the presence of the Ag nanoparticles pronounced absorption peaks at around 420 to 480 nm, depending on the amount of incorporated Ag and different preparation conditions. This absorption maximum is related by us, in accordance with other authors, to the surface plasmon loss of the Ag nanoparticles where the loss energy depends on the particle size and form, the concentration of the particles and the nature (dielectric constant) of the surrounding matrix.

HRTEM pictures showed the presence of Ag nanoparticles with sizes between 5 and 50 nm. The filling factor of Ag (within the fluorocarbon matrix) was about 0.3. Crystalline planes from the Ag nanoparticles could be observed with (200) and (111) orientation. The evaluation of the lattice spacing resulted in  $d_{200} = 0.204$  and  $d_{111} = 0.237$  nm which is within 1% of the bulk Ag values. The surface free energy of our films was determined by the observation of the contact angle of liquid drops, using water, ethyl alcohol and olive oil. The evaluation was done following the method of Zisman. We obtained a value around 15mN/m, which is approximately 50% of the value reported for bulk Teflon.

10:40am **TF-WeM9 Dewetting in Single and Bilayer Metallic Films under Pulsed Laser Irradiation**, *H. Krishna*, Washington University, *R. Sachan, N. Shirato, J. Strader*, University of Tennessee, *A.K. Gangopadhyay*, Washington University, *H. Garcia*, Southern Illinois University, *R. Kalyanaraman*, University of Tennessee **INVITED**

Metallic nanostructures and nanocomposites have many applications related to their magnetic, plasmonic and magneto-optical properties. Fabricating desired structures and compositions in a reliable and cost-effective manner is therefore of substantial importance to applications in energy harvesting, sensing and data processing. Here we will focus on the robust pattern formation characteristics of thermodynamically unstable single and bilayer metallic films. The unstable energy state manifests itself as spontaneous dewetting and self-organization under energetic radiation, such as from nanosecond pulse lasers. The ensuing patterns contain a fascinating range of nanostructures as well as physical properties. The general principle that explains the length-scale selection for this pattern formation is the balance between rates of free energy change and energy loss during film deformation. We have applied this principle to the single and bilayer systems and have found very good agreement with experimental observations. We will also briefly discuss our studies of nanoscale nucleation, size-dependent magnetic anisotropy, plasmonic behavior and the magneto-optical properties of some elemental and composite metallic materials made by this self-organization process.

\* This work is supported by NSF grants CAREER DMI-0449258, CMMI-0757589, DMR-0805258 and by Center for Materials Innovation grant # 94509A

11:20am **TF-WeM11 Subsurface Oxidation for Micropatterning Silicon (SOMS)**, *F. Zhang*, Brigham Young University, *K. Sautter*, Yield Engineering Systems, *R.C. Davis, M.R. Linford*, Brigham Young University

We introduce a straightforward patterning technique for native oxide-capped silicon to produce features of both nanometer and micron dimensions: subsurface oxidation for micropatterning silicon (SOMS). In this method, a stencil mask with, for example, ca. 5 micron features is positioned over a silicon surface. RF plasma oxidation of the substrate creates a pattern of thicker oxide in the exposed regions. Etching with HF or KOH produces very shallow (few nanometer) or much higher aspect ratio features (hundreds of nanometers deep) on silicon, respectively, where patterning is confirmed by atomic force microscopy, scanning electron microscopy, and optical microscopy. The oxidation process itself is studied under a variety of reaction conditions, which have not been thoroughly explored in the literature, including higher and lower oxygen pressures (2 and 0.5 Torr), a variety of powers (50 – 400W), different treatment times, and as a function of reagent purity (99.5% or 99.994% oxygen). A mathematical model of the results is derived. The reagent purity, even at the high level studied, is shown to influence the process. SOMS can be easily performed in any normal chemistry lab with a plasma generator. Because of its simplicity, it may have industrial viability.

11:40am **TF-WeM12 Variable-Thickness Patterns using Full-Wafer Dynamic Stencil Lithography**, *V. Savu*, EPFL, Switzerland, *S. Sansa, F. Perez-Murano*, CNM-IMB, CSIC, Spain, *J. Brugger*, EPFL, Switzerland

Stencil lithography is a shadow mask technique allowing patterning at full-wafer scale from micro to nanostructures by material deposition, etching or ion implantation. It offers unique opportunities for processing where standard lithography cannot be applied, such as on top of 3-dimensional and flexible/functionalized substrates [1]. In the dynamic stencil mode, the stencil and substrate move in-situ relative to each other during or in between depositions. This mode can be used for multi-material, variable thickness patterning [2]. Here we present the in-situ fabrication of variable-thickness structures by using dynamic stencil lithography.

The dynamic stencil setup consists of an x-y moving stage with 20 nm encoding resolution each and three z-stages on which the stencil is attached, and a fixed part which holds the substrate, as described in [3]. The x-y stage is programmed to move along various trajectories. The movement parameters are the (x,y) coordinates of the start and end point (corners), the gap between stencil and substrate, and the stencil speed (0.04-5  $\mu$ m/s).

By evaporating materials at a constant rate while changing the speed of the stencil, we obtained variable-height structures. We also varied substrate materials (SiO<sub>2</sub>, SiN) and parameters such as the deposition rate and the stencil-substrate gap. These structures were characterized by scanning electron microscopy and atomic force microscopy. We also analyzed the pattern transfer integrity from the stencil to the substrate as a function of stencil-substrate gap and aperture size.

Dynamic stencils are used here for patterning two-dimensional variable-height structures by material deposition through a stencil at 4" wafer scale. The contamination-free, parallel-processing, and versatile nature of dynamic stencil lithography provides custom applications with a novel solution.

[1] K. Sidler, O. Vazquez-Mena, V. Savu, G. Villanueva, M. A. F. van den Boogaart, and J. Brugger, "Resistivity measurements of gold wires fabricated by stencil lithography on flexible polymer substrates," *Microelectronic Engineering*, vol. 85, pp. 1108-1111, May-Jun 2008.

[2] J. L. Wasserman, K. Lucas, S. H. Lee, A. Ashton, C. T. Crowl, and N. Markovic, "Fabrication of one-dimensional programmable-height nanostructures via dynamic stencil deposition," *Review of Scientific Instruments*, vol. 79, p. 4, Jul 2008.

[3] V. Savu, M. A. F. v. d. Boogaart, J. Brugger, J. Arcamone, M. Sansa, and F. Perez-Murano, "Dynamic stencil lithography on full wafer scale," *Journal of Vacuum Science & Technology B*, vol. 26, pp. 2054-2058, 2008.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Benndorf, C.: TF-WeM6, 2  
Bernasek, S.: TF-WeM1, 1  
Brown, I.G.: TF-WeM5, 2  
Brugger, J.: TF-WeM12, 2

## — C —

Cattani, M.: TF-WeM5, 2  
Chichkov, B.N.: TF-WeM3, 1

## — D —

Davis, R.C.: TF-WeM11, 2  
Despont, M.: TF-WeM2, 1  
Drechsler, U.: TF-WeM2, 1  
Duerig, U.T.: TF-WeM2, 1

## — F —

Fowlkes, J.D.: TF-WeM4, 1  
Franzka, S.: TF-WeM3, 1  
Fuentes-Cabrera, M.: TF-WeM4, 1

## — G —

Gangopadhyay, A.K.: TF-WeM9, 2  
Garcia, H.: TF-WeM9, 2

## — H —

Hartmann, N.O.: TF-WeM3, **1**  
Hedrick, J.L.: TF-WeM2, 1  
Hensley, D.K.: TF-WeM4, 1

## — K —

Kalyanaraman, R.: TF-WeM9, **2**  
Knoll, A.W.: TF-WeM2, **1**  
Koch, J.: TF-WeM3, 1  
Krishna, H.: TF-WeM9, 2

## — L —

Linford, M.R.: TF-WeM11, 2

## — M —

Mathieu, M.: TF-WeM3, 1  
Melechko, A.V.: TF-WeM4, 1

## — O —

Ostendorf, A.: TF-WeM3, 1

## — P —

Pearce, R.: TF-WeM4, 1  
Perez-Murano, F.: TF-WeM12, 2  
Pires, D.: TF-WeM2, 1

## — R —

Rack, P.D.: TF-WeM4, 1

## — S —

Sachan, R.: TF-WeM9, 2  
Salvadori, M.C.: TF-WeM5, 2  
Sansa, S.: TF-WeM12, 2  
Sautter, K.: TF-WeM11, 2  
Savu, V.: TF-WeM12, **2**  
Seshabhattachar, S.: TF-WeM4, **1**  
Shirato, N.: TF-WeM9, 2  
Simpson, M.L.: TF-WeM4, 1  
Strader, J.: TF-WeM9, 2

## — T —

Talledo Coronado, A.F.: TF-WeM6, **2**  
Tao, F.: TF-WeM1, **1**  
Teixeira, F.S.: TF-WeM5, 2

## — V —

Vásquez Mazzoti, D.G.: TF-WeM6, 2

## — Z —

Zhang, F.: TF-WeM11, 2