Thin Film Division
Room: 110 - Session TF2+EM-WeA

Nanostructuring Thin Films
Moderator: A.V. Melechko, North Carolina State University

2:00pm **TF2+EM-WeA1 Templated Solid-State Dewetting for Patterning of Films**, ***C.V. Thompson***, *J. Ye, A.L. Giermann*, Massachusetts Institute of Technology **INVITED**

Most crystalline thin films are metastable in the as-deposited state, and will dewet to form islands when they are heated to temperatures that lead to sufficiently high atomic mobilities. This can happen well below the melting temperature of the film, so that the material remains in the form of a crystalline solid throughout the dewetting process. When unpatterned films dewet on flat substrates, the resulting islands have widely varying sizes and spacings. However, we have shown that substrate patterning can be used to control the solid-state dewetting process and to produce ordered arrays of monodispersed and crystallographically aligned islands from polycrystalline films. Recent experiments on patterned single-crystal films have allowed independent study of the various mechanisms that control structure evolution during solid-state dewetting. These include fingering instabilities, edge faceting, corner instabilities, pinch-off processes, and Rayleigh-like instabilities. Surface energy anisotropy plays a very important role in these processes, and for single-crystal films, leads to the formation of crystallographically aligned complex patterns of lines and islands that can be reproducibly controlled through pre-patterning.

2:40pm **TF2+EM-WeA3 Dynamics of Solid Thin-Film Dewetting in the Silicon-On-Insulator System**, ***E. Bussmann***, *F. Cheynis, F. Leroy, P. Müller*, CINaM-CNRS, France

Thin-film dewetting is a process wherein a film on a substrate spontaneously agglomerates into 3D islands, which in some instances are ordered. A detailed understanding of the mechanism and dynamics of dewetting is crucial, either to avoid the agglomeration, or to engineer organized arrays of nanostructures. Silicon-on-Insulator (SOI) films, which are promising substrates for microelectronics, undergo dewetting when annealed at >700°C under ultrahigh vacuum conditions. The Si film spontaneously transforms into an assembly of ordered nano-sized Si islands. Previous *ex-situ* studies of dewetted SOI films provided a qualitative description of the dewetting process [1-4]. However, the dewetting dynamics, as well as the thermodynamic driving forces and atomistic mechanisms at work, remained largely unclear. We simultaneously measure the real-time dewetting dynamics and the motion of surface atomic-steps (surface self-diffusion) using low-energy electron microscopy (LEEM) [5]. We observe the following scenario: (i) dewetting voids nucleate at defects in the Si(001) layer. In the early stages of dewetting, the area of the opening voids grows linearly with time, and the Si ejected from the voids accrues into a rim surrounding the dewetted area. (ii) As dewetting progresses, the rim undergoes an instability that leads to the formation of elongated Si fingers. Once the first fingers have formed, the void area grows as the square of time. (iii) Finally, the Si fingers undergo a Plateau-Rayleigh instability, breaking apart into 3D Si nano-islands. We compare our measurements of the morphological evolution of dewetting to a simple analytical model for dewetting void growth (based on surface diffusion, nucleation on the top of the 3D structures, and mass-conservation), and to Kinetic Monte Carlo simulations. The KMC simulations reproduce the qualitative features of the complex void shape evolution in detail, while the analytical model of void growth allows us to connect the void growth rate with the dewetting driving force. These approaches unambiguously show that the SOI dewetting process is surface-diffusion-limited and driven by surface and interface free-energy-minimization.

[1] D. T. Danielson *et al.*, J. Appl. Phys. 100, 83507 (2006).

[2] R. Nuryadi *et al.*, J. Vac. Sci. Technol. B, 20(1), 167 (2002).

[3] B. Yang *et al.*, Phys. Rev. B 72, 135413 (2005).

[4] E. Dornel *et al.*, Phys. Rev. B 73, 115427 (2006).

[5] E. Bussmann *et al.,* New J. Phys. 13 043017 (2011).

3:00pm **TF2+EM-WeA4 Self and Directed Assembly of Thin Metallic Films by Pulsed Laser Induced Dewetting**, ***Y. Wu***, University of Tennessee, *J.D. Fowlkes,* Oak Ridge National Laboratory, *L. Kondic,* New Jersey Institute of Technology, *J. Diez,* Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Argentina, *N.A. Roberts, P.D. Rack*, University of Tennessee

The synthesis and assembly of functional metallic nanomaterials is critical for realizing many important applications of nanoscience and nanotechnology, and metallic thin film dewetting has been an effective and low-cost approach to this end. In this study, we investigated dewetting of metal thin films via pulsed nanosecond laser melting. We also explore the dewetting and nanopattern formation of nanolithographically pre-patterned thin films of various shapes to understand initial and boundary conditions in guiding the assembly. More recently, nanolithography was used to impose the perturbation which ultimately led to an organized nanoparticle array. Specifically, liquid–phase pulsed laser induced dewetting (PLiD) was used to transform metallic thin film strips into nanoparticle arrays. We demonstrated that the assembly accuracy and precision could be drastically improved by merely imposing a synthetic sinusoidal perturbation onto the lateral surfaces of the thin film strip. The synthetic perturbations in the strip translated into an unstable varicose oscillation on the rivulet during retraction – a precise nanoparticle diameter and pitch emerged thereby superseding the otherwise naturally evolving modes predicted by the modified Rayleigh-Plateau instability. A nanoscale, synthetic perturbation was usefully imposed to "nudge" the natural, self–assembly dispersion toward significantly higher order.

4:00pm **TF2+EM-WeA7 Directed Self-Assembly of Ge Heteroepitaxial Quantum Dots with sub-35nm Spacing**, ***C. Petz,*** University of Virginia, *D. Yang, J. Levy,* University of Pittsburgh, *J.A. Floro*, University of Virginia

Artificially ordered Ge quantum dot (QD) arrays, where confined carriers can interact via spin coupling, may create unique functionalities such as spintronic bandgap systems. Development of such arrays for quantum computing requires fine control over QD size and spatial arrangement on the sub-35 nm length scale. We employ fine-probe electron-beam irradiation to locally decompose ambient hydrocarbons onto a bare Si (001) surface. These carbonaceous patterns are annealed in UHV, forming ordered arrays of nanoscale SiC precipitates that serve as templates for subsequent Ge quantum dot nucleation via strain-induced self-assembly during heteroepitaxy. The nanoprecipitates effectively reduce the critical thickness for Ge QD formation to below the 3-4 monolayers typical of Stranski-Krastanov growth in the Ge/Si (001) system. Thus, Ge QDs in the SiC-patterned regions nucleate prior to formation of randomly located QDs in the unpatterned areas. It is critically important to ascertain the variability in Ge QD size and placement, and ultimately to determine the crystalline quality and interface properties of these ultrasmall Ge dots on SiC nanoprecipitates. Using atomic force microscopy and cross-sectional transmission electron microscopy, we investigate the patterned surface morphology and internal structure of patterned QDs to develop a fundamental understanding of the Ge adatom behavior in the vicinity of local high lattice-mismatch nanoprecipitates. We find that Ge self-assembly at SiC sites depends on QD spacing and that the QD size is surface diffusion limited, suggesting that local alteration of the intermediate Si surface may repel Ge to higher lattice mismatched SiC sites. Support from the DOE Office of Basic Energy Sciences is gratefully acknowledged under grant number: DE-FG02-07ER46421.

4:20pm **TF2+EM-WeA8 Surface Functionalization of Zeolites and Nanoparticles: Understanding and Applying Plasma Modification Strategies for Unusually Shaped Particles**, ***J.C. Shearer***, *E.R. Fisher*, Colorado State University

Unusually shaped micron- and nanometer-sized particles are becoming key components in catalytic and biological applications. Zeolite particles are typically modified for ion-exchange and catalytic applications. Fe_2O_3 nanoparticles are widely used in biological applications such as MRI imaging and site-specific drug delivery, thereby creating a need for surface functionalization techniques to ensure biocompatibility. Plasma processing can effectively modify and implant functional groups onto flat substrates, and is non-directional. Thus, the primary focus here is on applying these plasma processes to unusually shaped materials and understanding the gas-phase chemistry and surface reactions that make these coatings viable. Previous work in our lab employed plasma-enhanced chemical vapor deposition to create composite SiO_2/TiO_2 nanoparticles. Here, we use plasma processing methods for the modification of zeolite surfaces and functionalization of Fe_2O_3 nanoparticles. Compositional and morphological

data demonstrate that the conformal treatment of particles was achieved and that the use of PECVD methods allowed for advanced control over surface modification and specific tailoring of the structure, composition, and growth characteristics of any deposited film. Insight into the modification and deposition process is provided by actinometric optical emission spectroscopy (AOES) and laser induced fluorescence spectroscopy (LIF), which allow characterization of the gas-phase species and their energetics (i.e. internal energies) for each system. To further investigate the functionalization of nanoparticle surfaces, additional studies explore the contributions of gas-phase OH radicals to the creation of SiO_2/Fe_2O_3 composite nanoparticles. Scatter coefficients and gas-phase density measurements derived from our imaging of radicals interacting with surfaces technique (IRIS) provides additional insight on the molecular-level chemistry occurring at the interface between gaseous plasma species and nanoparticle substrates. The operation and design of an in-house rotating drum reactor will be discussed as a potential method for adapting the composite nanoparticle fabrication to an industrial scale.

4:40pm **TF2+EM-WeA9 Role of Ion Flux on Alignment of Carbon Nanofibers Synthesized by DC Plasma on Transparent Insulating Substrates***, **R.C. Pearce**,* North Carolina State University*, A.W. Vasenkov,* CFD Research Corporation*, D.K. Hensley, M.L. Simpson, T.E. McKnight,* Oak Ridge National Laboratory*, A.V. Melechko*, North Carolina State University

A key factor to the implementation of vertically aligned carbon nanofibers (VACNFs) in devices is a more fundamental understanding of how to control fluctuations in the growth direction of the fibers. It has previously been hypothesized that the electric field is the primary factor in determining the orientation of fibers grown catalytically using plasma enhanced chemical vapor deposition (PECVD). Here we present results of carbon nanofiber synthesis on insulating substrates by dc plasma in the vicinity of grid electrodes. To perform these observations, VACNFS were synthesized on a fused silica substrate using direct current PECVD. To maintain continuous glow discharge above the substrate, a metal grid electrode layer (Cr) was deposited over silica with windows of exposed silica ranging in size from 200 µm to 1 mm. Observed trends in nanofiber alignment at the window-electrode interface suggests that the alignment is governed by the direction of the ion flux rather than the electric field at the substrate level. The proposed alignment mechanism is that ion sputtering of the carbon film on a catalyst particle the growth direction of the nanofibers. With this development, fiber growth direction can be better manipulated through changes in ionic flux direction, opening the possibility for growth of nanofibers on substrates with unique geometries.

5:00pm **TF2+EM-WeA10 High-Performance Poly-3-alkylthiophene-Carbon Nanotube Composites for Transparent Electrodes***, **S.L. Hellstrom**, R.Z. Jin, R.M. Stoltenberg, Z. Bao*, Stanford University

Flexible transparent electrodes are crucial for flat panel display and solar cell technologies. While carbon nanotube network electrodes show promise, their fabrication often involves insulating surfactants which worsen conductivity. As an alternative, we show that small amounts of conjugated semiconducting polymer added to nanotube dispersions enables straightforward solution deposition of uniform electrodes by spin-coating or drop casting. After doping, electrodes as good as 120 ohm/sq with 81% transmittance at 550 nm are obtained. Tuning system chemistry and deposition parameters allows control of tube bundle size, density, and alignment, and these may be correlated with electrode performance.

We also employ the selectivity of P3HT:CNT composites in wetting of and adhesion to different dielectric surfaces, to simultaneously fabricate and pattern organic electrodes with unprecedented nanotube density gradients and excellent feature resolution. We employ these to drive pentacene and C_{60} transistors that are competitive with those made using Au electrodes. We thereby suggest that this material system and fabrication technique has promise in applications requiring flexible, semitransparent, low-cost complementary circuits.

5:20pm **TF2+EM-WeA11 SiGe Nanomembranes: Defect-Free Single-Crystalline Growth Substrates for High- Quality Strained Epitaxial Materials***, **D.M. Paskiewicz**, B. Tanto, D.E. Savage, M.G. Lagally*, University of Wisconsin Madison

Silicon-Germanium semiconductor alloys are important in improving Group IV opto- and microelectronics. Typically, SiGe is used as a stressor to introduce strain into Si, thereby altering the electronic band structure [1, 2] or changing optical properties [3]. The SiGe stressor can be incorporated locally to strain small areas of Si uniaxially [2], or relaxed SiGe can be used as a substrate for growth of biaxially strained Si over large areas [1]. We will focus on the latter: using relaxed SiGe to induce global biaxial strain in Si. Conventional methods for creating relaxed SiGe substrates involve epitaxial growth on Si substrates and relaxation of the alloy *via* dislocations. The density of defects that reach the top relaxed SiGe layer can be limited though various techniques [4], but strain inhomogeneities and surface roughness created by the dislocations remain. We demonstrate the fabrication of SiGe nanomembranes (NM): fully *elastically* relaxed, smooth, single-crystalline sheets of SiGe alloy. A thin SiGe layer (less than the kinetic critical thickness for dislocation formation) is grown on a silicon-on-insulator (SOI) substrate with molecular beam epitaxy (MBE), followed by a Si capping layer of similar thickness to the Si template layer of the SOI. The SiO_2 layer of the SOI is selectively etched away, leaving the Si/SiGe/Si trilayer heterostructure free to strain share [5]. The Si layers of the trilayer are then selectively etched away, leaving a fully elastically relaxed SiGe NM. These SiGe NMs can be transferred to new handling substrates, bonded, and used as templates for growth of new defect-free materials.

A specific application involving strained Si/relaxed SiGe heterostructures is fabrication of 2-dimensional electron gas devices (2DEGs) that can be patterned and gated to confine individual electrons into quantum qubits with long spin coherence times [6]. These devices are very sensitive to changes in the electrostatic potential and thus require superb material quality. We compare the material quality of strained Si/SiGe heterostructures grown on SiGe NMs with those created on SiGe substrates relaxed *via* dislocations.

Research supported by DOE. Facilities support from NSF-MRSEC is acknowledged. DMP is supported by a NSF Graduate Research Fellowship.

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2. Chu et al., *Annu. Rev. Mater. Res.* **39** (2009) 203.

3. Jacobsen et al., *Nature* **441** (2006) 199.

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6. Simmons et al., *Phys. Rev. Lett.* **106** (2011) 156804.

5:40pm **TF2+EM-WeA12 Multilayer Barrier Coatings for Organic Photovoltaics***, **A.M. Coclite**, K.K. Gleason*, Massachusetts Institute of Technology

Barrier coatings, which prevent the permeation of water into OPV devices fabricated on flexible plastic substrates, are essential to extend the device lifetime. Such protective coatings are made of multilayer stacks where multiple dense, inorganic layers are alternated with soft, organic ones. The inorganic layer contains inevitably some pinholes and defects. The roles of the organic layer are (i) creating a tortuous and longer path among the defects of two successive inorganic layers (ii) filling the pores of the inorganic underlayer limiting the propagation of defects from one inorganic layer to the other and (iii) smoothening the substrate surface roughness.

In the past, we obtained good barrier properties (WVTR= 10^{-2} $g/cm^2/day$) with a hexalayer obtained by coupling initiated CVD (iCVD) and plasma enhanced CVD (PECVD). iCVD layers resulted in effective defect decoupling and good planarization of the substrate.[1]

Now a similar approach is investigated for the multilayer deposition in a large-area reactor (0.16 m^3), maintaining the same organosilicon precursor and the same reactor configuration for both deposition of silica-like and organosilicon layers.

SiO_x layers were deposited through PECVD in MW plasma at high power and high oxygen dilution. The silanol and organic groups were not detectable by IR spectroscopy, resulting in denser film if compared with the previous results.

A new process was used for the formation of organosilicon polymers with enhanced monomer structure retention compared to a conventional plasma deposition and faster deposition rate if compared to conventional iCVD processes from organosilicon monomer. We demonstrate that the monomer molecule remains substantially preserved in fact the C/Si ratio calculated from XPS data on the polymer was 4.3, close to the 3.7 C/Si elemental ratio of the monomer molecule.

The deposition of smoothening organic layers is demonstrated by depositing the coating on the top of a microsphere (1 µm in diameter) monolayer deposited over silicon wafers. Increasing the thickness of the coating, the degree of planarization (DP), both local (DLP) and global (DGP), increases. The DLP increases much faster than the DGP: when the coating is 1µm-thick the DLP is already 99%, for the global planarization instead a 1.8µm-thick-coating is needed to reach DGP= 99%.

The high density of the inorganic layer, the smoothness and planarization properties of the organic one make this approach particularly promising for the deposition of effective multilayer barrier coatings.

[1] Coclite, Ozaydin-Ince, Palumbo, Milella, Gleason, *Plasma Proc. Polym.*, **2010**, *7*, pp. 561

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