

## Thin Film

Room: B4 - Session TF-ThM

## Nanostructuring Thin Films II

Moderator: P.D. Rack, University of Tennessee

8:00am **TF-ThM1 Nanostructure of Gold Film Over Vertically Aligned Carbon Nanofiber Surface Impact on Immobilization of Alkanethiols**, *R. Desikan*, North Carolina State University, *T.E. McKnight*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *A.V. Melechko*, North Carolina State University

Chemical self-assembly has been widely used for several applications including surface modification and functionalization. The physics and chemistry of alkanethiol self-assembled monolayers (SAM) has been extensively studied. It is well known that SAM structures of alkanethiol are strongly influenced both by the surface structure of the underlying gold substrate. It has also been shown that the adsorption of alkanethiols onto gold surfaces having large, flat grains produces high-quality self-assembled monolayer. In this study we have investigated the effect of SAM formation over carbon nanofibers coated with gold thin film. The film nanostructure is strongly affected by the morphology of the surface on these high aspect ratio 3D features. The thiolated molecules are chosen due to the strong affinity of sulfur head groups with the gold surface of the carbon nanofibers. The difference in surface stress response alkanethiol of adsorption in vapor phase on large- and small-grained gold correlates well with differences in alkanethiol coverage and SAM structure on those substrates. We will present observations of how the surface structure of the underlying gold substrate influences the kinetics of SAM formation. It has been shown earlier that in the case of gold surfaces with small grain sizes (<100 nm), access to the high coverage, standing-up phase is inhibited. A comparison of annealed for increasing grained gold surfaces on the fibers to as deposited film will be discussed. The characterization of molecular coverage as a function of the gold grain size with an x-ray photoelectron spectroscopy will be presented.

8:40am **TF-ThM3 Spontaneous Growth of In-whiskers from In-Y Thin Films Prepared by Combinatorial Magnetron Sputtering Technique**, *T. Takahashi*, *A. Abdulkadhim*, *D. Music*, *J.M. Schneider*, RWTH Aachen University, Germany

In-Y binary thin films with a composition gradient were prepared using a combinatorial magnetron sputtering technique. In-whiskers grow spontaneously from the film surface at room temperature upon exposure to air. Whisker morphology and population vary with the In to Y ratio. An appreciable amount of In-whiskers is formed at film compositions close to In-25 at.%Y. The In-whisker thickness ranges from a few hundreds nanometers to a few micrometers.

In order to identify the whisker growth mechanism, temporal changes of the film surface upon air exposure were captured using scanning electron microscopy. X-ray micro diffraction was employed for studying the structural evolution during the In-whisker growth in air. The results show that the In-whiskers grow not from the tip but from the root. The whisker growth rate was as high as 150 nm/s. The growth of In-whiskers is found to be related to the incorporation of oxygen into the film during air exposure. Correspondingly, the In concentration within the film decreases as In-whiskers grow. The mechanism of the spontaneous In-whisker growth presented here can be understood based on the stress-induced extrusion of In-whiskers due to the selective room temperature oxidation of Y in sputtered In-Y thin films.

9:00am **TF-ThM4 Photothermally Induced Microchemical Functionalization of Organic Monolayers**, *A. Schroeter*, *B. Klingebiel*, *N.O. Hartmann*, University of Duisburg-Essen, Germany

Photochemical routines are widely recognized as a versatile means to fabricate multifunctional patterned organic monolayers with laterally alternating chemical terminations. The lateral resolution, in turn, usually is limited by optical diffraction, that is, the fabricated structures are not much smaller than the wavelength even when highly focusing optics are used. A simple routine for sub-wavelength nanopatterning of organic monolayers relies on photochemical processes, which take advantage of nonlinear effects [1]. In photochemical processing a focused laser beam is used to locally heat the substrate and initiate thermal decomposition of the monolayer. Silane-based monolayers can be patterned from the micrometer-range down to the sub 100 nm range. In analogy to photochemical routines, it is tempting to explore photochemical procedures which allow to locally functionalize organic monolayers. Here we report on a simple photochemical procedure for

local bromination of organic monolayers [2]. Surface-oxidized silicon samples are coated with alkylsiloxane monolayers. Local irradiation with a focused beam of an argon ion laser ( $\lambda = 514$  nm) in gaseous bromine leads to bromination of the monolayer in a confined micrometer-sized reaction zone. While irradiation induces photolysis of bromine molecules in the gas phase, the local temperature rise of the substrate in the focal area allows for bromination of the alkyl chains. Thus locally brominated surface structures are fabricated. In conjunction with other chemical transformations this provides an efficient route to a broad variety of functional groups. This allows to build up functional surface architectures via directed self-assembly of nanoscopic building blocks such as noble metal nanoparticles and stimuli-responsive polymers. Mechanistic aspects and prospects of photochemical routines in micro- and nanofabrication of multifunctional organic monolayers are discussed.

1. D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, *Nano Lett.* 6 (2006) 2358.

2. B. Klingebiel, A. Schröter, S. Franzka, N. Hartmann, *ChemPhysChem*, in press.

9:20am **TF-ThM5 Composite Nanoparticles Produced Using Plasma-Enhanced Chemical Vapor Deposition of SiO<sub>2</sub> and Amine-Containing Films**, *J.C. Shearer*, *E.R. Fisher*, Colorado State University

TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles are of significant importance in both chemical and biological applications. TiO<sub>2</sub> nanoparticles are used in paint, coatings, food, solar technology and many other areas. Fe<sub>2</sub>O<sub>3</sub>, as well as other magnetic nanoparticles, are used in the biomedical industry in drug delivery schemes as well as for magnetic resonance imaging contrast agents. Silica-coated TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles have distinct properties and enhanced functionality over those of uncoated nanoparticles. Plasma-enhanced chemical vapor deposition (PECVD) was employed to conformally coat TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles with SiO<sub>x</sub> and amine-containing films, thereby creating composite nanomaterials. Hexamethyldisiloxane (HMDSO)/O<sub>2</sub> plasmas were used to create SiO<sub>2</sub> and SiO<sub>x</sub>C<sub>x</sub>H<sub>y</sub>-coated nanoparticles and pulsed hexylamine (HexAm) plasmas were used to create amine-containing hydrocarbon materials, all of which were analyzed using Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and magnetic susceptibility. Films deposited on the nanomaterials showed little difference from those deposited on flat substrates. The performance of the TiO<sub>2</sub> nanoparticles was tested using UV-vis spectroscopy to determine dispersion characteristics of SiO<sub>x</sub>-coated TiO<sub>2</sub> materials, which can give information about the agglomeration of the nanoparticles in solution. Notably, the coated materials stay dispersed longer in polar solvents, suggesting the coated nanoparticles may be better suited for applications involving colloidal suspensions. Magnetic susceptibility characterized the magnetic properties of the Fe<sub>2</sub>O<sub>3</sub> nanoparticles before and after film deposition. Comparison of the mechanical and chemical properties of different composite nanomaterials will be discussed along with the influence of film composition on performance.

9:40am **TF-ThM6 Tailoring Local Conductivity by the Formation of Ag Nanoparticles in SiO<sub>2</sub> Xerogel Films**, *M.F. Bertino*, *R.J. Caperton*, *A.A. Baski*, Virginia Commonwealth University

Thin SiO<sub>2</sub> xerogel films (~200 nm) were fabricated by dip coating and were doped with Ag<sup>+</sup> by adding AgNO<sub>3</sub> to the parent solution. Nanoparticles were then fabricated inside the pores of these films by either exposing them to ultraviolet (UV) illumination or by locally injecting charge using a conducting atomic force microscope (CAFM). In both cases, reduction of the Ag<sup>+</sup> ions to the metallic state and the subsequent formation of Ag nanoparticles was observed by optical absorption spectroscopy and X-ray diffraction. Surprisingly, the formation of these Ag nanoparticles was accompanied by a decrease in the electrical conductivity of the films. For exposed regions with nanoparticle formation, CAFM measurements demonstrated no measurable current (< 1 pA) at sample bias voltages above 10 V. We attribute this decreased conductivity to a change in the morphology of the conducting Ag species in the film. Before reduction, Ag<sup>+</sup> ions are attached to negatively charged pore walls in a comparatively dense packing and produce a conducting film. After reduction with UV exposure or CAFM charge injection, the silver metal agglomerates into conducting nanoparticles that no longer form a percolated network, leading to insulating behavior. Local modification of the conductivity on the nanometer-scale is possible by operating the CAFM with an applied voltage above 6 V and scanning a defined pattern. Subsequent imaging of the area at lower voltage then shows insulating behavior in the previously patterned regions. Larger-scale patterning on the micron-to-mm scale is possible by utilizing a mask when exposing the film to UV illumination. Extensions of

this method to the fabrication of photonic and plasmonic devices is being explored.

10:40am **TF-ThM9 Synergistic Ag (111) and Cu (111) Texture Evolution in Phase Segregated  $\text{Cu}_{1-x}\text{Ag}_x$  Magnetron Sputtered Composite Thin Films**, *D.I. Filoti, A.R. Bedell, J.M.E. Harper*, University of New Hampshire

We investigated the texture and microstructure evolution of  $\text{Cu}_{1-x}\text{Ag}_x$  composite thin films through x-ray diffraction pole figures as a function of composition for  $x \leq 0.5$ . As-codeposited at room temperature by magnetron sputtering, the fcc composite  $\text{Cu}_{1-x}\text{Ag}_x$  emerge as a phase-segregated thin film, when the Ag volume fraction represents more than 15 at. % up to 50 at. %, or as a single phase thin film when Ag volume fraction represents less than 15 at. %. The texture evolution of Cu (111) and Ag (111) in phase-segregated Cu-Ag thin films proves to be synergistically enhanced when compared to pure copper or silver thin films. Not only is a stronger perpendicular (111) fiber texture obtained, but also an in-plane alignment of Ag (200) develops related to deposition direction and composition. By the use of transmission electron microscopy we observed a decrease in grain size in Cu-Ag composite films as compared with pure copper and silver films. These Cu-Ag thin films are being evaluated for antimicrobial applications.

11:00am **TF-ThM10 Plasmonic Phenomena in Indium Tin Oxide and ITO-Au Hybrid Films**, *S. Franzen, C. Rhodes, M. Cerruti, R.W. Gerber, M. Losego, J.-P. Maria, D.E. Aspnes*, North Carolina State University

For more than 100 years the plasmonic periodic table has been dominated by two elements, Ag and Au. The change in the surface plasmon polariton (SPP) signal in Au thin films is currently one of the most widely used methods for detecting binding interactions in biological systems. Despite broad interest, there has been sparing fundamental research into new plasmonic materials. Here, we elucidate some equivalences regarding plasmonic phenomena in conducting metal oxides, specifically indium tin oxide (ITO), and Au. In contrast to Ag and Au, conducting metal oxides offer the possibility of tuning both the location of the metallic resonance and its width according to deposition conditions. We investigate properties of ITO and ITO/Au layers by reflectance spectra  $R_p$  and  $R_s$  obtained for light polarized parallel and perpendicular, respectively, to the plane of incidence. Data were obtained in the Kretschman configuration. These data reveal two distinct types of plasmonic phenomena, one due to a capacitive-type oscillation that can only occur for very thin conducting films and the second being the usual surface plasmon resonance. One or the other can be realized either by changing the ITO thickness or by depositing either metallic or nanostructured Au on the ITO to change boundary conditions. The results can be understood completely through a combination of the Drude model for free carriers in a metal, Bruggeman effective-medium theory, and the Fresnel equations. This provides a new dimension for engineering plasmonic phenomena for investigations of molecules adsorbed at interfaces.

11:20am **TF-ThM11 Micro and Nanostructured Interfaces for Therapeutic Delivery**, *T.A. Desai*, University of California, San Francisco  
**INVITED**

Efficient drug delivery remains an important challenge in medicine. Continuous release of therapeutic agents over extended time periods and in accordance to a pre-determined temporal profile; local delivery at a constant rate to overcome systemic toxicity; improved ease of administration, and increasing patient compliance are some of the unmet needs of the present drug delivery technology. This talk will discuss in vivo drug delivery strategies that capitalize on the strengths of micro and nanofabrication. By taking advantage of our ability to control topography and chemistry at submicron size scales, we have developed organic and inorganic interfaces which modulate cell function while at the same time allow for controlled drug release kinetics. Due to our ability to create monodisperse features (pores, wires, and hollow tubes) as small as several nanometers in a variety of non-planar biocompatible materials, these interfaces offer advantages in their reproducibility, stability, and their ability to intimately contact cell and tissue surfaces. Such nanoengineered interfaces may be optimized for biomolecular selectivity and surface bioactivity, leading to unique interfacial properties not achieved through existing drug delivery approaches. Nanotechnology can add functionality to current drug delivery platforms while becoming an enabling technology leading to new basic discoveries in the biological sciences.

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