Thin Film
Room: B3 - Session TF1+SE-TuM

Glancing Angle Deposition I
Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am **TF1+SE-TuM1 Nanorod Structures for Energy Conversion**, ***N.A. Koratkar***, Rensselaer Polytechnic Institute **INVITED**

Oblique angle deposition (OAD) is a technique which allows for fabrication of unique nanostructures, which cannot be grown by advanced lithographic techniques. OAD is simple, fast, cheap, has high mass production capability and can generate unique two- and thee-dimensional nanostructures with large aspect ratio and controllable porosity, shape and symmetry. The fact that these nanostructures can be integrated onto a substrate platform makes them practical for many realistic applications. In this talk I will demonstrate the application of nanorods grown by OAD in various key device applications of today's energy starved society. The first is nanostructured Si anodes for rechargeable Li-ion batteries with higher capacity. The second is the development of Zinc Oxide (ZnO) and Indium Tin Oxide (ITO) nanorods by magnetron sputtering at low temperatures and their use as enhanced transparent conducting electrodes for polymeric photovoltaic cells. The third is the use of Pt nanorod based electrode architectures for proton exchange membrane fuel cells and the fourth is the use of Cu nanorods architectures for enhanced nucleate boiling which has strong implications for the management of thermal energy.

8:40am **TF1+SE-TuM3 Nanophotocatalysts Engineered by Glancing Angle Deposition Method**, ***W. Smith***, *Y. Zhao*, University of Georgia

TiO_2 has long been used as an efficient and effective photocatalyst material, with applications in water purification, water splitting for hydrogen generation, clean windows, and many others. The photocatalytic efficiency of TiO_2 can be enhanced by increasing its surface area as well coupling it with another semiconductor which can create a charge separation effect. There are many methods to produce high surface area nano-sized TiO_2 such as sol-gel, hydrothermal, and ball-milling, but these techniques are governed by surface chemistry and random aggregation, and are difficult to control the overall size and morphology of the nanoparticles. These issues can be fixed by utilizing an oblique angle deposition (OAD) technique and glancing angle deposition (GLAD) technique, that can create ordered nanorod arrays with tunable height, separation, density and heterostructures. With these unique advantages, we systematically studied the photocatalytic rate of methylene blue versus the TiO_2 nanorod height, and found a scaling relationship that can be interpreted by a surface reaction model. We also created WO_3-TiO_2 two-layer thin film, tilted nanorods, and vertical nanorods by e-beam deposition, OAD, and GLAD. Two important factors played a role in the observed photocatalytic properties; the crystal phase of each material, and the interfacial area between TiO_2 and WO_3. The best sample was found to be the GLAD multi-layer nanorod array, which showed an enhancement up to 3 times over single layer TiO_2 GLAD nanorods. The GLAD structure had a higher interfacial area between TiO_2 and WO_3 than other samples. To maximize the interfacial area between the two materials, a dynamic shadowing growth (DSG) method was used to create a core-shell nanorod array. WO_3 nanorods were first grown on a bare substrate using GLAD to serve as the "core". A TiO_2 "shell" was then deposited such that the entire WO_3 "core" nanorod was covered. The photocatalytic decay rate for these core-shell samples again showed further improvement over single layer TiO_2 thin films and multi-layer c-TiO_2/a-WO_3 films by 13 and 3 times respectively.

These results show that the GLAD based nanofabrication technique is a versatile tool to design new photocatalytic nanostructures. With more structural and material engineering, better photocatalyst structures can be engineered.

9:00am **TF1+SE-TuM4 Enhanced Optical Absorption and Photoconductivity Response of Indium Sulfide Nanorod Arrays**, ***M.F. Cansizoglu***, *T. Karabacak, H.W. Seo,* University of Arkansas at Little Rock, *R. Engelken*, Arkansas State University

Indium (III) sulfide is a wide bandgap and photoconductive material that has attracted attention due to its potential applications in optical sensors and in photovoltaic devices. High optical absorption in active regions of these devices is one of the key parameters that determine their performance especially in solar cell and photodetector applications. In this study, we show that indium sulfide nanorod arrays deposited by glancing angle deposition (GLAD) technique have superior optical absorption and low reflectance properties compared to conventional flat thin film coatings. Our GLAD nanorods had about 96% absorption in the sub-600 nm spectrum, while much thicker and denser thin films of indium sulfide was able to absorb only 80% of the incident light in the same spectrum. Due to the high optical absorption, a significant photoconductivity response was also observed in the nanorod samples, whereas no measurable photoresponse was detected in conventional thin films. In addition, we give a preliminary description of the enhanced light absorption properties of the nanorods by using Shirley-George Model that predicts enhanced diffuse scattering and reduced reflection of light due the rough morphology.

9:20am **TF1+SE-TuM5 Oblique Angle Polymerization**, ***M.C. Demirel***, Penn State University

The growth of spatially organized structures is of considerable fundamental interest, since it may provide us with important clues to the way in which organized structures form in Nature. A closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. The organized structures in Nature are formed through evolutionary processes, and these complex molecules and features are built using molecular protein machinery. Synthetic polymers, that mimic biological materials in their designs, form organized structures too. We have demonstrated that nanostructured polymer thin films can be fabricated by an oblique angle polymerization method. [1-2] These structures are composed of approximately 40,000,000 aligned columns (approximately 100-150 nm in diameter) per square millimeter similar to the gecko footpad or insect wing. These structures have high aspect ratio and the production technique does not require any template, lithography method or a surfactant for deposition. This approach allows us to tune the chemical properties of nanostructured surfaces and film morphology to control the physicochemical properties of the resulting films, such as hydrophobicity, porosity, electrochemistry, chemical reactivity, surface energy and crystallinity. We have recently functionalized nanostructured polymer films for controlled release and delivery of organics and synthetic molecules. Structured polymer brushes are envisioned to be useful in for specific controlled drug release, metallization (SERS and catalyst applications), tissue targeting as well as antifouling applications. [3-5]

Cetinkaya, M., Malvakdar, N., Demirel, M.C., "Power-Law Scaling of Structured Poly(p-xylylene) Films Deposited by Oblique Angle", JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS, Vol. 46, pg 640-648, 2008.

Cetinkaya, M., Boduroglu, S., Demirel, M.C. "Growth of Nanostructured Thin Films of Poly(p-xylylene) Derivatives by Vapor Deposition", POLYMER, Vol.48, pg. 4130-4134, 2007

Demirel, M.C., Cetinkaya, M., Singh, A., Dressick W.J., " A Non-Covalent Method for Depositing Nanoporous Metals via Spatially Organized Poly(P-xylylene) Films", ADVANCED MATERIALS, Vol.19, pg.4495-4499, 2007

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Kao, P., Malvadkar N., Wang, H. Allara, D., Demirel, M.C., "Surface Enhanced Raman Detection of Bacteria on Metalized Nanostructured Poly(p-xylylene) Films " Vol. 20, pg. 3562-3565, ADVANCED MATERIALS, 2008.

9:40am **TF1+SE-TuM6 Structural and Optical Properties of Metal Sculptured Thin Films on Large-Scale Prepatterned Substrates**, *D. Schmidt, T. Hofmann,* ***E. Montgomery***, University of Nebraska-Lincoln, *B. Mbenkum,* Max Planck Institute for Metals Research, Germany, *M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) metal nanostructures are of particular research interest in modern material science and engineering, due to their intriguing properties, which can differ considerably from their bulk counterparts. These size- and structure-driven properties in such 3D metal nanostructures credit themselves for potential implementation in optical, electro-mechanical, and electromagnetic systems.

We utilize glancing angle physical vapor deposition, which exploits physical shadowing and varying particle incidence azimuth for fabrication of 3D nanostructures from metals arranged in sculptured thin films (STFs). While such nanoscaffolds (typically in geometries of (slanted) columns, chevrons, screws, or spirals) are randomly distributed on untreated substrates, organized growth can be achieved on prepatterned surfaces. Self-assembled block copolymer nanolithography and nanosphere lithography are promising techniques to accomplish wafer-scale prepatterning. The desired spacing of the resulting hexagonal pattern can be tailored based on polymer chain length and nanosphere radius, respectively. Both methods are superior to conventional and electron beam lithography techniques because of small structure sizes achieved in the order of a few nanometers and large scale preparation.

This presentation elucidates our work on structure-related optical properties of different STFs from various metals grown on untreated as well as prepatterned silicon substrates by electron-beam evaporation at an oblique angle of incidence. Generalized spectroscopic ellipsometry is employed to determine the anisotropic optical constants (refractive index *n* and extinction coefficient *k*) of the thin films in the spectral range from 400 nm to 1650 nm. All investigated STFs show extreme birefringence as well as dichroism. We observe that optical properties depend rather on geometry than material [1,2].

[1] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Appl. Phys. Lett. **94**, 011914 (2009).

[2] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Opt. Lett. **34**, 992 (2009).

10:40am **TF1+SE-TuM9 On the Uniformity of Films Fabricated by Glancing Angle Deposition**, ***N.G. Wakefield***, *J.C. Sit*, University of Alberta, Canada

Films fabricated using the glancing angle deposition technique are subject to significant variations in important film parameters across a sample due to varying geometric conditions at each point on the substrate. This is a serious fundamental problem, as non-uniformities in aspects such as film thickness or porosity can drastically change a film's properties across even a small sample size. This means that film properties can vary rapidly, and undesirably, with position over a substrate and attempting to scale technologies based on glancing angle deposition to large areas presents a major challenge. This paper presents a method to quantify the non-uniformities in these quantities, starting from a simple geometric framework, applicable to physical vapor deposition at low pressures. In this work, this method is applied to glancing angle depositions done at a fixed deposition angle, but with arbitrary azimuthal substrate rotation. Quantities such as the effective deposition angle and the mass flux at any point on the substrate can be determined purely from the geometry of the deposition setup. Predicting further quantities such as the film porosity and thickness requires additional, material specific information that is easily obtainable. For a TiO2 deposition at $\alpha = 70°$ on a 10 cm substrate, dependent on the film's structure, porosity and thickness non-uniformities are found to range from ±1.7% to ±8.2% and ±1% to ±30% respectively. Experimental values were obtained using Mueller matrix spectroscopy and showed excellent agreement. The technique described here is general and can be applied to glancing angle deposition setups having arbitrary substrate size and throw distance. The ability to accurately model the gradients in quantities such as the film porosity, allows for a combinatorial approach to examine film properties such as refractive index, absorption or conductivity across a single substrate. Further improvements to the model should allow for the treatment of depositions done at varying deposition angles and with curved substrates.

11:00am **TF1+SE-TuM10 Nanostructured Tungsten and Tungsten Trioxide Films Prepared by Glancing Angle Deposition**, ***D. Deniz***, *R.J. Lad*, University of Maine

The sensitivity of chemiresistive metal oxide gas sensors can be markedly increased by fabricating nanostructured films with very high surface to volume ratio. In this work, nanostructured tungsten (W) and tungsten oxide (WO_3) films were fabricated using pulsed direct current (DC) magnetron sputtering of a W target with a glancing angle deposition (GLAD) geometry. The major parameters that were varied included substrate temperature, deposition rate, substrate rotation, Ar/O_2 plasma composition, and post-deposition thermal treatments. The stoichiometry of the nanostructured films was characterized by X-ray photoelectron spectroscopy (XPS), and the structure and morphology were investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (SEM). Metallic W nanorods were formed by sputtering in a pure Ar plasma at room temperature and they crystallized in a simple cubic β-phase with W(100) texture. Subsequent annealing at 500 °C in air transformed the nanorods to textured triclinic WO_3 structure but the nanorod morphology was retained. Stoichiometric WO_3 films grown in Ar/ O_2 plasma at room temperature had an amorphous structure and also exhibited a nanorod morphology. Post-deposition annealing at 500 °C in air induced crystallization to the triclinic WO_3 phase and also caused a morphological change into a very nanoporous network. The differences in the chemiresistive response to each of these high surface area nanoengineered films to CO_2 and CH_4 gas exposure will be presented.

11:20am **TF1+SE-TuM11 Dual Magnetron Oblique Sputtering of Biaxially Oriented ZnO Thin Films on Amorphous Substrates**, ***B.L. Stevens***, *S.A. Barnett*, Northwestern University

This talk will describe results on deposition and characterization of biaxially oriented ZnO thin films on amorphous substrates. Biaxially-oriented ZnO thin films on low-cost substrates are of interest for ZnO-based devices and as "substrates" for subsequent growth of devices based on AlN, GaN, InN, and their alloys. Expensive single crystal substrates, which are typically used to achieve the requisite crystalline perfection of the epitaxial device layers, could be replaced by biaxially-textured ZnO substrates if sufficiently good orientation can be achieved.

The dual magnetron oblique sputtering (DMOS) geometry utilized two dc magnetron sputter sources, with metallic Zn targets, positioned opposite each other and at angles of 20 to 40° relative to the substrate normal. Sputtering was carried out in an oxygen-rich $Ar\text{-}O_2$ atmosphere. Substrates were Corning 7059 glass, Corning 1737F glass, or Si (001) that had been oxidized to produce an amorphous SiO_2 surface layer. Cross-sectional SEM showed reasonably dense as-deposited films even without substrate heating. The as-deposited films were under considerable compressive stress, as measured by x-ray peak position, in agreement with prior results on sputtered ZnO. Atomic-force microscopy measurements on as-deposited 1.5 μm thick films showed relatively high rms roughnesses of 8.3 nm.

The ZnO films exhibited (002) out-of-plane orientation, as suggested by θ-2θ x-ray scans and verified by x-ray pole figures that were completed for selected samples. Sputtering from a single target (instead of the usual dual-target geometry) caused a shift in the out-of-plane orientation, causing the (002) plane normal to be up to 10° off normal. X-ray scans as a function of azimuthal angle Φ were carried out to detect reflections from (101) planes. The strongest biaxial orientation was observed when the sputter sources were placed at 30° from the substrate normal, with Φ-scan peaks exhibiting a full width half maximum (FWHM) value of 23°. Elevated substrate temperature during deposition, up to 600°C, decreased the orientation in the films, yielding a ~17% increase in Φ FWHM. Post deposition annealing at up to 1000°C substantially improved the degree of biaxial orientation, decreasing the Φ-scan FWHM by ~60%. The effects of a range of deposition and post-deposition annealing conditions on the film orientation will also be reported. The orientation mechanism also will be discussed.

11:40am **TF1+SE-TuM12 A Slice of GLAD: Use of Focused Ion Beam Tomography to Characterize Titania Thin Films**, ***K.M. Krause***, University of Alberta, Canada, *D. Vick*, NRC National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Focused ion beam (FIB) tomography allows for the serial slicing and imaging of a sample volume on the order of several nanometers to microns thick. With this technique, a focused beam of ions rasters across the specimen surface, milling it layer-by-layer. In tandem, a scanning electron microscope (SEM) images the exposed surface at the removal of each individual slice. The series of SEM images can then be post-processed with custom or commercially available software to create a 3D reconstruction of the milled volume.

As FIB tomography has progressed over the years, the range of materials, structures, and size scales has been expanded. Various analysis have been carried out with FIB, including the study of how grain boundaries in Ni alloys influence crack propagation and how the geometry of buried Ge quantum dot superlatices depends on the growth of supporting materials layers [1 – 3]. In the present work we report on the use of ion beam milling and concurrent SEM imaging to probe the properties of titanium dioxide nanostructured thin films fabricated using the glancing angle deposition (GLAD) technique [4].

Our titania films are deposited at oblique angles, while substrate rotation is employed, on silicon wafers. The resultant films have a columnar structure with spacing between columns determined by the deposition angle and characteristics determined by the rotation speed and deposition rate. To support the porous GLAD films during FIB slicing, a photoresist is spun into the film and then baked, forming a heterogeneous solid. The photoresist not only provides support for the nanostructures as they are sliced, but also offers good atomic number (Z) contrast to the titania. The GLAD films are then sliced and imaged using a Zeiss NVision 40 Crossbeam® workstation. Captured images are post-processed using MATLABTM and commercially available JEOL TEMographyTM software packages.

While column morphology and geometric properties of GLAD films have been well studied, investigations of columnar structure have been limited to SEM and TEM. Here, we demonstrate that the FIB technique can be used to provide a spatially discrete view of GLAD intra-column and inner-column porosity and structure. Analysis of these properties is ongoing and current experimental results will be presented.

References

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4. K. Robbie, M.J. Brett, A. Lakhtakia, Nature 384, 616 (1996).

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