

Tuesday Morning, November 1, 2011

Thin Film Division

Room: 104 - Session TF+SE-TuM

Glancing Angle Deposition (GLAD) I

Moderator: T. Karabacak, University of Arkansas at Little Rock

8:20am **TF+SE-TuM2 Progress in Glancing Angle Deposition Technology for Practical Applications**, M. Suzuki, Kyoto University, Japan **INVITED**

Recently, advanced top-down processes for the fabrication of nanostructures have been developed; however, these processes are long predated by the process of shadowing growth by glancing angle deposition (GLAD), which affords the fabrication of the self-assembled nanostructures over a much larger area at significantly lower costs. In the past two decades, significant progress has been made in the development of 3D nanomorphologies well-controlled by the GLAD such as the zigzag and helix morphologies. Much effort has also been expended to gain a theoretical and numerical understanding of the growth mechanism of nanostructures in order to improve their morphology. Many researches are being carried out in academia to investigate the useful properties of nanocolumnar thin films, such as magnetic anisotropy, birefringence, dichroism, and optical activity *induced by nanoshapes*; high-performance catalysis and electrodes *using large surface area*; and various *size effects*. On the other hand, most companies seem hesitant to introduce the GLAD technique in the factory because of the prejudice that obliquely deposited thin films are not durable and reproducible. However, some products of obliquely deposited thin films are already being manufactured, although their production processes have not necessarily been disclosed. In this presentation, we discuss the previous products and investigations of GLAD thin films and demonstrate that this prejudice can be overcome. In addition, we introduce our recently commercialized products manufactured by GLAD, namely, surface enhanced Raman substrate¹ and low-reflectivity wire-grid polarizers². Because GLAD films have the great potential of enabling humankind to overcome the energy and environmental problems it confronts, it is important to encourage the industry to adopt GLAD by removing the prejudice against GLAD films.

[1] M. Suzuki *et al.*, "Au Nanorod Arrays Tailored for Surface-Enhanced Raman Spectroscopy," *Analytical Sciences* **23**, 829 (2007).

[2] M. Suzuki *et al.*, "Low-Reflective Wire-Grid Polarizers with Absorptive Interference Overlayers," *Nanotechnology* **21**, 175604 (2010).

9:00am **TF+SE-TuM4 Engineering Columnar Nanostructures for Organic Photovoltaics**, R.T. Tucker, Univ. of Alberta, Canada, D.A. Rider, NRC-Nat. Inst. for Nanotech., Canada, J.G. Van Dijken, M. Thomas, B.J. Worfolk, A. Lalany, K.M. Krause, Univ. of Alberta, Canada, M.D. Fleischauer, NRC-Nat. Inst. for Nanotech., Canada, M.T. Taschuk, Univ. of Alberta, Canada, K.D. Harris, NRC-Nat. Inst. for Nanotech., Canada, J.M. Buriak, M.J. Brett, Univ. of Alberta, Canada

Organic photovoltaics (OPVs) represent one possible route to widespread adoption of solar energy production [1]. The most promising OPV technology to date has been the bulk heterojunction, a photoactive mixture which bridges the gap between exciton diffusion lengths (~15 nm) and typical device length scales (~200 nm). However, bulk heterojunctions are typically disordered, which can limit charge extraction and thereby reduce OPV performance. The ideal OPV bulk heterojunction structure has been identified as ordered interpenetrating columnar electron donor and acceptor layers [2]. The interface morphology of such structures may be fabricated with glancing angle deposition (GLAD), a well-developed, robust nanostructuring technique that has been demonstrated for numerous materials at the length scales required for high quality OPV devices.

Here we present a summary of organic solar cell research utilizing GLAD at the University of Alberta. GLAD's flexibility lends itself to structuring both the transparent conductor layer as well as the donor and acceptor photoactive layers. We have demonstrated GLAD structuring of indium tin oxide (ITO), copper (II) phthalocyanine (CuPc), and fullerene (C60). ITO nanopillars fabricated by GLAD have been incorporated as three dimensional high surface area electrodes in organic photovoltaic devices [3]. The nanostructured electrodes demonstrated 30% improved performance compared to planar ITO anodes, due to increased optical absorption and high surface area. Typical OPV donor and acceptor materials, CuPc and C60, have also been successfully structured by the GLAD technique [4,5]. Advanced motion control algorithms, designed to

form thinner columns, were used to optimize the material nanostructures and produce highly desirable ordered bulk heterojunctions when coupled with complementary polymers. In the case for GLAD C60 devices, the short-circuit current was double that of bulk heterojunction devices. The GLAD technique has proven to be an incredibly useful method for fabricating and tuning electrode and bulk heterojunction morphologies in OPVs.

[1] H. Spanggaard and F.C. Krebs, *Sol. Energy Mater. Sol. Cells* **83** 125-146 (2004)

[2] F. Yang and S.R. Forrest, *ACS Nano* **2** (5), 1022-1032 (2008)

[3] D.A. Rider *et al.*, *Nanotechnology* **22** (8), 085706 (2011)

[4] J.G. Van Dijken *et al.*, *J. Mater. Chem.* **21** (4), 1013-1019 (2011)

[5] M. Thomas *et al.*, *ACS Appl. Mater. Interfaces* (in press, 2011)

9:20am **TF+SE-TuM5 Enhanced Photoconductivity Response of Glancing Angle Deposited Indium Sulfide Nanorod Arrays for Photodetector Device Applications**, H. Is, M.F. Cansizoglu, T. Karabacak, University of Arkansas at Little Rock

Photoconductivity (PC) in semiconductors can be detected by measuring the change in electrical conductivity when the material is exposed to light. Photosensitive materials with high PC response can be useful especially for photodetector applications. Compared to conventional thin film geometry, semiconducting nanostructures can provide enhanced photoresponse due to their low dark conductivity and superior capability of absorbing light, which leads to an enhanced PC response even to the minimal changes in light intensity. Glancing angle deposition (GLAD) provides a unique capability of producing nanostructured arrays of various materials with controlled shapes, size, and separation. In this study, we fabricated semiconducting indium sulfide nanorod arrays by GLAD on ITO coated glass substrates in various lengths and capped them with a silver film as metal contact to form a proof-of-concept photodetector device. PC response of these devices was measured at different wavelengths with altered light intensities. We show that GLAD nanorods have a superior PC response than conventional thin film, which is believed to be mainly due to their enhanced light trapping and high optical absorption property.

10:40am **TF+SE-TuM9 Catalytic Nanomotor Control: Design Techniques Using Dynamic Shadowing Growth**, J.G. Gibbs, Y.P. Zhao, University of Georgia

Catalytic nanomotors with nanometer-to-micrometer dimensions convert chemical energy into mechanical work via catalysis allowing for autonomous self-propulsion. They are an emerging nanotechnology field and promise important technological advances in drug delivery, transport, assembly, and other processes at the nano-scale. Catalytic nanomotors are inorganic analogues of cellular motor proteins that convert chemical energy into work through stored energy. One of the greatest challenges in this field is the manipulation and direct control of motion and swimming behaviors.

We focus upon the geometric design of catalytic nanomotors to modulate motion behaviors. To achieve this goal, a dynamic growth technique must be implemented. Most research uses template-directed electroplating (TDEP) allowing only simple geometries. We use dynamic shadowing growth (DSG) for fabrication which is a dynamic process allowing for construction of a much wider range of structures and shapes.

Depositing different materials and controlling the overlapping area is the first method of motion modulation used. To alter the swimming speed of a spherical nanomotor, Au is overlapped with the Pt-catalyst to varying degrees; the Au surface area A is changed systematically. The average moving speed u is found to follow the scaling relationship, $u \propto A^{-1/2}$, which agrees with the self-electrophoresis mechanism.

Swimming behaviors can also be altered by geometrical design, easily implemented by DSG making the technique useful to engineer different types of motion. Various swimming behaviors are exhibited by altering the geometry, and/or changing the location of the Pt catalyst accomplishable. Two very similar structures were fabricated and move based upon the location of the catalyst. Multi-component rotational nanomotors consisting of Pt coated TiO₂ nanoarms grown upon ~ 2.01 μ m diameter silica microbeads are designed by dynamic shadowing growth. When exposed to hydrogen peroxide, H₂O₂, the structures rotate about an axis through the center of the microbead and perpendicular to the TiO₂ nanoarm at a rate of 0.15 Hz per % H₂O₂ concentration. The other nanomotors are tadpole-like structures that swim in large sweeping circular trajectories. The swimming trajectories are fine-tuned by altering the arm length and orientation

exploiting geometry-dependent hydrodynamic interactions at low Reynolds number. The curvature, angular frequency, and radius of curvature of the trajectories change as a function of arm length. Simulations based on the method of regularized Stokeslets are also described and correctly capture the trends observed in the experiments.

11:00am **TF+SE-TuM10 Fabrication of Cr-doped TiO₂ Nanorod Arrays by Oblique Angle Co-Deposition and Their Photocatalytic Properties**, *G.K. Larsen*, University of Georgia, *R. Fitzmorris*, *J.Z. Zhang*, University of California Santa Cruz, *Y.P. Zhao*, University of Georgia

In order to achieve efficient photocatalytic behavior in the visible light range, transition metal ions are often doped into TiO₂. Of these transition metal dopants, Cr appears superior in extending the photoresponse of TiO₂ into the visible range. However, different fabrication methods have produced mixed results regarding the effect of the Cr dopant on photocatalytic efficiency. In this study, a unique fabrication method, oblique angle co-deposition (OACD), is used to deposit a well-aligned array of Cr-doped TiO₂ nanorods that exhibit optical absorption in the visible region. These films are compared with TiO₂ nanorod arrays fabricated by oblique angle deposition (OAD). Due to the similarity of fabrication methods, the effect of the dopant on the structural, optical, and photocatalytic properties of TiO₂ can be isolated. The Cr dopant alters the TiO₂ lattice structure, with an increase in the crystallization temperature of the anatase phase and a decrease in the rutile crystallization temperature. Additionally, Cr is found to segregate out of the TiO₂ matrix and migrate to grain boundaries and the surface of the nanorods. The photocatalytic efficiency and IPCE of the Cr:TiO₂ films is reduced when compared to intrinsic TiO₂ due to changes in the photocatalyst's surface and charge transport properties as a result of the formation of intergranular Cr(VI) oxide clusters. The presence and the effects of the Cr(VI) phase is the result of exceeding the solubility limits of Cr within the TiO₂ lattice.

11:20am **TF+SE-TuM11 Optimal Conditions for Visualization of Fingerprints with the Conformal-Evaporated-Film-By-Rotation Technique**, *D.P. Pulsifer*, *S.A. Muhlberger*, *R.J. Martín-Palma*, *R.C. Shaler*, *A. Lakhtakia*, Pennsylvania State University

The conformal-evaporated-film-by-rotation (CEFR) technique was investigated for use as a development technique to visualize sebaceous fingerprints of forensic importance. A variation on oblique angle deposition, the CEFR technique requires the substrate holder to rapidly rotate about a perpendicular axis. The combination of an obliquely directed, collimated vapor flux and rapid rotation of the substrate gives rise to a conformal coating on the residue left behind on a substrate by the friction ridges of the finger. The coating has a closely packed nanocolumnar morphology. We conducted a systematic study of various deposition parameters in order to identify those conditions which are optimal for the development of fingerprints with the CEFR technique. We varied: base pressure during deposition, vapor flux angle with respect to the substrate plane, substrate rotation rate, deposition rate, and final film thickness. By qualitatively comparing fingerprints before and after development for various values of each deposition parameter, we were able to identify optimal conditions for development. For all depositions chalcogenide glass of nominal composition Ge₂₈Se₆₀Sb₁₂ was used to coat sebaceous fingerprints placed on glass microscope slides. We found the optimal conditions to be: a vapor flux angle of 10 deg as measured from the substrate plane, a rotation rate of 3 rps, a deposition rate of 1 nm/s, a final film thickness of 500 nm, and a deposition pressure of 0.1 mTorr. These values are close to those reported previously for CEFR coating of fingerprints with the exception of the base pressure. An optimal base pressure of 0.1 mTorr significantly relaxes the vacuum requirements of an evaporation chamber to be used for this purpose, making the technique very accessible to forensic scientists and law enforcement agencies. This work was supported by Grant No. 2010-DN-BX-K232 from the U.S. Department of Justice.

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