

# Wednesday Morning, October 20, 2010

## Thin Film

Room: San Miquel - Session TF+SE-WeM

## Glancing Angle Deposition (GLAD) I

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

8:00am **TF+SE-WeM1 Soft Nanostructured Films for Biomedical Applications**, *M.C. Demirel*, Pennsylvania State University **INVITED**

Anisotropic textured surfaces represent key structural components utilized by various animals and plants to gain a competitive advantage for survival. For example, a closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. These structures are composed of millions of aligned columns per square millimeter, which create novel anisotropic properties. We have demonstrated that these structures can be fabricated synthetically by an oblique angle polymerization (OAP) method. OAP 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. In this talk, we will describe unique anisotropic physicochemical properties (i.e. morphing/folding, wetting, and friction) of well-ordered arrays of nano-rods/tubes, which mimic biological structures at the microscopic scale. We will also present results concerning the use of these films for biomedical and biosensors applications.

8:40am **TF+SE-WeM3 Growth Temperature Controlled Morphology of Ge Nanocolumns**, *C. Khare, J. Bauer, J.W. Gerlach*, Leibniz Institute of Surface Modification (IOM), Germany, *B. Fuhrmann*, Martin-Luther-University Halle, Germany, *T. Höche, B. Rauschenbach*, Leibniz Institute of Surface Modification (IOM), Germany

Germanium films with manifold nanostructures are grown by ion beam sputter glancing angle deposition (GLAD). Morphological shape variations were introduced through variation of the substrate temperature ( $T_S$ ) and differently patterned silicon substrates. Pre-patterned substrates served as seeds for growing structures assisting the formation of a periodic nanostructure array. Nanocolumns grown on a bare Si(100) substrate demonstrated an altered morphology that can be controlled by the substrate temperature. At elevated substrate temperature ( $T_S / T_M > 0.3$ ), surface diffusion-driven mass transport as a result of increased adatom mobility augmented fibrous-columnar and intra-columnar growth. Further increment of the substrate temperature ( $T_S / T_M > 0.45$ ) exhibited column merging and column broadening. Additionally, significant changes in the overall film thickness representing changes in the film porosity were observed. Similar merging and broadening characteristics were also exhibited on SiO<sub>2</sub> nanosphere templated substrates. For the films deposited at elevated substrate temperatures, XRD measurements showed the growth of polycrystalline films. TEM analysis confirmed the growth of large crystallites at elevated substrate temperatures. Thus, growth of Ge nanostructures with tailored morphology can be grown by substrate pre-patterning and by utilizing substrate temperature induced effects.

9:00am **TF+SE-WeM4 Glancing Angle Deposited Platinum Nanorod Arrays with Enhanced Electrocatalytic Activity for Oxygen Reduction Reaction in PEM Fuel Cells**, *W.J. Khudhayer, A.U. Shaikh, T. Karabacak*, University of Arkansas at Little Rock

In this work, we have investigated the electrochemical properties of vertically aligned, single-layer, low loading, carbon-free and single crystal Pt nanorod arrays as a potential cathode material in polymer electrolyte (PEM) fuel cells. These nanorods of different lengths in the range of 20-600 nm were produced by glancing angle deposition (GLAD) technique with Pt loading values of 0.016-0.5 mg/cm<sup>2</sup>. Electrodes of conventional carbon supported Pt nanoparticles (Pt/C) were also prepared for comparison with Pt nanorods for their electrochemical properties. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were utilized to study the morphology and crystallography of Pt nanorods. SEM and XRD results reveal that Pt nanorods are well-isolated, vertically aligned, and single-crystal with atomically sharp tips. The single-crystal property allows enhanced electrochemical activity and reduced surface oxidation, while the isolated nature of the rods in lateral directions can provide a channeled porosity for effective transportation of gases in a PEM fuel cell. The electrochemical activity of Pt nanorods as well as Pt/C was evaluated using cyclic voltammetry (CV). CV results show that Pt nanorod electrocatalysts reduce oxygen to water at a more positive potential than that of Pt/C, indicating that our catalyst has a lower oxygen overpotential due to the enhanced electrode

porosity, single-crystal property, and the dominance of the preferred crystal orientation for oxygen reduction reaction (ORR). In addition, a series of CV scans show that our catalyst is more stable than Pt/C in the acidic environment. Finally, in order to get a fair comparison for high surface area catalysts, detailed thin-film rotating disk electrode measurements at room temperature were performed on 200 nm long Pt nanorods as well as Pt/C for comparison to calculate the most important kinetics parameters (Tafel slopes, exchange current density, Pt mass-specific activity and area-specific activity), which are the accepted measures of true catalysts activity towards ORR. These results reveal the enhanced mechanism and kinetics of ORR on Pt nanorods compared to Pt/C.

9:20am **TF+SE-WeM5 Hydrogen Storage Properties of Magnesium Nanotrees by Glancing Angle**, *M.F. Cansizoglu, T. Karabacak*, University of Arkansas at Little Rock

Among many solid state materials for hydrogen storage, magnesium hydride (MgH<sub>2</sub>) combines a hydrogen capacity of 7.6 wt % with the benefit of the low cost of production and abundance. The main difficulties for implementing MgH<sub>2</sub> are slow absorption/desorption kinetics and high reactivity towards air and oxygen, which are also common issues in most lightweight metal hydrides. Previously, improvements in hydrogen storage and release properties have been reported by using nanostructured magnesium that can be obtained through various fabrication methods including ball-milling, mechanical alloying, and vapor transport. In this study, we investigate the hydrogen absorption and desorption properties of magnesium "nanotrees" fabricated by glancing angle deposition (GLAD) technique, and also conventional Mg thin films deposited at normal incidence. Mg nanotrees are about 15 μm long, 10 μm wide, and incorporate "nanoleaves" of about 20 nm in thickness and 1.2 μm in lateral width. A quartz crystal microbalance (QCM) gas absorption/desorption measurement system has been used for our hydrogen storage studies. Nanostructured and thin film Mg have been deposited directly on the surface of the gold coated unpolished quartz crystal samples. QCM hydrogen storage experiments have been performed at temperatures ranging between 100-300°C, and at H<sub>2</sub> pressures of 10 and 30 bars. QCM measurements revealed that Mg nanotrees have better storage characteristics compared to Mg thin films. They can reach hydrogen storage values of about 4.80 wt% at 100°C, and up to about 6.71 wt% (which is close to the theoretical maximum storage value of Mg) at temperatures lower than 150°C. The significant enhancement in hydrogen absorption properties of Mg nanotrees is believed to originate from novel physical properties of their nanoleaves. These structures are very thin (~20 nm) and both surfaces are exposed to hydrogen enhancing the diffusion of hydrogen together with a decreased diffusion length. In addition, nanostructured Mg have been observed to be quite resistant to surface oxidation, which is believed to be due to the single crystal property of the Mg nanoleaves.

9:40am **TF+SE-WeM6 Fabricating Crystalline ZnO Nanorods by Glancing Angle Deposition**, *J.M. LaForge, M.T. Taschuk, M.J. Brett*, University of Alberta, Canada

Zinc oxide possesses a combination of properties, including semiconductor electronic behaviour, optical transparency, and piezoelectricity, that make it an interesting candidate for energy scavenging, photovoltaics, and chemical sensing applications (1, 2). Several unique nanostructures may be formed with ZnO, with a variety of growth methods that exploit the difference in surface energy between the low-index crystal faces of the wurtzite ZnO crystal leading to preferential growth along the c-axis.

Glancing angle deposition (GLAD) is assumed to operate effectively under conditions of limited surface diffusion so that growth occurs from geometric shadowing of an incoming particle flux. While amorphous GLAD films are typical, there are numerous crystalline films reported in the literature, including ZnO (3). This suggests that in certain material systems growth kinetics play a role in GLAD growth. However, the conditions under which GLAD produces crystalline films has not been thoroughly investigated or explained.

We have selected ZnO to investigate these issues for two reasons: first, the technological applications outlined above, and second, to explore the material growth properties which can produce crystalline structures. This makes it an ideal candidate for studying nanostructure morphology and crystal properties as a function of process parameters, including deposition rate, pitch and throw distance. Optimal growth conditions for zinc oxide nanorod films occurred for pitch values in the vicinity of 1 nm to 10 nm. Study of the post aspect ratio and areal post density suggests that typical GLAD growth occurs for deposition rates <0.005 nm sec<sup>-1</sup> and that growth kinetics begin to contribute significantly at deposition rates >0.01 nm sec<sup>-1</sup>. Films deposited at pitch values between 0.001 nm to 6.5 μm are crystalline

and textured, and greater texturing is achieved for conditions of decreased surface diffusion.

- (1) Wang, Z. L. *Journal of Physics: Condensed Matter*. **2004**, *16*, R829-R858.
- (2) Ye, C.; Fang, X.; Hao, Y.; Teng, X.; Zhang, L. *The Journal of Physical Chemistry. B*. **2005**, *109*, 19758-65.
- (3) Teki, R.; Parker, T.; Li, H.; Koratkar, N.; Lu, T.-M.; Lee, S. *Thin Solid Films*. **2008**, *516*, 4993-4996.

10:40am **TF+SE-WeM9 Optical, Magnetic, Magneto-Optical and Electrochemical Properties of Sculptured Thin Films**, E.B. Schubert, D. Schmidt, T. Hofmann, A.C. Kjerstad, E. Montgomery, S. Schöche, M. Schubert, University of Nebraska - Lincoln

Bottom-up and self-organized three-dimensional (3D) structure design on the nanoscale opens a new field in nanostructure based thin film engineering with a broad range of practical applications for sensors, optical coatings, photovoltaic devices or biomaterials, for example. Sculptured thin films (STF's) belong to this group of thin films and current research creates exciting new knowledge about the unique material properties that are related to shape, dimension, and distribution of the nanostructures within the thin film ensemble. The following paper presents new sculptured thin film properties obtained from material analysis using optical, magnetic, magneto-optical and electrochemical characterization techniques. [1-5] Material properties have been quantified from model analysis and results from our investigations lead to original device designs for applications such as highly-sensitive mass balances, subwavelength antireflection coatings, magneto-optical memory and chemical sensors.

- [1] E. Schubert, *Contributions to Plasma Physics* **47**, 545 (2007).
- [2] D. Schmidt, B. Booso, T. Hofmann, E. Schubert, A. Sarangen, and M. Schubert, *Appl. Phys. Lett.* **94**, 011914 (2009).
- [3] D. Schmidt, B. Booso, T. Hofmann, E. Schubert, A. Sarangan, and M. Schubert, *Opt. Lett.* **34**, 992 (2009).
- [4] D. Schmidt, A. C. Kjerstad, T. Hofmann, R. Skomski, E. Schubert, and M. Schubert, *J. Appl. Phys.* **105**, 113508 (2009).
- [5] D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, *Appl. Phys. Lett.* **96**, 091906 (2010).

11:00am **TF+SE-WeM10 Stress Behavior of Obliquely Sputtered Ta Films on Glass Substrates**, S.U. Jen, P.H. Chiang, Academia Sinica, Taiwan, Republic of China

Ta films were obliquely deposited on glass substrates by magnetron sputtering method using the parameters: deposition angle  $\alpha = 60^\circ$ ; deposition temperature  $T_S = 298, 373, 473,$  and  $573$  K; Ar working gas pressure  $P_{AR} = 2, 7.5,$  and  $15$  mTorr; film thickness  $t_f = 100$  nm. From X-ray diffraction, atomic force microscopy, cross-section transmission electron microscopy, and Auger depth profile analysis, we conclude that: [1] the axis of each columnar grain is inclined at an angle  $\beta \approx 35^\circ$  with respect to the film normal; [2] in-plane grain aggregates show some vestiges of the chain-like structure, whose long axis is perpendicular to the plane of incidence (i.e. the transverse or width direction of the sample); [3] oxygen atoms are found inside the film; especially located in the columnar gaps (or microvoids) between neighboring grains. The stress of each film was measured via Stoney equation. The main results in regard to the stress behavior of this series of Ta films are summarized below: [a] the intrinsic stress  $S_i$  is always tensile and dominant over the thermal stress  $S_T$ ; [b] the total stress is anisotropic with the longitudinal stress being larger than the transverse stress; [c] as  $T_S$  increases,  $S_i$  becomes less tensile. Result [a] is reasonable because Ta is a high melting point material.<sup>1</sup> Especially, in the oblique-deposition case, the formation of gaps becomes more obvious. Hence, much larger tensile stress (than in the normal-deposition case) arises from the attractive interaction of oxygen atoms across the gaps. Result [b] is a consequence of the self shadowing effect, which is already manifested in the conclusion [2] above. Result [c] is due to the fact that as  $T_S$  is higher, there is a structure transition from zone I to zone T, and oxygen atoms are less likely to be incorporated into the film.

<sup>1</sup> G. Guisbiers, O. Van Overschelde, M. Wautelet, *Acta Materialia* **55**, 3541(2007).

11:20am **TF+SE-WeM11 Role of Columnar Nanostructures on Static and Dynamic Wetting Properties of Silver Film**, D. Singh, J. Singh, IIT Delhi, India

The study of wetting has always been a very active field of research. In recent years, the interest in this field is stimulated by nanoengineering the surface to meet the requirements of various biological, chemical and industrial applications by modifying their wetting properties. In the present study, we have investigated the effect of silver nanocolumns on the static as well as dynamic wettability of surface. The nanocolumns of about 400 nm

length and 150 nm diameter ( $\alpha = 85^\circ$ ) were grown by oblique angle deposition method over the Si(100) substrate. The effect of these nanocolumns on static wetting behavior was studied by performing sessile drop contact angle measurements using de-ionized water. A significant enhancement in the hydrophobicity of silver surface with contact angle value of  $108^\circ$  was observed (see supplement file, Fig. 1). To ensure that the observed changes in wetting behavior are due to the influence of nanocolumns, the measurements were carried out for different surface features ranging from plane to nanocolumnar film (grown for  $\alpha = 0^\circ, 65^\circ, 75^\circ$  and  $85^\circ$ , see SEM images in supplement file, Fig.2). Contact angle was observed to increase gradually from  $94^\circ$  to  $96^\circ$  with increase in oblique angle ( $\alpha$ ) from  $0^\circ$  to  $75^\circ$ . A drastic increase in contact angle was observed for nanocolumnar surface grown at  $\alpha = 85^\circ$ . For these silver samples the rms (root mean square) surface roughness was found to follow almost the same pattern as that of contact angle with  $\alpha$ , suggesting the dependence of wettability on surface roughness. The observed results were explained following the Cassie-Baxter model considering the silver nanocolumns to form a silver-air composite surface. To investigate the effect of nanocolumns on dynamic wetting property, the contact angle measurements for higher sample surface temperature ( $T_s = 80^\circ\text{C}$ ) were performed and the rate of change of contact angle of water drop for an interval of 10 sec was measured. This transition rate of contact angle values was found to increase drastically for the nanocolumnar surface (see the supplement file, Fig.3). It shows that the nanocolumnar growth affects not only the static contact angle by making the surface hydrophobic but also greatly influences the surface temperature dependent dynamic wetting behavior of water drop. This study provides a basic understanding of the wetting behavior of nanocolumnar surface as well as shows the possibility to tune the surface wettability for meeting the requirements of various industrial applications.

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