Advanced Surface Engineering
Room: 204 - Session SE+TF+NC-ThA

Glancing Angle Deposition (GLAD) II

Moderator: D. Gall, Rensselaer Polytechnic Institute

2:00pm **SE+TF+NC-ThA1 Glancing Angle Deposition at the Nano-Bio Interface**, ***Y. Zhao***, University of Georgia **INVITED**

Glancing angle deposition (GLAD) technique is a physical vapor deposition method to design three-dimensional nanostructures by programming the vapor incident angle and substrate azimuthal rotation. This method offers large area growth of aligned nanorod arrays with additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. With recent advance in a multilayer deposition procedure, one can design complex and multifunctional heterogeneous nanostructures. In addition, with a co-deposition system of two or more sources, novel nanocomposites or doped nanostructure arrays can be produced, which results in nanostructures with different morphology. Here, I will highlight our recent progress in multi-component nanorod array fabrication and their potential biological applications. We find that aligned silver nanorod array substrates can be used as a high sensitive virus and bacteria sensor base on surface enhanced Raman spectroscopy (SERS) principle. This SERS based sensor can be used to detect the molecular fingerprints of several important human respiratory viruses including respiratory syncytial virus, rhinovirus, adenovirus, human immunodeficiency virus, influenza virus, and bacteria, with high sensitivity and selectivity, and to discriminate between different virus/bacterium strains. Using a unique multilayer deposition configuration, catalytically driven nanomotors have been fabricated and demonstrated, which can directly convert chemical energy into mechanical energy. This device holds a great potential to mimic smart biological systems via hybrid organic-inorganic nanostructures.

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2:40pm **SE+TF+NC-ThA3 Growth and Characterization of Magnesium, Magnesium Alloy, and Doped TiO_x Sculptured Thin Films (STFs)**, ***S.M. Pursel***, *M.W. Horn, B.A. Shaw*, The Pennsylvania State University

Bioabsorbable materials such as magnesium, which is essential for cellular function, have recently been studied for use in heart stents, bone plates and screws, and dental and orthopedic implants. However, the use of vapor deposition to form non-equilibrium magnesium alloys has had little if any commercial interest even though certain properties of these alloys, namely corrosion resistance, can be improved. Engineering of surface morphology using dip coatings and etching has been used in biomedical materials to enhance certain application specific surface properties. Sculptured thin film (STF) technology potentially provides a path to merge the advantages of non-equilibrium alloy formation and engineering nanoscale surface morphology. We present here our results utilizing a vapor co-deposition scheme to improve nucleation and corrosion properties of magnesium alloys. By utilizing co-deposition with materials such as titanium, yttrium, zirconium, and others the growth mode of magnesium can be modified and the solid solution limit can be surpassed leading to an improvement in corrosion resistance. Characterization of the growth of magnesium alloy thin films has been done utilizing various alloying elements, substrate temperatures, post-deposition treatments, and substrate positions (to deposit STFs). The results point towards a growth mode controlled by crystallization effects that are not common in higher melting temperature materials. The results of the study are presented in terms of x-ray diffraction data, microscopy analysis of growth evolution, and corrosion testing. We will also present results that extend our work on TiO_x chiral STFs utilizing the circular Bragg phenomenon (CBP) for sensor applications. The CBP is observed in the circularly polarized transmission spectrums of chiral STFs as a stop band for co-handed light. The location and shape of this stop band is dependant on the material properties among other factors. Using an impurity material from a second source may allow added sensitivity for sensor applications while maintaining STF morphology and function.

3:00pm **SE+TF+NC-ThA4 Performance and Response Time of Nanostructured Relative Humidity Sensors**, ***M.T. Taschuk***, *J.J. Steele, M.J. Brett*, University of Alberta, Canada

Applications requiring relative humidity (RH) measurement will require differing sensitivity, range of humidity operation, and response times. These properties are determined by the properties of the sensing medium: material, porosity, surface area, pore size distribution and morphology. We have been investigating the use of glancing angle deposition (GLAD) for the fabrication of RH sensors with interdigitated electrode (IDE) substrates.[1,2] While GLAD offers some significant advantages for RH sensors, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. The response of our devices depend on the extremely large low frequency dielectric constant of water adsorbed to metal oxides, which can results in a three order of magnitude change in capacitance as RH is increased from 0 to 100%. We have recently employed an electromagnetic model with simple dielectric mixing laws to compare our device performance with literature values for dielectric constants[2]. Further work is ongoing to include structural effects in the dielectric mixing laws to improve accuracy. Response time varies with the size and nature of pores in our sensors, which in turn relies on column properties such as diameter and surface roughness. Experimental values for response time of the GLAD RH sensors have been reported, but a neither a model nor thorough study of response time as a function of deposition angle and film thickness has been presented. Constructing a model for our devices requires an understanding of the diffusivity of GLAD films, the interaction between water vapour and TiO2, and the electromagnetic behaviour of IDE devices. In this paper we characterize the performance and response time of GLAD RH sensors as a function of film thickness and deposition angle. The microstructure column radius as a function of film thickness and deposition angle is investigated. A 1D numerical model describing response time of our devices is developed, which includes diffusion, adsorption and IDE physics. The modeling results are compared with our experimental data, and demonstrates that response time of our sensors is dominated by adsorption.

[1] J.J. Steele, G.A. Fitzpatrick, and M.J. Brett. IEEE Sensors Journal, Vol. 7:955 – 956, 2007.
[2] J.J. Steele, M.T. Taschuk, and M.J. Brett. IEEE Sensors Journal, (In Press), 2008.

3:20pm **SE+TF+NC-ThA5 Patterned Ag Nanorod Arrays as SERS Substrates by Template Mediated Oblique Angle Deposition**, ***Y. Liu***, *Z. Zhang, Y. Zhao*, University of Georgia

Surface enhanced Raman scattering (SERS) is widely used in the analytical, biomedical, clinical, environmental, and security applications. The practical application of a SERS-based sensor requires an efficiency SERS substrate which can not only provide a high enhancement factor, but also be uniform, stable and reproducible. In this work, a highly ordered, uniform and periodic patterned Ag nanorod arrays as SERS substrates are fabricated by combining electron beam lithography (EBL) and oblique angle deposition (OAD) techniques. Two dimensional nano Au post arrays with different separations are fabricated by EBL. There are only very weak SERS signal can be detected after the Au post arrays are treated by a 1 μL 10^{-4} M BPE (trans-1,2-bis (4-pyridyl) ethene) droplet. However, after a layer of ~ 400 nm Ag nanorods are deposited on those BPE treated Au post array, strong SERS signals have been obtained. Furthermore, the SERS intensities become more than 8 times stronger, after the Ag arrays are further treated by a droplet of 1μL 10^{-5} M BPE. These results demonstrate that most SERS signals could come from the molecules adsorbed on the side surfaces of the Ag nanorods, rather than the ends. The SERS signal is also strongly dependent on the separation of the Au posts. A numerical calculation on the electric field enhancement has been carried out to confirm this result.

4:00pm **SE+TF+NC-ThA7 Quantification of Porosity and Deposition Rate of Nano-Porous Films Grown by Oblique Angle Deposition**, ***D.J. Poxson***, *F.W. Mont, M.F. Schubert, J.K. Kim, E.F. Schubert*, Rensselaer Polytechnic Institute

We propose analytic formulas accurately predicting the refractive index and film thickness of obliquely deposited thin films for a given incident angle. Recently, it was shown that accurate control of the refractive index of physical-vapor deposited thin film materials can be achieved through the use of oblique-angle deposition. Refractive index tunability and low refractive index (low-n) films are highly desirable for a variety of optical applications. For example, broadband antireflection coatings, omni-directional reflectors, distributed Bragg reflectors, optical micro-resonators, light-emitting diodes, photovoltaic solar cells, and optical interconnects. While the qualitative tenets of oblique-angle deposition were demonstrated over a century ago, no quantitative formulas for the porosity and deposition rate have been described in the literature. In this work, we propose a model relating the porosity and deposition rate of a material to its vapor flux incidence angle for oblique-angle deposition. Our model is based upon geometrical arguments, employs a single fitting parameter, and takes into account surface diffusion. We have measured the refractive index and thickness for SiO_2 and indium tin oxide (ITO) nano-porous films deposited over a wide range of deposition angles ($0° < \theta < 90°$). The porosity of a material is determined from the measured refractive index. Comparison of experimental SiO_2 and ITO porosity values and deposition rates with theory reveals excellent agreement. The theoretical model allows for the predictive

control of refractive index, porosity, and deposition rate for all deposition angles, potentially a very useful tool in the development of high quality low-n optical coatings. Furthermore, given the set of basic assumptions used, we expect these formulas to be valid for a wide range of materials.

4:20pm **SE+TF+NC-ThA8 Sculptured Thin Films from Aluminum**, ***E.B. Schubert***, *T. Hofmann, D. Schmidt, M.M. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) structure design of chiral materials on the nanoscale is a current demand in modern material science and engineering and various intriguing applications are foreseen for example in the fields of optics, electromechanics or electromagnetic. Glancing angle deposition is a method which allows for "bottom-up" fabrication of 3D shaped and tailored chiral nanostructures arranged in sculptured thin films (STF). We will present an investigation of the growth of STF's from aluminum on highly p-type doped silicon substrates by using either ion beam sputtering or electron beam evaporation. Various growth schemes have been used to obtain films with different nanostructure shapes such as posts, plates, screws or spirals. The films have been characterized regarding their optical and electrical properties by means of 4x4 Mueller-Matrix ellipsometry, IR spectroscopic ellipsometry and electrical measurements. Whereas Mueller-Matrix Ellipsometry reveals an optical response which can be related to the symmetry of the three-dimensional nanostructures,[1] the IR data give hint to electron or lattice absorptions. We found that the IR optical response depends on the shape of the nanostructures. STF's from aluminum plates for example show a strongly metallic behavior, whereas films containing Al spirals show multiple resonances, with a periodic spectral distance of 7.2 THz between neighboring absorption features. The IR optical data for the Al nanocoils are discussed in terms of coupled inductance and capacitance pairs, where the inductance is formed from the coil itself and the depletion layer capacitance is created on the footprint of the metallic Al coil with the highly p-type doped Si substrate. A Drude-like background term, which accounts for free carriers in the aluminum nanospirals was also used during sample regression. It is found, that resistivity and free mean path of the electron depends of the shape of the Aluminum nanostructures as well. This behavior is verified by electrical measurements under dc conditions.

[1] D. Schmidt, E. Schubert, and M. Schubert, phys. stat. sol. (a) 205, 748 (2008).

4:40pm **SE+TF+NC-ThA9 Mueller Matrix Ellipsometry Studies of the Optical Properties and Structure of Serial Bi-Deposited Titanium Oxide Sculptured Thin Films**, *N.J. Podraza, S.M. Pursel,* The Pennsylvania State University, *R.W. Collins,* University of Toledo, ***M.W. Horn***, The Pennsylvania State University

In this work, titanium oxide (TiO_2) chiral sculptured thin films (STFs) are fabricated using serial bi-deposition (SBD) electron beam evaporation and studied using Mueller matrix ellipsometry (MME). Chiral STFs are of interest for a wide range of applications in optoelectronic devices such as photovoltaics, microelectronic devices, microcavities, biological sensors, and bioabsorption devices. These films can be described as assemblies of upright, parallel, helical columns. Their helicoidal morphology, being periodic, engenders the circular Bragg phenomenon: circularly polarized light couples to the helices present in the film, if the handedness of the light and the STF coincide, resulting in enhanced reflectance in the Bragg regime spectral range. TiO_2 STFs fabricated using SBD are of particular interest for fundamental studies due to its high bulk index of refraction and films prepared using this technique can be fabricated to exhibit Bragg resonances in the visible spectral range at wavelengths ~450-650 nm. Although normal incidence transmission and reflection measurements can demonstrate this behavior, it is often impossible to discern the various optical and structural properties of optically anisotropic materials like STFs. MME, however, allows us to extract each of the principal indices of refraction (n_x, n_y, n_z) as well as the microstructural parameters such as film thickness and the initial polar and in-plane orientation of the helices. The complete Mueller matrices for SBD TiO_2 STFs are measured using a dual-rotating compensator spectroscopic ellipsometer over a spectral range from 250-825 nm in transmission mode at normal incidence ($\Theta_i = 0^0$) and non-normal incidence ($5 \leq \Theta_i \leq 55^0$). The normal incidence measurements provide the principal indices of refraction and the microstructure, while the non-normal incidence measurements allow us to monitor the blue-shift in the Bragg resonance with increasing angle of incidence. The fundamental understanding gained from MME is expected to provide assistance in further engineering and optimizing these types of materials for specific applications requiring control of the Bragg resonance feature.

5:00pm **SE+TF+NC-ThA10 Low Hydrogen Desorption Temperature of Hydrided Pd Coated Novel Mg Nanoblades**, ***F. Tang***, *T. Parker, H.-F. Li, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

We grew Mg nanoblades standing nearly vertically on the substrates by oblique angle vapor deposition. The thickness of the nanoblades along the vapor incident direction ranges from ~15 nm to ~30 nm at a vapor incident angle ~75°, while the width perpendicular to the incident vapor direction is as wide as a few hundred nm.[1] These novel nanoblade structures have several advantages over the bulk materials for hydrogen storage: such as a large surface-area-to-mass ratio of ~60 m^2/g and ultrathin thickness (~22 nm), which will significantly enhance the kinetics of hydrogen absorption/desorption. The spacing between the nanoblades can also accommodate the large volume change ($Mg \leftrightarrow MgH_2$) during hydrogenation/de-hydrogenation processes. We have studied hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades coated with Pd as a catalyst, using in situ temperature desorption spectrum (TDS), ex situ scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Pd coated Mg nanoblades were hydrogenated at a pressure of 1 bar with substrate held at ~333 K for ~15 hours. The de-hydrogenation property of the hydrided Pd/Mg/Pd nanostructure was characterized in situ by TDS, which showed that the hydrided nanostructure has a low hydrogen desorption temperature at ~365 K. Through a combinational microstructure by TEM and TDS analyses of hydrided nanoblades as well as hydrided nanoblades covered with additional Mg layers, we found that the effect of Pd catalyst on reducing the hydrogen desorption temperature is significantly stronger than the conventionally proposed grain size and strain effects. The ex situ SEM images showed that the hydrided Pd/Mg/Pd and hydrided Pd/Mg (one sided Pd coating) nanoblades became highly curved. Various shapes such as circular, helical or spiral have been formed in the hydrided Pd/Mg nanoblade films. The formation of these curly structures could be related to the strain induced by the partial decomposition of MgH_2 after the sample was exposed to air. The understanding of hydrogenation/de-hydrogenation properties of Pd coated Mg nanoblades could help us in designing promising nanoscale metal hydrides for hydrogen storage with low desorption temperatures. FT was supported by the NSF award 0506738 and TP was supported by the DOE (education) GAANN P200A030054.

[1] F. Tang, T. Parker, H.-F. Li, G.-C. Wang, and T.-M. Lu, J. of Nanosci. and Nanotechnol. 7, 3239 (2007).

5:20pm **SE+TF+NC-ThA11 Improving Stiffness of Silicon Chevrons by 1.2 MeV Ar^{+8} Ion Irradiation**, ***R. Nagar***, Indian Institute of Technology Delhi, *C. Patzig, B. Rauschenbach,* Leibniz-Institute of Surface Modification Leipzig, Germany, *P. Kumar, D. Kanjilal,* Inter-University Accelerator Centre, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Five-armed silicon chevrons were grown by oblique angle ion beam sputter deposition on Si(111) substrates pre-patterned with 260 nm diameter silica spheres and 500 nm diameter polystyrene spheres. The patterning spheres self-assemble in hexagonal network, act as nucleation sites, and control the dimensions as well as the distance between the growing chevrons. The chevron arms are about 500 nm long, 350 nm wide and 200 nm thick with odd numbered arms making an angle of about 45° and even numbered arms an angle of about 55° from the vertical. In order to tailor the mechanical strength of the chevron coatings, the samples were irradiated with 1.2 MeV Ar^{+8} ions at liquid nitrogen temperature at different fluences of 10^{15}, 10^{16} and 10^{17} ions/cm^2. The range of Ar ions in the amorphous Si matrix as determined by the simulation code SRIM is about 1.1 μm. Therefore, the Ar ions traverse the complete length of the chevrons before getting implanted in the Si(111) substrate. The spring constant of the chevrons was determined by force-distance spectroscopy using an atomic force microscope. Results show that the spring constant of the irradiated Si chevrons grown on 260 nm diameter silica spheres increases from 480 N/m for pristine to 1320 N/m for a fluence of 10^{16} ions/cm^2. For chevrons grown on 500 nm diameter polystyrene spheres, an increase from 370 N/m for pristine to 1325 N/m for fluence of 10^{17} ions/cm^2 is observed. Thus, irradiated chevrons are stiffer as compared to pristine ones. Finite element analysis of chevrons provides an insight into the dynamics of the resulting deformations when the chevrons are loaded. The modeling establishes that for these odd-armed chevrons a vertically downward load results in a torque about the base of the chevrons. The load produces a significantly larger lateral stress/displacement relative to the vertical, thus making them more robust to the loading force. Investigations by micro-Raman and glancing angle X-ray diffraction suggest that the Ar irradiation fosters a transformation from amorphous to poly-crystalline Si. The improved mechanical strength of the chevrons indicates that ion irradiated chevron coatings are capable of withstanding higher loads as compared to pristine coatings without getting delaminated.

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