Thin Film
Room: 11 - Session TF+SE+NS-WeM

Glancing Angle Deposition (GLAD)

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

8:00am **TF+SE+NS-WeM1 Tunable-Refractive-Index Materials – A New Class of Optical Thin-Film Materials with Applications in Solid-State Lighting and Solar Photovoltaics**, ***E.F. Schubert***, Rensselaer Polytechnic Institute **INVITED**

Among the properties of optical materials, the refractive index is a most fundamental one. It determines many optical characteristics such as Fresnel reflection, Bragg reflection, Snell refraction, diffraction, and the phase and group velocity of light. The refractive indexwas introduced centuries ago by Isaac Newton who correlated the refractive index with the relative strength of refraction at the liquid-to-air interface.He realized that the degree of refraction is proportional to the mass densityof the liquid, and therefore called the new optical quantity the "opticaldensity." Nowadays, this key quantity is known as the "refractive index."

Among transparentdense materials, MgF_2 has the lowest refractive index: $n = 1.39$. Air and other gases have a refractive index very close to 1.0 but these materials are not viable forthin-film optoelectronic applications. Therefore, there are no dense materials witha refractive index in the range $1.0 < n < 1.39$. That is, this range has remained unavailable and unexplored.

Over the last few years, a new class of materials, tunable-refractive-index materials, has been developed. Optical thin-film materials, with a refractive index as low as 1.05, have been demonstrated. The tunable-index materials are based on nano-porous materials, such as, for example, nano-porous SiO_2, nano-porous indium-tinoxide (ITO), and nano-porous TiO_2. The porosity can be precisely controlled by using oblique-angle deposition, a technique in which the substrate is at non-normal angle with respect to the deposition source. Whereas dense films form for normal-incidence deposition, porous films with aself-organizing nano-structure form for oblique-angle deposition.

In this presentation, we will present examples of novel structures and devices that exploit the newly gained controllability of the refractive index. Devices to be discussed include distributed Bragg reflectors, light-emitting diodes, and solar cells, along with the performance enhancements enabled by the control of the refractive-index.

8:40am **TF+SE+NS-WeM3 Nanostructured Homogenous CdSe/TiO_2 Composite Visible Light Photoanodes Fabricated by Oblique Angle Codeposition**, ***G.K. Larsen***, University of Georgia, *B.C. Fitzmorris*, University of California Santa Cruz, *C. Longo*, University of Campinas, Brazil, *J.Z. Zhang*, University of California Santa Cruz, *Y.-P. Zhao*, University of Georgia

A unique fabrication method, oblique angle codeposition, is used to deposit well-aligned nanorod arrays and thick films of homogenously mixed CdSe/TiO_2 composites. The structural, optical, and photoelectrochemical properties of the films are investigated using a variety of experimental techniques. Ultrafast exciton dynamics are studied using femtosecond transient absorption (TA) spectroscopy. The CdSe/TiO_2 composites are compared with pure CdSe and TiO_2 filmsin order to determine their utility for photoelectrochemical (PEC) applications and to understand the mechanisms underlying the observed behaviors. The morphology of the deposited nanorods changes with film composition due to atomic collisions occurring in the vapor column, which can be modeled using a simplified Keller-Simmons expression. Furthermore, the two phase evaporation process of CdSe creates three different cluster types within the TiO_2 film structures: isolated Se, Se-deficient CdSe, and Se-rich CdSe. The prevalence of each cluster type is dependent on predicted film composition, and each is affected differently by open-air annealing. Isolated Se can be incorporated into the TiO_2 lattice, resulting in low energy rutile phase. Se-deficient CdSe clusters crystallize preferentially into cubic CdSe and are easily oxidized into CdO, while Se-rich CdSe clusters crystallize into hexagonal CdSe and are more stable. Furthermore, each of these cluster types interacts differently with the surrounding TiO_2 matrix, resulting in diverse optical and PEC behaviors. Interestingly, the stoichiometry of the CdSe domains is more important than overall CdSe content within the film in determining the structural, optical, and PEC properties of the films. The composite nanorod structure is a more efficient photoanode under visible light illumination than both the pure CdSe and TiO_2 nanorod array films. The higher efficiency of the composite films is attributed to efficient charge transfer and separation in the homogenously mixed composite. This is confirmed by the extremely high electron injection rate from CdSe into TiO_2 observed in the ultrafast TA studies.

9:00am **TF+SE+NS-WeM4 Control the Biaxial Texture of Vertically Aligned Nanostructures using Oblique Angle Sputtering Deposition with Substrate Flipping Rotation**, ***G.-C. Wang***, *L. Chen*, *T.-M. Lu*, Rensselaer Polytechnic Institute

It is known that oblique angle deposition can be used to grow 3D nanostructures with a variety of morphology such as nanorods and nanospirals. For a selective set of materials, the technique can also produce a preferred crystal orientation, particularly a biaxial texture where the texture selection occurs in both the out-of-plane and in-plane directions. Most frequently biaxial texture created using the oblique angle deposition is in the form of slanted nanorods. It is desirable to produce a biaxial structure in the form of vertically aligned nanostructures which may be useful as a buffer layer to grow functional films on top of it. In this talk we will discuss several strategies to grow vertically aligned nanostructures including nanorods with a biaxial texture by dynamically varying the incident flux angle with respect to the surface normal during deposition. A particularly robust technique to achieve this goal is a flipping rotation scheme where the substrate is rotated continuously at a fixed speed around an axis lying within and parallel to the substrate [1]. This is very different from the conventional substrate rotation mode where the rotational axis is perpendicular to the substrate surface. In the flipping rotational mode the incident flux is perpendicular to the rotational axis, and the incident flux angle changes continuously. Mo vertical nanorod films, grown on amorphous substrates under three orders of magnitude different rotation speeds, different flipping directions, and different ending deposition angles, were characterized using scanning electron microscopy. For texture characterization of these Mo nanostructures we used our newly developed reflection high energy electron diffraction surface pole figure technique [2]. Despite very different morphologies, such as 'C'-shaped, 'S'-shaped, and vertically aligned nanorods grown by the flipping rotation, the same (110)[1-10] biaxial texture with an average out-of-plane dispersion of ~15° was observed. In contrast, we showed that only a fiber-textured Mo film was obtained by using the conventional rotation mode with a fixed incident flux angle. These biaxial Mo vertical nanorod films have potential applications as buffer layers to grow near-single crystal semiconductor films through nanoheteroepitaxy. These films may find important applications in energy conversion and light emitting devices.

Work was supported by the NSF DMR-1104786.

[1] L. Chen, T.-M. Lu, and G.-C. Wang, Nanotechnology 22, 505701 (2011).

[2] F. Tang, T. Parker, G.-C. Wang, and T.-M. Lu, J. of Physics D: Applied Physics 40, R427 (2007).

9:20am **TF+SE+NS-WeM5 Flux Engineering to Control In-Plane Crystal and Morphological Orientation**, ***J.M. LaForge***, *G. Ingram*, *M.T. Taschuk*, *M.J. Brett*, University of Alberta, Canada

Texture evolution during oblique angle deposition (OAD) and glancing angle deposition (GLAD) is of fundamental interest and important applications. As the distribution of size, shape and orientation of crystal grains impacts film electrical, optical, magnetic and mechanical properties control over texture evolution is important to optimizing performance. Morphology and crystal texture of OAD or GLAD nanostructured films is influenced by the orientation of the substrate relative to the collimated vapor flux, namely angle of incidence and the azimuthal angle, during deposition. Previous work has demonstrated control over the out-of-plane orientation through changes in the angle of incidence or azimuthal motion of substrate (e.g. stationary or continuous rotation).[1][2] However, work on the development of in-plane orientation has focused on material kinetic effects, such as deposition temperature, residual gas concentration, and deposition rate rather than substrate motion.[3][4]

We have deposited iron nanocolumns that have a tetrahedral apex and an out-of-plane texture (fiber texture) at a deposition angle of 88° under continuous substrate rotation. It is possible to induce in-plane crystal texture and morphological orientation by engineering the azimuthal distribution of the flux to match the symmetry of the nanocolumns (i.e. 3-fold rotational symmetry). Thus, biaxially textured nanocolumns with an in-plane alignment that is predominantly controlled by substrate motions (or flux configuration) can be created using this technique. In principle, this method could be generalized to nancolumns with 4-fold and 6-fold azimuthal symmetry and therefore provides a mechanism to form biaxially textured, nanostructured films from a variety of materials deposited on amorphous or crystalline substrates.

[1] P. Morrow, F. Tang, T. Karabacak, P.-I. Wang, D.-X. Ye, G.-C. Wang, T.-M.T.-M. Lu, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films***2006**, *24*, 235.

[2] R. Krishnan, T. Parker, S. Lee, T.-M. Lu, *Nanotechnology***2009**, *20*, 465609.

[3] K. Okamoto, T. Hashimoto, K. Hara, M. Kamiya, H. Fujiwara, *Thin Solid Films***1985**, *129*, 299-307.

[4] K. Okamoto, T. Hashimoto, K. Hara, M. Kamiya, H. Fujiwara, *Thin Solid Films***1987**, *147*, 299-311.

9:40am **TF+SE+NS-WeM6 Bi-axial Texture Development in AlN Layers during Off-axis Sputter Deposition**, ***R. Deng***, *D. Gall*, Rensselaer Polytechnic Institute

Polycrystalline AlN layers were deposited by pulsed-DC reactive magnetron sputtering from a variable deposition angle α = 0-84° in 5 mTorr pure N2 at room temperature. X-ray diffraction pole figure analyses show that layers deposited from a normal angle (α = 0°) exhibit fiber texture, with a random in-plane grain orientation and the c-axis tilted by 42±2° off the substrate normal, yielding wurtzite AlN grains with the {10-12} plane approximately parallel (±2°) to the substrate surface. However, as α is increased to 45°, two preferred in-plane grain orientations emerge, with populations I and II having the c-axis tilted towards and away from the deposition flux, by 53±2° and 47±1° off the substrate normal, respectively. Increasing α further to 65 and 84°, results in the development of a single population II with a 43±1° tilt. This developing bi-axial texture is attributed to a competitive growth mode under conditions where the adatom mobility is sufficient to cause inter-grain mass transport but insufficient for the thermodynamically favored low energy {0001} planes to align parallel to the layer surface. Consequently, AlN nuclei are initially randomly oriented and form a kinetically determined crystal habit exposing {0001} and {11-20} facets. The expected direction of its highest growth rate is 49±5° tilted relative to the c-axis, in good agreement with the 42-53° measured tilt. The in-plane preferred orientation for α > 0° is well explained by the orientation dependence in the cross-section of the asymmetric pyramidal nuclei to capture off-normal directional diffusion flux. The observed tilt is ideal for shear mode electromechanical coupling, which is maximized at 48°.

10:40am **TF+SE+NS-WeM9 Engineered Indium Tin Oxide Nanowhiskers via Vapour Liquid Solid Glancing Angle Deposition**, ***A.L. Beaudry***, *R.T. Tucker, J.M. LaForge, M.T. Taschuk,* University of Alberta, Canada, *M.J. Brett*, University of Alberta, Canada and The National Institute for Nanotechnology

The vapour liquid solid (VLS) nanowire growth technique has been recently modified with spatially modulated vapour flux through glancing angle deposition (GLAD).[1,2] Using this new technique, named VLS-GLAD, our group has demonstrated improved morphological control over indium tin oxide (ITO) nanowhiskers.[1] Single crystal ITO nanowhiskers are grown via a self-catalyzed VLS growth mechanism, resulting in branched structures.[3] VLS-GLAD exhibits improved control over the diameter, spacing, branching density and branching orientation of ITO nanowhiskers. As the angle of deposition is increased to glancing angles, there is a transition from a dense interconnected network to a porous film of individual ITO nanowhisker structures. In addition, branching was found to increase significantly with increasing deposition angle. This result is attributed to an increase in the proportion of vapour flux incident on the sides of the structures, resulting in an increase in self-catalytic VLS growth of branches. This effect has been used to engineer branch morphology and orientation. Vapour flux rate modulation at glancing angles results in further in-situ control over ITO nanowhisker features. HRTEM imaging revealed a continuation of crystal planes from the trunk into the branch. XRD results indicated single crystal cubic bixbyite structures with a <400> growth direction. Haacke's figure of merit was used to assess the suitability of ITO nanowhisker films as transparent electrodes.[4]

[1] Beaudry, A.L. et al. *Nanotechnology* **23**, 105608 (2012).

[2] Alagoz, A.S. and Karabacak, T. *MRS Proceedings* **1350**, (2011).

[3] Castañeda, S.I. et al. *Journal of Applied Physics* **83**, 1995 (1998).

[4] Haacke, G. *Journal of Applied Physics* **47**, 4086 (1976).

11:00am **TF+SE+NS-WeM10 CoPt Nanopillars for Advanced Media by Glancing Angle Deposition**, ***H. Su***, *A. Natarajarathinam, S. Gupta*, The University of Alabama

We report for the first time the fabrication of CoPt+AlN "granular nanorods" utilizing glancing angle deposition (GLAD) on a multi-gun, planetary sputtering system. Initially, AlN was deposited by reactive sputtering from an Al target while CoPt multilayers were simulataneously sputtered using cobalt and platinum targets. Various ratios of Co and Pt, ranging from Co80Pt20 to Co50 Pt50, were used to deposit CoPt-AlN nanorods with different AlN volume percentages. X-ray diffraction (XRD), electron dispersive X-rays (EDX), scanning electron microscopy (SEM), and alternating gradient magnetometry(AGM) were employed to characterize the structural and magnetic properties, respectively. SEM micrographs indicated that the nanorods were approximately 16 nm in diameter, the angle between the substrate plane and the growth direction was about 78 degrees, while the lengths of the nanorods ranged from 30 to 50 nm, depending on deposition time. The angles between the substrate plane and incident flux ranged from 47 degrees to 82 degrees as the substrate presented itself at different angles to the target during the planetary deposition. The composition of CoPt-AlN has been studied by EDX for different ratios of AlN. M-H loops showed that the planetary GLAD sample had twice the coercivity of the flat sample.

We have also compared stationary vs. planetary GLAD, and sequential deposition of AlN/CoPt multilayers with true co-deposition, using an annular CoPt target with an Al insert. Simulations of the deposition have been carried out to gain a better understanding of where the AlN segregates with respect to the CoPt grains. These preliminary results indicate a novel and promising approach to nanopatterned graded media that is the subject of intense research in the data storage industry.

11:20am **TF+SE+NS-WeM11 Through-post Electrical Characterization of GLAD Thin Films**, ***A. Lalany***, *R.T. Tucker, M.T. Taschuk,* University of Alberta, Canada, *M.D. Fleischauer,* University of Alberta and The National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Glancing Angle Deposition (GLAD) [1] thin films are increasingly used in optoelectronic applications that benefit from their unique optical properties or ultra-high surface area. GLAD produces porous nanostructured thin films which have found applications as high surface area electrodes. Potential performance benefits of these nanostructured thin-films for optoelectronic devices include, but are not limited to, increased charge extraction [2]. Suitable electrical conductivity along the length of GLAD structures (normal to substrate plane) is necessary to exploit a GLAD film's high surface area for electronic devices. However, optimization of GLAD films for these devices has proven difficult without direct measurements of post resistivity.

In-plane resistivity measurements of metals and conductive oxide GLAD films have been performed [3-5], showing increasing in-plane resistivity with increasing oblique deposition angle (due to decreased film density resulting in fewer conductive pathways). Electrical anisotropy has also been observed, with differing in-plane resistivity for different nanocolumn orientations [3-5]. Through post conductivity measurements present additional challenges - it has been shown that as crystallite grain size approaches the range of bulk electron mean free path, column-boundary scattering effects begin to dominate standard bulk-scattering mechanisms [6]. As such, the extensive boundaries present in GLAD structures can result in complex electrical behavior. While several attempts have been made to access through-post electrical properties, results have been limited to relative measures or are extremely low yield processes [7, 8].

We require a measurement technique that is both time and cost effective, statistically robust, and has high yield. This has been achieved with a Kelvin Cross-Bridge Resistor architecture specifically designed to measure through-post resistivity. Our devices can measure resistivities between 100 μΩ cm < ρ < 11 GΩ cm, and we have successfully measured through-post conductivities for Indium-tin-oxide (ITO) and Cr GLAD films. Here, we will present device fabrication, validation and current experimental results.

[1] M.M. Hawkeye et al., J. Vac. Sci. Technol. A 25 (2007) 1317.

[2] D.A. Rider et al., Nanotech. 22 (2007) 0857060.

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[4] K.D. Harris et al., Adv. Funct. Mater. 18 (2008) 2147.

[5] D. Vick et al., J. Vac. Sci. Technol. A 24 (2006) 156.

[6] A. Besnard et al., J. Phys. D: Appl. Phys. 44 (2001) 215301.

[7] M.F. Canslzoglu et al., ACS Nano. 4 (2010) 733.

[8] S.P. Chiu et al., Nanotech. 20 (2009) 105203.

11:40am **TF+SE+NS-WeM12 Direct Label-Free Detection of microRNA Using a Multi-well SERS Chip Fabricated By Oblique Angle Deposition**, ***J.L. Abell***, University of Georgia, *J.M. Garren,* Georgia Health Science University, *J.D. Driskell,* Illinois State University, *R.A. Tripp, Y.-P. Zhao*, University of Georgia

Direct label-free nucleic acid detection is a desirable yet challenging task. The current mainstay detection and screening technologies, namely polymerase chain reaction (PCR) and DNA microarrays (i.e. DNA chips), rely heavily upon the use of extrinsic reporter molecules to detect the

hybridization of a probe sequence to a target sequence. Removing the need for external labels reduces the cost and complexity of DNA detection assays. This, however, requires a sensing platform capable of highly sensitive, specific, direct chemical analysis. Surface-enhanced Raman spectroscopy (SERS) is an analytical technique capable of detecting highly resolved chemical signatures with superior sensitivity, and can be used to determine the relative quantities of a compound adsorbed on a nano-structured metal surface. The challenge for SERS detection is to produce a large area, uniform and highly sensitive substrate. Here, we report the use of Ag nanorod (AgNR) SERS substrates fabricated by oblique angle deposition (OAD) for microRNA (miRNA) detection. With such a large area (wafer size) and uniform response (signal intensity variation ≤ 10%) of the AgNR substrates, we have developed a simple molding technique to pattern the substrates into multi-well arrays. We demonstrate a 40-well 1" x 3" glass slide allowing for parallel screening of multiple specimens with uniform response. This multiwell substrate has been used in conjunction with a linear least squares (LS) analysis method by assuming that the SERS spectrum of miRNA is a convolution of the individual signals of each of the four A, C, G, and T components, where the contribution of each source signal to the total DNA signal is weighted by the relative quantities of A, C, G, and T present within the sequence. Experimentally we have demonstrated this method for detection and differentiation of four different DNA sequences. In addition, we show for the first time the subtle spectral changes observed after label-free hybridization can be quantified with LS to confirm the capture of the target sequence. This study reveals that the use of OAD SERS substrate could be a potential technique to replace to current microarray technique for DNA/RNA detection.

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