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

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

8:00am **SE+TF+NC-ThM1 Sculptured Thin Films: Something Old, Something New, Something Borrowed, Something Blue**, ***A. Lakhtakia***, Pennsylvania State University **INVITED**

Sculptured thin films (STFs) are assemblies of parallel shaped columns with nanoscale features.[1] The demonstrated optical and biological functionalities of STFs suggest their classification as nanoengineered metamaterials. Deliberate engineering of the shape of columns was accomplished about 35 years before the formal conceptualization of STFs as optical materials in the early 1990s. Thereafter, the language of liquid crystals was borrowed to describe their optical constitutive properties. The design of columnar morphology for STF-based devices to engineer the optical polarization state became well-established about five years ago. The research front for optical applications of STFs now comprises electrically controllable optical filters, light sources of specific polarization states, and plasmonics. High-quality optical performance may necessitate post-deposition processes that result in blue-shifting of spectral features. In contrast, high precision in morphology appears unnecessary for using STFs as platforms for cell cultures.

[1] A. Lakhtakia and R. Messier, Sculptured Thin Films (SPIE Press, 2005).

8:40am **SE+TF+NC-ThM3 Randomness and Roughening in Glancing Angle Deposition**, ***K. Robbie***, *T. Brown*, Queen's University, Canada, *S. Asgharizadeh, M. Sutton*, McGill University, Canada

The unique highly-porous nanostructures created with Glancing Angle Deposition are a direct result of the randomness inherent to the condensation of atomic or molecular vapors. This randomness arises through quantum indeterminism in the atom-by-atom evaporation of the source material. At one extreme of film growth conditions, when adatom diffusion is high, the influence of vapor-substrate geometry is minimized and the resulting films are typically dense with isotropic structure and properties - in essence this is the regime of molecular beam epitaxy. When adatom mobility is reduced (e.g. through reduced temperature or the introduction of a reactive gas) geometrical effects become increasingly important and a balance develops between roughening due to the random arrival of atoms and smoothing due to the reduced, but still finite, adatom diffusion. Films grown under these conditions with normal-incidence vapor can be quite dense, yet the film surface will always roughen due to the random arrival of the vapor atoms, eventually resulting in a cauliflower-like fractal morphology. The unique nanostructures of GLAD are created when geometrical shadowing is used to amplify randomness-induced roughening - requiring the vapor to arrive at an angle larger than approximately 70 degrees from the substrate normal. We present here the first experimental observation, through x-ray reflectivity (XRR) measurements of thin silicon films, of the transition to the glancing angle growth regime. We find that film porosity increases as a function of thickness in the GLAD regime, whereas it decreases with thickness under the same growth conditions yet with nearer-normal vapor incidence. Silicon films deposited at room temperature onto rapidly rotating substrates exhibit linearly increasing density as a function of thickness when deposited at vapor incidence angles of less than 70 degrees, and linearly decreasing density (increasing porosity) when deposited at incidence angles above 70 degrees. We also show that significant 'filling-in' can occur during glancing-angle growth, where vapor deposits some distance below the growing film surface. These XRR measurements provide valuable new insight into the glancing angle deposition growth process, and will help to refine film nanostructure simulation and design models.

9:00am **SE+TF+NC-ThM4 Scaling of Nanorods during Glancing Angle Deposition: Effect of Surface Diffusion**, ***S. Mukherjee***, *D. Gall*, Rensselaer Polytechnic Institute

Ta, Al, and Cr nanorods, 65–430 nm wide and 440 nm tall, were grown by glancing angle sputter deposition onto continuously rotated Si(001) substrates from a deposition angle of 84º at substrate temperatures T_s = 300–1125 K. Surface diffusion is negligible at low homologous temperatures $T_s/T_m < 0.08$ (T_m: melting point) and for systems with a high activation energy for surface diffusion E_m. This leads to a chaotic growth process where the surface morphological evolution is controlled by long-range shadowing interactions and the rod width w (= 58 nm) at a constant height h (= 400 nm) is material independent. However, at higher growth temperatures, w increases with T_s and scales with T_s/T_m for all investigated metals as well as for data from the literature. This is attributed to an increase in the average island size on the growth surface which results in additional shadowing interactions and a chaotic divergence in the microstructure. Applying mean-field nucleation theory and non-linear dynamics within the kinetically limited growth regime yields a Lyapunov exponent λ of 0.033 for the divergence from the zero-temperature morphology and an effective E_m that scales with the melting point according to $E_m = 2.46kT_m$. The data also suggests a transition from a 2D to a 3D island growth mechanism as T_s increases from below to above a critical temperature $T_c = 0.24T_m$. The growth exponent p decreases monotonously from 0.5 to 0.31 as T_s increases from 300 K to T_c, in agreement with Meakin and Krug's model and Mullins-Herring model for 2+1 dimensional moving interfaces. However, p exhibits a discontinuity at Tc and becomes anomalous ($p > 0.5$) for $T_s > T_c$.

9:20am **SE+TF+NC-ThM5 Glancing Angle Deposition on Rotating Patterned Substrates: Experiment and Simulation**, ***C. Patzig***, Leibniz-Institute of Surface Modification Leipzig, Germany, *T. Karabacak*, University of Arkansas at Little Rock, *B. Fuhrmann*, Martin-Luther-University Halle, Germany, *B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany

When glancing angle deposition is combined with a continuous substrate rotation, the growth of nanostructures with various shapes such as vertical posts, spirals and screws is possible. The shape is controllable with the ratio $\rho = r/\omega$ of the deposition rate r to the rotational speed ω. Besides the control of ρ, other deposition parameters such as the deposition angle β between particle flux and substrate normal, or the substrate temperature can be used to alter morphology and density of the grown sculptured thin films. Additionally, the use of a patterned substrate as an array of artificial seeds for the incoming deposition flux can lead to the growth of periodically arranged nanostructures. Here, nano sphere lithography was used to structure Si(100) substrates with Au dots in both hexagonally close packed and honeycomb arrangement as templates for the subsequent glancing angle deposition that was done by ion beam sputter deposition of a Si target. The influence of ρ, β, and the height of the Au seeds h on the morphology of the Si nanostructures for the case of the honeycomb pattern is discussed and compared with Monte Carlo simulations of glancing angle deposited sculptured thin films on templated substrates. It is found that in both experiment and simulation, depending on ρ either periodically arranged spiral-like or vertical column-like structures are grown, whereas changing β from 0° to a glancing 85° shifts the film morphology from dense with honeycomb-like arranged caps over partially grown together nanocolumns with hexagonally arranged pores in-between to separated nanostructures that replicate the templates honeycomb arrangement. Additionally, it was found both experimentally and in simulations that glancing angle sputter deposition on rapidly rotating substrates causes nanocolumns with triangular cross section on honeycomb templates and with circular cross sections on hexagonally close packed templates, showing that not only the inter-seed-distances, but also the symmetry of the template pattern influences the form of the growing nanostructures.

9:40am **SE+TF+NC-ThM6 Fabrication of Inclined Nano-Rough Columns by Combined Glancing Angle Deposition (GLAD) and Colloidal Lithography for Biological Applications**, ***A. Dolatshahi-Pirouz***, *M. Foss, D. Sutherland, J. Chevallier, F. Besenbacher*, University of Aarhus, Denmark

Recently there has been an increasing focus on methods to produce surfaces with a varying topography on the nanometer length scale for applications in e.g. biotechnology, photonics, and catalysis, since the nanoscale surface topography is known to influence the performance in these areas. Here, colloidal lithography is combined with glancing angle deposition (GLAD) to generate well-separated platinum nano-rough columns with a brush like appearance. The columns were fabricated by physical vapor deposition (PVD) with an e-gun evaporator onto surfaces pre-coated with polystyrene particles with a diameter at 137 nm by colloidal lithography at different deposition angles between the substrate and incoming flux (θ = 35, 10 and 5) as well as different depositions times. The effect of θ and deposition time t on the morphological characteristics of the nano-columns was investigated by utilizing scanning electron microscopy (SEM) and subsequently analyzing the images in order to determine the height, width and inclination angle of the nano-rough columns. From the SEM images we observe that the morphology of the nano-rough columns depend on the angle of incidence and as the deposition angle approaches grazing incidence sharp brush like columnar protrusions are grown on the colloidal particles, while more smoothly shaped surface features are grown at higher deposition angles. Moreover, by changing the incidence angle of the incoming flux,

well-separated nano-rough columns can be synthesized with an angle of inclination ranging from 26 to 90 degrees. As the deposition time increases the height and width of the nano-rough columns follows a power law and increases accordingly. The power law exponents for the height and width increment as function of the deposition time both depends on the angle of incidence decreasing from 1.06 ± 0.04 to 0.81 ± 0.16 and 0.71 ± 0.07 to 0.19 ± 0.01, respectively, as the deposition angle decreases from 35 to 5 degrees. The change in the power law exponents indicates that the kinetics of the growth of the nano-rough columns is influenced by surface diffusion and shadowing effects. Moreover, from the power law exponents we were able to tailor inclined nano-rough columns with the same height and an inclination angle ranging from 90 to 26 degrees. The nano-rough surfaces are currently being used in cell experiments which indicate that inclined nano-rough columns can be used to guide the cellular behavior on a surface.

10:40am **SE+TF+NC-ThM9 Growth of Al Nanowhiskers on the Patterned Substrate by Glancing Angle Deposition at High Temperature**, ***M. Suzuki***, *R. Kita, K. Hamachi, K. Nakajima, K. Kimura*, Kyoto University, Japan

Recently, we have found that peculiar metal (Al, Fe, Ag, Au etc.) nanowhiskers grow when metal is deposited at a glancing angle on a high-temperature substrate (HT-GLAD). The key factors for producing nanowhiskers are a glancing deposition angle larger than 80° and a temperature higher than almost half of the melting point of the metal. Since the growth of the nanowhiskers may be concerned with the general crystal growth mechanisms, an understanding of the growth mechanisms will provide a novel technique to fabricate nanostructures. Further, if the growth of nanowhiskers is controlled, metal nanowhiskers will become important components for nanoelectromechanical devices because of their mechanical compliance, high electric and thermal conductance, catalysis, plasmonic properties, magnetism, etc. In order to understand the effect of the detailed geometric deposition condition on the growth of nanowiskers, we have demonstrated HT-GLAD of Al on a heated substrate with trench patterns. Al was deposited on a surface-oxidized Si(110) substrate using an electron beam (EB) evaporation apparatus specially designed for HT-GLAD. Six groups of trenches with a nominal width of 1, 3, 5, 10, 15, and 20 μm, respectively, and a depth of 1.7 μm were prepatterned along the direction. The substrate temperature during the deposition was maintained constant at a temperature of 390 °C. By choosing an appropriate substrate attitude during the deposition, the deposition angle on the sidewalls of the trenches was kept constant at 85°, while that on the surface was varied between 55° and 87°. The amount of Al deposited on the sidewalls was 30 nm in average thickness for all samples. The number of nanowhiskers growing on the sidewalls significantly increased with deposition angle on the surface. This suggests that Al atoms deposited in front of the growing nanowhiskers play an important role in the growth of nanowhiskers. The directive migration and/or reflective scattering are possible candidates for the transport process of the deposited atoms.

11:00am **SE+TF+NC-ThM10 Characteristic Length Scale of Nanorods**, ***H. Huang***, RPI

Glancing angle deposition has led to numerous exotic structures of nanorods. It is natural to ask: what makes nanorods nano. Following the discovery of three-dimensional Ehrlich-Schwoebel barrier, we have discovered a new length scale that dictates the formation of crystalline nanorods. This presentation starts with the physics origin of such length scale, and continues with atomistic simulations demonstrating the variation of the length scale and validation experiments, and ends with design of nanosynthesis based on the knowledge of this new length scale & its experimental validation. It is interesting to note that this length scale is the very reason that nanorods synthesis is possible, even though nanorods had been realized long time ago (and it was patented a decade ago).

11:20am **SE+TF+NC-ThM11 Crystalline Organic Nanocolumn Arrays**, ***J. Zhang***, *I. Salzmann, P. Schaefer, J.P. Rabe, N. Koch*, Humboldt University Berlin, Germany

Nanocolumn arrays based on organic semiconductor materials have significant potential for realizing various devices, such as sensors, field emitters, and nanoelectronic devices, on large-area flexible substrates at room temperature. In our work, crystalline nanocolumnar arrays of two widely studied organic semiconductors, i.e., Fullerene (C_{60}) and pentacene were fabricated by glancing angle deposition (GLAD), and characterized by scanning electron microscopy and X-ray diffraction. For both materials, column diameters of typically 100 nm are found on the transparent conductive oxide ITO at the rotation speed of 3 rpm (rounds per minute), essentially independent of column height (up to 360 nm for pentacene). However, on Si-oxide only C_{60} formed nanocolumns, while pentacene exhibited a morphology resembling that obtained by regular normal incidence deposition. The difference is attributed to the different molecular surface diffusion lengths on the substrate. Furthermore, the morphology of nanocolumns on ITO grown by GLAD is studied for molecular materials forming amorphous and crystalline solids. Amorphous tris(8-hydroxyquinoline)aluminum nanocolumn arrays were obtained at sample rotation speeds varying from 0.3 rpm to 30 rpm. For crystalline pentacene, a nanocolumn array formed at a rotation speed of 3 rpm, while a wide distribution of column heights and shapes was formed at rotation speeds of 0.3 rpm and 30 rpm. The incoming molecular flux and molecular diffusion length on column surface, both determined by rotation speed, were found to govern the resulting morphology of crystalline pentacene nanocolumns on ITO.

11:40am **SE+TF+NC-ThM12 Competitive Growth Mechanisms of Aluminum Nitride Thin Films Deposited by Off-Normal Reactive Magnetron Sputtering**, ***D. Deniz***, University of New Hampshire, *T. Karabacak*, University of Arkansas at Little Rock, *J.M.E. Harper*, University of New Hampshire

We have recently shown that AlN (0002) (c-axis) is tilted abruptly towards the deposition direction as N2 concentration is increased in N2/Ar sputtering gas mixtures. Here we present a Monte Carlo simulation model to describe the phenomenon of sudden c-axis AlN tilt. The model is based on the assumption that AlN islands with their c-axis parallel to substrate normal and AlN islands with tilted c-axis coexist at the initial stages of the growth and they can provide the adatoms with different surface mobilities. It is believed that the adatom mobilities are quenched when N2 concentration reaches a certain amount in the reactive sputtering of AlN. Our model further assumes that adatom mobility differences on different islands result in a growth rate difference of the islands. At the initial stages of the growth, AlN islands with tilted c-axis grow taller due to the lower adatom mobility on these islands. As they grow taller they win the competition and stop the further growth of AlN islands with their c-axis parallel to substrate normal due to shadowing effect. Monte Carlo simulations revealed that the shadowing effect combined with different adatom mobilities promotes the sudden c-axis tilt in AlN thin films.

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