Advanced Surface Engineering
Room: San Miquel - Session SE+TF-WeA

Glancing Angle Deposition (GLAD) II
Moderator: K. Robbie, Queen's University, Canada

2:40pm **SE+TF-WeA3 Nanorods by Extreme Shadowing: New Pictures and New Physics**, ***D. Gall***, Rensselaer Polytechnic Institute **INVITED**

Glancing angle deposition (GLAD) uses an oblique deposition angle to exacerbate atomic shadowing during physical vapor deposition to create underdense layers consisting of nanorods with engineered shapes and three-dimensional composition variations. This growth process is intrinsically chaotic. However, initial substrate pattering combined with temporal changes in the deposition fluxes yield surprisingly regular nanostructure arrays. The questions about the theoretical minimum feature size as well as rod branching, merging, and broadening is discussed by presenting statistical morphology data from various metals deposited over a large temperature range. The rod width follows a power law scaling where the growth exponent depends linearly on the island nucleation length scale, but exhibits a discontinuity at 20% of the melting point, associated with a transition from a 2D to a 3D island growth mode. Different metals show excellent quantitative agreement when scaled to the melting point, yielding a single homologous activation energy of 2.46 for surface diffusion on curved nanorod growth fronts, applicable to all metallic systems at all temperatures. The onset of bulk diffusion near 50% of the melting point during such growth under exacerbated shadowing conditions leads to a direct transition from an underdense (zone I) structure to a dense (zone III) structure. Applications include nanostructured fuel cell electrodes, active components of nano pressure sensors, and lubricant transport channels for high-temperature self-lubrication.

4:00pm **SE+TF-WeA7 Quasi-periodic Pattern Formation on Columnar Thin Films by Ion Beam Erosion at Oblique Incidence**, ***M. Suzuki***, *H. Moriwaka, K. Nakajima, K. Kimura*, Kyoto University, Japan

It is well known that obliquely deposited thin films show various shape related properties due to not only their complex columnar shapes but also their unique surface morphology. For example we have succeeded to prepare in-line aligned noble metal nanorod arrays on a template layer with anisotropic surface roughness originating from the bundled columns created by serial-bideposition technique (SBD)[1]. Our nanorod arrays show the excellent surface enhanced Raman scattering properties. However, it is difficult to avoid the irregularities in size and shapes of the columns in the obliquely deposited thin films. On the other hand, recently, much attention has been paid on the pattern formation by ion beam erosion (IBE) at oblique incidence. When the flat surface is irradiated with the ion beam, quasi-periodic ripple patterns are self-organized. These ripple patterns seem to be more regular than the morphology found in the obliquely deposited thin films. However, the ripples in IBE surface are too gentle to use their functionaries or to use them as a template for the shadowing growth. In this work, we tried to reduce the irregularities of columnar shapes of obliquely deposited thin films by IBE.

Layers of Ge with an anisotropic surface morphology were prepared by SBD technique on a Si substrate. During the SBD, the deposition angle for Ge measured from the surface normal was fixed at an angle of 82°, while the azimuthal angle was changed rapidly by 180° with each deposition of an approximately 10 nm thick layer. After 15 cycles of SBD, Ge layers with an thickness of 300 nm were obtained. The surface of the Ge layer was irradiated with Xe^+ ions of 5 keV up to the fluence of 0.5, 1.5, 3.0×10^{16} ions /cm^2 at an angle of incidence of 45° or 70° The planes of incidence of Ge vapor and Xe^+ ions are perpendicular to each other.

The average aspect ratio of the surface corrugation is 1.4 for the non-irradiated Ge films and significantly increases with increase of fluence. At the fluence of 3.0×10^{16} ions /cm^2, the aspect ratio reaches 7 mainly due to the elongation of the surface corrugation along the incident direction of the ion beam. The width of the surface corrugation is wider for 45° incidence than 70° incidence. Remarkably, distinct periodicity is found in the autocorrelation images of the SEM of the surface. These results are understood in terms of the directive sputtering toward the forward direction of the ion beam and the redeposition of the sputtered atoms, and are characteristic for the ion beam erosion of the porous materials.

1. M. Suzuki, et al., Appl. Phys. Lett., **88**, 203121 (2006).

4:20pm **SE+TF-WeA8 Shadowing Effect of Patterned Seeds in Glancing Angle Deposition**, *D. Soma*, ***D.-X. Ye***, Virginia Commonwealth University

Glancing angle deposition (GLAD) technique has been developed by several groups including us in the past few years to produce three-dimensional nanostructures of a large variety of material. This technique combines oblique angle deposition with substrate manipulations in a physical vapor deposition system. The shadowing effect is the dominant growth mechanism resulting in the formation of various nanostructure arrays by programming the substrate rotation in polar and/or azimuthal direction. On patterned seeds, the shadowing effect strongly depends on the geometric parameters of the seed arrays, i.e. the aspect ration of individual seeds, and the separation and arrangement of the seeds. In this talk, we will study those geometric parameters using a (2+1)-dimensional Monte Carlo simulation. In our simulation, we couple the shadowing effect and ballistic aggregation with rotating oblique incident particles. The uniformity of the nanostructures grown on the seeds will be investigated. The results of this study will provide a guideline for the design of seeds to achieve uniform size nanostructures by using GLAD.

4:40pm **SE+TF-WeA9 Control of Phase Formation in Metal Oxide GLAD Films**, ***R.T. Tucker***, University of Alberta, Canada, *A.E. Schoeller*, *M.D. Fleischauer*, NRC - National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Glancing angle deposition (GLAD) has found application in a wide range of fields requiring porous, high surface area thin films, including sensors, optics, and energy devices. [1] This diversity is due in large part to the wide range of compatible materials, including metals, semiconductors, and organic compounds. Metal oxides are of particular interest for energy storage and conversion applications since they can be tuned for a combination of transparency, electrical conductivity, and chemical and thermal stability. Achieving the desired stoichiometric phase is essential for controlling desirable metal oxide properties. Here we discuss the challenges associated with achieving phase control in porous GLAD films.

Metal oxide GLAD films typically deposit in an amorphous state, so post-deposition processing is one route used to access a particular crystallinity and stoichiometry. Thermal annealing conditions depend on the desired phase: anatase TiO_2 readily forms at a few hundred degrees Celsius in air; Ti_4O_7 generally requires longer anneals at high temperatures (1000 ºC) in a reducing atmosphere (eg. H_2 in carrier gas). [2] Annealing temperature, duration, and environment (e.g. oxidizing vs. reducing atmosphere) can all have an impact on film morphology, since coalescence or softening of structures is greatly enhanced at temperatures near the melting point of the metal oxide. Both the porosity of the film and the strength of the reducing atmosphere affect the extent of oxygen removal and morphology changes at relatively high temperatures, while still allowing access to a wide range of compositions (e.g Ti_nO_{2n-1}, n = 2 - 9), phases (e.g. monoclinic, tetragonal, or orthogonal Nb_2O_5) and the associated optical, electronic, and thermal properties.

We will present methods to retain the porosity and structure of GLAD thin films while achieving desired stoichiometry and phase via post-deposition annealing, with a specific focus on phase and crystallinity characterization using x-ray diffraction. We will attempt to correlate results from the Ti-O and Nb-O systems with results from other systems of interest (e.g. W-WO_3) [3] as part of a better understanding of phase formation in porous thin films.

[1] M.M. Hawkeye and M.J. Brett, J. Vac. Sci. & Tech. A, **25**, 1317 (2007).

[2] J.R. Smith *et al*, J. Appl. Electrochem., **28**, 1021 (1998).

[3] D. Deniz *et al.*, Thin Solid Films, **518**, 4095 (2010).

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5:00pm **SE+TF-WeA10 A Fan-Shadowing Model in Oblique Angle Deposition**, ***B. Tanto***, Rensselaer Polytechnic Institute, *G.A. Ten Eyck*, Sandia National Laboratories, *T.-M. Lu*, Rensselaer Polytechnic Institute

Recently oblique angle deposition has been used in a wide range of important, unique applications. The column angle of the obliquely deposited columnar structures is an important parameter that determines their mechanical, optical, and chemical properties. Unfortunately this angle can be greatly affected by materials and processing conditions which are too complex to model and predict. Existing models such as the tangent rule and cosine rule are independent of materials and processing conditions and therefore in general have a limited ability to predict the column angle. We present a semi empirical model that includes the effects of materials and processing conditions. We show that our model is able to accurately predict column angle analytically for a wide range of obliquely deposited amorphous Ge for two different sets of processing conditions. We also show how this model can be used to predict other useful quantities, such as porosity and column width.

The model uses the fact that the deposition on a line (or wire) results in a fan structure due to a self-shadowing effect with a fan angle that depends on materials and processing conditions. We first show how columnar structures can be generated by analytically applying global shadowing between the fan structures growing on adjacent lines. The columnar structures obtained possess geometrical properties (such as column width and column merging) that are consistent with columnar structures observed in experiment and simulation. We show how the exact shape and time evolution of the columnar structure can be calculated based on the knowledge of the fan shape. Once the exact shape of the columnar structure is known, various useful quantities can also be obtained: column angle, porosity, and column width. We experimentally verified our model by depositing amorphous Ge on line seeded substrate and on a flat substrate. The model agrees with experiments done on both substrates.

Finally, we describe relatively simple experimental setups that can be used for fast and convenient measurement of the fan geometry at various processing conditions, such as flux rates and temperatures. These fan geometry data obtained on normal incident flux can then be used to predict the columnar structure geometries for the whole range of incident flux angles and for all the various processing conditions.

5:20pm **SE+TF-WeA11 Investigation of the Nanorod-Structuring Threshold in Glancing Angle Deposition (GLAD)**, ***D. Deniz***, *R.J. Lad*, University of Maine

Thin films of tin (Sn), aluminum (Al), gold (Au), ruthenium (Ru), tungsten (W), ruthenium dioxide (RuO2), tin dioxide (SnO2) and tungsten trioxide (WO3) were grown by glancing angle deposition (GLAD) to determine whether a nanostructuring threshold condition can be quantified as a function of both substrate temperature and melting point of the material. Films were grown using both DC and pulsed DC magnetron sputtering with continuous substrate rotation over the temperature range from 18 – 800oC. Film morphologies, structures, and compositions were characterized by high resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Films were also grown in non-GLAD configurations for comparison. For the elemental metals, it is found that nanorod-structuring occurs for materials with melting points higher than that of Al (660°C) when films are grown at room temperature with a relatively small rotation rate of ~5 rpm. For the oxide materials, our results indicate that a critical substrate temperature (TS) to melting point (TM) ratio exists, above which GLAD nanorod-structuring becomes ineffective because the adatom mobilities become large enough for non-kinetically limited film nucleation and growth processes to occur, similar to those operative in a non-GLAD growth configuration.

Authors Index

Bold page numbers indicate the presenter