

## Advanced Surface Engineering Division Room A215 - Session SE+AS+TF-WeA

### Nanostructured Thin Films and Coatings

**Moderators:** Mehran Golizadeh, Montanuniversität Leoben, Austria, Suneel Kodambaka, University of California Los Angeles

#### 2:20pm SE+AS+TF-WeA-1 Structural and Optical Properties of Pulsed-Laser Deposited $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Thin Films, *Mallesham Bandi, V Zade, R Chintalapalle*, University of Texas at El Paso

In the course of demand for wide band gap semiconductors in modern electronic devices,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is extensively studied for the last two decades due to its wide range of applications such as field effect devices, switching memories, high temperature gas sensors, photocatalysts, deep-UV photodetector and transparent conducting electrode etc. However, fabricating device quality thin films and understanding the optical properties is an active timely research to exploit  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> into wide range of optoelectronic device applications. We report on the effect of deposition parameters on the structure and optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> fabricated by Pulsed Laser Ablation onto a wide range of substrate materials. Polycrystalline thin films were fabricated on silicon and sapphire substrates with varying substrate temperatures and oxygen partial pressures, which resulted in various morphologies. To study the effect of morphology on optical properties polycrystalline thin films were analyzed using spectroscopic ellipsometry. Moreover, epitaxial thin films of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were fabricated on C-plane sapphire and MgO (100) oriented substrates. A more detailed account of structure, growth behavior and optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> will be presented and discussed.

#### 2:40pm SE+AS+TF-WeA-2 Structural, Electrical, and Optical Properties of Mo-Ga Alloy Thin Films, *Nivedita Lalitha Raveendran, R Chintalapalle*, University of Texas at El Paso

Materials with thermal stability and can establish a stable contact for component layers are highly desirable for the design and development of advanced high power electronic device technologies. In this context, the present study investigates the effect of growth temperature on the structural, morphological, optical and electrical properties of the thin films of rarely investigated Mo-Ga alloy system. The objective is to understand the growth behavior, structure, electronic properties and thermal stability of Mo-Ga thin films for application in Ga<sub>2</sub>O<sub>3</sub> based devices. In the present work, Mo-Ga thin films of ~350 nm thickness were fabricated on Si (100) substrates by sputter-deposition. The deposition temperature was varied in the range of 25-700°C. X-ray diffraction analysis of the deposited samples indicate the realization of nanocrystalline films at 500°C, and beyond 500°C deterioration in crystallinity was noticed. A shift in Bragg's position towards higher angle was evident with increase in substrate temperature, which could be attributed to substrate temperature induced residual stresses. Moreover, formation of non-stoichiometric thin films was observed at higher deposition temperature (>500°C). The optical properties of the deposited thin films were obtained by spectroscopic ellipsometry and a detailed analysis of the electrical properties of the thin films were also carried out. The results will be presented and discussed to establish the structure-composition-property correlation.

#### 3:00pm SE+AS+TF-WeA-3 Metallic Glass: From Coating to First-Ever Nanotube Arrays, *Jinn P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China

Thin film metallic glass (TFMG) is a new class of multi-component metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties because of their amorphous structure. Thin films prepared by physical vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In the first part of my talk, I will present some important TFMG properties and applications we have discovered in recent years. Then, the metallic glass nanotubes (MGNTs) on Si fabricated by a simple lithography and sputter deposition process for very large-scale integration is introduced. This first-ever metallic nanotube array is awarded by *American Chemical Society* (ACS) at nano tech Japan 2018 in Tokyo. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes

hydrophobic, repelling water. By heating/cooling the array, the surface hydrophobicity is changed. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device and, with an applied electric voltage to the heating device underneath, so that the arrays are functioned as biomimetic artificial suckers for thermally adhesion response [3].

### References

- [1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.
- [2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, *Biosensors and Bioelectronics*, 102 (2018), 129-135.
- [3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, *Nanoscale*, 10 (2018) 1366-1375.

#### 3:20pm SE+AS+TF-WeA-4 Tin Oxide Nanoaggregate Fragmentation and Restructuring during Supersonic Impaction based Thin Film Deposition Processes, *Souvik Ghosh, X Chen, C Li, B Olson, C Hogan*, University of Minnesota, Minneapolis

Aerosol deposition (AD) is a versatile technique for printing thin films. During AD, gas-suspended particles are impacted inertially on a target surface at high velocities. Subsonic impaction processes often lead to highly porous, weakly bound depositions. High-speed supersonic deposition, however, can lead to denser, mechanically robust coatings of metals & metal oxides. Supersonic deposition is hence a potential low temperature route to the additive manufacturing of thin films (<1  $\mu$ m to >10  $\mu$ m) of a variety of materials.

However, the mechanism of film densification & consolidation remains poorly understood, particularly because AD can function with spherical or fractal-like agglomerated particles, from both dry powder feeds & aerosol synthesis processes. In an effort to better understand AD, we examined the mechanism of thin film formation via supersonic impaction of SnO<sub>2</sub> nanoaggregates on alumina, where we observed the formation of mechanically robust SnO<sub>2</sub> thin films. SnO<sub>2</sub> nanoaggregates were synthesized via flame spray pyrolysis (FSP) of Tin 2-Ethylhexanoate. These nanoaggregates characterized via differential mobility analysis shows a broad size distribution in the 40 nm -300 nm mobility diameter range. X-ray diffraction analysis of as-collected powders confirmed the formation of nano-crystalline SnO<sub>2</sub>. To understand morphological changes to aggregates during high speed deposition, a differential mobility analyzer was used prior to deposition to select aggregates within a prescribed mobility diameter. The aggregates were then deposited electrostatically at low velocity (at atmospheric pressure) & supersonic speeds after passing through a 200  $\mu$ m throat width, slit-type, conically contoured converging-diverging nozzle. With low speed deposition, we observed highly branched, chain like aggregates; while after supersonic deposition, we observed denser aggregates with significantly lower number of particles. Images hence suggest that the aggregates fragment & restructure during supersonic impaction.

Fragmentation & restructuring was quantified by image analysis of TEM images to determine their projected radii of gyration, perimeter, end-to-end distance, & projected area. These four parameters were then compared to those from in-silico projections of quasifractal aggregates, enabling extrapolation of the 3D architectures of deposited particles. Plots of the number of primary nanoparticles in aggregates as functions of their inferred radii of gyration confirmed that supersonic deposition leads to both (1) fewer primary particles per aggregate (fragmentation) & (2) for a given number of primary particles, smaller radii of gyration (restructuring).

#### 4:20pm SE+AS+TF-WeA-7 From Gas-ion to Metal-ion-controlled Irradiation: A Paradigm Shift in the Thin Film Growth by Magnetron Sputtering, *Grzegorz Greczynski*, Linköping University, Sweden; *I Petrov, J Greene*, University of Illinois at Urbana-Champaign; *L Hultman*, Linköping University, Sweden

ION IRRADIATION IS A KEY TOOL FOR CONTROLLING THE NANOSTRUCTURE, PHASE CONTENT, AND PHYSICAL PROPERTIES OF REFRACTORY CERAMIC THIN FILMS GROWN AT

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low temperatures ( $T_s$ ) by magnetron sputtering. However, in contrast to gas-ion bombardment, the effects of metal-ion irradiation on properties of these films have not been extensively studied due to (i) low metal-ion concentrations during standard dc magnetron sputtering (DCMS), and (ii) difficulties in separating metal-ion from gas-ion fluxes. These issues were recently resolved with our development of high-power pulsed magnetron sputtering (HiPIMS), in which pulsed substrate bias is applied in synchronous to the metal-ion-rich portion of each pulse.<sup>1</sup> Careful choice of sputtering conditions allows exploitation of gas rarefaction effects such that the charge state, energy, and momentum of metal ions incident at the growing film surface can be tuned.

The results of time-resolved mass spectrometry analyses performed at the substrate position during HiPIMS and HiPIMS/DCMS co-sputtering of transition-metal (TM) targets in Ar and Ar/N atmospheres are reviewed. Knowledge of the temporal evolution of metal- and gas-ion fluxes is essential for precise control of the incident metal-ion energy and minimizing the role of gas-ion irradiation. Also, covered are the growth of TM nitride and boride alloys by metal-ion synchronized HiPIMS. In contrast to gas-ions, a fraction of which are trapped at interstitial sites, metal-ions are primarily incorporated at lattice sites resulting in much lower compressive stresses. In addition, the closer mass match with the film-forming species results in more efficient momentum transfer and provides the recoil density and energy necessary to eliminate film porosity at low  $T_s$ . Several novel film-growth pathways are described: (i) nanostructured N-doped  $bcc\text{-CrN}_{0.05}$  films combining properties of both metals and ceramics, (ii) fully-dense, hard, and stress-free  $\text{Ti}_{0.39}\text{Al}_{0.61}\text{N}$ , (iii) single-phase cubic  $\text{Ti}_{1-x}\text{Si}_x\text{N}$  with the highest reported SiN concentrations, (iv) unprecedented AlN supersaturation in single-phase NaCl-structure  $\text{V}_{1-x}\text{Al}_x\text{N}$ , (v) a dramatic increase in the hardness, due to selective heavy-metal-ion bombardment during growth, of dense  $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$  and  $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$  films deposited with no external heating, and (vi) simultaneous increase in both hardness and toughness of  $\text{Zr}_{1-x}\text{Ta}_x\text{B}_y$  layers deposited with synchronized Ta<sup>+</sup> irradiation.

Finally,  $\text{Ti}_{1-x}\text{Ta}_x\text{N}$  alloys grown with no external heating are shown to produce high-quality Cu diffusion barriers and provide excellent corrosion protection for stainless-steel substrates.

<sup>1</sup> G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *J. Vac. Sci. Technol. A* 30 (2012) 061504

**5:00pm SE+AS+TF-WeA-9 Atomic Layer Deposition of Silver Thin Film on Polydimethylsiloxane (PDMS), Sarah Hashemi Astaneh, C Sukotjo, C Takoudis, University of Illinois at Chicago**

Two types of samples were prepared in this work:

- 1- Silver coated PDMS
- 2- Silver coated PDMS with interlayer of  $\text{TiO}_2$

For type 1 samples: Silver deposition was done in the costume-built ALD system. ( $\text{Ag}(\text{fod})$  ( $\text{Pet}_3$ )) was used as a silver precursor and dimethyl amineborane ( $\text{BH}_3$  ( $\text{NHMe}_2$ )) was used as a reducing agent. Silver bubbler and dimethyl amineborane bubbler temperatures were kept at 96 °C and 50 °C, respectively. The reactor pressure and temperature was kept at 500 mtorr and 115 °C during deposition, respectively.

For type 2 samples: prior to silver coating, deposition of  $\text{TiO}_2$  on PDMS was done in a commercial ALD system (Kurt J. Lesker 150 LE). Tetrakis (dimethylamido) titanium (IV) (TDMAT™) was used as the metal oxide precursor and maintained at 70 °C in the bubbler during all depositions. Ultra high purity  $\text{N}_2$  was used as a carrier gas as well as purging gas.  $\text{O}_3$  was used as an oxidizer for this ALD reaction and it was prepared using a UV-ozone generator placed immediately upstream of the deposition chamber to reduce ozone decomposition in delivery line as described in our previous studies. The reactor pressure and temperature was kept at ~1000 mtorr and 120 °C during  $\text{TiO}_2$  deposition. This process leads to ~9 nm of  $\text{TiO}_2$  interlayer on PDMS.

Right after this step,  $\text{TiO}_2$  coated PDMS samples were transferred to the custom-built ALD system and silver deposition was carried on in the costume-built ALD system similar to type 1 samples.

In each of the above runs, simultaneously; same thin film was deposited on p-type Si (100) silicon wafer (University wafer Inc, USA) and used as a reference substrate to determine deposited film thickness.

The growth and composition of the silver on top of PDMS samples were analyzed with X-ray photoelectron spectroscopy (XPS) using Kratos AXIS-165 equipped with monochromatic Al K $\alpha$  X-ray source operating at 15kV

and 10 mA. As can be seen in figure 1, Ag 3p, Ag 3d peaks appeared clearly on Si,  $\text{TiO}_2$  coated Si and  $\text{TiO}_2$  coated PDMS substrates.

**5:20pm SE+AS+TF-WeA-10 Fabrication of 2D Photonic Crystals using Block Copolymer Lithography on Flexible Substrates and Fibers for Wearable Technology, Wade Ingram, R Spontak, J Jur, North Carolina State University**

Block copolymer lithography is a method of transferring a self-assembled pattern from the block copolymer to the substrate using vapor phase infiltration of metal or metal-organic precursors into select polymer domains. The process is able achieve sub-10 nm resolution and can be used for electronic or photonic device fabrication. In our research, we seek to use block copolymer lithography to template polymer films and textile fibers for applications in wearable electronics and advanced light absorption in garments.

Deriving inspiration from nature, 2D photonic crystals are fabricated using polystyrene-block-polymethylmethacrylate (PS-b-PMMA) copolymers. Through thermal and solvent vapor annealing, the block copolymer self-assembles into uniform domains with long-range order across the substrate. Subsequent exposure to common gas precursors like trimethylaluminum will result in a hybrid material forming from the exposed carbonyl functional groups in the PMMA domain. Etching steps in  $\text{O}_2$  plasma or selective solvents results in a patterned nanostructure of the metal or metal-organic material deposited on the substrate. These structures are imaged using scanning electron microscopy before and after etching, as well as with atomic force microscopy in tapping mode to understand how robust they are. Further characterization using infrared and ultraviolet-visible spectroscopy is performed to generate plots showing how these unique nanostructures interact with light from UV through IR wavelengths. This work aims to understand how block copolymer lithography on polymeric and flexible substrates can eventually be applied to polymer fibers for functional textiles.

**5:40pm SE+AS+TF-WeA-11 Use of an Einzel Lens to Enhance Electrohydrodynamic Printing Technology, Matthew Strohmayer<sup>1</sup>, A Dhall, P Ramesh, N Tokranova, C Ventrice, Jr., SUNY Polytechnic Institute**

Additive manufacturing (AM) shows great promise for both research and industrial applications. The main advantages of AM include limited waste and the ability to build complicated structures. The most common techniques for AM are fused deposition manufacturing, digital light printing, and ink jetting. All of these techniques suffer from resolution and material limitations. Recently, a cost-effective, versatile method of high-resolution printing called electrohydrodynamic (EHD) printing has been introduced. This method allows for spatial resolution in the hundreds of nanometers. This process works similarly to a typical ink jetting system, except instead of the ink/polymer being pushed out of a tip, it is pulled out by an applied electric field. This allows for the resultant droplet to be smaller than the needle diameter. Electrostatic repulsion of the charged droplets limits the ultimate resolution of this technique. To overcome this resolution limitation, we have incorporated an Einzel lens into the system to focus the droplets. This helps the droplets overcome the repulsive Coulomb interaction, leading to better spatial resolution. To validate this approach, simulations were performed to test for different parameters, including droplet size changes and lens optimization. This was then used to build a real system.

<sup>1</sup> ASSD Student Award Finalist

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