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

3:00pm **SE+AS+TF-WeA3 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-WeA4 Tin Oxide Nanoaggregate Fragmentation and Restructuring during Supersonic Impaction based Thin Film Deposition Processes**, ***Souvik Ghosh,*** *X. Chen, C. Li, B. Olson, C.J. 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 μm to >10 μm) 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_2 nanoaggregates on alumina, where we observed the formation of mechanically robust SnO_2 thin films. SnO_2 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_2. 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 μm 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-WeA7 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.E. Greene,* University of Illinois at Urbana-Champaign*; L. Hultman,* Linköping University, Sweden **INVITED**

Ion irradiation is a key tool for controlling the nanostructure, phase content, and physical properties of refractory ceramic thin films grown at 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.[1] 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*-$CrN_{0.05}$ films combining properties of both metals and ceramics, (ii) fully-dense, hard, and stress-free $Ti_{0.39}Al_{0.61}N$, (iii) single-phase cubic $Ti_{1-x}Si_xN$ with the highest reported SiN concentrations, (iv) unprecedented AlN supersaturation in single-phase NaCl-structure $V_{1-x}Al_xN$, (v) a dramatic increase in the hardness, due to selective heavy-metal-ion bombardment during growth, of dense $Ti_{0.92}Ta_{0.08}N$ and $Ti_{0.41}Al_{0.51}Ta_{0.08}N$ films deposited with no external heating, and (vi) simultaneous increase in both hardness and toughness of $Zr_{1-x}Ta_xB_y$ layers deposited with synchronized Ta^+ irradiation.

Finally, $Ti_{1-x}Ta_xN$ alloys grown with no external heating are shown to produce high-quality Cu diffusion barriers and provide excellent corrosion protection for stainless-steel substrates.

[1] 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-WeA9 Atomic Layer Deposition of Silver Thin Film on Polydimethylsiloxane (PDMS)**, ***Sarah Hashemi Astaneh,*** *C. Sukotjo, C.G. 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 TiO_2

For type 1 samples: Silver deposition was done in the costume-built ALD system. (Ag(fod) (Pet_3)) was used as a silver precursor and dimethyl amineborane ((BH_3 ($NHMe_2$)) 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 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 N_2 was used as a carrier gas as well as purging gas. 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 TiO_2 deposition. This process leads to ~9 nm of TiO_2 interlayer on PDMS.

Right after this step, 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 Kα 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, TiO_2 coated Si and TiO_2 coated PDMS substrates.

5:20pm **SE+AS+TF-WeA10 Use of an Einzel Lens to Enhance Electrohydrodynamic Printing Technology**, ***Matthew Strohmayer***[1], *A. Dhall, P. Ramesh, N. Tokranova, C.A. 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.

[1] **ASSD Student Award Finalist**

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