Tuesday Morning, November 8, 2016

Advanced Surface Engineering
Room 101C - Session SE+NS+TF+TR-TuM

Nanostructured Thin Films and Coatings

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Robert Franz, Montanuniversität Leoben, Austria

8:00am **SE+NS+TF+TR-TuM1 Design and Predictive Synthesis of Thin Films and Coatings***, P.A. Salvador, **Gregory Rohrer**,* Carnegie Mellon University **INVITED**

A fundamental challenges in materials synthesis is to obtain a specific targeted composition in a functional crystal structure. For example, the synthesis of hexagonal BN is relatively easy, but synthesizing thick films of cubic BN is more difficult. In other words, we cannot currently predict exact synthesis conditions of many targeted polymorphs, and so their formation is often left to lengthy "design-of-experiments" (DOE) methodologies or, more commonly, basic trial-and-error practices. It is essential to improve the output of computational and physical experimental practices to move closer to predictive synthesis and design of coatings.

This talk will describe some recent results of a methodology called combinatorial substrate epitaxy (CSE), which we have used to understand the preferred epitaxial orientations (PEOs) of a wide range of heteroepitaxial structures and to fabricate various novel metastable materials. In this approach, the target compound is deposited on polished polycrystalline substrates, rather than commercial single crystals or buffer layers. The primary hypotheses underpinning CSE is that the each grain surface in the polycrystalline substrate can be treated as the equivalent of a single-crystal surface in a traditional DOE experiment, therefore providing every combination of substrate orientation in a single experiment. The local structure is probed in a scanning electron microscope using electron backscatter diffraction and automated orientation assignments. The method not only allows for hundreds of experiments to be carried out in a single growth run, it has the unique advantage of not being restricted to the use of commercially available single crystals.

This talk will focus on three important observations. First, when a film is grown on a polycrystal, the growth occurs by grain-over-grain epitaxy. In other words, films can grow on microcrystalline substrates in the same way they grow on millimeter scale substrates, or every grain is in an independent observation of growth. Second, there are PEOs, regardless of the substrate surface plane, and these can be easily predicted. For many of the cases we have observed, the PEO is the one that aligns the closest packed planes and directions in the eutactic (nearly close packed) arrangement of oxide ions in different structures. Third, we have already fabricated new and novel metastable coatings using this methodology, where novel substrates provide the epitaxial template to control phase formation. Observations relative to functional ceramics, including examples from the BO_2, B_2O_3, ABO_3, A_2BO_4, and $A_2B_2O_7$ families, will be described.

8:40am **SE+NS+TF+TR-TuM3 Nanoscale Atomic Arrangement in Multicomponent Thin Films Synthesized Far-from-Equilibrium***, V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, **Kostas Sarakinos**,* Linköping University, Sweden

Synthesis of multicomponent thin films using vapor fluxes with a modulated deposition pattern is a potential route for accessing a wide gamut of atomic arrangements and morphologies for property tuning. In the current study, we present a research concept that allows for understanding the combined effect of flux modulation, kinetics and thermodynamics on the growth of multinary thin films. This concept entails the combined use of thin film synthesis by means of multiatomic vapor fluxes modulated with sub-monolayer resolution [1], deterministic growth simulations and nanoscale microstructure probes. Using this research concept we study structure formation within the archetype immiscible Ag-Cu binary system showing that atomic arrangement and morphology at different length scales is governed by diffusion of near-surface Ag atoms to encapsulate 3D Cu islands growing on 2D Ag layers [2]. Moreover, we explore the relevance of the mechanism outlined above for morphology evolution and structure formation within the miscible Ag-Au binary system. The knowledge generated and the methodology presented herein provides the scientific foundation for tailoring atomic arrangement and physical properties in a wide range of miscible and immiscible multinary systems.

[1] "*A METHOD OF CONTROLLING IN-PLANE COMPOSITIONAL MODULATION*", Patent Pending Application, PCT/EP2014/052831.

[2] V. Elofsson, G.A. Almyras, B. Lü, R.D. Boyd, and K. Sarakinos, "*Atomic arrangement in immiscible Ag-Cu alloys synthesized far-from-equilibrium*", Acta Mater. 110, 114 (2016).

9:00am **SE+NS+TF+TR-TuM4 Is *Intrinsic* Nanocrystalline Stability Practically Achievable? Insights from Investigations with Pt-Au Alloys***, **Nicolas Argibay**, T.A. Furnish, D.P. Adams, P. Lu, M. Chandross, M.A. Rodriguez, B.L. Boyce, B.L. Clark, M.T. Dugger,* Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been proposed recently, supported by some notable demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of stress on this stability. In this presentation we present results of an investigation on the stress and temperature dependent nanocrystalline stability of a noble-metal alloy (Pt-Au) in the form of sputter co-deposited thin films. In situ XRD and TEM annealing revealed an extraordinary degree of thermal stability, confirming literature predictions. Tribological experiments and molecular dynamics simulations were used to further explore the impact of stress as a destabilizing factor.

9:20am **SE+NS+TF+TR-TuM5 Improved Mechanical Properties In Tungsten-Molybdenum Nanostructured Thin Films***, **Gustavo Martinez**, C.V. Ramana,* University of Texas at El Paso

Preventing materials failure and improving the performance of materials in nuclear reactors demand novel materials to serve under extreme environment conditions. For nuclear applications, tungsten (W) has been alloyed in the past with La and Re to improve its performance and properties including low fracture and high ductile to brittle transition. In this work, molybdenum (Mo) solute atoms were added to W matrix with the intention of creating interstitial point defects in the crystals that impede dislocation motion, increasing the hardness and young modulus of the material. Nanostructured W-Mo thin films with variable Mo content were deposited by the sputter-deposition. W-Mo films were stabilized in bcc structure of W. Studies showed that as grain size formation increases the residual stress distribution will reach the maximum and stabilize after a deposition temperature of 350 °C. The residual stress still continues to follow a parabolic pattern, indicating that the stresses mainly depend on grain organization rather than atomic packing. From Nano-scratch testing, it is found that depth penetration decreases with increasing sputtering temperature. The effect of Mo on the overall mechanical properties improvement in W-Mo nanostructured thin films will be presented and discussed.

Keywords: Tungsten-Molybdenum Thin Films, Mechanical Properties, Nano-Indentation

9:40am **SE+NS+TF+TR-TuM6 Hierarchical Monolith Scaffolds for Silicon Lithium Ion Battery Electrodes***, **Kevin Laughlin**,* Brigham Young University

Research has shown stable high gravimetric capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). High stability operation however requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode. Here we present work on a hierarchical approach to structuring carbon nanotube based carbon monoliths that provide for electrode stress management on multiple scales.

11:00am **SE+NS+TF+TR-TuM10 Technological Developments in Coatings for Components and Cutting Tools***, **Roel Tietema**,* IHI Hauzer Techno Coating B.V., Netherlands*; D. Doerwald,* Hauzer, Netherlands*; R. Jacobs, G. Negrea, I. Kolev, J. Zhu, J. Landsbergen,* Hauzer **INVITED**

Nanostructured and amorphous coatings play an important role in today's industrial applications. This is the case both in applications for cutting tools, as well as in applications for components.

In cutting tools nanostructured coatings with high hardness, including hot hardness, and ductility have been extremely helpful to increase the productivity of the machining process. On one hand superlattice multilayers have shown here great benefits and on the other hand nanocrystallites in the material have been created to give the coating materials an inherent high hardness and ductility.

In automotive coatings these material properties were leading to technological breakthroughs as well. First coatings on the market were nanostructured WC-C:H sputtered coatings, developed by Prof. Dimiggen of Fraunhofer IST. These developments were soon followed by hybrid a-C:H coatings, combining the WC-C:H developments with a multilayered structure to achieve a gradual adaptation of the Young's modulus of the relatively soft steel as base material to the very hard a-C:H-DLC top layer. In this way it has been possible to produce coatings with a very high ductility, despite the high hardness. Hardness values as applied today on components are ranging from 2000-2500 HV for a-C:H coatings up to 4000-7000 HV for ta-C coatings.

The importance of petreatment and post treatment steps for cutting tools and components, being as important as the actual coating step, will be addressed in this talk.

The main focus in this talk will be on the equipment aspects. Several technologies for cutting tools and for components will be presented. The equipment design and even the selection of most suitable process technology is however also strongly determined by the productivity. Besides technological properties of the coating there is a focus on the cost reduction of the coating per coated part. Cost reduction is main driver in many fields, especially in the field of components. Reduction of the cost of ownership leads to a tendency to use fast processes in large systems, respectively application of in-line systems.

11:40am **SE+NS+TF+TR-TuM12 Influence of Transition Metal Dopants on Target Poisoning and Oxidation Mechanisms of Reactively Sputtered γ-Al_2O_3 Thin Films***, **Helmut Riedl,** B. Kohlhauser,* TU Wien, Institute of Materials Science and Technology, Austria*; V. Paneta,* Uppsala University, Sweden*; C.M. Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; P.H. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The outstanding oxidation resistance, thermo-mechanical stability and chemical inertness of Al_2O_3 attracts particular attention in various industrial applications. Especially, in the field of protective barrier coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. Apart from the fact that the deposition of the thermodynamically stable α-Al_2O_3 is strongly limited by the depositing temperature, the formation of electrically isolating Al_2O_3 at the target surface leads to massive arcing processes and destabilizes the deposition process. These problems could be overcome by varying the powering method to pulsed DC and especially RF sputtering, but at the cost of decreased deposition rates and plasma densities.

Therefore, we study in detail the influence of small amounts of transition metals such as M = Cr, Nb, Mo, and W on the process stability and coating properties of reactive DC sputter deposited $(Al_{1-x}M_x)_2O_3$ thin films. To keep the influence of the alloying elements on the outstanding properties of alumina as low as possible only targets with alloying contents of x = 2 and 5 at.% are investigated. All micro-alloyed targets allow for significantly improved process stability and massively reduced arcing processes at the target as compared to the non-alloyed Al target. The morphology of all coatings deposited is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the Cr, Mo, and W containing coatings are slightly enhanced by solid solution hardening in comparison to pure Al_2O_3 obtaining e.g. hardness values of about 25 GPa. In contrast, alloying contents of about 1 at.% Nb are already degrading the mechanical properties of alumina thin films. The significantly enhanced process stability when using Cr, Mo, and W alloyed Al targets, leads to coatings with improved thin film quality. Therefore, the oxidation resistance of these films even outperform the Al_2O_3 DC sputtered film.

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