

# Wednesday Afternoon, November 1, 2017

## Advanced Surface Engineering Division

Room: 11 - Session SE+2D+NS+SS+TF-WeA

### Nanostructured Thin Films and Coatings

**Moderators:** Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

2:20pm **SE+2D+NS+SS+TF-WeA1 Plasma Process Development and Optimized Synthesis of TiB<sub>2</sub> Coatings from DC Magnetron Sputtering, High Power Impulse Magnetron Sputtering, and DC Vacuum Arc.** *Johanna Rosen*, Linköping University, Sweden **INVITED**

The use of high power impulse magnetron sputtering (HiPIMS) or cathodic arc for the synthesis of TiB<sub>2</sub> coatings will drastically increase the amount of ionized species impinging on the substrate compared to regular DC magnetron sputtering. In particular for HiPIMS, it is possible to control the flux of ionized species by varying the pulse frequency, which allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant.

We show that the additional energy supplied during film growth in the HiPIMS process, compared to regular DC sputtering, results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to  $\geq 42$  GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Furthermore, we show that the energy supplied to the film surface is influenced by when the bias is applied relative to the HiPIMS pulse. Based on charge-state-resolved plasma analysis it is found that by applying the bias in synchronous with the HiPIMS pulse, a higher fraction of B<sup>+</sup> ions will constitute the total flux of bombarding ions. This results in a lower residual stress compared to coatings deposited under bombardment of mainly Ar<sup>+</sup> ions.

Finally, we also present results from TiB<sub>2</sub> synthesis based on DC vacuum arc, and a route for attaining a stable, reproducible, and close to fully ionized plasma flux of Ti and B by removal of the external magnetic field. Plasma analysis shows increased ion charge states as well as ion energies compared to HiPIMS. Furthermore, while regular DC magnetron sputtering and HiPIMS typically give a B to Ti ratio above 2, the arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

3:00pm **SE+2D+NS+SS+TF-WeA3 Multi-technique Approach for Studying Co-sputtered M-Si-O Thin Films.** *Lirong Sun*, General Dynamics Information Technology, *N.R. Murphy*, Air Force Research Laboratory, *J.T. Grant*, Azimuth Corporation

In this work, the M-Si-O thin films (M: Al and Ta) were prepared through reactive pulsed DC magnetron co-sputtering of M and Si targets in an O<sub>2</sub>/Ar mixture. The M fraction [M/(M+Si)] of different chemical compositions (M<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>), as determined through X-ray photoelectron spectroscopy (XPS), was varied between 0 and 100% by changing sputtering power applied to the M targets. The film thickness, refractive index (n) and extinction coefficient (k) were determined by *in situ* spectroscopic ellipsometry (iSE). Concurrent with ellipsometry measurements, the *in situ* stress evolution of the films, as correlated to the M fraction, was investigated using a multi-beam optical sensor (MOS) system. The MOS system was used to measure both intrinsic stress resulting from the deposition process as well as thermal stress evolved during heating/cooling process. Data obtained through stress monitoring during heating and cooling was used to calculate the coefficient of thermal expansion (CTE). The density and crystallinity of the films were measured by X-ray diffraction and X-ray reflectivity, respectively. Transmission and reflectance of the films were carried out by UV-Vis-NIR spectroscopy. Finally, this study derives a process-property-microstructure relationship correlating the optical constants, CTE, intrinsic stress, and M fraction.

3:20pm **SE+2D+NS+SS+TF-WeA4 Ultra-high Vacuum Magnetron Sputter-deposition of Zr/Al<sub>2</sub>O<sub>3</sub>(0001): Effect of Substrate Temperature on Zr Thin Film Microstructure and Thermal Stability of Zr-Al<sub>2</sub>O<sub>3</sub> Interfaces.** *K. Tanaka*, *J. Fankhauser*, University of California at Los Angeles, *M. Sato*, Nagoya University, Japan, *D. Yu*, *A. Aleman*, *A. Ebnonnasir*, *C. Li*, University of California at Los Angeles, *M. Kobashi*, Nagoya University, Japan, *M.S. Goorsky*, *Suneel Kodambaka*, University of California at Los Angeles

Zr thin films are grown on Al<sub>2</sub>O<sub>3</sub>(0001) substrates in an ultra-high vacuum deposition system via dc magnetron sputtering of Zr target in Ar atmosphere

at temperatures T<sub>s</sub> between 600 °C and 900 °C. The as-deposited layer surface structure and composition are determined *in situ* using low-energy electron diffraction and Auger electron spectroscopy, respectively. Bulk crystallinity and microstructures of the samples are determined using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 °C  $\leq$  T<sub>s</sub> < 750 °C, we obtain fully dense, hexagonal close-packed structured Zr(0001) thin films with smooth surfaces. At T<sub>s</sub>  $\geq$  750 °C, the Zr layers are porous, exhibit {0001} texture, and with rough surfaces. Energy dispersive x-ray spectra obtained from the Zr/Al<sub>2</sub>O<sub>3</sub> interfaces reveal the formation of Zr-Al intermetallic compounds, whose thickness increases exponentially with increasing T<sub>s</sub>. We attribute the formation of this interfacial layers to fast diffusion of Zr and reaction with the Al<sub>2</sub>O<sub>3</sub> substrate.}

4:20pm **SE+2D+NS+SS+TF-WeA7 Structural, Mechanical, Optical Properties of Molybdenum Incorporated  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Nanocrystalline Films for Extreme Environment Applications.** *Anil Battu*, *S. Manandhar*, *C.V. Ramana*, University of Texas at El Paso

Recently, gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) has been attracting the attention of researchers as a suitable material for different extreme environment applications, such as high power electronics, optoelectronics, ultraviolet transparent conductive oxides, and gas sensors.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> exhibits the highest thermal and chemical stability, which makes the material interesting for high-temperature oxygen sensor applications. However, the response time and sensitivity must be improved. In recent years, doping Ga<sub>2</sub>O<sub>3</sub> with the suitable metal ions has been considered to alter the electronic properties and to improve sensor performance. In this context, the present work was performed on using a mechanically resilient metal (Mo) to incorporate into Ga-oxide (GMO) to provide excellent physical and thermo-mechanical characteristics. The GMO nanocomposite films with variable Mo contents (0-11.23 at%) were sputter-deposited onto Si(100) by varying the sputtering power in the range of 0-100 W. The effect of Mo on the crystal structure, mechanical properties and optical properties of GMO nanocomposite films is significant. While Mo content  $\leq$  4 at% retains the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> phase, higher Mo content induces amorphization. Molybdenum incorporation into  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, reduces the grain-size leading to amorphous nature of the entire film as well as surfaces. The nanoindentation studies indicate the remarkable effect of structural evolution and Mo content on the mechanical properties of the deposited GMO thin films. While Mo incorporation increases the hardness from 25 to 36 GPa, elastic modulus decreases. Mo-induced red-shift in the band gap is significant in GMO films. Based on the results, a structure-property relationship is established in Mo incorporated Ga<sub>2</sub>O<sub>3</sub> films.

4:40pm **SE+2D+NS+SS+TF-WeA8 Investigating Mass Transport and other Events underlying Rapid, Propagating Formation Reactions in Pt/Al Multilayer Films.** *David Adams*, *M.J. Abere*, *C. Sobczak*, *D.E. Kittell*, *C.D. Yarrington*, *C.B. Saltonstall*, *T.E. Beechem*, Sandia National Laboratories

Metallic thin film multilayers that undergo rapid, self-propagating exothermic reactions are of interest for several applications including advanced joining technology. Reactive multilayers, such as commercially available Ni-Al, have been developed as a heat source to locally solder or braze dissimilar materials. A local heating approach is of great benefit for joining temperature-sensitive components and metastable structures. The development of new materials for reactive joining requires an improved, detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we describe recent studies of a more highly exothermic reactive multilayer system (Pt/Al). Thin Pt/Al multilayers exhibit rapid propagating reactions with flame speeds as high as 100 m/s and internal heating rates  $> 1 \times 10^7$  K/s. Equimolar designs are characterized by a substantial heat of formation,  $\sim 100$  kJ/mol. at., which is approximately twice that of Ni/Al. Our discussion of equimolar Pt/Al multilayers will focus on the thermal and mass transport characteristics which underly their self-propagating reactions. We have utilized advanced thin film characterization techniques to probe the thermal conductivity of different Pt/Al multilayers having various periodicities. This acquired information is used within the framework of an analytical method developed by Mann et al. (J. Appl. Phys. 1997) to estimate the mass transport properties of Pt/Al multilayers subjected to high heating rates. The analytical model accounts for layer thicknesses, compositional profiles near interfaces, flame temperatures, heats of reaction, and adiabatic temperatures in order to predict reaction wavefront velocity and its variation with multilayer design.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

5:00pm **SE+2D+NS+SS+TF-WeA9 Adaptive Ceramic Coatings for Extreme Environments**, *Samir Aouadi*, University of North Texas, *C. Muratore*, University of Dayton, *A.A. Voevodin*, University of North Texas

**INVITED**

This talk will provide an overview of the latest research developments in the design and exploration of hard coatings with high temperature adaptive behavior in tribological contacts. The initial focus of the talk will be on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Adaptive mechanisms will also be discussed and will include metal diffusion and formation of lubricant phases at worn surfaces, thermally- and mechanically-induced phase transitions in hexagonal solids, contact surface tribo-chemical evolutions to form phases with low melting point, and formation of easy to shear solid oxides. All of these adaptive mechanisms are combined in nanocomposite coatings with synergistic self-adaptation of surface structure and chemistry to lubricate from ambient temperatures to 1000 °C and provide surface chemical and structural reversibility during temperature cycling to maintain low friction coefficients. Changes in the structural and chemical properties of these materials as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on *ab initio* calculations and molecular dynamics simulation methods. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

5:40pm **SE+2D+NS+SS+TF-WeA11 Ultralow Wear of Stable Nanocrystalline Metals**, *Nicolas Argibay*, *T.A. Furnish*, *T.F. Babuska*, *C.J. O'Brien*, *J.F. Curry*, *B.L. Nation*, *A.B. Kustas*, *P. Lu*, *M. Chandross*, *D.P. Adams*, *M.A. Rodriguez*, *M.T. Dugger*, *B.L. Boyce*, *B.G. Clark*, Sandia National Laboratories

The existence of intrinsic thermodynamically stable nanocrystalline binary metal alloys has been recently proposed and supported by demonstrations of stability through annealing of powders. There is a great deal of interest in understanding the impact of mechanical stress on this stability. In this presentation we discuss the results of an investigation on the stress and temperature dependent stability of a nanocrystalline noble-metal alloy (Pt-Au) in the form of sputtered thin films. We show that stabilization of nanocrystalline structure can impart low friction ( $\mu \sim 0.2-0.3$ ) and remarkable wear resistance, 100x lower than any previously reported metal.

6:00pm **SE+2D+NS+SS+TF-WeA12 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, *Daniel Edström*, *D. Sangiovanni*, *L. Hultman*, *I. Petrov*, *J. Greene*, *V. Chirita*, Linköping University, University of Illinois at Urbana-Champaign

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. The essential feature in the disordered alloys, as reported for ordered alloys, is the increased occupancy of electronic  $d-t_{2g}$  metallic states, which allows the selective response to tensile/shearing stresses, and explains the enhanced toughness confirmed experimentally for VMoN films.

Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack.

New DFT calculations suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC. A comprehensive electronic structure analysis, as well as stress/strain curves DFT-based calculations, carried out for the newly formed ternary TMC alloys, reveal similar trends between shear-stressed TMN and TMC compounds, and predict VMoC as the best candidate alloy with enhanced ductility.

**KEYWORDS:** nitrides, carbides, toughness, hardness, ductility.

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