## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B1-1-ThM

## PVD Coatings and Technologies I

**Moderator: Frank Kaulfuss**, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

8:20am **B1-1-ThM-2 Optimization of RF Magnetron Sputter Deposition of Ultrathick Boron Carbide Coatings***, Alison Engwall (engwall1@llnl.gov),* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; L. Bayu Aji, S. Shin, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Boron carbide is a material of interest as an ablative layer for inertial confinement fusion (ICF) applications due to its robust physical properties and uniform amorphous structure. However, growing boron carbide films to thicknesses of >50 µm, as needed for ICF, presents many challenges. Our approach to the optimization of two main process parameters (the target-to-substrate distance and Ar gas pressure) for the deposition of boron carbide coatings by RF magnetron sputtering is based on a combination of film characterization, plasma diagnostics, and modeling. Monte Carlo simulations of ballistic sputtering and gas-phase atomic transport are benchmarked by selected measurements of the deposition rate, residual film stress, and plasma parameters monitored with an electrostatic probe. We describe results of this study of parameter space and ultimately demonstrate the deposition of >50 µm-thick boron carbide coatings with close-to-zero residual stress.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

8:40am **B1-1-ThM-3 Hybrid Technologies for Wear Protective Coatings With Adaptive Behavior***, Andrey Voevodin (andrey.voevodin@unt.edu),* University of North Texas, USA **INVITED**

Physical Vapor Deposition (PVD) technologies offer a suite of methods for surface engineering, where the broad range controls of the deposited flux chemical composition, density, ionization state and energy allow for the growth of wear reducing materials with complex compositions and structures tailored for an adaptive behavior in variable environments and temperatures.For example, the hybridization of magnetron sputtering and pulsed laser deposition had led possibility to embed transition metal dichalcogenides into hard ceramic matrices which had open a range of adaptive coating capable to operate over the broad range of environment humidity and temperature by self-changing the contact surface chemistry and structure in response to the environment change. The hybrid processes for the formation of adaptive wear protective coatings were further expanded to include combinations of PVD methods with other methods, e.g. laser texturing and electro-spark deposition, had led to additional avenues for realization of robust wear protective coatings with adaptive behavior to operate under high contact loads and speeds.The presentation reviews developments of adaptive wear protective coatings produced with hybrid PVD methods and places perspectives for future opportunities.

9:20am **B1-1-ThM-5 Cylindrical Magnetron Deposition of TiAlN Coatings with HiPIMS***, Veronika Simova (veronika.simova@polymtl.ca), O. Zabeida, L. Varela Jimenez, J. Qian, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Rotating cylindrical magnetrons have several important benefits in comparison with widely used planar magnetrons, making them interesting for large-scale industrial applications. Due to their rotation, target erosion is uniform that results in a much higher target utilization (70% or more) and a high stability during reactive sputtering processes. Moreover, better cooling efficiency allows one to use higher power densities and, consequently, higher deposition rates can be achieved. This makes cylindrical magnetron sputtering (CMS) well adapted for HiPIMS.

In the present work, we investigated the use of CMS for the fabrication of $Ti_{0.5}Al_{0.5}N$ as a model hard coating extensively used for the protection against harsh environments such as those seen in aerospace and manufacturing. We studied the effect of pulsed-DC and HiPIMS deposition conditions (frequency of 0.91 kHz, duty cycle of 91% and 9.1%, respectively) on the microstructure, mechanical properties, residual stress and stress depth profiles. In addition, *in situ* real-time plasma monitoring by optical emission spectroscopy (OES) was applied for the study of the process and of the film growth conditions.

By applying the substrate bias, the coating hardness increased from 20 GPa (no bias) up to 30 GPa for a bias of -60 V without any additional heating. This increase in hardness is in good correlation with the increase in compressive stress from -0.9 GPa to -5.5 GPa and corresponding decrease in the grain size (from 16 nm to 9 nm). The stress depth profiles clearly show a steep gradient in compressive stress increasing from the substrate interface towards to the coating surface.

Substrate heating results in further enhancement of the mechanical properties, accompanied by a considerably lower compressive stress and its gradient. Consequently, when combining substrate heating with substrate biasing, hard TiAlN coatings with even lower compressive stress can be produced (-2.3 GPa).

The results clearly show that the substrate bias and heating can effectively be used to tune the mechanical properties and residual stress and stress depth profiles of TiAlN coatings.

9:40am **B1-1-ThM-6 Development of VC-based Early Transition Metal Carbide Superlattices via Compound Target Magnetron Sputtering***, Barbara Schmid (barbara.schmid@tuwien.ac.at), N. Koutná, R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee Composite Materials, Germany*; E. Pitthan Filho, D. Primetzhofer,* Uppsala University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides are known to feature high thermal and mechanic stability as well as high melting points, sometimes above 3500 K, and can be regarded as ultra-high temperature ceramics (UHTC). The huge downsides to those materials is the high inherent brittleness.

Superlattice architecture describes the alternation of coherently grown nanolayers of two or more materials. By creating such superlattices, optical, magnetic, electronic, tribological, or mechanical properties can be influenced. The hardness but also the toughness of superlattice materials can be significantly higher than their monolithically grown components.

Therefore, we developed superlattice structures of selected transition metal carbides combined with VC as well as performed bilayer period variations between 2 and 50 nm.

The selected carbide combinations are based on density functional theory simulations, which revealed VC containing films as most promising candidates to have an improved toughness behavior due to the superlattice structure.

All coatings are developed via DC magnetron sputtering using the respective ceramic targets. Their characterization includes X-ray diffraction, scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy, elastic recoil detection analysis, nanoindentation and in-situ micromechanical investigations.

10:00am **B1-1-ThM-7 New Approach to Ceria-Based Electrolyte Deposition by Reactive Magnetron Sputtering***, Kamel Ouari (kamel.ouari@utt.fr), E. Zgheib, S. Achache,* LASMIS, University of Technology of Troyes, France*; M. Arab Pour Yazdi, A. Billard, P. Briois,* FEMTO-ST, University of Technology of Belfort-Montbéliard, France*; F. Sanchette,* LASMIS, University of Technology of Troyes, France

Low-Temperature Solid Oxide Fuel Cells (LT-SOFC) represent a future technology for clean and efficient power generation from renewable sources. Low-temperature operation can make SOFC technology technically useful, i.e. less manufacturing cost and with more stable long-term performance. However, it also brings significant challenges in cell fabrication, especially in producing thin and dense electrolyte films with good mechanical and electrical properties. Magnetron sputtering is one of the advanced techniques used to develop micrometer coatings. Although it is a scalable industrial process, it also has drawbacks, such as low oxide deposition rates. Ceria-based electrolytes, Ce(Gd, Sm)O2, are one of the most promising alternatives to the conventional SOFC electrolyte, Yttria-Stabilised Zirconia (YSZ), due to their high ionic conductivity at low temperatures (< 600°C). Thus, in this work, optimized electrolytes for LT-SOFCs are deposited by reactive pulsed DC magnetron sputtering. The objective is to obtain dense coatings of a few micrometres with high deposition rates. Coatings were deposited using an DEPH 4 system (DEPHIS, Etupes, France) to prove their feasibility on a large scale. We report two new methods for depositing high-quality electrolyte layers by reactive magnetron sputtering, one involving sub-stoichiometric coating and the other stoichiometric without using any control systems (e.g. optical emission spectroscopy, target voltage, mass spectrometry, or other). The sub-stoichiometric films require ex-situ annealing to fully oxidize them. The deposition rates are in the order of that of the metal mode of the reactive deposition method. Moreover, the discharge voltage and overall pressure stabilize after a few minutes. Investigations are focused on growth, physico-electrochemical characterizations of Gd- and Sm-doped ceria as a function of deposition parameters (bias, O2 flow rate, etc.), and performance tests of LT-SOFCs with 2, 5 and 10 µm thick sputtered electrolytes.

10:20am **B1-1-ThM-8 Sputter-Deposited Zr-Cu Thin Film Metallic Glasses: Microstructure and Properties Control of as-Deposited Films and Impact of Ultra-Short Pulsed Laser Irradiation Treatments on the Film's Structure***,* ***Alejandro Borroto (alejandro.borroto@univ-lorraine.fr),*** Institut Jean Lamour - Université de Lorraine, France*; M. Prudent,* Laboratoire Hubert Curien - Université de Lyon, France*; S. Bruyère,* Institut Jean Lamour - Université de Lorraine, France*; F. Bourquard,* Laboratoire Hubert Curien - Université de Lyon, France*; D. Pilloud, D. Horwat,* Institut Jean Lamour - Université de Lorraine, France*; M. Leroy,* IREIS, Groupe HEF, France*; P. Steyer,* MATEIS, INSA Lyon, Université de Lyon, France*; J. Colombier, F. Garrelie,* Laboratoire Hubert Curien - Université de Lyon, France*; J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

Owing to their amorphous structure, metallic glasses (MGs) have emerged as a new class of materials with remarkable properties compared with their crystalline counterpart. Using physical vapor deposition methods such as sputtering, MGs can be prepared in the form of thin film metallic glasses (TFMGs). Thus, the microstructural control inherent to the sputtering process can be exploited to tailor the properties of TFMGs. Meanwhile, laser irradiation is a well-established technique for surface functionalization, allowing the generation of ripples known as laser-induced periodic surface structures (LIPSS).However, a lack exists on the laser-induced surface functionalization of MGs, most of the studies are focused on the laser irradiation-crystalline material interaction.

Here, sputter-deposited Zr-Cu thin films, largely known for their good glass forming ability, are used as a model system and studied over a wide range of compositions. Our results are divided into two parts. First, we report on the influence that the energy of the sputtered atoms arriving at the substrate (controlled here through the deposition pressure) has on the structure, microstructure, and properties of the deposited films. We demonstrate that by increasing the deposition pressure, a composition-dependent transition from a denser to a columnar microstructure occurs. This microstructural transition directly affects the residual stress state as well as the electrical and optical properties of the deposited TFMGs. In particular, we show that there is a threshold in the deposition pressure below which the resistivity of the films remains constant. Second, we report on the laser-induced structural changes occurring at the surface and near-surface in Zr-Cu thin film metallic glasses. Hence, we study the influence that the alloy composition has on the crystallization process induced by laser irradiation. Transmission electron microscopy is used to study the evolution of the film's structure, microstructure, and composition after laser irradiation. In particular, we demonstrated the feasibility of laser treatment to obtain periodic surface structures of different geometries in TFMGs. Our results shed new light on the laser-amorphous material interaction process, opening a new avenue for future applications.

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