Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP2-1-WeM

HIPIMS, Pulsed Plasmas, and Energetic Deposition I

Moderators: Arutiun P. Ehiasarian, Sheffield Hallam University, UK, **Tetsushide Shimizu**, Tokyo Metropolitan University, Japan

8:00am **PP2-1-WeM-1 Alpha-alumina thin films at low temperature: how R-HiPIMS process parameters influence purity and crystallinity*, Célia Dieudonné [celia.dieudonne@icmcb.cnrs.fr]*,** ICMCB, France*; Marjorie Cavarroc-Weimer,* Safran, France

Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS) is emerging as a highly effective technique for the deposition of high-quality insulating metal oxide coatings. There are numerous process parameters. Some are similar to those of reactive conventional magnetron sputtering (working pressure, gas ratio, substrate temperature etc.), while others are similar to those of pulse use (frequency, time-off etc.). This study highlights the potential of R-HiPIMS to produce dense, homogeneous, and pure alpha-alumina (α-Al_2O_3). High ionization rates and peak power densities inherent to R-HiPIMS play a crucial role in promoting film densification and stabilizing the α-Al_2O_3 phase. The influence of other process parameters including oxygen partial pressure, working pressure, target power density, and substrate temperature on film microstructure is investigated. Special attention is given to the effect of the bias configuration of the steel substrate, comparing the presence of α-Al_2O_3 when the substrate is grounded or at a floating potential. This aspect constitutes a major focus of the study, as the substrate bias state significantly affects the energy and flux of incoming ions, as well as the overall plasma–substrate interaction during deposition. A mechanism to stabilize α-Al_2O_3 is proposed.

8:20am **PP2-1-WeM-2 Influence of Pulse Parameters in Multi-Pulse Hipims on Reactive Mode Transition for VO_2 Thin Film Deposition*, Erdong Chen [chen-erdong@ed.tmu.ac.jp]*,** *Rina Watabe,* Tokyo Metropolitan University, Japan*; Stephanos Konstantinidis,* University of Mons, Belgiums, Belgium*; Daniel Lundin,* Linköping University, Sweden*; Tetsuhide Shimizu,* Tokyo Metropolitan University, Japan

Vanadium dioxide (VO2) undergoes a thermochromic phase transition around 68°C, changing from a tetragonal to a monoclinic structure accompanied by a substantial change in optical and electrical properties, which can be used in e.g., smart windows. However, synthesizing single-phase VO2 films via reactive sputtering remains challenging due to 1) the wide range of vanadium-oxygen (V-O) stoichiometries, and 2) the need to grow the proper crystalline phase, leading to a limited process window with a very narrow phase transition from VOx to VO_2.

In this study, these challenges were addressed by regulating the peak current (Ipk) in reactive multi-pulse High-Power Impulse Magnetron Sputtering (HiPIMS) to control the reactive mode transition. The number and on-time of micro-pulses were systematically varied to elucidate the relationship between the incident ion flux and Ipk evolution as a function of O_2 gas flow, using ion mass spectrometry.

With this approach, a linear increase in Ipk was achieved upon O_2 introduction, mitigating the abrupt current drop and reducing process hysteresis typically observed in single-pulse HiPIMS. This enabled more stable control over VO_2 deposition and improved the deposition rate within the transition regime.

As a result, VO_2 crystalline thin films were successfully deposited on ZnO/glass substrates. Thermochromic measurements revealed a resistivity change of over two orders of magnitude across the phase transition occurring at approximately 50 °C.

8:40am **PP2-1-WeM-3 Bipolar HiPIMS Discharges: Principles, Diagnosticsand Thin Film Deposition Strategies*, Jiří Čapek [jcapek@kfy.zcu.cz]*,** *Tomáš Kozák, Andrea Dagmar Pajdarová, Mina Farahani, Tomáš Tölg,* University of West Bohemia in Pilsen, Czechia **INVITED**

The properties of thin films depend on their microstructure, crystal structure, and residual stress, which are influenced by the mobility of adatoms during growth. In magnetron sputtering, the adatom mobility can be enhanced via ion bombardment by applying a bias voltage. High-power impulse magnetron sputtering (HiPIMS) offers greater control by delivering high-power density pulses, producing a high fraction of ionized species and enhanced ion bombardment, even without a substrate bias. However, a bias voltage may still be needed to control low-energy ions. Recently, bipolar HiPIMS, where a positive voltage pulse follows the main negative voltage pulse, has been suggested to be used instead of a substrate bias voltage.

This presentation summarizes our research on bipolar HiPIMS. Plasma analyses using the Langmuir probe and mass spectroscopy revealed that plasma parameters evolve similarly regardless of positive pulse parameters or distance from the target, though their values differ. During the initial phase of the positive pulse, a large potential difference (up to 200 V), high electron temperature (up to 150 eV), and a significant drop in electron density were observed. After this part, the difference between the potentials and the electron temperature is low. The time-averaged spectra of ions exhibit a prominent high-energy peak. It is shown that the position of the peak can be varied by the positive pulse amplitude, its magnitude scales with the pulse length, and its width can be slightly influenced by the length of the delay interval.

Special attention is devoted to the deposition of films on insulating surfaces. Biasing such surfaces becomes ineffective because the plasma-substrate potential difference necessary for ion acceleration almost vanishes once the surface is charged by the incident plasma ions. We propose the utilization of chopped bipolar HiPIMS (featuring several short positive pulses replacing a single long positive pulse) to enhance energy flux to such insulating surfaces. Results show that for an insulated surface with low capacitance, bipolar pulse configurations do not significantly increase energy flux to the surface due to its rapid charging by plasma ions. Conversely, high surface capacitance facilitates an increase in energy flux even for a long positive pulse. For medium surface capacitance (tens of nF), chopping the positive pulse in bipolar HiPIMS effectively increases the energy delivered to the film by discharging the surface in the off-times. Optimal conditions for the deposition of thin films will be discussed based on this systematic study of various unipolar and bipolar pulse configurations.

9:20am **PP2-1-WeM-5 Synthesis-Dependent Phase Evolution in the W–N System: A Case Study with HiPIMS and N+ ion source*, Oleksandr Pshyk [oleksandr.pshyk@empa.ch]*,** *Kerstin Thorwarth, Nathan Rodkey, Sebastian Siol,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Many nitride compounds exhibit relatively wide homogeneity ranges, which usually simplify their synthesis. However, some complex nitrides, such as W-N, contain numerous stable ground-state phases as well as metastable phases. Some of these phases have been computationally predicted to possess extraordinary properties, especially the nitrogen-rich compounds. In contrast, some of these phases have a very narrow homogeneity range, which, combined with variations in synthesis conditions, complicates their controlled synthesis. Exploring such a complex phase space becomes even more challenging when non-equilibrium synthesis methods, such as physical vapor deposition (PVD) methods, are employed. Therefore, understanding the phase evolution sequences within the W-N system under the exceptional synthesis conditions provided by high power impulse magnetron sputtering (HiPIMS) can help identify the conditions necessary for the synthesis of unique nitride compounds.

In this report, we present a comprehensive exploration of the basic synthesis parameter space for W-N thin films using HiPIMS. In addition to varying the nitrogen partial pressure (and thus the nitrogen-to-tungsten ratio), we investigate the effects of substrate temperature, substrate bias potential, and substrate-to-target distance on phase formation. We show how the phase fractions within each composition window change with variations in these process parameters. Furthermore, to elucidate the role of N_2 gas dissociation and ionization on phase evolution, we perform W-N thin film deposition assisted by an electron cyclotron wave resonance nitrogen plasma source. Our results reveal that the synthesizability of the two most commonly reported W-N phases synthesized using PVD methods - the NaCl-structured WN_x and WC-structured WN_x phases - strongly depends on the nitrogen concentration in the films set by substrate temperature or substrate bias. Furthermore, the boundaries between different phases are highly sensitive to the deposition rate, which is determined by the substrate-to-target distance. We analyze and discuss these results in the context of plasma characteristics at different nitrogen partial pressures and substrate-to-target distances.

The findings presented here can serve as a guide for synthesizing other compounds within complex phase diagrams that contain numerous stable and metastable phases within narrow homogeneity ranges.

9:40am **PP2-1-WeM-6 Development and Optimization of CrN and CrSiN Hipims Coatings for Enhanced Tool Performance in Cryogenic Machining of Ti6Al4V**,
Gaya CHETTOUH [gaya.chettouh@utt.fr], University of Technology of Troyes (UTT), France*; Soufyane ACHACHE, Lamine GUEYE,* Université de Technologie de Troyes, France*; Yoann PINOT,* École Supérieure Nationale d'Arts et Métiers de Cluny, France*; Frederic SANCHETTE, Mohamed EL GARAH,* Université de Technologie de Troyes, France*; Corinne NOUVEAU,* École Supérieure Nationale d'Arts et Métiers de Cluny, France

Cryogenic machining is a sustainable alternative to conventional cutting fluids, reducing environmental impact while improving cooling efficiency at the tool–workpiece interface. This study develops protective coatings for cutting tools used in the cryogenic machining of Ti6Al4V titanium alloy. Although Ti6Al4V offers excellent mechanical strength and corrosion resistance, its poor machinability due to low thermal conductivity, high hardness at elevated temperatures, and strong chemical reactivity remains challenging.

Coatings are commonly applied to tungsten carbide tools to enhance their mechanical and tribological behavior. Lin et al. [1] showed that CrN deposited by modulated pulsed power magnetron sputtering (MPPMS) reached a hardness of 26 GPa and a Young's modulus of 330 GPa, while Si addition (6.3 at. %) by pulsed DC sputtering increased hardness and modulus to 38 GPa and 395 GPa, respectively. This work reports on the enhancement of CrN and CrSiN coatings deposited by high power impulse magnetron sputtering (HiPIMS). Deposition parameters, including nitrogen flow, target duty cycle, bias voltage, and bias pulse synchronization (T_{on})—were optimized to improve film adhesion and density.

Microstructural and phase analyses were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). Nanoindentation revealed a maximum hardness of 33.2 GPa and modulus of 317 GPa at T_{on} = 110 µs. Tribological tests with a rotary tribometer showed friction coefficients between 0.51–0.53 against Ti6Al4V balls, with a minimum wear volume of 1.24 × 10^{-5} mm^3/Nm at T_{on} = 210 µs. Coatings deposited at T_{on} = 210 µs and 310 µs also exhibited superior adhesion, with critical loads (LC_3) of 4.5 N and 4.15 N, respectively. The CrN coating at T_{on} = 210 µs offered the best balance between mechanical and tribological performance, highlighting the key role of bias pulse synchronization in HiPIMS coatings.

Finally, the effect of Si incorporation was studied using a hybrid HiPIMS/pulsed DC mode to deposit CrSiN coatings containing 0–10 at. % Si. The influence of Si on microstructure and mechanical properties was compared with the optimized CrN reference. Coatings were then tested under cryogenic conditions to assess their machining performance. The corresponding results are presented.

[1] Lin et al. Surf. Coat. Technol., vol. 216, p. 251–258, 2013

11:00am **PP2-1-WeM-10 Nanopatterned Nanolayer TiN/NbN Coatings as Plasmonic and Wear Resistant Antimicrobial Materials**,
***Arutiun P. EHIASARIAN [a.ehiasarian@shu.ac.uk]**, Arunprabhu Arunachalam Sugumaran,* Sheffield Hallam University, UK*; Ryan Bower, Ming Fu,* Imperial College London, UK*; David Owen, Ethan Muir, Yashodhan Purandare, Papken Ehiasar Hovsepian,* Sheffield Hallam University, UK*; Peter K. Petrov, Rupert Oulton,* Imperial College London, UK*; Thomas Smith,* Sheffield Hallam University, UK

Light-activated antimicrobial materials based on superhard nanoscale multilayer coatings are a novel class of materials which avoid eluting toxic heavy metals, are activated by visible light and are resistant to wear. High Power Impulse Magnetron Sputtering (HIPIMS) has been used to fabricate TiN / NbN nanoscale multilayers, whose surface was patterned into a nanoscale spike array using reactive ion etching to create features that amplify light-induced surface plasmon resonance. The film bilayer thickness was tailored and graded to enhance the toughness of the nanospikes and improve their resistance to sliding wear as evaluated in pin-on-disk tests and SEM observations. A highly activated plasma chemistry was observed in the HIPIMS environment with metal-to-gas ion momentum ratios reaching 4 for NbN and 2.7 for TiN at pulse duration of 200 µs. These conditions stabilised a (200) crystallographic texture for the nanolayer stacks. A high density microstructure observed in AFM curbed plasmon losses by reducing the density of scattering centres at grain boundaries. Preferential oxidation of NbN on the surface detected through XPS was responsible for deteriorating the plasmonic figure of merit of the films as observed through ellipsometry. Pump-probe laser measurements showed significant increases in the lifetime of active electron species in the films due to trapping of hot carriers by oxygen vacancies such as Nb^{3+} and Ti^{3+}, with Nb being more sensitive due to a higher enthalpy of its oxide. An enhanced Raman scattering was observed from nanospike regions. Antimicrobial activity of up to 4-log kill was observed *for Staphylococcus aureus* and *Pseudomonas aeruginosa* bacteria under UV illumination.

11:20am **PP2-1-WeM-11 Nitride thin films and R-HiPIMS parameter selection: a machine learning approach**,
***Julien Neyrat [julien.neyrat@safrangroup.com]**, Marjorie Cavarroc-Weimer, Edern Menou, Thomas Vaubois,* Safran, France*; Dominique Michau, Angéline Poulon-Quintin,* CNRS-ICMCB, France

Reactive High-Power Impulse Magnetron Sputtering (R-HiPIMS) is a very efficient process to elaborate high quality thin films (dense, continuous, smooth, homogeneous and nanostructured) thanks to a high-ionized plasma and to high peak power densities applied to the metallic target during short pulses. However, R-HiPIMS involves numerous parameters. Some are similar to reactive conventional magnetron sputtering (working pressure, ratio of gazes, substrate temperature...), others are specific to R-HiPIMS with the use of pulses (frequency, duration ...). This is why a new approach combining traditional knowledge-based approaches with data-driven methodologies that require artificial intelligence and machine learning algorithms is proposed. First, the links existing between film microstructures and R-HiPIMS parameters, based on design of experiments, is introduced for vanadium nitride thin films selected for tribological applications. Their excellent lubrication ability at high temperature with the formation of self-lubricant oxides, makes them excellent candidates. Second, a numerical approach is introduced to facilitate/accelerate the R-HiPIMS parameter selection. Based on the previous experimental data base, using machine-learning tools, different classification and regression models are trained. The aim is to show how this approach could be useful to predict film microstructure from process parameters and then, tribological properties.

11:40am **PP2-1-WeM-12 Effect of Coating on the Crystal Structure and Properties of VN Coatings Deposited by HiPIMS**,
Te-I Huang [dd113011513@gapp.nthu.edu.tw], Department of Engineering and System Science National Tsing Hua University, Taiwan

Vanadium nitride (VN) is one of the promising coating materials for cutting tools due to its excellent mechanical properties such as high hardness and low wear rate; especially the formation of Magnéli-phase oxides at high temperature can significantly lower the friction coefficient and increase the wear resistance. In our previous study, we found that the mechanical properties and thermal stability of VN coatings were influenced by the crystal structure, where VN phase with hexagonal crystal structure (h-VN) exhibits higher hardness and better oxidation resistance compared with cubic VN (c-VN) phase. Although VN with mixed cubic and hexagonal phases were produced, the process parameters that could enhance the transition from c-VN to h-VN remain uncertain. In this study, VN coatings having different c-VN/h-VN ratios with thickness ranging from 500 to 1750 nm were deposited on Si substrates using high-power impulse magnetron sputtering (HiPIMS). The phase evolution and microstructure of the VN coatings were examined using X-ray diffraction (XRD) and scanning electron microscopy, respectively. The distribution of c-VN and h-VN phases in the VN coatings were observed using transmission electron microscopy. Residual stress of the coatings was determined using laser curvature method and XRD. The variation of residual stress, hardness, and electrical resistivity were correlated to the crystal structure of the VN coatings. The results reveal that increasing coating thickness may promote the transition from c-VN to h-VN, thereby affecting the mechanical performance of the VN coatings.

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