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

HiPIMS, Pulsed Plasmas and Energetic Deposition I

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8:00am **PP2-1-WeM-1 Energetics and Chemistry of Cathodic Arc Ti-N Plasma: A Combinatorial Investigation Using Experimental Probes and Fluid Mechanical Modelling**, ***Nikolaos Giochalas [nikolaos.giochalas@liu.se]***, Linköping Univ., IFM, Nanostructured Materials Div., Sweden; *Grzegorz Greczynski,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *Ferenc Tasnadi,* Linköping Univ., IFM, Theoretical Physics Div., Sweden; *Lina Rogström, Magnus Odén,* Linköping Univ., IFM, Nanostructured Materials Div., Sweden

Cathodic Arc Deposition, a commonly used PVD process of growing hard coatings, involves high fluxes of ions and electrons in a dense, expanding plasma. The composition of the arc plasma may vary significantly within the deposition chamber, and the source-to-substrate distance impacts the coating growth conditions. This study investigates the Ti-N plasma generated by a 100 mm, dc-operated arc source at 20 V and 120 A, in an 1 Pa N_2 ambient within a cylindrical, lab-scale HV chamber. A combinatorial approach of experimental probes and finite element fluid mechanical modelling is used to understand the varying plasma composition in terms of ions, neutrals, and radicals, and their corresponding fluxes. The measured and simulated ion species are Ti^{1+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, TiN^{1+}, TiN^{2+}, N_2^{1+}, and N^{1+}. The dominant ion species in every probed spatial configuration is Ti^{2+}, while Ti^{1+} follows closely and equalizes the energetic footprint of Ti^{2+} when the distance from the source is increased. Atomic Nitrogen ions maintain a significant presence throughout the plasma volume, largely due to a sustained emission from the nitrided Ti-source surface, N_2 dissociation and charge exchange collisions. In general, the plasma density and average charge state follow a decreasing trend for distances larger than 35 cm from the source, where the presence of Ti^{3+} and Ti^{4+} is suppressed. At the same time, TiN-ions retain their presence, leading to different growth conditions at the substrate, depending on the chosen distance from the source.

8:20am **PP2-1-WeM-2 Exploring the Microstructure and Mechanical Properties of TiZrMbTaMoN Highentropy Alloy Nitride Coating: Effect of Nitrogen Content**, ***Sen-You Hou [housenyou23@gmail.com]***, National Tsing Hua University, Taiwan, China; *Po-Yu Chen,* National Tsing Hua University, Taiwan; *Bih-Show Lou,* Chang Gung University,Taiwan; *Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

The highpower impulse magnetron sputtering (HiPIMS) generates highdensity plasma through higher instantaneous pulse currents, resulting in thin films with fewer defects, higher density, and densermicrostructure. In this work, a combination of HiPIMS and radio frequency power supply system was used to deposit TiZrNbTaMoN highentropy alloy (HEA) thin films with varying nitrogen contents on Si wafer,AISI304 and 420 stainless steel substrates. The cross-sectional morphology, composition, and crystal structure of thin films were analyzed using scanning electron microscopy, electron probe microanalyzer, X-ray diffraction, andtransmission electron microscope, respectively. Subsequently, potentiodynamic polarization corrosion tests were conducted on the HEA thin films in 3.5 wt.% NaCl aqueous solution using an electrochemical workstation to evaluate their corrosion resistance. We found that TiZrNbTaMoN HEA nitride coatings exhibited a hardness of up to 29 GPa, along with outstanding corrosion resistance.The effect of nitrogen content on the phase, mechanical properties, and corrosion resistance of TiZrNbTaMoN HEA thin films was discussed in this work.The potential applications for the TiZrNbTaMoN HEA thin filmsin the machining industries were proposed.

8:40am **PP2-1-WeM-3 Insights into the Carbon HiPIMS Discharge: Ionized Flux Fraction and Ion Energy Distribution**, ***Tetsuhide Shimizu [simizu-tetuhide@tmu.ac.jp]***, *Ryo Sakamoto, Erdong Chen,* Tokyo Metropolitan University, Japan; *Caroline Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *Peter Klein,* Masaryk University, Czechia; *Daniel Lundin,* Linköping University, Sweden

Magnetron sputtering-based physical vapor deposition (PVD) has gained considerable attention for the synthesis of functional carbon and carbide coatings, such as tetrahedral amorphous carbon (ta-C), due to its scalability, cost-effectiveness, and uniform film deposition capabilities. In this context, enhancing the ionization degree of carbon using high-power impulse magnetron sputtering (HiPIMS) presents a promising opportunity to expand its applicability. Therefore, substantial progress has been made toward increasing carbon ionization in HiPIMS discharge, through techniques such as adding neon (Ne) gas and employing bipolar pulse schemes. However, the ionization fraction of carbon achieved by HiPIMS remains significantly lower than other techniques, e.g. filtered cathodic vacuum arc (FCVA) and pulsed laser deposition (PLD), presenting significant challenges to its adoption as an alternative approach. Despite these limitations, effectively utilizing the carbon ions generated in HiPIMS discharges requires a detailed quantitative understanding of the ionization fraction, their transport to the substrate, and their role in film growth. In this study, we aim to quantitatively investigate the ionized flux fraction and ion energy distributions in HiPIMS carbon discharges using argon (Ar) as the working gas, correlating these metrics with key process parameters. To achieve this, plasma diagnostics were performed using a magnetically shielded charge selective quartz crystal microbalance (ionmeter), time-of-flight (TOF) mass spectrometry, and time-resolved optical emission spectroscopy, with particular focus on the effects of the peak discharge current density, working gas pressure, and magnetic field. Our results demonstrate that the ionized flux fraction of carbon increases with higher peak current density, lower working pressure, and weaker magnetic fields. The maximum ionized flux fraction of ~12% was observed at a peak current density of 3.1 A/cm² under the weakest magnetic field configuration at a working pressure of 0.6 Pa. Furthermore, the ion energy distribution functions (IEDFs) revealed a distinct high-energy tail exceeding 100 eV, a feature not commonly observed in conventional HiPIMS discharges involving metal targets. Using time-resolved optical emission imaging, we also investigated the kinetic mechanisms underlying the acceleration of these high-energy carbon ions. This study highlights the importance of process parameter control in achieving efficient carbon ionization and transport, which is essential for advancing HiPIMS as a viable technique for carbon coating technologies.

9:00am **PP2-1-WeM-4 Reactive Mode Transition in Multi-Pulse HiPIMS Discharge of Vanadium in Ar/O2 Gas Mixtures**, ***Erdong Chen [chen-erdong@ed.tmu.ac.jp]***, *Tetsuhide Shimizu,* Tokyo Metropolitan University, Japan; *Caroline Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *Stephanos Konstantinidis,* University of Mons, Belgium; *Daniel Lundin,* Linkoping University, Sweden

Vanadium dioxide (VO2) is a thermochromic material that undergoes a metal-insulator transition (MIT) at approximately 68°C, resulting in significant alterations in optical and electrical properties. However, the formation of single-phase VO2 films is challenging in reactive sputtering due to the wide range of vanadium-oxygen (V-O) stoichiometries [1], leading to a limited process window. Based on the relationship between the oxidation state on the target surface and peak current in reactive high-power impulse magnetron sputtering (R-HiPIMS) systems [2], hysteresis examinations were performed to assess peak current evolution in response to variations in oxygen gas flow, aiming to identify an optimal process window for VO2 fabrication. An abrupt decline in peak current was observed upon increasing the O2 gas flow to 1 standard cubic centimeter per minute (sccm), accompanied by a relatively large hysteresis window, which hindered process stabilization and suggested the formation of vanadium pentoxide (V2O5) on the target surface. To address these challenges, we employed a novel approach utilizing very short, multi-pulse sequences in the R-HiPIMS process. This method eliminated the abrupt drop in peak current and reduced the hysteresis window by 36.6%, facilitating improved control over the VO2 deposition process. Additionally, multi-pulse HiPIMS (m-HiPIMS) enhanced both the ionization flux fraction and deposition rate while effectively managing arcing phenomena. Further analysis revealed characteristic variations in peak current (Ipk) as a function of O2 gas flow, with distinct peak current values and waveforms for each micro-pulse. Pulse on time and the number of micro pulses were also investigated to find a suitable process condition for VO2 deposition using multi-pulse mode R-HiPIMS. Comprehensive investigations into these micro-pulses were conducted using mass spectrometry to correlate findings with the surface chemistry of the vanadium target. The growth and properties of the deposited films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallinity of VOx films and their electrical and optical performance were evaluated.

9:20am **PP2-1-WeM-5 HiPIMS goes Ferroelectric: Improving the Remnant Polarization and Leakage in Ferroelectric AlScN for Memory Applications***, Federica Messi, Jyotish Patidar, Nathan Rodkey,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Morgan Trassin,* ETH Zurich, Switzerland*; **Sebastian Siol [sebastian.siol@empa.ch]**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The increasing demands of big data and AI necessitate breakthroughs in energy-efficient computing and data storage. Ferroelectric nitrides, such as aluminum scandium nitride (AlScN), show great potential for non-volatile memory technologies due to their high remnant polarization, temperature stability, and compatibility with current semiconductor manufacturing processes.

The performance of ferroelectric nitrides is directly linked with their structural properties. The remnant polarization can be improved by increasing the c-axis orientation of the film, whereas the leakage current density can be improved by optimizing the microstructure. Point defects however negatively affect the breakdown behavior of the material, which represents a major challenge in the deposition of ferroelectric thin films.

Metal-ion synchronized high-power impulse magnetron sputtering (MIS-HiPIMS) can be used to accelerate film-forming metal ions onto the growing film, resulting in enhanced crystalline quality, improved c-axis texture, and a compact microstructure. Building on our recent successful demonstration of MIS-HiPIMS for piezoelectric thin films [1] we leverage the unique advantages of the technique for the deposition of ferroelectric AlScN with excellent performance.

Through a combinatorial study, we investigate the influence of HiPIMS on the ferroelectric properties of $Al_{1-x}Sc_xN$ films while correlating these properties with crystallinity and Sc composition. Our optimized deposition process successfully yields $Al_{1-x}Sc_xN$ films on Si substrates with performance that is otherwise only achieved using epitaxial growth.[2] Compared with previous reports using conventional sputtering the HiPIMS films show significantly enhanced remanent polarization with values of > 170 $\mu C/cm^2$ while maintaining comparable coercive fields of 5.0 MV/cm. Notably, our findings reveal that the remanent polarization remains stable even with increasing scandium concentrations. At the same time the leakage current densities are among the lowest reported to date.[3] These results can be explained by the excellent c-axis texture enabled by HiPIMS. In the future HiPIMS could enable dense ferroelectric films with low thickness to reduce the switching potential. To our knowledge this is the first report of ferroelectric switching in HiPIMS-deposited nitride thin films. Overall, the results are more than promising and highlight the potential of HiPIMS for the development of defect-sensitive electronic thin films.

[1] Patidar et al. Physical Review Materials 8 (9), 095001, 2024

[2] Deng et al. Journal of the American Ceramic Society, **107**, (3), 2023

[3] Yazawa et al. arXiv preprint arXiv:2407.14037, 2024

9:40am **PP2-1-WeM-6 Controlling Film Growth by Changing the Target Thickness***, **Diederik Depla [Diederik.Depla@ugent.be]**, Farzaneh Ahangarani Farahani, Andreas Debrabandere,* Ghent University, Belgium

This paper summarizes a series of experiments demonstrating the significance of energetic species during DC magnetron sputter deposition. The first example focuses on the phase composition of tungsten (W) films, which can consist of a mixture of a-W and b-W crystals. Various mechanisms have been proposed to explain phase selection, including substrate heating due to plasma exposure and residual gas pressure. However, a broad parameter scan rules out these trends and shows that the phase composition can be quantitatively correlated with the flux of reflected neutrals with energies exceeding the displacement energy threshold. To establish this correlation, the phase composition is quantitatively determined using X-ray diffraction (XRD) analysis and combined with test particle Monte Carlo simulations to evaluate the energy of the reflected neutrals. The energy of these neutrals is defined by binary collisions between argon (Ar) and tungsten (W) atoms and the initial energy of the argon ions, which is set by the discharge voltage. Increasing the target thickness results in a lower magnetic field strength and, consequently, a higher discharge voltage. This effect allows the phase composition to be tuned by just adjusting the target thickness. The role of target thickness is further illustrated in a study on the percolation film thickness during the growth of silver (Ag) thin films. In-situ four-point probe resistance measurements are used to investigate the initial nucleation of these films. A power-law correlation between the percolation thickness and the deposition flux is observed, with the correlation exponent adjustable through variations in target thickness. Both studies highlight that reporting only the discharge power during experiments omits essential information critical for other researchers.

F. Ahangarani Farahani, D. Depla. “Phase Composition of Sputter Deposited Tungsten Thin Films.” *Surface and Coatings Technology*, vol. 494 (2024) 131447

11:00am **PP2-1-WeM-10 Effect of Nitrogen Content on the Microstructure, Mechanical, and Anti Corrosion Properties of AlCrNbSiTiN High Entropy Alloy Films Fabricated by High Power Impulse Magnetron Sputtering***, **Sheng-Jui Tseng [pprayray0915@gmail.com]**,* National Taipei University of Technology, Taiwan*; Chia-Lin Li,* Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; Yung-Chin Yung,* National Taipei University of Technology, Taiwan*; Bih-Show Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taiwan*; Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) films, especially the HEA nitride coatings, have attracted much attention from industries and researchers due to their unique mechanical properties and corrosion resistance. In this work, the AlCrNbSiTiN HEA coatings were fabricated on Si wafers, AISI 420 and 304 stainless steel plates by high power impulse magnetron sputtering. To investigate the impact of equimolar AlCrNbSiTi target poisoning ratios (ranging from 10 to 90 %) and the nitrogen contents on the phase, microstructure, mechanical, and anti corrosion properties of AlCrNbSiTiN coatings, a plasma emission monitoring (PEM) feedback control system was employed during sputtering. A systematic analysis of the microstructure and mechanical properties was conducted. The chemical compositions of HEA coatings were investigated by a field emission (FE) electron probe microanalyzer. FE-scanning electron microscopy and transmission electron microscopy were used to examine the microstructure of HEA films. Additionally, X-ray diffraction was employed to assess grain size, lattice constants, and crystallinity. A series of mechanical property tests, including hardness, adhesion, wear, and residual stress measurements were performed. The potentiodynamic polarization test of coatings in the 0.5 M H2SO4 aqueous solution was examined. It is anticipated that the AlCrNbSiTi HEA film exhibited an amorphous structure. With increased nitrogen contents and target poisoning ratios, the AlCrNbSiTiN HEA nitride films transformed into a face-centered cubic structure. The HEA nitride films are projected to show enhanced hardness and elastic modulus, primarily due to the formation of a saturated metal nitride phase and solid solution strengthening from multiple elements. Based on the experimental results, the effects of target poisoning and nitrogen contents on the phase, microstructure, mechanical properties, and corrosion resistance of AlCrNbSiTiN coatings were discussed in this study.

11:20am **PP2-1-WeM-11 Effects of High-Power Impulse Plasma Source (HiPIPS) Parameters on the Properties of Aluminum Thin Films Synthesized at Atmospheric Pressure***, **Brianna Hoff [brianna.hoff@mines.sdsmt.edu]**, Forest Thompson, Nathan Madden, Grant Crawford,* South Dakota School of Mines and Technology, USA

High vacuum is required for conventional physical vapor deposition (PVD) techniques which restricts the application space that benefits from the dimensional stability, functionality, and chemically benign processing afforded by PVD thin films. Motivated by this limitation, a high-power impulse plasma source (HiPIPS) has been developed for surface engineering at atmospheric pressure. HiPIPS technology utilizes high-voltage, low duty cycle DC pulses to generate a plasma discharge between a consumable feedstock (cathode) and a conductive plasma jet nozzle (anode). The plasma is forced out of the nozzle by high flow rates of process gas where it subsequently interacts with a substrate which may be biased to increase the kinetic energy of ionized species. The HiPIPS design enables high plasma density to be achieved while maintaining low average power. In this study, processing-microstructure-property relationships are reported for the HiPIPS deposition of metallic aluminum (Al) films. Argon (Ar) was used as the working gas, and Al thin films were deposited at atmospheric pressure by utilizing Al alloy electrodes. HiPIPS system design variables and plasma discharge characteristics were correlated with the mechanical, compositional, and microstructural properties of the Al films. Film characterization was conducted via adhesion testing, energy dispersive x-ray spectroscopy, transmission electron microscopy, and atomic force microscopy. In this presentation, HiPIPS parameters which lead to desirable film qualities are discussed.

11:40am **PP2-1-WeM-12 Enhancing CrAl Ionization in HiPIMS Using Auxiliary Targets: Insights from Time-Averaged OES**, ***Kai-Shawn Tang [a0966877063@gmail.com]***, *Ying-Xiang Lin, Chih-Yen Lin, Yi-Hui Lee, Wan-Yu Wu,* National United University, Taiwan

Recently, High-Power Pulsed Magnetron Sputtering (HiPIMS) technology, due to its high ionization rate, has enabled increased ion bombardment during film growth, resulting in dense and smooth films. Previous studies using Bipulse-HiPIMS to deposit Ag-Cu and Ti-Cu films showed that, compared to unipolar mode, Ag-Cu co-sputtering significantly increased the ionization of Ag, while Ti-Cu co-sputtering greatly enhanced the ionization of Cu. These findings suggest that, in the Bipulse-HiPIMS process, the selection and configuration of targets, as well as the tuning of each target's parameters, are closely related to the ionization rate of plasma species.

CrAlN possesses excellent oxidation resistance; however, ternary metal nitride films are no longer sufficient to meet current demands. Therefore, we further investigated quaternary metal nitride films, doping with elements such as Cr, Ti, and Zr to enhance mechanical properties and oxidation resistance. This study uses Bipulse-HiPIMS co-sputtering, with CrAl as the main target at a fixed power of 1.5 kW and Cr, Ti, and Zr as auxiliary targets. Since Cr has a relatively high second ionization energy (16.49 eV), whereas Ti and Zr have second ionization energies of 13.58 eV and 13.13 eV respectively, Ti and Zr are expected to ionize more readily than Cr. The Bipulse-HiPIMS technique aims to assist the ionization of the less readily ionized material (Cr) by more easily ionized materials. Time-averaged OES was used to measure the effect of different target materials on the plasma spectrum during the process.

The auxiliary target power was increased from 0.2 kW to 0.8 kW, observing plasma conditions on the CrAl target. It was found that plasma intensity was lowest in single-target mode, while the addition of an auxiliary target significantly enhanced plasma intensity. The study showed that as auxiliary target power increased, the intensities of Cr^+, Ar^+, N_2^+, N_2^{2+}, and Cr^0 in the plasma also increased. Next, with the auxiliary target power fixed at 0.5 kW, the auxiliary target's duty cycle was varied from 3% to 15%. Under different duty cycle conditions, it was observed that lower duty cycles led to increased Cr^+ and Al^+ intensities, with minimal differences in N_2^+ and N_2^{2+}, while Ar^+ intensity increased with higher duty cycles. The effect of different auxiliary targets is also demonstrated.

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