Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B8-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderator: Martin Rudolph, Leibniz Inst. of Surface Eng. (IOM), Germany

1:20pm **B8-2-ThA-1 Diagnosing Bipolar HiPIMS Plasmas Using Laser Thomson Scattering (Virtual Presentation)***, **James Bradley (j.w.bradley@liv.ac.uk)**, M. Law,* University of Liverpool, UK **INVITED**

A laser Thomson scattering (LTS) experiment has been developed to measure the temporal and spatial evolution of the electron temperature T_e and density n_e in HiPIMS plasmas. The circular magnetron source furnished with a tungsten target has been operated in both unipolar and asymmetric bipolar pulsing modes. The LTS measurements made in the magnetic trap and on the centre-line are complemented by time-resolved Langmuir probe data as well as plasma optical emission measurements.

In conventional unipolar mode, during the HiPIMS pulse (on-time), the LTS measurements of n_e are seen to peak at 6.9×10^{19} m^{-3}, falling by two orders of magnitude some 300 µs into the afterglow. The value of T_e is seen to rise and fall during the negative pulse on-time as the discharge moves from one dominated by argon to metal vapour. Langmuir probe measurements are in good agreement with the LTS data.

When the source is operated in asymmetric bipolar pulsing mode, the pulse on-time results on the discharge centreline are similar to the unipolar case, however during the positive pulse periods we see significant electron heating in which T_e can rise to values comparable to the those measured in on-time. The on-set of the rises in T_e are significantly delayed relative to the start of the positive pulse, with the delay time decreasing with the magnitude of the positive voltage. The local electron density on the centreline n_e is seen to decay significantly more quickly in the afterglow than for the corresponding unipolar pulsing case. Optical emission intensities show the presence of W(I) lines well into the afterglow. The phenomenon of plasma electron heating in the positive pulse is believed to be due to the existence of a transient reverse discharge, in which the vessel walls become an effective cathode.

LTS measurements in the magnetic trap however, show no such anomalous electron heating in the positive pulse period. These observations are discussed in terms of electron cross-field transport from wall to different regions of the plasma.

2:00pm **B8-2-ThA-3 Time Resolved IEDF, EEDF and Q/M of a HiPIMS Discharge for Different Pulse Conditions, Pressures, and Probe Orientations***, Z. Jeckell,* University of Illinois at Urbana Champaign, USA*; D. Barlaz,* University of Illinois Urbana Champaign, USA*; W. Huber, T. Houlahan, I. Haehnlein,* Starfire Industries, USA*; **Brian Jurczyk (bjurczyk@starfireindustries.com)**,* Starfire Industries LLC, USA*; D. Ruzic,* University of Illinois Urbana Champaign, USA

Zachary Jeckell[1], David Barlaz[1], David Kapelyan[1], Wolfgang Huber[2], Thomas Houlahan[2] Ian Haehnlein[2], Brian Jurczyk[2], David N[1]. Ruzic[1]

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This work investigates the temporal evolution of both the electron energies as well as the ion energies during a variety of high-power impulse magnetron sputtering conditions utilizing the positive voltage reversal, known as the Positive Kick, including pulse conditions and pressures ultimately to better understand the physics needed to tailor future depositions. This work was carried out using the HIDEN PSM probe which allows for time resolved ion energy and q/m measurements enabling differentiation between working gas ions and target ions, as well as identification of higher ionization states.Sputtered neutral distribution, low-energy sputtered ions, ionized process gases and accelerated ions from the near-magnetron magnetic trap influence the deposited film based off the modified Thornton-Anders diagram for HiPIMS plasmas. The differentiation between charged species showcases the time evolution of the $M_{magentictrap}^+/Ar_{magentictrap}^+$ and the $M_{bulkplasma}^+/Ar_{bulkplasma}^+$ ratios which are useful for optimizing pulse conditions to efficiently transport metal ions to the substrate and to aid in the selection of process recipes with suitable ratios. The IEDF measurements are paired with time resolved EEDF data acquired from a custom sampling circuit capable of discretizing increments of the duration of one HiPIMS pulse with the Positive Kick. Performed by sweeping voltages, an array for I-V-T are formed that allows for the EEDF to be calculated for all times t. Commentary on plasma potential evolution and expansion is given in relation to the measured IEDF at different on-axis and off-axis locations via linear motion feedthrough.

2:20pm **B8-2-ThA-4 Metal-Ion Synchronized Reactive HiPIMS of AlScN for Piezoelectric Applications***, **Jyotish Patidar (jyotish.patidar@empa.ch)**, K. Thorwarth, T. Amelal, S. Zhuk, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The growing demand for highly integrated piezoelectric micro-electro-mechanical systems motivates the development of novel piezoelectric thin films. AlN in wurtzite structure is a promising candidate for a number of piezoelectric applications due to its high temperature stability and linear frequency response. Isovalent alloying of AlN with Sc is a successful strategy to enhance its piezoelectric coefficient. The heterostructural nature of the alloy system, however leads to low miscibility and a high degree of structural frustration for high Sc concentrations. Consequently, to achieve highly textured AlScN films using conventional magnetron sputtering high deposition temperatures or epitaxial stabilization are needed.

In this work, we present the development of a metal-ion synchronized reactive high-power impulse magnetron sputtering (MIS-HiPIMS) approach for AlScN that could lead to advantages over the current state-of-the-art. HiPIMS is rarely employed for the synthesis of electro-ceramics or semiconductors, since the highly energetic synthesis environment often results in a large number of bulk defects. However, MIS-HiPIMS enables the control of the incident ions kinetic energy while simultaneously reducing the ion-implantation and consequently the bulk-defect concentration in the film. [1]

The MIS-HiPIMS approach presented here is based on reactive HiPIMS sputtering of Al combined with direct current (DC) sputtering of Sc in Ar/N atmosphere. The ion-energy-distribution at the substrate is recorded using a time and energy-sensitive quadrupole mass spectrometer. Subsequently, the negative substrate bias is synchronized on the Al-rich part of the pulse. The HiPIMS pulse pattern, as well as the timing of the synchronization is varied to tailor the microstructure and texture of the AlN thin films. In addition, the non-equilibrium solubility of Sc in AlN is investigated as a function of the incident ion kinetic energy. The materials are fully characterized with respect to their phase constitution, structure and composition using state-of-the-art techniques including high-resolution X-ray diffraction, Rutherford backscattering spectroscopy, elastic recoil detection analysis as well as hard X-ray photoelectron spectroscopy. For selected samples, the transverse piezoelectric coefficients $e_{31,f}$ are compared.

A successful demonstration of a MIS-HiPIMS process for highly textured AlScN could enable the deposition on temperature sensitive substrates, such as polymer foils, but also the functionalization of surfaces with high aspect ratios and would enable a variety of exciting new applications.

[1] Greczynski, G. *et al.J. Vac. Sci. Technol. A***2019**, *37* (6), 060801.

2:40pm **B8-2-ThA-5 Selective Metal Ion Irradiation Using Bipolar HiPIMS: A New Route to Tailor Film Nanostructure and the Resulting Mechanical Properties***, **Ivan Fernandez (IVAN.FERNANDEZ@NANO4ENERGY.EU)**,* NANO4ENERGY SLNE, Spain

Metal ion irradiation combining HiPIMS discharges and pulsed bias synchronization has been demonstrated in the recent years to be a powerful method to achieve an accurate control on film nanostructure and phase control for the deposition of Transition Metal (TM) Nitrides [1]. It allows the deposition of films with optimum mechanical properties as well as reduced accumulated stress compared to the films deposited with gas-ion bombardment in Direct Current Magnetron Sputtering (DCMS). The selective attraction of metal ions at the substrate position optimizes the metal ion energy and momentum required during film growth.

In this presentation we extend this concept of selective metal ion irradiation by combining Bipolar HiPIMS with conventional DC magnetron sputtering operation and DC biasing. The concept of Bipolar HiPIMS was introduced some years ago by different groups and consist in applying a positive pulse with controlled pulse width and amplitude voltage after the conventional HiPIMS negative pulse [2]. This positive pulse allows the accurate acceleration of the positive metal ions towards the substrate, thus, promoting improved film properties such as reduced stress, higher film densification, improved mechanical properties - such as hardness or wear resistance- or better coverage of 3D complex parts. Moreover, it has been recently demonstrated that using bipolar HiPIMS with a substrate at ground potential (comparable to negative biased) results in a similar ion current profile as in conventional HiPIMS with a synchronized pulsed bias with the same delay and timing as the positive pulse [3].

This new coating process has been used for the deposition of hard, dense Transition Metal (TM) Nitrides commonly used in the metalworking industry. This manuscript studies the influence of Nb and Cr ion irradiation on the mechanical properties of TiAlN films, as they show a high large difference in mass. The description of the process as well as the resulting properties (microstructure, hardness, stress and texture) will be presented in this paper.

References:

[1] G. Greczynski et al.,). "*Metal-ion subplantation: A game changer for controllingnanostructure and phase formation during film growth by physical vapor deposition*". J.Appl. Phys. 127, 180901 (2020).

[2] G. Eichenhofer, I. Fernandez, and A. Wennberg, "*Industrial use of HiPIMS and the hiP-V hiPlus technology*," Vak. Forsch. Prax. 29, 40 (2017).

[3] R. Viloan et al., "*Copper thin films deposited using different ion acceleration strategies in HiPIMS*" *Surface* & Coatings Technology 422 (2021) 127487

3:00pm **B8-2-ThA-6 Ion Beam Sputter Deposition of Gallium Oxide Thin Films***, D. Kalanov, Y. Unutulmazsoy,* ***André Anders (andre.anders@iom-leipzig.de)****, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides unique opportunities to control the sputtering and growth processes and to study the correlations between them. The process provides intrinsic heating to the growing film by energetic particles, which can be used to tune various thin film properties, such as microstructure (incl. film density) and crystalline phase.

Gallium oxide is a material of high technological interest because of its unique properties, such as a wide bandgap and a high breakdown field strength. It enables the use of the material, for instance, in ultra-high-power electronics. To fully exploit the potential of gallium oxide thin films, high crystalline quality is needed. The IBSD is a process proven to be capable of growing films of such quality. In contrast to magnetron sputtering, IBSD does not have the unwanted highly energetic (several 100 eV) negative ion component, which causes defects.

The present report covers a systematic study of ion beam sputter deposition of gallium oxide thin films by investigating the fundamental correlations between (i) process parameters (sputtering geometry, ion species, ion energy, oxygen partial pressure), (ii) properties of secondary, sputtered and scattered particle species, and (iii) thin films.

The properties of secondary particles are studied by measuring energy distributions of ions, sputtered and scattered from the target. It is shown that changes in the sputtering geometry and energy of primary ions give control over the high-energy tail of the distribution. The composition of the film-forming flux is compared between processes with primary Ar^+ and O_2^+ beams, by varying the background oxygen pressure. Thin films are deposited for the same process configurations, and characterized regarding growth rate, density, roughness, crystallinity, and chemical composition. Presented systematic analysis may help to improve the process for depositing films of high crystalline quality at different substrate conditions (elevated temperatures, various substrate materials).

3:20pm **B8-2-ThA-7 The Promise of Data-Driven Methods for Diagnostics and Control of Plasma Interactions with Surfaces***,* ***Ali Mesbah (mesbah@berkeley.edu)****,* University of California Berkeley, USA **INVITED**

Data-driven methods can create unprecedented opportunities for real-time diagnostics and control of low-temperature plasmas (LTPs), which are increasingly used for treatment of heat and pressure sensitive (bio)materials in surface etching/functionalization, environmental, and biomedical applications. Some of the main challenges in modeling and control of LTP applications arise from their inherent complexity and variability. Firstly, the dynamics of LTPs are highly nonlinear and spatio-temporally distributed, which are hard to model due to their mechanistic complexity. Secondly, the LTP effects on complex surfaces are generally poorly understood. And thirdly, LTPs exhibit run-to-run variations and time-varying dynamics, whereby LTP treatments may be carried out under similar conditions, but yield different results. In this talk, we will demonstrate the usefulness of learning-based diagnostic and predictive control approaches for LTP treatment of complex surfaces. We will discuss how advanced machine learning and optimization methods can be leveraged to learn the complex plasma and surface dynamics in real-time, toward safe and high-performance LTP treatment of complex surfaces.

4:00pm **B8-2-ThA-9 Colored Random Noise of Cathodic Arcs: What Is It? Should We Care?***,* ***Andre Anders (andre.anders@iom-leipzig.de)****, K. Oh, D. Kalanov,* Leibniz Institute of Surface Engineering (IOM), Germany

Cathodic arcs are well established as the plasma source of a high-rate deposition technology, delivering hard and corrosion-resistant coatings, which are often based on nitrides but also on oxides, carbides, and multilayers and nanocomposites thereof.Through clever configurations of magnetic field, gas supply locations and choice of substrate location, the effects of arc plasma fluctuations or "noise" are mitigated and/or utilized. The physical origin of such noise lies in non-stationary cathode spot processes.Cathode spots, the small locations of current concentration and plasma generation, are known to be greatly affected by the chemical and microstructural properties of the cathode surface.Therefore, it should be expected that not all noise is equal but dependent on the cathode material and surface conditions.One can quantify the type of noise through their power spectral density and define a colored random noise (CRN) index, which lies between 1 (white noise) and 2 (brown noise), and it can even be greater than 2 when events are coupled due to strong feedbacks.In this contribution we summarize the findings, primarily based on FFT (fast Fourier transform) analysis of streak images of cathode spot plasma in vacuum, in argon, nitrogen, and oxygen.We show that the CRN index of cathode spots in vacuum is slightly larger than 2, indicating a general random walk behavior but with feedback, which is likely due to the influence of spot plasma on the ignition of the next spots.Argon as a process gas has no discernable influence on the CRN index, whereas nitrogen and especially oxygen reduce the index.This seems to be related to "easier" ignition of spots in the presence of a compound layer.A compound layer makes it easier for spots to ignite relatively far away from the original spot, but also to repeatedly ignite at about the same position.In the latter case, the spot may appear macroscopically stationary.The spot processes are orders of magnitude faster than the deposition duration and therefore, from a deposition point of view, the fluctuating plasma flow is generally considered with its "noise-averaged" properties.

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