Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B8-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Tiberiu Minea, Université Paris-Saclay, France, **Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

8:00am **B8-1-ThM-1 the Role of He (23S1) Metastable Atoms to Generate High Current Density in Pulsed Magnetron Discharge*, Abderzak FARSY (abderzak.el-farsy@universite-paris-saclay.fr),*** Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France*; E. Morel,* SuperGrid Institute, France*; T. Minea,* Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France

Magnetically enhanced plasmas are used in various applications of low-temperature plasmas including magnetron sputtering and Hall-effect thrusters. In magnetron discharge technologies for sputtering applications, the use of the magnetic field allows the electron confinement yielding for the increase of the plasma density by 1-2 orders of magnitude and the increase of the deposition rate. High power impulse magnetron sputtering (HIPIMS) is a recent ionized physical vapor deposition where a pulsed power supply delivers a huge peak power during a short pulse to achieve a very high ionization degree (>50%) of the metallic sputtered vapor.

In this contribution, we focused on the time-resolved characterization of gas temperature and the density of He (2^3S_1, 19.82 eV) metastable atoms in the ionization region of magnetron plasma operated with a graphite target (2 inch in diameter) and a high current density range (10-20 A/cm^2) within a pulse of 50 µs. Those characterizations are combined with the electrical ones of the cathode voltage and the discharge current. The temporal evolution of He metastable atoms velocity distribution functions (AVDFs) was measured using Time Resolved Tunable Diode Laser Absorption spectroscopy (TR-TDLAS), see figure 1 in supplemental document. A diode laser, accorded to provide 30 pm wavelength range without mode hop and centered at λ_0=1082.909 nm, was used to probe the He $2^3S_1 - 2^3P_0$.

In our conditions, the measured TR-TDLAS profile is affected only by the Doppler broadening; all other mechanisms are negligible. Thus, from the analysis of TR-AVDFs, the gas temperature and He metastable atoms density are calculated (figure 2b in supplemental document), we assumed that the He ground state and the He metastable have the same temperature. The main result obtained by those diagnostics is that the He metastable atoms density reaches the maximum by a time-shift with the current maximum. The He metastable atoms density reaches the maximum at 20 µs whereas the discharge current at 31 µs. In the presentation, this behavior will be used to discuss the role of the He metastable atoms to generate the high current density. Since the measurements were carried out in the ionization region, the He metastable atoms density is affected by electron density and temperature and also by the gas rarefaction effect. Therefore, the effect of cathode voltage, the gas pressure and the discharge current will be presented and discussed.

8:20am **B8-1-ThM-2 Transport of Ions and Neutrals in HiPIMS Studied by Particle-Based Simulations*, Tomas Kozak (kozakt@ntis.zcu.cz),*** University of West Bohemia, Czechia

High-power impulse magnetron sputtering (HiPIMS) technique is being increasingly used for deposition of films due to its ability to deliver more energy into the growing film via target material ions. The sputtered target material atoms are ionized in the high-density plasma above the target. Some of these ions return onto the target due to the structure of the plasma potential above the target. To understand the effect of the pulse shape and other discharge parameters on the ion return probability is very important for the optimization of the ionized fraction, the energy and the total flux of film-forming atoms on the substrate.

A 3D computer simulation employing the direct simulation Monte Carlo (DSMC) method was developed to bridge the gap between existing volume-averaged (less detailed) and particle-in-cell (very detailed) models. The presented simulation can directly calculate the return probability and the related ionized fraction of the target material species on the substrate for a given (time-dependent) spatial distribution of the plasma potential which is estimated based on recent experimental studies. Moreover, the simulation provides time- and space-resolved densities of atoms and ions in the discharge plasma and their fluxes to various surfaces (including energy distributions). The calculated densities are in a good agreement with density maps obtained by optical methods. The ionized fraction on the substrate is found to strongly depend on the plasma potential drop across the ionization region above the target while the ion return probability changes only weakly (around the value of 0.9). This highlights the importance of accurate determination of the ion return probability. By comparing the simulation results with experimental data (such as, ionized fraction, deposition rate), other unknown discharge parameters can be determined.

The simulation also provides quantitative evaluation of the gas rarefaction effect which is found to significantly reduce the process gas density between the target and the substrate (during and after the HiPIMS pulse). Additionally, the effects of various collisional processes in the plasma or the effect of varying plasma potential (*e.g.*, due to spokes) can be studied by the simulations.

8:40am **B8-1-ThM-3 Kinetic Investigation of Electron Heating in HiPIMS Discharges*, Bocong Zheng (bcong.zheng@gmail.com),*** Fraunhofer USA*; Y. Fu,* Tsinghua University, China*; K. Wang, T. Schuelke,* Fraunhofer USA*; Q. Fan,* Michigan State University, USA **INVITED**

We provide a self-consistent and complete description of discharge characteristics of high power impulse magnetron sputtering (HiPIMS) through fully kinetic 1d3v particle-in-cell/Monte Carlo collision (PIC/MCC) simulations. As HiPIMS employs much higher transient power than conventional DC magnetron sputtering (DCMS), more physical processes need to be considered in its simulations, such as Coulomb collisions between charged species, sputtering winds, i.e. gas rarefaction due to momentum exchange between the sputtering species and the background gas, ionization of metal ions from the sputtering species, and secondary electron emission induced by these multi-charged metal ions. This study considers all of the above processes and on this basis provides a detailed description of the HiPIMS discharge characteristics, including discharge runaway, electron dynamics, and sputtering winds. Some important conclusions previously obtained from the global model are confirmed by this *ab initio* kinetic simulation. During the discharge runaway process, i.e., the transition from the low-current DCMS regime to the high-current HiPIMS regime, metal ions gradually replace gas ions as the dominant ones, and the electron energization transitions from sheath energization to Ohmic heating of the ionization region. These results are beneficial for the design and optimization of HiPIMS discharges in practical applications.

9:20am **B8-1-ThM-5 The Influence of the Magnetic Field on the Discharge Parameters of a High Power Impulse Magnetron Sputtering Discharge*, Martin Rudolph (martin.rudolph@iom-leipzig.de),*** Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Intstitute of Technology, Sweden*; H. Hajihoseini,* University of Iceland*; . Raadu,* KTH Royal Institute of Technology, Sweden*; T. Minea,* Université Paris– Saclay, France*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linköping University, IFM, Sweden

The magnetic field of a magnetron is crucial for the working principle of magnetron sputtering. This becomes apparent in particular for high power impulse magnetron sputtering (HiPIMS), where changes in the magnetic field are known to strongly affect the discharge current and voltage waveforms. For examples, for discharges with the peak discharge current kept constant, the discharge voltage decreases with stronger magnetic fields. Simulating these discharges using the Ionization Region Model provides insights into the discharge physics. We reveal that the decreasing discharge voltage has the effect that a higher fraction of the input power is used for electron heating rather than for accelerating ions. This is because stronger magnetic field increases the fraction of the discharge voltage that drops over the ionization region which enhances Ohmic heating. As a result, the discharge voltage can be lower to reach the same peak discharge current. For discharges operated with the discharge voltage kept constant, the peak discharge current increases for stronger magnetic fields. The reason is again that a higher fraction of the input power is directed to the electrons, the discharge becomes more energy efficient. This increases the electron density which lowers the discharge impedance and enables the discharge to run at a higher discharge current. Indeed, we find a close link between the evolution of the electron density and that of the discharge current during the pulse. This suggests that the discharge current can be used as a handle to adjust the electron density of a HiPIMS discharge and by that, to adjust the probability that a sputtered atom is ionized in the ionization region.

9:40am **B8-1-ThM-6 Digitalisation Strategies for a Digital Twin of the Synthesis of Functional Materials by High Power Impulse Magnetron Sputtering and Other Plasma PVD Processes***, **Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk)**, A. Arunachalam Sugumaran, P. Hovsepian,* Sheffield Hallam University, UK*; C. Davies, P. Hatto,* Ionbond UK

Optical emission spectroscopy (OES) was combined with process parameters to monitor all stages of both High Power Impulse Magnetron Sputtering (HIPIMS) and conventional magnetron sputtering processes to provide a robust method of determining process repeatability and a reliable means of process control for quality assurance purposes. Strategies for the in-situ real-time monitoring of coating thickness, composition, crystallographic and morphological development for a CrAlYN/CrN nanoscale multilayer film were developed.Equivalents to the ion-to-neutral ratio and metal-to-nitrogen ratios at the substrates were derived from readily available parameters including the optical emission intensities of Cr I, N_2 (C-B) and Ar I lines in combination with the plasma diffusivity estimated from the ratio of substrate and cathode current densities.The optically-derived equivalent parameters identified the deposition flux conditions which trigger the switch of dominant crystallographic texture from (111) to (220) observed in XRD pole figures and the development of coating morphology from faceted to dense for a range of magnetron magnetic field configurations.

The work paves the way to implementation of machine learning protocols for monitoring and control of these and other processing activities, including coatings development and the use of alternative deposition techniques.The work provides essential elements for the creation of a digital twin of the PVD process to both monitor and predict process outcomes such as film thickness, texture and morphology in real time.

10:00am **B8-1-ThM-7 Decrease of the Interfacial Adhesion to Polymers and Pharmaceuticals Through Modification of Steel Surfaces by PVD and CVD Techniques***, M. Lima,* University of Minho, Portugal*; R. Silva,* University of Aveiro, Portugal*; F. Ferreira,* University of Coimbra, Portugal*; F. Oliveira, R. Silva,* University of Aveiro, Portugal*; A. Cavaleiro, **Sandra Carvalho (sandra.carvalho@dem.uc.pt)**,* University of Coimbra, Portugal

The adhesion is a thermodynamic parameter that quantifies the interatomic and intermolecular interaction between two surfaces and involves chemical, physical, and rheological phenomena [1]. Many industrial processes are affected by adhesion phenomena occurring during the contact of two surfaces with different properties.

An example is the demolding stage of the injection molding process because small fractions of the polymers frequently remain adhered to the mold surface, producing defective polymeric parts (~2 % of the injected parts are rejected) and reducing the mold lifetime [2].

On the other hand, the production of pills and tablets in the pharmaceutical industry is limited by the interaction between the punch and the powder. Different factors such as chemical composition, excipients, particle sizes, melting and compression points of the pharmaceuticals, and the surface properties of the punch determine the success of the drug compaction. The compaction and surface finishing of the pills will directly influence the disintegration and drug dissolution leading to diverse and undesired drug absorption kinetics [3].

Solving adhesion problems in these specific industries will reduce the generation of waste and increase productivity.

There are different ways to optimize the demolding process, such as temperature and humidity optimization, applied demolding and molding forces, or modification of the steel surface using physical vapor deposition (PVD), plasma treatments, and chemical vapor deposition (CVD) methods.

This work will report the development of coatings deposited by atomic layer deposition as well as magnetron sputtering onto steel surfaces to reduce the adherence of both polymeric and pharmaceutical materials. Coatings with different chemical and physical properties presented different surface energy values and this parameter was related to the adhesion of the polymers or the pharmaceuticals to the surfaces. Additionally, the steel coated surfaces were characterized by different techniques (SEM, XRD, FTIR, XPS, nanoindentation, OCA) to disclose the adhesion mechanisms. The coated surfaces with the lowest surface energy showed in a simulated injection process (polymers) and a powder compression machine (pharmaceuticals), the most promising results.

References

[1] R. Matjie et al., Fuel, 181 (2016) 573-578.

[2] M.J. Lima et al., ACS Appl. Nano Mater., 4 (2021) 10018-10028.

[3] V. Mazel et al., Int. J. Pharm., 442 (2013) 42-48.

10:20am **B8-1-ThM-8 Target Erosion Effects During Hipims Deposition of Ultrathick Au-Ta Alloy Films***, J. Bae,* General Atomics, USA*; A. Engwall, L. Bayu Aji, S. Shin, A. Baker, J. Moody, **S. O. Kucheyev (kucheyev@llnl.gov)**,* Lawrence Livermore National Laboratory, USA

Gold-tantalum alloy films are of interest for biomedical and magnetically-assisted inertial confinement fusion (ICF) applications. Here, we systematically study properties of Au-Ta alloy films deposited by high-power impulse magnetron sputtering (HiPIMS) from alloyed targets. By varying substrate tilt, bias, and HiPIMS pulsing parameters, properties of Au-Ta films can be controlled in a very wide range, including residual stress from -2 to +0.5 GPa, density from 12 to 17 g/cm^3, and electrical resistivity from 50 to 4500 micro-Ohm cm. Emphasis of this presentation will be on understanding and controlling effects of target wear/erosion, which strongly influences film properties during the long runs required for depositing >10-micron-thick coatings for ICF hohlraums. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

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