Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderators: Simizu Tetuhide, Tokyo Metropolitan University, Japan, **Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

2:00pm **PP2-2-ThA-3 Strategies for Low Temperature Reactive Deposition of Crystalline TiO_2 Thin Films***, Tomas Kubart (tomas.kubart@angstrom.uu.se),* Uppsala University, Department of Electrical Engineering, Sweden **INVITED**

Titanium dioxide thin films have a multitude of different applications. While the amorphous TiO_2 has excellent optical properties and very good conductivity, the presence of defects leads to an increased recombination. For this reason, crystalline thin films of TiO_2 are desirable for photocatalysis as exemplified by plasmonic photoconversion devices for production of chemical molecules or oleophobic surface treatment by photofixation of SO_2 on anatase surfaces. In general, there is a great interest in deposition techniques that enable phase control of oxide thin films with TiO_2 being the prominent example.

This contribution deals with reactive HiPIMS deposition of TiO_2 thin films. First, experiments with a relatively long target-to-substrate distance are presented. It is shown that in the absence of substrate heating, all deposited films are X-Ray amorphous. Despite that, films prepared by an optimized HiPIMS process exhibit up to 3 times higher photocatalytic activity evaluated by photodegradation of stearic acid, as compared to reference pulsed DC films prepared using the same setup. High oxygen partial pressure is required to achieve the enhanced photocatalytic performance. Increased ion energy, however, has a detrimental effect on the photoactivity. The deposition conditions have also pronounced impact on the crystallization kinetics of the thin films as illustrated by in-situ GIWAXS studies.

When the target-to-substrate distance is reduced, the crystallinity of the as-deposited films is greatly improved. Growth of anatase as well as rutile can be achieved by changing the total deposition pressure. Even here, the HiPIMS process facilitates crystallization of the films as compared to pulsed DC. The deposition, however, results in a pronounced unintentional heating of the substrate. The heat input to the substrate is characterized and results from alternative experiments are presented.

In summary, the HiPIMS deposited films clearly outperforms the ones prepared by pulsed DC. Although the exact growth conditions are dependent on the deposition geometry and specifics of the deposition setup, some general trends can support the process development.

2:40pm **PP2-2-ThA-5 Plasma Dynamics of Individual HiPIMS Pulses Investigated by High-Frame-Rate Camera***, Matjaz Panjan (matjaz.panjan@ijs.si),* Jozef Stefan Institute, Slovenia

Plasma of high-power impulse magnetron sputtering (HiPIMS) discharges is not azimuthally homogenous instead it is concentrated in dense angular regions called spokes [1]. These regions are organized in periodic or quasi-periodic patterns, typically have triangular shape and rotate with velocities of several km/s. Spokes are also present in other types of magnetron discharges. They have been observed in DC magnetron sputtering [2] and RF magnetron sputtering discharges [3].

In this work, we studied the dynamics of HiPIMS plasma with microsecond time resolution using a high-frame-rate camera. The individual pulses were investigated for different Ar pressures (0.25-2 Pa) and peak currents (10-400 A). The experiments show three distinct stages in the plasma dynamics and self-organization with increasing discharge current. From the pulse onset and up to currents of 25-50 A the dynamics is similar to one observed in DCMS discharges. Spokes rotate in the -**E×B** direction with velocities from 4 km/s to 15 km/s and exhibit elongated triangular shape. The growth rate in discharge current strongly influences the spoke velocity – spokes rotate faster for higher growth rates. This DCMS-like stage is followed by a chaotic plasma reorganization with the formation of irregular patterns and complex spoke propagation. As current increases above approximately 50 A, plasma starts to form regular patterns with triangular spoke shape. During this stage, spokes rotate in the **E×B** direction with velocities from 6 km/s to 9 km/s. The spoke velocity depends on the pressure but is practically independent of the discharge current. Spokes rotate faster at lower pressures than at higher pressures. Remarkably similar plasma evolution is observed for pulses with comparable discharge current waveforms.

[1] A. P. Ehiasarian *et al.Appl. Phys. Lett.,* **100** (2012) 114101

[2] M. Panjan *et al.Plasma Sources Sci. Technol.*, **24** (2015) 065010

[3] M. Panjan *J. Appl. Phys.*, **125** (2019) 203303

3:00pm **PP2-2-ThA-6 PowerFlex 500CG: A New HiPIMS Machine for Microtools Coating***, Tommaso Ceccatelli Martellini (tommaso.ceccatellimartellini@protectim.com),* Protec Surface Technologies, USA*; G. Coletta,* Protec Surface Technologies, Italy

A new PVD platform for the deposition of ultra-smooth hard coatings on microtools is introduced: the PowerFlex 500CG. This PVD machine is based on HiPIMS technology and allows the reliable deposition of multiple industrial coatings (TiSiN-based, AlCrN-based or sputter taC) for demanding applications such as high precision machining of hardened steel (HRC60), TiAlV or Al-alloys. The current cutting applications require coatings with extremely high smoothness, durability, and thermal resistance as well as tailored stress and toughness. The performance of the PowerFlex 500CG machine will be described in this paper, including its new etching protocol allowing in-situ microtool edge preparation or a stable reactive sputtering process to improve deposition rate. Finally, a comparison with the industrial benchmark coatings for high precision machining is presented.

3:20pm **PP2-2-ThA-7 Toward Decoupling the Effects of Kinetic and Potential Ion Energies: Ion Flux Dependent Structural Properties of Thin (V,Al)N Films Deposited by Pulsed Filtered Cathodic Arc***, Yeliz Unutulmazsoy (yeliz.unutulmazsoy@iom-leipzig.de), D. Kalanov, K. Oh,* Leibniz Institute of Surface Engineering (IOM), Germany*; S. Karimi Aghda,* RWTH Aachen University, Germany*; J. Gerlach, N. Braun,* Leibniz Institute of Surface Engineering (IOM), Germany*; F. Munnik,* Helmholtz-Zentrum Dresden - Rossendorf, Germany*; A. Lotnyk,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Schneider,* RWTH Aachen University, Germany*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany

Multiply charged ions formed in pulsed filtered cathodic arc process carry significant kinetic and potential energy which contributes to the formation of dense, adherent and macroparticle-free thin films. While the impact of kinetic ion energy on thin film formation during energetic processes such as cathodic arc deposition is well explored, the effects of ion potential energy are less known. We aimed to decouple the contribution of ion kinetic and potential energy regarding the structural effects on the forming thin films. To reach that goal, different arc source configurations are utilized in the filtered cathodic arc experiment including biasing the plasma in relation to the grounded substrate and applying an external magnetic field at the source. Charge-state-resolved energy distribution functions of ions measured at the substrate positions revealed the differences in plasma properties between the arc source configurations, and applying external magnetic field is found to be the primary tool to increase the ratio of multiply charged ions. Thin films of metastable cubic (V,Al)N films are deposited using different electrical configurations and characterized in detail. The resulting thin films demonstrate the possibility to deposit crystalline films without substrate heating due to “atomic scale heating” stemming from the high flux of multiply charged ions, namely the ions carrying significant kinetic and potential energy, in the case of an external magnetic field. However, additional complexity added by the high flux needs further research to distinguish the sole effects of ion flux and ion potential energy on the structure of a forming thin film.

4:20pm **PP2-2-ThA-10 Tough Plasmonic Titanium Nitride Films Deposited by High Power Impulse Magnetron Sputtering***, E. Muir,* Sheffield Hallam University, UK*; R. Bower, P. Petrov,* Imperial College of Science, Technology and Medicine, UK*; **Arutiun P. Ehiasarian (A.Ehiasarian@shu.ac.uk)**,* Sheffield Hallam University, UK

TiN is one of the most plasmonically active and environmentally robust materials with photocatalytic function. However thin films suffer from high optical losses due to a high uptake of C and O impurities at grain boundaries. Densification of the microstructure through High Power Impulse Magnetron Sputtering (HIPIMS) deposition improves the optical properties, however the influence of plasma chemistry is not known. This study utilises constant-current HIPIMS as a technology to achieve high pulse-to-pulse reproducibility and overall operational stability in the discharge in a wide operating window. Time-resolved optical emission spectroscopy reveals a gas-rich ignition phase with duration of 30 µs which develops into a metal-rich phase where the metal component is continuously pumped over 70 µs while the plasma density remains constant. A steady metal-dominated state is reached for pulse durations above 100 µs. Films deposited during the ignition stage were markedly different than those deposited when the discharge develops into the “pumping” and “steady state” regimes, for a constant peak and average power. Differences are observed in the crystallographic texture shifting from a strong (111) to a stronger (200) component confirmed by XRD pole figures, and H_{IT}^3/E_{IT}^2 ratio (toughness) increasing dramatically from 0.2 to 0.3 GPa for a nano-hardness increase from H_{IT} = 33 to 34 GPa. The changes are correlated with the grain morphology observed by AFM. All films were deposited without heating or substrate bias and exhibited excellent plasmonic properties with a single wavelength of electric permittivity near zero and low optical losses represented by the imaginary component of the electric permittivity as determined from modelling of ellipsometry data. The antimicrobial properties of the films will be discussed.

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