Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP2-2-WeA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

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

2:00pm **PP2-2-WeA-1 Introducing an Ionization Region Model for Reactive High-Power Impulse Magnetron Sputtering**, ***Daniel Lundin* *[daniel.lundin@liu.se]***, *Joel Fischer,* Linköping University, Sweden*; Martin Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; Jon Tomas Gudmundsson,* University of Iceland **INVITED**

High-power impulse magnetron sputtering (HiPIMS) is a physical vapor deposition (PVD) technique in which short pulses of high instantaneous power are applied to a magnetron cathode to significantly increase the degree of ionization of the film-forming material. This generally results in an improved coating quality including reduced surface roughness, increased density, and increased coverage on complex 3D geometries. In addition, reactive HiPIMS has also been shown to display a reduced hysteresis behavior compared to reactive DC magnetron sputtering. If we can properly control the internal process parameters, this will likely have a great impact on the way compound coatings are being deposited, since it allows for stable operation in the desired transition zone and consequently a dramatically increased deposition rate, while still preserving other inherent advantages of HiPIMS.

In this work we take the first steps towards a more detailed understanding of the reactive HiPIMS process by introducing a novel reactive ionization region model (R-IRM). The R-IRM is based on the established ionization region model (IRM), which has been extended to incorporate an extensive nitrogen reaction set together with all the additional complexities arising from the addition of a reactive gas. We use the R-IRM to study the internal process parameters of reactive HiPIMS discharges that are difficult to investigate experimentally by applying the model to a set of HiPIMS discharges of Ti in various Ar/N_2 mixtures and with different external process parameters. The temporal evolution of the densities of the different plasma species, their fluxes towards the substrate, as well as the ionization and back-attraction probabilities obtained from the model give valuable insights into how key properties influencing film growth, such as the material flux composition and charge state of film-forming ions, are affected by the choice of the external process parameters. We furthermore observe, that with the small relative flow rates of N_2 typically needed to obtain stoichiometric coatings, nitrogen only plays a minor role in the plasma chemistry.

2:40pm **PP2-2-WeA-3 Energy Contributions in the Reactive Sputter Deposition of TiO_2 Thin Films**, ***Daniel Fernandes [daniel.f.fernandes@angstrom.uu.se]***, *Lars Österlund, Tomas Kubart,* Uppsala University, Angstrom Laboratory, Sweden

The growth of crystalline TiO_2 thin films by physical vapor deposition techniques typically requires a deposition temperature well above 200°C. Energetic flux of film forming species can reduce the growth temperature. To this end, the use of HiPIMS has already been proposed. Moreover, the growth in a reactive oxygen atmosphere opens the parameter space even further by introducing excited and ionized oxygen species to the process.

The goal of this study is to decouple the contributions of the deposition temperature and species generated in the reactive HiPIMS discharge to the growth of crystalline TiO_2. Deposition systems with different chamber geometries were used, where the main difference was the distance between the sputtering target and the substrate holder. The crystallinity of resulting films was investigated by conventional GIXRD and compared to pDCMS (pulsed direct current magnetron sputtering) reference processes. To evaluate the energetic input in each process, a simple heating model based on radiative heat exchange between elements at different temperatures, was implemented. Based on the measured substrate temperature evolution and assuming an effective chamber wall cooling, the steady-state temperature and the energy per deposited particle during deposition were estimated.

The film crystallinity was strongly affected by the target-to-substrate distance. All films deposited with a long distance were amorphous while short distance resulted in crystalline films. Short deposition distance resulted in pronounced heating of the growing film since the substrate is in the denser plasma. Even so, identical growth conditions resulted in a better crystalline quality for HiPIMS films. The difference in steady-state temperature does not fully justify the contrast in crystallinity, where 480 K and 464 K were estimated for HiPIMS and pDCMS, respectively. The estimated energy input per deposited Ti atom was higher for HiPIMS, predicted to be approximately 1.5 keV, while for pDCMS it was 1.25 keV. These values are considerably higher than the kinetic energy of ions generated by HiPIMS. Therefore, other energetic components to the process need to be considered to understand the mechanisms behind crystallization, e.g. the contribution of hot electrons in HiPIMS discharges.

3:20pm **PP2-2-WeA-5 Influences of Target Poisoning on the Phase, Microstructure, and Mechanical Properties of Crmonbtiwc High Entropy Alloy Carbide Thin Films Grown by a Superimposed Highpower Impulse and Medium-Frequency Magnetron Sputtering System**, ***Tse Wei Chen [gagamodo@gmail.com]***, *Chia-Lin Li,* Ming Chi University of Technology, Taiwan*; Bih Show Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan*; Jyh Wei Lee,* Ming Chi University of Technology, Taiwan

Since the high entropy alloy (HEA) materials were proposed by Prof. Yeh in 2004, they have been widely studied due to their outstanding mechanical and physical properties. HEAs refer to alloys consisting of at least five elements, with each element's content not exceeding 35 at.%. This compositional constraint prevents any single element from dominating the material's behavior, resulting in unique characteristics arising from the collective contribution of multiple elements. Compared with traditional binary or ternary alloy carbide coatings, HEA carbide coatings have superior performances, such as high hardness, good wear, and corrosion resistance. In this study, an equimolar CrMoNbTiW target was employed to deposit CrMoNbTiWC carbide thin films on 420 stainless steel, 304 stainless steel, and silicon wafer substrates via different target poisoning ratios by a superimposed highpower impulse magnetron sputtering (HiPIMS-MF) system. During the sputtering process, the CrMoNbTiW target poisoning ratios were controlled from 10% to 90% by the feedback control of acetylene gas flow ratios and the optical emission signal intensity of Cr species using a plasma emission monitoring feedback control system. The film thickness and cross-section morphologies were analyzed using field emission scanning electron microscopy and transmission electron microscopy. The crystal structure of the thin film was evaluated by X-ray diffraction.The chemical composition analysis revealed that the carbon content increased from 20.0 at.% to 88.3 at.% as the target poisoning ratio increased from 10 to 90%. The HEA carbide film exhibited an FCC phase. A maximum hardness of 25.1 GPa was obtained for the HEA carbide film containing 53.0 at.% carbon. The friction coefficient of thin film decreased with increasing carbon contents. The impact of target poisoning ratio and carbon content on the phase, microstructure, and mechanical properties of CrMoNbTiWCHEA carbon thin films were discussed in this work.

3:40pm **PP2-2-WeA-6 Novel Superimposed HiPIMS/RF Sputtering Process on a Single Magnetron**, *Mark Günter,* Melec GmbH, Germany*;* ***Caroline Adam [c.adam@physik.uni-kiel.de]***, Melec GmbH, Kiel University, Germany

Reactive sputtering of dielectric films poses significant challenges, primarily due to target poisoning, which can lead to arcing, hysteresis, and generally lower deposition rates [1]. RF (radio-frequency, 13.56 MHz) is a stable option for arc-free processes, even though the films can be porous and grow at lower rates than in DC or MF (mid-frequency) mode. HiPIMS (high power impulse magnetron sputtering) is known to deposit dense films, however the tendency for arcing is higher due to the high peak voltages [1].

To provide stable deposition conditions, a hybrid sputtering process is investigated where HiPIMS and RF are simultaneously applied to the same cathode. For this purpose, a Melec SPIK3000A HiPIMS generator is connected alongside an RF generator and a conventional matchbox to the magnetron. An additional filter (Aurion Anlagentechnik GmbH) is necessary to avoid RF reflection into the HiPIMS generator. The radio-frequency can be either applied continuously or by superposition in the on or off-time of the HiPIMS pulses. The film deposition experiments are complemented by plasma diagnostics with energy-resolved mass spectrometry [2] and so-called non-conventional diagnostics as the passive thermal probe [3].

The addition of an RF plasma provides pre-ionization for the HiPIMS pulses, yields to a faster HiPIMS current rise and allows to reduce the process pressure. This phenomenon was already investigated for the superposition of HiPIMS with DC [4] or MF [5]. During reactive sputtering of Al_2O_3 and SiO_2, the addition of RF substantially mitigates arcing, as evidenced by the resulting films, which show a remarkable decrease in droplet density. The deposition rates of the HiPIMS and RF power add up in the superimposed process achieving a higher overall deposition rate.

Proof of principle for a combination of RF and HiPIMS excitation on one magnetron has been established and opens up a new route for arc-free deposition of Al_2O_3 and other oxidic layers. Further investigations will include the influence and optimization of pulse parameters as well as the effect of the ratio between the average HiPIMS and RF power.

[1] A. Anders, J. Appl. Phys. 121, 171101 (2017).

[2] J. Benedikt et al., J. Phys. D: Appl. Phys. 45 (2012) 403001.

[3] H. Kersten et al., Thin Solid Films 377–378 (2000) 585–591.

[4] P. Vašina et al., Plasma Sources Sci. Technol. 16 (2007) 501–510.

[5] W. Diyatmika et al., Surf. Coat. Technol. 352 (2018) 680–689

4:00pm **PP2-2-WeA-7 Towards Ti-Si-C MAX-based coatings via reactive cathodic arc evaporation: Advanced Characterization and Process Optimization**, ***Arno Gitschthaler [arno.gitschthaler@tuwien.ac.at]**, Rainer Hahn,* TU Wien, Institute of Materials Science and Technology, Austria*; Jürgen Ramm, Carmen Jerg,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; Szilárd Kolozsvári, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Eleni Ntemou, Daniel Primetzhofer,* Uppsala University, Sweden*; Helmut Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

MAX phases are a unique class of nanolaminated compounds that combine properties of metals and ceramics, offering electrical and thermal conductivity alongside creep, oxidation, and corrosion resistance. Consequently, there is growing interest in synthesizing relatively phase pure MAX phase PVD coatings for a broad range of applications. However, the successful development of MAX-based coatings for next-generation technologies requires a comprehensive understanding of the relationships between the deposition processes, chemical composition and phase formation. Among the various MAX phases, the thin film synthesis of the Ti-Si-C system has been the focus of research for quite some time [1], [2]. Yet, reducing the synthesis temperature to below 650 °C remains a major challenge, as it limits compatibility with metallic substrates and therefore practical use. Regarding this issue, cathodic arc evaporation has great potential due to its elevated ionization degree.

Thus, a variety of Ti-Si-C coatings have been grown by arc evaporating metallic targets (Ti or TiSi) in reactive plasma atmospheres (Ar, SiH_4 & C_2H_2 or Ar & C_2H_2) at 550 °C in an industrial coating plant. To improve adhesion to metallic substrates and to prevent element diffusion between the coating and the substrate, a thin Ti interlayer was applied. The first challenge was the adjustment of the reactive gas flow rates in order to maintain the narrow stoichiometric window during film growth and ensure the formation of Ti-C and Si nanolayers. Final confirmation of the selected deposition approaches was provided by the precise determination of elemental composition using elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS). Subsequently, the focus was on the phase characterization of the Ti-Si-C MAX phases and its most competitive phases (*e.g.* TiC and Ti_5Si_3C) through various laboratory and synchrotron X-ray diffraction (XRD) techniques, such as BBXRD, GIXRD, HT-GIXRD and CSnanoXRD. In particular, the high energy X-rays used for transmission nanodiffraction experiments allowed accurate phase identification and provided valuable insights into preferred growth directions. Overall, it has been successfully demonstrated for the first time that Ti-Si-C MAX-based coatings can be synthesized by reactive CAE at temperatures below 650 °C.

[1] J.-P. Palmquist *et al.*, “Magnetron sputtered epitaxial single-phase Ti3SiC2 thin films,” *Appl. Phys. Lett.*, vol. 81, no. 5, pp. 835–837, Jul. 2002.

[2]J. Alami *et al.*, “High-power impulse magnetron sputtering of Ti–Si–C thin films from a Ti3SiC2 compound target,” *Thin Solid Films*, vol. 515, no. 4, pp. 1731–1736, Dec. 2006.

4:20pm **PP2-2-WeA-8 Influence of Pulse Duration on Plasma Chemistry and Thin Film Growth of Plasmonic Titanium Nitride Deposited by Constant Current Regulated HIPIMS**, ***Ethan Muir [e.muir@shu.ac.uk]**, Arutiun Ehiasarian,* Sheffield Hallam University, United Kingdom*; Ryan Bower,* Imperial College London, UK*; Yashodhan Purandare,* Sheffield Hallam University, United Kingdom

Plasmonic materials require very high temperatures to manufacture and are not available by conventional methods, this study develops a low temperature process to satisfy this demand.

Typically, plasmonic Titanium Nitride thin films produced via PVD methods are deposited at temperatures between 600-800 °C. The Titanium Nitride films produced for this study were deposited at room temperature, ensuring they are CMOS-compatible and consequently, reducing the energy consumption of the process. Titanium Nitride thin films are ideal for real-world applications, due to their high hardness and corrosive resistance, extending the lifetime of components the films are applied to. This study aims to produce films for photocatalytic applications with longer lifetimes than currently produced photocatalytic materials such as nanoparticles.

This study documents the results of an investigation into the effect of pulse duration within constant-current HIPIMS discharges, specifically investigating the effects on plasma chemistry, temporal evolution and on the changes to thin film texture of films produced from these discharges. Pulse durations ranging from 40-200µs were studied. Time-Averaged Optical Emission Spectroscopy (OES) and Time-resolved OES have been conducted on a series of discharges with different pulse durations. The data obtained from the Time-Resolved OES shows three stages that can be used to characterise the generation of the discharge: Gas Rarefaction, Pumping and Steady State. Time-resolved and Time-averaged mass spectrometry studies were also conducted which verify the data obtained via OES. There is proof of an increase in electron temperature within the discharge whilst current and voltage remain constant. Titanium Nitride films were produced from the different discharges studied to investigate the role that pulse duration and plasma chemistry plays on the texture of the produced films via x-ray diffraction (XRD). Bragg-Brentano scans and pole figures show how the crystallographic structure of the film changes with the changing pulse duration and the effects it has on the grain sizes and stress within the film on micro and macro scales. Nanohardness and toughness were measured for each of the produced samples showing how the mechanical properties of the film are affected by the pulse duration. These films optical properties have also been studied using ellipsometry to determine their real and imaginary permittivity, to assess their plasmonic capabilities within the visible spectrum.

4:40pm **PP2-2-WeA-9 Monitoring Vanadium Nitride Thin Film Deposited by Reactive Hipims: From Microstructure to Properties**, ***Julien Neyrat [julien.neyrat@safrangroup.com]**, Marjorie Cavarroc,* Safran, France*; Angeline Poulon,* CNRS, Université de Bordeaux - ICMCB, France

Among hard coatings materials, transition metal nitrides proved to be valuable candidates with excellent mechanical properties and both chemical and thermal stabilities. This study proposes to show the interest of Reactive High-Power Impulse Magnetron Sputtering (R-HiPIMS) process to produce Vanadium nitride thin films. Thanks to a high ionization degree of the sputtered metal and to high peak power densities applied to the target during few tens of microseconds pulse, deposited films are dense and homogeneous. The influence of several process parameters (target peak power density, N_2 partial pressure, total gas (Ar + N_2) pressure and pulse parameters) on film microstructure are reported. The obtained structures were investigated by X-ray diffraction (GIXRD and θ-2θ) and both scanning and transmission electron microscopy. Discharge composition and electrical characteristics according to processing parameters were studied by optical emission spectroscopy and Langmuir probe measurements. The VN obtained microstructure depends strongly on processing parameters especially pulse parameters and gas parameters which affect the incoming species energy at the substrate. The VN microstructure formation is discussed with respect to conditions promoting both adatoms mobility on the substrate surface and ionized species into the plasma. Comparison of mechanisms involved during the formation of the microstructure depending on the process parameters is presented as well as characterization of mechanical properties (mechanical and electrical) of deposited layers.

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