Thin Films Division
Room A122-123 - Session TF+SE-MoA
HiPIMS and Reactive HiPIMS for Novel Thin Films

Moderators: Joe Becker, Kurt J. Lesker Company, Megan Holtz, Cornell University

1:40pm **TF+SE-MoA-1 The Influence of the Magnetic Field on the Deposition Rate and Ionized Flux Fraction in the HiPIMS Discharge**, *H Hajihoseini,* University of Iceland, Iceland*; M Cada, Z Hubicka,* Academy of Sciences of the Czech Republic, Czech Republic*; S Unaldi,* LPGP Université Paris-Sud, France*; M Raadu, N Brenning,* KTH Royal Institute of Technology, Sweden*; **Jon Tomas Gudmundsson**,* University of Iceland, Iceland*; D Lundin,* LPGP Université Paris-Sud, France

Three different ways to quantify the degree of ionization in sputtering magnetrons are discussed [1]. Then we move on to explored the effect of the magnetic field strength |**B**| and geometry (degree of balancing) on the deposition rate and ionized flux fraction F_{flux} in dc magnetron sputtering (dcMS) and high power impulse magnetron sputtering (HiPIMS) when depositing titanium. The HiPIMS discharge was run in two different operating modes. The first one we refer to as ’fixed voltage mode’ where the cathode voltage is kept fixed at 625 V while the pulse repetition frequency is varied to achieve the desired time average power (300 W). The second mode we refer to as ’fixed peak current mode’ is carried out by adjusting the cathode voltage to maintain a fixed peak discharge current and by varying the frequency to archive the same average power. Our results indicate that the dcMS deposition rate is weakly sensitive to variations in the magnetic field while the deposition rate during HiPIMS operated in fixed voltage mode changes from 30% to 90% of the dcMS deposition rate as |**B**| decreases [2]. In contrast, when operating the HiPIMS discharge in fixed peak current mode the deposition rate increases only slightly with decreasing |**B**|. In fixed voltage mode, for weaker |**B**| the higher the deposition rate, the lower the F_{flux}. The measured quantities, the deposition rate and ionized flux fraction, are then related to the ionization probability α_t and the back attraction probability of the sputtered species β_t. We show that the fraction of the ions of the sputtered material that escape back attraction increases by 30% when |**B**| is reduced during operation in fixed peak current mode while the ionization probability of the sputtered species increases with increased discharge current when operating in fixed voltage mode.

[1] A. Butler, N. Brenning, M. A. Raadu, J. T. Gudmundsson, T. Minea and D. Lundin, *Plasma Sources Science and Technology*, **27**(10) (2018) 105005

[2] H. Hajihoseini, M. Čada, Z. Hubička, S. Unaldi, M. A. Raadu, N. Brenning, J. T. Gudmundsson and D. Lundin, *Plasma*, submitted for publication, April 2019

2:00pm **TF+SE-MoA-2 HIPIMS and Magnetron Sputtering of Niobium for use in Josephson Junctions**, ***George Major**, M Linford,* Brigham Young University

Niobium (Nb) is a technology-critical element with superconductive properties, and applications in electronics, superconductors, and particle accelerators. Thin film niobium is commonly deposited by magnetron sputtering. Properties of Nb thin films must be precisely tuned for applications, e.g., Josephson Junctions, as surface roughness, crystallite size, and apparent elastic modulus can affect superconducting film properties. To create a Josephson Junction, a thin film of Al (4 to 10 nm) is deposited on top of a smooth Nb film (ca. 100 nm). The functionality of this Al film is inversely related to its thickness. The smoother the film onto which the Al is deposited, the thinner it can be. High-power impulse magnetron sputtering (HIPIMS) is an emerging method for physically depositing thin films. HIPIMS produces a high degree of ionization of sputtered material and a high rate of molecular gas dissociation, which results in high density films. Various metals, including Ti and Ta, have been successfully deposited by HIPIMS, showing dense, smooth microstructures free of large-scale defects. Here, Nb thin films are deposited using magnetron sputtering and HIPIMS. These films are characterized by AFM, TEM, XPS, and SEM. Ellipsometry is used to study their optical properties and to determine their optical constants. HIPIMS should result in lower surface roughness compared to magnetron sputtering. The resulting films will lead to improved superconductive devices.

2:20pm **TF+SE-MoA-3 Thin Film Crystal Growth of Oxides, Nitrides and Carbindes using High Impulse Magnetron Sputtering**, ***Jon-Paul Maria**,* The Pennsylvania State University **INVITED**

This presentation will discuss thin film crystal growth using reactive pulsed magnetron sputtering specifically in the region referred to as high power impulse magnetron sputtering, or HIPIMS. HIPIMS is characterized by duty cycles less than approximately 10%, and magnetron power densities in excess of 1 kW/cm^2. These intense impulses produce high ionization fractions of both the gas and sputtered species, they can be sustained in atmospheres containing substantial fractions of O_2 or N_2 with only modest re-sputtering, and they can be tuned so as to minimize target poisoning. Pulsed dc plasmas have been applied routinely to promote thin film adhesion, to achieve high deposition rates, and to produce extremely hard and wear resistant coatings. Their introduction to electronic materials has been much less rapid.

The intent of this presentation is to demonstrate the utility of pulsed dc plasmas, and specifically the HIPIMS regime, for electronic materials, including oxides, nitrides and carbides which require reactive environments that can in many cases can be challenging to realize. Three case studies will be presented: 1) epitaxial growth of CdO thin films for IR optoelectronic applications, 2) epitaxial growth of GaN thin films for wide bandgap applications, and 3) entropy-stabilized carbides for extreme environments. The basic instrumentation of this interesting plasma method will be discussed, and how it offers advantages for controlling defect chemistry, and this transport properties, in CdO, for enabling epitaxy at surprisingly low temperatures in GaN, with excellent control of surface morphology, and for achieving high carbon content in rocksalt carbides, and thus high hardness. In all cases the specific connections between plasma parameters, temperature, pressure, growth mode, and ultimately physical properties will be stressed. The intent is to demonstrate how this less-well explored region of plasma processing space offers possible advantages to crystal growth of electronic materials of contemporary interest.

3:00pm **TF+SE-MoA-5 Reactive Bipolar High Power Impulse Magnetron Sputtering (B-HiPIMS) for Deposition of High Entropy Carbides**, ***Trent Borman**, M Hossain, J Maria,* The Pennsylvania State University

Sputtered carbide thin films frequently feature significant carbon sub-stoichiometry irrespective of the source materials, while amorphous-C or a-C:H secondary phases begin to precipitate with as many as 1/3 or more of the carbon sites vacant in the rock salt structure. In reactive sputtering it is often necessary to sputter in the compound regime in order to achieve a higher carbon stoichiometry, however this comes with the penalty of reduced sputter yield. Reactive HiPIMS can avoid carburization of the target through gas rarefaction and high target etch rates. While this is beneficial for process stability, carbide microstructural evolution is still limited by the low homologous temperature achievable in thin film deposition (0.25-0.3T_{melt}). Recently, bipolar-HiPIMS has been discussed as a means of tailoring the bombardment in order to drive microstructural development through momentum transfer and thermalization of kinetic energy.

The authors will discuss the reactive synthesis of high entropy carbide films from metal alloy targets using Bipolar High-Power Impulse Magnetron Sputtering (B-HiPIMS) in a mixed Ar/CH_4 atmosphere. The effects of bipolar pulse voltages and lengths on microstructural, compositional, and phase development will be discussed. Additionally, the impacts of order of magnitude changes in sputter pulse length on the formation of carbide thin films will be reported. This work investigates a broad range of carbon stoichiometries: from metallic films and carbon deficient carbides to near stoichiometric carbides and carbide/amorphous-carbon nanocomposites. This enables investigation of the property trends as a function of carbon content, as it is presently unclear if the diverse trends observed in the binary carbides persist in a high entropy system or are overshadowed by the high entropy metal sublattice.

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3:20pm **TF+SE-MoA-6 High Density Titanium Oxide and Silicon Oxide Films Deposited by Current-Controlled High Power Impulse Magnetron Sputtering**, ***Arutiun P. Ehiasarian**, P Hovsepian, D Loch,* Sheffield Hallam University, UK

High density transparent oxide layers on glass can improve the environmental viability of photovoltaics, displays, and low emissivity layers in glazing as well as aid the photocatalytic deactivation of organic contaminants. High Power Impulse Magnetron Sputtering (HIPIMS) produces high density microstructures and high hardness due to the delivery of an ionised metal and dissociated oxygen deposition flux to the substrates.

TiOx and SiOx films were produced in a cluster tool by reactive HIPIMS of a pair of metallic targets in an Ar-Oxygen atmosphere. The HIPIMS process was carried out by controlling the current within the pulse. This resulted in the elimination of stability issues associated with runaway currents for all target poisoning states from metallic to fully poisoned. TiOx was deposited by a fast plasma ignition and a constant current during pulses of up to 200 microseconds. Electron cooling and gas rarefaction were observed sequentially during the initial stages if the pulse. These were followed by a steady increase in metal ion emission at constant power input. SiOx was deposited using a current ramp and shorter pulses of up to 20 microseconds and a bipolar operation. In the transition mode oxygen was emitted mainly from the target whilst in the filly poisoned mode it was detected in the gas phase by time-resolved optical emission spectroscopy. TiOx films deposited without additional heating or substrate biasing had good transparency and a refractive index which increased continuously as the oxygen flow reduced from 45 to 13% reaching a maximum value of 2.55 at a wavelength of 550 nm. The films comprised a mixture of rutile and anatase phase with HIPIMS deposition producing higher fractions of rutile compared to bipolar pulsed DC operation. The HIPIMS films reached higher refractive index of 2.55 compared to 2.47 for bipolar pulsed DC. The hardness of the films and its relation to process conditions are discussed. The morphological density was extremely high as confirmed by a 2 orders of magnitude reduction in corrosion current in potentiodynamic polarisation tests on 304 stainless steel substrates. SiOx microstructural density, refractive index and hardness are discussed.

4:00pm **TF+SE-MoA-8 Epitaxial Growth and Surface Morphology of Thin Film GaN via HiPIMS**, ***Kevin Ferri****, E Runnerstrom,* Pennsylvania State University*; A Klump, Z Sitar, R Collazo,* North Carolina State University*; J Maria,* The Pennsylvania State University

GaN is a desirable wide bandgap semiconductor for applications as blue and UV emitters as well as high temperature, high power, and high frequency electronic devices. In order to overcome the low reactivity of gallium with nitrogen at low temperatures, thin film GaN deposition techniques such as Metal Organic Chemical Vapor Deposition often use high pressure growth at temperatures in excess of 1000 °C. While higher temperatures allow for high crystal quality thin film GaN with favorable morphology, this presents challenges to abrupt junction formation due to fast diffusion rates that cause dopant migration during deposition. It is thus advantageous to find avenues to lower the deposition temperature for GaN to a region where controlled doping can occur. While doing so, it is imperative to maintain epitaxy and growth morphology for device fabrication.

In this presentation, we demonstrate that reactive High-Power Impulse Magnetron Sputtering (HiPIMS) is an effective low temperature alternative for depositing high quality, epitaxial GaN thin films. In contrast to conventional direct current (DC) or radio frequency (RF) sputtering, pulsed DC provides the needed kinetic energy and ionization fraction to establish a sufficiently reactive environment to promote full nitridation. This can be challenging with many other Ga sources. More specifically, the low duty cycle regime of pulsed DC known as HiPIMS provides access to kW/cm^2 peak power densities without target degradation and thus dramatically increased gallium reactivity. In addition, adding an opposite polarity voltage pulse between the target bombarding events, known as a kick pulses, further allows one to tailor both the adatom landing energy on the substrate surface, and mitigate target poisoning.

This unique capability set enables us to prepare high crystal quality epitaxial GaN thin films with smooth surface morphologies characterized by c/2 steps and terraces at temperatures below 500 °C. The presentation will focus on the relationships between sputtering parameters including voltage, kick pulse, pulse length, and duty cycle, on GaN thin film crystal quality, surface morphology, and growth rate. Preliminary transport properties will be reported.

4:20pm **TF+SE-MoA-9 Reactive HiPIMS Deposition of a Thick Cu:CuCNx Multilayered Nano-composite Coating Material for Improving Machining Process Performance in Rough Turning**, ***Md.Masud-Ur Rashid****, C Nicolescu,* KTH Royal Institute of Technology, Plasmatrix Materials AB, Sweden*; A Archenti,* KTH Royal Institute of Technology, Sweden*; G Shuai,* KTH Royal Institute of Technology*; R Tomkowski,* KTH Royal Institute of Technology, Sweden

Vibrations in metal cutting process such as turning have detrimental effect on productivity, finished surface roughness of workpiece and cutting insert life. During machining process high frequency vibration (equal to or above 10000 Hz) causes micro cracks to the cutting insert, which facilitate the failure of cutting insert and consequently resulted in higher roughness on workpiece surface. In this study a reactive high power impulse magnetron sputtering (R-HiPIMS) deposition process was used to deposit a thick copper and copper-carbon nitride (Cu:CuCNx) multilayered nano-structured composite coating, with higher stiffness and damping properties, on the shim. This coated shim was then used to suppress the high frequency vibration during rough turning operation. Scanning electron microscopy (SEM) of the coating cross section as well as energy dispersive x-ray spectroscopy (EDS) mapping of the cross-section confirms the multilayered structure with the presence of different rations of copper (Cu), carbon (C), and nitrogen (N). The Cu:CNx coating thickness was measured to be approximately 100 µm. The average surface hardness (SH) and cross-sectional hardness (CSH), measured by Vickers-microhardness indention, were found to be 353.2 HV and 149.5 HV respectively. Insert wear measurement after 30 minutes of rough turning process, reveals that the studied 100 µm Cu:CuCNx multi-layered composite coating material can reduce the tool wear by 60.5%. The average roughness value (Ra) of the work piece material is also reduced by 8.76% in case of using Cu:CNx coated shim comparing to conventional shim.

4:40pm **TF+SE-MoA-10 The Residual Stress Control in Hard Metal Films by Energetic Deposition**, ***Y.G. Li****, Y Qu, Z Jiang, M Lei,* Dalian University of Technology, China

For energetic deposition, ion bombardment was an important factor independent of grain size for influencing the residual stress, and the energy and flux were critical parameters to determine the residual stress evolution. In this work, modulated pulsed power magnetron sputtering (MPPMS) and deep oscillation magnetron sputtering (DOMS) were employed to control the energy and flux with or without bias to modulate the ion bombardment for intrinsic stress generation. The films thickness was selected at 0.2, 0.5, 1.5 and 3.0 µm to give a comparative study of the intrinsic stress, and thermal stress was not considered since the effect of thermal stress made no major influences. It was found that the thin films all showed compressive residual stress with thickness under 1 µm, and the residual stress of Cr thin film was lower than that of the Nb thin film under similar thickness. The residual stress of DOMS Nb thin film was always higher than MPPMS Nb thin film, however the residual stress of DOMS Cr thin film was equivalent to MPPMS Cr thin film. The ion irradiation effect should be the dominating effect responsible for the difference between Nb and Cr thin films, since Nb generated more Nb^{2+} ions than Cr in energetic deposition. For Cr thin films, the grain size and deposition rate were also important influencing factors, fine grain size and high deposition rate promoted the formation of compressive residual stress. For energy deposition, the effect of secondly charged ions in the film growing front should be concentrated to establish a proper kinetic model for intrinsic stress generation.

5:00pm **TF+SE-MoA-11 Advanced HIPIMS Coatings Through Kick Pulse Technology**, ***Jason Hrebik****,* Kurt J. Lesker Company

HIPIMS coating technology has been rapidly growing over the past few years due to the availability of R&D scale supply offerings. This has resulted in many new breakthroughs in application enhancement, production scalability, and efficiency. The number of applications where HIPIMS is now considered is also advancing. Breakthroughs in HIPIMS controllability have enabled researchers to find a variety of ideal operating parameter sets for various performance requirements. One of the most significant technical advances is a reverse positive kick pulse. This option provides a significant variable for driving out film stress in HIPIMS applications and increasing yield rates, which have been a major downside to HIPIMS in the past. These advances open up new possibilities for the technology and the enhancement of many thin film applications. This presentation will highlight examples of these applications along with the advantages associated with HIPIMS and the Kick pulse technology. It will show how these advances can be scaled to larger scale production applications and provide examples of what enhancements can be expected.

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