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

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Prof. Jon Tomas Gudmundsson, University of Iceland, **Dr. Tiberiu Minea**, Université Paris-Saclay, France

2:00pm **B8-1-WeA-1 Impact of Selective Acceleration of High-mass Ions - Low Temperature Growth of Stress-free Single Phase α-W Films**, ***Tetsuhide Shimizu,*** Tokyo Metropolitan University, Japan*; H. Du,* Guizhou University, China*; R. Boyd, R. Viloan, D. Lundin,* Linköping University, IFM, Sweden*; M. Yang,* Tokyo Metropolitan University, Japan*; U. Helmersson,* Linköping University, IFM, Sweden **INVITED**

Efficient metal-ion-irradiation during film growth with the concurrent reduction of gas-ion-irradiation, are realized for high-power impulse magnetron sputtering (HiPIMS) by the use of a synchronized, but delayed, pulsed substrate bias. In this way, the growth of stress-free, single phase α-W thin films is demonstrated without additional substrate heating or post-annealing. By synchronizing the pulsed substrate bias to the metal-ion rich portion of the discharge, tungsten films with a <110> oriented crystal texture are obtained as compared to <111> orientation obtained using a continuous substrate bias. At the same time, a reduction of Ar incorporation in the films are observed, resulting in the decrease of compressive film stress from σ = 1.80 to 1.43 GPa when switching from continuous to synchronized bias. This trend is further enhanced by the increase of the synchronized bias voltage, whereby a much lower compressive stress σ = 0.71 GPa is obtained at *U*s = 200 V. In addition, switching the inert gas from Ar to Kr has led to fully relaxed, low tensile stress (0.03 GPa) tungsten films with no measurable concentration of trapped gas atoms. Room-temperature electrical resistivity is correlated to the microstructural properties, showing lower resistivities for higher *U*s and having the lowest resistivity (14.2 μΩcm) for the Kr sputtered tungsten films. Moreover, we showed a very low resistivity of 13.9 μΩcm at an ultra-thin thickness of ~10 nm grown on SiO_2 without substrate heating or post annealing. The realization of self-ion-irradiation by accelerated W^+ ions in HiPIMS discharge has an important role at the growth phase of nucleation and island growth, and consequently to the development of larger grains. These results illustrate the clear benefit of utilizing selective metal-ion-irradiation during film growth as an effective pathway to lead grain growth and to minimize the compressive stress induced by high-energetic gas ions/neutrals during low temperature growth of high melting temperature materials.

2:40pm **B8-1-WeA-3 Modeling of High Power Impulse Magnetron Sputtering Discharges with Tungsten Target**, ***Swetha Suresh Babu,*** University of Iceland*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; D. Lundin,* Linköping University, Sweden*; T. Shimizu,* Tokyo Metropolitan University, Japan*; J. Fischer,* Linköping University, Sweden*; J. Bradley,* University of Liverpool, UK*; J. Gudmundsson,* University of Iceland

The ionization region model (IRM) is applied to model a high power impulse magnetron sputtering discharge with a tungsten target. The IRM gives the temporal variation of the various species and the average electron energy, as well as internal discharge parameters such as the ionization probability and the back-attraction probability of the sputtered species. In the initial stage of the pulse argon ions dominate the discharge until the tungsten ions take over remain as the dominating ions to the end of the pulse. We demonstrate how the contribution of the W^+ ions to the total discharge current at the target surface increases with increased discharge voltage for peak discharge current densities $J_{D,peak}$ in the range 0.33 - 0.73 A cm^2 [1]. For the sputtered tungsten the ionization probability increases, while the back-attraction probability decreases with increasing discharge voltage. Furthermore, we discuss the findings in terms of the generalized recycling model and compare to experimentally determined deposition rates and find good agreement. The IRM is then validated against experimental determination of particle densities and electron temperature by comparison to the temporal evolution of the electron density and the electron temperature determined by Thomson scattering measurements and the temporal evolution of the relative neutral and ion densities determined by optical emission spectrometry.

[1] S. S. Babu et al. Plasma Sources Sci. Technol. 31 (2022) 065009

3:00pm **B8-1-WeA-4 Combinatorial Deposition of Highly Oriented AlScN Films Using Synchronized-HiPIMS for Piezoelectric Applications**, ***Jyotish Patidar,*** *S. Zhuk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; M. Ghosh, A. Wieczorek, K. Thorwarth, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Piezoelectric micro-electro-mechanical systems (MEMS) are one of the building blocks of modern electronics and are used in many applications such as RF filters, resonators, and sensors. AlN has been one of the standard materials for such applications due to its high-temperature stability and linear frequency response. Significant improvements in the piezoelectric response can be achieved by isovalent alloying of AlN with Sc.[1] The heterostructural nature of the alloy system, however, leads to low miscibility and a high degree of structural frustration for high Sc concentrations, and thus decreased texture of the films.

In this work, we present the utilization of synchronized-HiPIMS along with a combinatorial deposition approach to deposit highly oriented AlScN films. The combinatorial deposition approach discussed here is based on the co-sputtering of Al and Sc in a reactive environment and provides us an opportunity to probe the properties of films with different Sc contents and temperatures in fewer depositions.[2] The synchronization of substrate bias with the metal-ion-rich part of the sputter plasma is done. This effectively reduces Ar-ion incorporation and consequently helps in the growth of textured films at lower deposition temperatures.[3]

The combinatorial libraries of AlScN are deposited with different biasing conditions, essentially changing the kinetic energy of oncoming species. The solubility limit of Sc in AlN is demonstrated to change with varying bias conditions and deposition temperatures. The improvement in the texture of the films and its correlation with stress is investigated. In addition, the influence of closed-field and open-field plasma (obtained by changing the magnetic configuration of sputter guns in the chamber) is discussed in tailoring the phase, structure, and stress in the films. The combinatorial libraries are fully characterized with respect to their phase constitution, structure, composition, stress, and piezoelectric coefficients using state-of-the-art techniques. Selected libraries are mapped for d_{33} values on doubly-polished Si wafers.

A successful deposition of textured AlScN film using synchronized HiPIMS will enable the deposition on structured as well as temperature-sensitive substrates which would be beneficial for a variety of exciting applications.

[1] Akiyama, Morito, et al. *Advanced Materials***2009,** 21 (5), 593-596.

[2] Talley, Kevin R., et al. *Physical Review Materials***2018**, 2 (6), 063802.

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

3:20pm **B8-1-WeA-5 Fabrication of TiZrNbTaFeBN Coatings Using Superimposed HiPIMS-MF Systems: Mechanical and Chemical Properties Evaluation**, *I. Moirangthem, S. Chen, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*;* ***Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

Equimolar high entropy alloys and their coatings have shown improved chemical and mechanical properties as compared to the conventional alloys and their coatings. Various combinations of transition-elements in equimolar ratios and their nitrides have been explored recently in search of alloys with excellent mechanical and chemical properties. In this study, oneTiZrNbTaFeN and six TiZrNbTaFeBN high entropy nitride coatings were deposited on p-type Si (100), AISI 304 and AISI 420 stainless steel substrates by utilizing a superimposed HiPIMS-MF power system for the equimolar TiZrNbTaFe alloy target and a radio frequency (RF) power source for the boron target. The RF power of the boron target was varied from 125 W to 900 W to control the boron content while the nitrogen flow rate was maintained at a constant. The microstructures, phases and surface roughness of the alloy coatings were investigated by a field emission scanning electron microscope, X-ray diffractometer and atomic force microscope, respectively. The hardness and fracture toughness were measured using nanoindentation test and microhardness test. A pin-on-disk tribometer was used to study the wear characteristic of the alloy coatings. The effect of heat treatment, oxidation and potentiodynamic polarization of the coatings were also examined. The mechanical and chemical properties of TiZrNbTaFeBN high entropy alloy coatings were explored in this work.

3:40pm **B8-1-WeA-6 Effect of Synchronous Bias Mode with Different Duty Cycles on Microstructure and Mechanical Properties of AlTiN Coatings Deposited by HiPIMS Process**, *J. Tang,* Department of Electronic Engineering, Lunghwa University of Science and Technology, Taiwan; *S. Huang,* ***I-Hong Chen****, G. Shen,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan; *F. Yang,* Department of Materials Engineering, Ming Chi University, Taiwan; *C. Chang,* Department of Materials Engineering,Center for Plasma and Thin Film Technologies, Ming Chi University, Taiwan

In the present work, we evaluated the synthesis of AlTiN coatings through HiPIMS with variable duty cycle (3%, 6%, 12%, 18%) under synchronous pulse-DC (SP-DC) bias and with trigger delay 50 ms bias (TD50). The influence of these processing conditions on the microstructure and mechanical properties of AlTiN was investigated. FE-SEM analysis results showed a highest deposition rate of 22.1 nm/min when TD50 with 3% duty cycle. The results of EPMA and XRD show that when the Al/Ti ratio x is between 0.71 to 0.74, the h-AlN structure will be generated. The results of TEM and nanoindenter analysis show that the DC bias transforms into synchronous bias boosting the bias output time (increasing duty cycle) will refine the AlTiN grains from about 150 to 20 nm, increasing the hardness from 22.7 to 24.7 GPa.Meanwhile, the residual stress of AlTiN thin film increased from 0.2 to -1.51 GPa, and obtain a higher adhesion strength 54.8 N on synchronous bias with 6% duty cycle condition. Therefore, the both duty cycle and trigger delay under synchronous pulse-DC bias also can as an important function of HiPiMS process parameter.

Keywords: synchronous bias, duty cycle, high-power impulse magnetron sputtering, AlTiN coating

4:00pm **B8-1-WeA-7 Bipolar HiPIMS: A New Route to Deposit Advanced Coatings on 3D Complex Geometries**, *I. Fernandez, J. Santiago-Varela, P. Diaz-Rodriguez,* NANO4ENERGY SLNE, Spain; *L. Mendizabal, C. Zubizarreta,* IK4 TEKNIKER, Spain; ***Ambiörn Wennberg****,* NANO4ENERGY, Spain

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 [1]. 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.

This paper shows experimental results for the deposition of uniform coatings solutions on 3D complex geometry components used different application sectors: cutting tools and punches for aerospace and medical industry, plastic injection moulding for packaging or Through Substrate Vias (either Silicon or Glass) in electronic engineering for high performance interconnection in 3D integrated circuits.

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

4:20pm **B8-1-WeA-8 On the Control of the Composition of NbC Films Deposited by HiPIMS from a Compound Target: Plasma Diagnostics**, ***Tomáš Kozák****, M. Farahani, A. Pajdarová,* University of West Bohemia, Czechia; *A. Bahr, R. Hahn, H. Riedl,* TU Wien, Austria; *P. Zeman,* University of West Bohemia, Czechia

Transition metal carbides are refractory materials possessing extremely high melting temperatures, outstanding mechanical strength, excellent electrical conductivity, and good chemical stability. Non-reactive high-power impulse magnetron sputtering (HiPIMS) of NbC films from a single compound target is an attractive deposition method because of its simplicity and scalability. The film composition (C/Nb ratio), microstructure and, consequently, mechanical properties, can be controlled by varying the power density in the pulse [1].

This presentation focuses on explaining the observed change in the composition ranging from C-rich films to stoichiometric NbC films corresponding to an increase in the pulse-averaged power density (realized by shortening the pulse length) [1]. The Nb and C atoms sputtered from the target are under the influence of multiple processes that together affect their transport towards the substrate (including the sputtering rate and angular distribution, scattering off the process gas atoms, ionization in the high-density plasma and return of ions onto the target or loss of ions to chamber walls). These processes are expected to be manifested differently for Nb and C, due to their disparate elemental properties, such as atomic mass and ionization potential.

To untangle the influence of the above-mentioned plasma processes on the C/Nb ratio in the films, Nb^+ and C^+ fluxes at the substrate position were measured by energy-resolved mass spectroscopy and trends in the ratios of Nb and C neutral and ion species at various positions in the discharge were monitored by optical emission spectroscopy. These experimental results are supported by a theoretical analysis of the target composition and of the transport of plasma species in the discharge, employing a pathway discharge model and particle-based simulations. The aim of this presentation is to provide a general understanding applicable to magnetron sputtering of various multi-component targets.

[1] A. Bahr, T. Glechner, T. Wojcik, A. Kirnbauer, M. Sauer, A. Foelske, O. Hunold, J. Ramm, S. Kolozsvári, E. Ntemou, E. Pitthan, D. Primetzhofer, H. Riedl, R. Hahn, Non-reactive HiPIMS deposition of NbCx thin films: Effect of the target power density on structure-mechanical properties, *Surf. Coat. Technol.***444** (2022) 128674.

4:40pm **B8-1-WeA-9 Comparative Study of DC and HIPIMS Discharge Characteristics of Cylindrical Magnetron in Open and Confined Space**, ***Wojciech Trzewiczyński****, A. Oniszczuk, W. Gajewski,* Trumpf Huettinger Sp. z o.o., Poland; *M. Betiuk, A. Mirońska,* Łukasiewicz Research Network – The Institute of Precision Mechanics, Poland

This paper discusses discharge characteristics of a Cr cylindrical magnetron with multi-toroidal plasma geometry in Ar atmosphere. This particular shape of the magnetron enables applications of coatings on surfaces previously inaccessible to magnetron sputtering - in confined spaces, such as: the interiors of pipes or barrels. Direct current magnetron discharge sources are often characterized by current-voltage characteristics of the form $I \propto V^q$. It has been suggested that the exponent q provides an index to the effectiveness of the magnetic electron confinement in a magnetron discharge[1]. An application of a magnetron in a confined space can significantly influence the magnetic field and thus the electron confinement. Therefore, we have examined the I-V characteristics of DC, pulsed DC and HIPIMS discharge of Cr cylindrical magnetron with multi-toroidal plasma geometry in Ar atmosphere in open and confined space realized by a A570 Gr. 36 steel pipe. The q parameter of the exponential function Id (Ud) describing current-voltage waveforms was determined. The study confirms that the type of discharge and magnetron surroundings significantly affects the value of q.

[1] G. Y. Yeom and John A. Thornton; Journal of Applied Physics 65, 3816 (1989)

5:00pm **B8-1-WeA-10 A Hybrid Plasma Model for Cr Thin Films Deposition by Deep Oscillation Magnetron Sputtering**, *J. Gao,* Dalian University of Technology, China; *F. Ferreira,* University of Coimbra, Portugal; ***M.K. Lei****,* Dalian University of Technology, China

A time-dependent hybrid plasma model composed of a zero-dimensional global model and a two-dimensional fluid model is proposed for the simulation of plasma chemistry and transportation during the Cr thin films deposition by deep oscillation magnetron sputtering (DOMS). The global model deals with the plasma reactions in the ionization region near the target with the discharge voltage and current waveforms as an input. The metal discharge mechanisms in DOMS is investigated based on the temporal plasma characteristics. The DOMS plasma possesses a characteristic of alternating gas/metal discharge in the time domain. The discharge transits from gas dominated to metal dominated at charging voltage from 360 V to 400 V. At charging voltage higher than 360 V, the metal self-sputtering comes into the runaway regime temporarily as indicated by the self-sputtering parameters exceeding unity, generating the dense and metal-rich plasma. The output of the global model is then connected to the 2D fluid model as a boundary condition to simulate the high-density plasma transportation in the diffusion region through the entire macropulse period. The fluxes of film-forming species including neutral metal atoms and metal ions as well as the energy transferred to the growing films are calculated in the fluid model. The DOMS deposition rate loss and microstructure transformation of the deposited thin films are explained by the calculation results according to the structure zone diagram. The decreased grain size and elevated nano-hardness of the deposited Cr thin films are attributed to the structure transition from zone I to zone T due to the efficient metal ion bombardment to growing thin films as the charging voltage increases.

5:20pm **B8-1-WeA-11 Optimization of Si Addition on AlTiN and AltiCrN Coatings Synthesized by Hipims for the Stability of the Mechanical and Thermal Properties and Development of a Multilayer Architecture Coating**, ***Patrick Choquet***, Luxembourg Institute of Science and Technology (LIST), Luxembourg

Influence of different concentrations of Si into AlTiN and AlTiCrN coatings and multilayer architecture deposited by HIPIMS is discussed in two sections. The first one reports on the crystallographic phase stability investigations done by XRD, the microstructural TEM observations and the micromechanical studies to understand the role of the Si addition on these two nitride coatings. It was noticed that the Full Width at Half Maxima (FWHM) that can be correlated to the coating grain size, increases with Si addition for AlTiSiN coatings but not in the case of AlTiCrSiN coatings. The instrumented value for the wear resistance of these strain-hardened nitride coatings (Hardness/Young's Modulus ratio) was estimated to 0.09 for both coatings independently of the Si content and compared to the multilayer coating. The second discusses the investigations on the oxidation mechanisms and the kinetics of the oxide growth at 950 °C for various durations, mainly through a detailed description of the oxide layers by combining the investigations of X-ray Diffraction, Transmission Electron Microscopy, Dynamic Secondary Ion Mass Spectrometry and the Atom Probe Tomography of the different coatings. Thank to isotopic oxidation tests with sequential time duration $^{16}O/^{18}O$ and SIMS depth profile analyses, the rule of cationic diffusion process and the growth mechanism for each oxide scales have been proposed to explain the oxidation kinetics. Concerning the thermal resistance of the AlTiN coating at 950 °C, the introduction of Si below 5 at.% has largely increase the oxidation set point, from 800 °C to 950 °C (or even highest). The oxidation study for AlTiCrSiN coating has reported a different oxide scale morphology, a pure TiO_2-rutile nearer the surface, followed by the Al-rich oxide, then mixed oxide region of $(AlCr)_2O_3$ with small islands of TiO_2 and an amorphous SiN_x surrounding the different oxide. A regular oxidation kinetic has been recorded for the AlTiCrSiN coating and no influence of the addition of Si has been recorded. For the moderate Si contents, thanks to an optimization of nanoscale thicknesses, a multilayer TiAlSiN/TiAlCrSiN coating architecture can inhibit the formation of TiO_2 top-layer and also promotes the formation of Al-rich protective oxide layer.

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