

Plasma and Vapor Deposition Processes

Room Town & Country A - Session PP1-2-MoA

PVD Coatings and Technologies II

Moderators: Christian Kalscheuer, IOT, RWTH Aachen, Qi Yang, National Research Council of Canada

1:40pm **PP1-2-MoA-1 From PVD to CVD to ALD - Changes in Demand for Semiconductor Interconnect Metals**, *Estrelita (Lita) Shon-Roy*, TECHCET, USA

PVD Technology has been used for more than 50 years as a method to deposit interconnect metal in semiconductor device technology, however this has changed dramatically as device technology has driven chip manufacturing processes toward CVD and now ALD technology. Lita Shon-Roy will present the current and future outlook on metallization used for semiconductor device production and the key technical and market drivers behind the increasing use of CVD and ALD technology for chip process development. As an expert in materials markets and trends, Shon-Roy will discuss market drivers alongside technical challenges leading to the development of new/different metal precursor materials.

2:00pm **PP1-2-MoA-2 Material-Dependent Loss in Deposition Rate of High Power Impulse Magnetron Sputtering Discharges**, *Martin Rudolph*, Leibniz Inst. of Surface Eng. (IOM), Germany; *Kateryna Barynova*, University of Iceland; *Nils Brenning*, KTH Stockholm, Sweden; *Swetha S. Babu*, University of Iceland; *Joel Fischer*, *Daniel Lundin*, Linköping University, Sweden; *Michael A. Raadu*, KTH Stockholm, Sweden; *Jon Tomas Gudmundsson*, University of Iceland, Sweden

High power impulse magnetron sputtering is an ionized physical vapor deposition technique in which the sputtered metal flux from the target is partially ionized. This enhances film properties like density and adhesion. At the same time, some of the produced metal ions are back-attracted to the target and therefore lost from the deposition process. We show that this loss in deposition rate is largely dependent on the sputter yield of the target material. Here, two extremes can be distinguished: 1) Discharges with low sputter yield targets are dominated by argon, and 2) discharges with high sputter yield targets are metal-rich. In the first case, the electron temperature must be significantly higher to enable sufficient ionization of predominantly the working gas to generate the experimentally observed high discharge currents. In those discharges we find strong electron energization by Ohmic heating in the ionization region extending beyond the cathode sheath. In the second case, we find that Ohmic heating is considerably weaker compared to the low sputter yield discharges. At the same time, frequent collisions with metal atom cool the electron population, which leads to a decrease in electron temperature. By examining a range of different target materials using the Ionization Region Model (IRM) we find a consistent trend of decreasing back-attraction probability and electron temperature as the sputter yield of the target material increases. A lower electron temperature increases the mean free path of ionization of sputtered species, shifting the average location of ionization away from the target. The much weaker electric fields at those locations compared to the target vicinity, ultimately facilitates ion escape toward the substrate, which thus explains the observed reduction in back-attraction.

2:20pm **PP1-2-MoA-3 Effect of Acetylene Gas Flow Rates on Target Poisoning, Phase Composition, Microstructure, Mechanical Properties and Corrosion Resistance of AlCrNbSiTiC High Entropy Alloy Carbide Thin Films**, *Hsiang Yu Tsai*, *Yung Chin Yang*, National Taipei University of Technology, Taiwan; *Chia Lin Li*, Ming Chi University of Technology, Taiwan; *Bih Show Lou*, Chang Gung University, Taiwan; *Jyh Wei Lee*, Ming Chi University of Technology, Taiwan

High entropy alloy carbide (HEAC) differs from conventional carbides, which are typically composed of one or two metallic elements. HEAC demonstrates remarkable properties, including an extremely high melting point, enhanced hardness, and superior wear resistance. In this study, AlCrNbSiTiC HEAC thin films with varying carbon contents were deposited using a superimposed high power impulse magnetron sputtering (HiPIMS) and medium-frequency (MF) sputtering technique by a plasma emission monitoring (PEM) feedback control system. The optical emission signal of Cr element was monitored under different argon/acetylene gas flow ratios and the target poisoning effect was studied by the PEM system. The cross-sectional morphology, chemical compositions, and crystal structure of the films were characterized using field emission scanning electron microscopy

(FE-SEM), FE-electron probe microanalyzer (FE-EPMA), and X-ray diffraction (XRD), respectively. The mechanical properties of the HEAC thin films, including hardness, elastic modulus, adhesion, and wear resistance, were evaluated using nanoindentation, scratch testing, and pin-on-disk wear testing. The corrosion resistance of HEAC films in the 0.5M sulfuric acid aqueous solution was explored. This study systematically investigated the influence of target poisoning ratios and carbon content on the phase composition, microstructure, mechanical properties, and corrosion resistance of AlCrNbSiTiC HEAC thin films. Potential applications of these HEACs films were also proposed in this work.

2:40pm **PP1-2-MoA-4 Duplex Coating Process by Plasma Enhanced Magnetron Sputtering**, *Jianliang Lin*, Southwest Research Institute, USA

Metallic substrates can be treated by a combination of nitriding and subsequent deposition of a physical vapor deposition (PVD) coating to improve coating adhesion, wear/abrasion resistance, and corrosion resistance. The combination of the two processes is known as duplex treatment. In general, conventional nitriding treatment and PVD coating deposition are typically performed as two separate processes in distinct facilities and environments. Consequently, the lead time and production cost are not optimized. We present a duplex coating process by integrating plasma nitriding and magnetron sputtering using hot filament assisted and plasma enhanced magnetron sputtering (PEMS) within the same facility. In the process, a global nitrogen plasma is generated by impact ionization from electrons emitted from the hot filaments and attracted towards the substrate surface for nitriding. In this study, the effects of the PEMS process on the structure and properties of the nitrided stainless steel have been studied. The PEMS treated stainless steel exhibited greatly improved surface hardness, wear resistance, and hydrophobicity in oil formula. In addition, duplex TiSiCN and DLC coatings deposited using the integrated process showed improved mechanical properties and adhesion as compared to the coatings deposited without the duplex treatment.

3:00pm **PP1-2-MoA-5 Influence of Post-Heat Treatment on Structural, Photocatalytic, Dielectric, and Tribological Properties of TiO₂/Al/TiO₂ Multilayer Thin Films**, *Anand Joshi*, *Mahendra Singh Rathore*, *Unnati Joshi*, Parul University, India

The purpose of this study was to evaluate the impact that post-heat treatment has on the structural, physical, photo-catalytic, and dielectric properties of multilayer structures of thin films composed of TiO₂/Al/TiO₂. Radiofrequency (RF) magnetron sputtering and direct current (DC) magnetron sputtering were used to deposit a multilayer of titanium dioxide and aluminum on glass and silicon substrates at room temperature. The flow rate of argon gas was kept constant. After that, the films that had been deposited were annealed in air for three hours at temperatures ranging from 200 degrees Celsius to 500 degrees Celsius. After that, samples that had been deposited and annealed were characterised by employing techniques such as X-ray diffractometer, scanning electron microscopy (SEM), and atomic force microscopy. The purpose of these techniques was to explore the structural and physical properties of the samples that had been deposited and annealed. The technique of energy dispersive spectroscopy was utilised in order to investigate the impact that temperature has on the constituent composition. Experiments were conducted in the presence of ultraviolet (UV) light and sunlight to investigate the catalytic behaviour of samples against MB and RHD dye. Temperature was found to be a significant factor in the improvement of the percentage of dye degradation. Both the unaltered and the annealed samples were subjected to analytical examinations of their dielectric characteristics, AC conductivity, dielectric loss, and tangent loss. Interdiffusion of Al atoms in TiO₂ matrix as a result of annealing demonstrates an improvement in the characteristics and potential usefulness of the material as a catalyst and electrode material for applications involving energy storage. In addition, a pin-on-disc tribometer has been utilised in order to evaluate the tribological characteristics of the coating. An in-depth discussion has been held regarding the potential mechanisms of tweaking the properties, as well as the potential applications of these qualities.

3:20pm **PP1-2-MoA-6 Reactive Magnetron Sputtering to Design 2D Cobalt Nitride - Carbon Nanotube Bucky paper Hybrids: Co-N Phase Diagram Screening and Thin Film Porosity Enhancement**, *Saraf Khan*, 3 Rue Mademoiselle 54000 Nancy, France

The decade ahead brings the challenge of eco-friendly generation of hydrogen fuel. Seeking substitutes, transition metal nitrides, far less studied than metal oxide so far, have the potential to serve as platinum free alternatives. This study explores synthesis of flexible, free standing cobalt

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nitride thin films deposited onto multi-walled carbon nanotube 2D films (buckypapers) to further serve as electrochemical electrodes. The reactive magnetron sputtering technique which allows to control the purity, stoichiometry, crystalline structure of the grown thin films is used to synthesize several cobalt nitrides. These latter are here characterized with complementary techniques to ascertain the nature of the synthesized cobalt nitride. When deposited onto flat silicon substrates, dense cobalt nitride thin films are obtained while disorganized porous nanostructures of Co₃N are formed on the carbon nanotube surface.

4:00pm PP1-2-MoA-8 Optimizing Bi Stoichiometry in Bi_{0.5}Na_{0.5}TiO₃ Thin Films Deposited via Low-Pressure RF Magnetron Sputtering in Ar Plasma, Zikriya Khan, University of Mons (UMONS), Belgium; Kristiaan Temst, Catholic University of Leuven, Belgium; Denis Rémiens, Polytechnic University of Hauts-de-France; Stéphanos Konstantinidis, University of Mons (UMONS), Belgium

Depositing Bismuth-based thin films by the sputtering technique often results in a non-stoichiometric excess of Bi across various materials, including the ferroelectric piezoelectric Bi_{0.5}Na_{0.5}TiO₃. This phenomenon is attributed to the lower scattering of heavier sputtered species in the plasma phase. Common mitigation strategies include multi-target sputtering to control Bi flux and promoting Bi re-evaporation at elevated growth temperatures by exploiting its temperature-sensitive sticking coefficient. Herein, we systematically investigate this issue, focusing on BNT thin film deposition without *in-situ* substrate heating and using a mixed-powder target by single-cathode RF Magnetron sputtering in Ar plasma. Compositional analysis of the films via EDX and RBS reveals a 25-30% excess of Bi by sputtering a stoichiometric Bi_{0.5}Na_{0.5}TiO₃ (BNT50/50) target. Simulations indicate a relatively unhindered transfer of Bi towards the substrate while other species are impeded by the background gas, as shown by the target sputtering combined with species transport using TRIM and SIMTRA codes, respectively. Reducing the sputtering yield of Bi by adjusting the target composition to Bi_{0.35}Na_{0.5}TiO_{2.8} (BNT35/50) eliminates the excess Bi from the BNT films. This study provides a clear insight into the origin of bismuth excess and a route map for its regulation inside the Bi-based thin films deposited via the sputtering technique.

Keywords: “Bi_{0.5}Na_{0.5}TiO₃”, “Thin Films”, “Bi Excess”, “Magnetron Sputtering”, “Powder Targets”, “Ar Plasma”.

4:20pm PP1-2-MoA-9 The Effect of an Additional Cooled Graphitic Anode to the Magnetron Sputtering of Al Films, Daniela Shealsey Jacobo Mora, Stephen Muhl, Marco Antonio Martínez Fuentes, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México
In this work, aluminum (Al) thin films were deposited onto glass substrates using a two-plasma system. A standard 2” MAK DC magnetron sputtering and an additional water-cooled anodic plasma. The second anodic plasma was generated using a graphite electrode placed approximately 5 cm from the magnetron. We found that the anodic plasma generated additional argon ions, which were incorporated in the magnetron discharge. These additional ions changed the characteristic of the magnetron discharge and the deposition of the aluminum atoms. Here we report the dependence of the changes as a function of the position of the anode and the temperature of the graphite electrode. Similarly, we report the changes in the properties of the films, hardness, and wear resistance as a function of the experimental parameters, gas pressure, MS voltage, and the voltage applied to the graphite anode, as well as the deposition rates measured by optical profilometry.

4:40pm PP1-2-MoA-10 Low Temperature Deposition of Silicon Nitride Thin Films by Reactive RF Diode Sputtering, Rakesh Singh, Ferrotec Inc., USA
Silicon nitride films have drawn increasing attention due to their high demand in various engineering applications. Considering many disadvantages of chemical vapor deposition (CVD) such as high process temperature and hydrogen contamination, reactive RF diode sputtering is an alternative method to produce high quality SiN_x films. In this work, we report synthesis of SiN_x films at low temperature by reactive RF diode sputtering.

Target power density, substrate bias, reactive gas (Ar+N₂) composition, and working pressure are some of the parameters that significantly influence the composition and optical properties of the films. SiN_x films with variable refractive index (1.9 to 2.2 at 632 nm) were obtained by changing Ar to N₂ ratio in the reactive gas mixture. Target-substrate gap was adjusted to improve the thickness uniformity and achieve 1-Sigma of <1% over 200 mm Si wafer.

5:00pm PP1-2-MoA-11 Experimental and Simulative Investigation of Crack Growth in TiAlCrN PVD Coatings, Ujjwal Suri, Felix Weber, Christoph Broeckmann, Institute of Applied Powder Metallurgy and Ceramics (IAPK) at RWTH Aachen e.V., Germany; Kirsten Bobzin, Christian Kalscheuer, Xiaoyang Liu, RWTH Aachen University, Surface Engineering Institute (IOT), Germany
Hard physical vapor deposition (PVD) coatings are widely used as protective layers on cemented carbide tools due to their exceptional mechanical properties. However, these coatings can be susceptible to damage and cracking. Gaining a deeper understanding of how the coating microstructure influences the cracking behavior is essential. Moreover, most tool wear prediction does not include the effect of the cracking behavior. Thus, crack initiation and propagation under external loads and its contribution to tool wear should be investigated. A precise micromechanical simulation of cracks could enhance the accuracy of tool wear simulations in cutting applications.

This study combines experimental and mesoscale simulation to investigate the cracking behavior of a TiAlCrN PVD coated cemented carbide tool. Initially, nanoindentations coupled with inverse FEM simulations are conducted to determine mechanical properties of coatings, specifically Young's modulus and parameters for the Ludwik-Hollomon model. These properties are then applied to simulate high-load nanoindentation at a macroscopic scale. Subsequently, scanning electron microscopy (SEM) is applied to characterize the grain morphology. Using this data, a representative finite element model is developed. Numerical simulations of the local crack initiation and growth are performed based on the implemented model in combination with the extended finite element method (XFEM). SEM micrographs taken after indentation are analyzed to study crack behavior, enabling a correlation between experimental results and numerical simulations.

The combined experimental and detailed numerical modelling approach facilitates insights into how microstructural parameters including grain size and orientation influence crack growth in the coating system. This study presents a combined analysis using experimental nanoindentation and a mesoscopic simulation model of the nanoindentation to investigate the crack growth in PVD coated cemented carbide. The correlation of experimental and simulative results allows a detailed study of the interaction of microstructure and crack growth in PVD coatings. Models comparable to the one here presented may be used in future work for optimization of coated cemented carbide tools.

5:20pm PP1-2-MoA-12 Determination of Mechanical Properties of PVD Tool Coatings Using Machine Learning, Kirsten Bobzin, Christian Kalscheuer, Xiaoyang Liu, Surface Engineering Institute - RWTH Aachen University, Germany

The wear resistance of physical vapor deposition (PVD) coatings is heavily influenced by their elastic and plastic properties. These properties serve as essential inputs for finite element method (FEM) simulations to predict tool wear, including the elastic modulus for the characterization of elastic properties and parameters of the Johnson-Cook model for the description of the plastic behavior. A precise determination of these parameters is required for simulation of tool wear. In this study, machine learning models are developed to directly map load-depth curves from nanoindentations on TiAlSiN and TiAlCrN coatings to parameters of coatings in FEM. An FEM simulation model of nanoindentation is employed to generate a dataset comprising load-depth curves resulting from a wide range of input material properties. Several machine learning models including support vector regression (SVR), multilayer perceptron (MLP), long short-term memory (LSTM) and gated recurrent unit (GRU) are then trained, validated, and compared using this dataset. The input to these models consists of simulated load-depth curves, with the target being parameters required for the definition of the material in commercial FEM softwares. Among these machine learning models, GRU achieves the best prediction performance. Ultimately, GRU is used to predict material parameters of TiAlSiN and TiAlCrN coatings based on experimental load-depth curves. FEM simulations using the GRU-predicted material parameters show excellent alignment with experimental measurements, achieving accurate results in a single iteration without further parameter adjustments. The determined parameters can be directly used as reasonable inputs for further FEM simulations as parts of a Greybox model to predict tool wear during cutting.

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