Monday Morning, May 12, 2025

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP1-1-MoM

PVD Coatings and Technologies I

Moderators: Dr. Qi Yang, National Research Council of Canada, **Dr. Christian Kalscheuer**, IOT, RWTH Aachen, Germany

10:00am **PP1-1-MoM-1 Complementary Cutting-Edge Plasma Monitoring Techniques for Process Development, Production Control and Machine Learning (ML)***, **Thomas Schütte [schuette@plasus.de]**, Jan-Peter Urbach, Peter Neiß, Marius Radloff, Hokuto Kikuchi,* PLASUS GmbH, Germany **INVITED**

As specifications in the thin film industry become more and more demanding, high production yields and cost effective production becomes a major factor in this competitive market. Increasing demands for better specifications and lower scrap rates drive the demand for efficient process control systems.

In addition, data analysis using artificial intelligence (AI) and machine learning (ML) technologies has made tremendous progress in recent years, sparking interest in using these methods for the diagnostics and control of plasma applications. To utilize this capability, a large number of data sets from complementary process diagnostics methods are required.

This presentation will highlight the opportunities and advantages of utilizing the latest developments in real-time in-situ data acquisition of different diagnostic techniques in a single system: Spectroscopic plasma process monitoring acquires data from the actual process plasma whereas in-situ broadband photometric measurements gather properties of the growing coating such as film thickness or color values. In addition, time-resolved electrical measurements of generator power, voltage and current provide valuable electrical process information especially in pulsed plasma applications.

Selected plasma applications are used to illustrate how process variations influence the results of the different measurement techniques. Consequently, by combining different methods and analyzing the complementary data in real-time, interdependencies between process and product properties become visible and can be used to achieve more accurate and reliable process control. At the same time the collected data can be fed into the analysis using AI and ML techniques to improve product quality and long-term production stability.

Real-time process control examples combining different diagnostic methods will be presented and first approaches to the application of ML methods will be illustrated using various coating applications from industry and R&D, such as metallic and reactive sputtering, HIPIMS and PECVD processes for tribological, optical and glass coating processes.

10:40am **PP1-1-MoM-3 Plasma Diagnostics and Thin Film Synthesis Using an Industrial-Sized DC Vacuum Arc Source with Magnetic Steering and a TaB₂ Cathode***, **Igor Zhirkov [igor.zhirkov@liu.se]**, Andrejs Petruhins, Ali Saffar Shamshirgar,* Materials Design Division, Linköping University, Sweden*; Philipp Immich,* IHI Hauzer Techno Coating B.V., Netherlands*; Szilard Kolozsvári, Peter Polcik,* PLANSEE Composite Materials GmbH., Germany*; Johanna Rosen,* Materials Design Division, Linköping University, Sweden

Due to physical and chemical characteristics of transition metal borides, thin films thereof are gaining increasing attention as protective hard coatings. Most publications in this area focus on TiB_2, synthesized through various physical vapor deposition (PVD) techniques. Tantalum diboride, TaB_2, is characterized by a hardness comparable to TiB_2, but with an elastic modulus ~ 2 times lower. It results in a combination of high strength and high resistance to elastic and plastic deformation, for potential use in protective coating industry. However, there are no reports on deposition of TaB_2 coatings with DC vacuum arc, a process commonly used in industry, in particular with magnetic steering. In this work, we present analysis of the process (cathode weight loss, film deposition rate), plasma composition, and the (micro-) structure and composition of the cathode as well as of films, using a Hidden EQP mass-energy analyzer, SEM, XRD, and XPS. The study is performed using an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. The TaB_2 cathodes were provided by PLANSEE Composite Materials GmbH. The magnetic arc steering system, based on variation of magnitude of electrical current flowing through the solenoid placed behind the cathode, allows tuning of the strength of the magnetic field at the center point of the cathode surface in the range ± 8 mT (different polarity). The steering system is found to improve the stability of the arcing process and result in more smooth erosion of the cathode surface. Plasma analysis performed at base pressure (10^{-5} Torr) shows peak ion energies consistent with the velocity rule, around 140 and 10 eV for Ta and B, respectively. The ion energies, the ion charge states, and the plasma ion compositions were found to be strongly affected by the operating pressure, with a plasma ion composition showing a lower B content (~ 60 % Ta and ~ 40 % B at base pressure) compared to the cathode stoichiometry. Even lower B ion signals were recorded at higher pressures. The plasma properties were correlated to the deposited thin films, their composition and structure. The lack of B within the deposited films was found to be less pronounced than for the plasma ions. Altogether, the results show that DC vacuum arc can be used for TaB_2 depositions with stability provided by the magnetic steering.

11:00am **PP1-1-MoM-4 Novel Approach in Cathodic Arc Evaporation Enabling Precise Control Over Energy of Deposited Ions in Industrial Conditions***, **Martin Ucik [m.ucik@platit.com]**,* Masaryk University, Czechia

Introduction

Commonly, in cathodic arc evaporation (CAE), where multiple elements are contained in a coating, materials of several targets are simultaneously evaporated. This evaporated material, being near-complete ionization due to the exceedingly high power densities in cathode spots with significant number or even predominance of multiply charged ions (2+, 3+, etc.), is condensed onto the substrate under applied bias which is constant. Therefore, often the currents and the substrate bias need to be optimized in order to avoid undesirable effects such as delivering excessive energy to the growing coating.

With a new approach of pulsed arc and synchronized bias relative to the arc pulses, we are now able to select which evaporated material is accelerated towards the substrate at what applied voltage, therefore controlling the delivered energy or, in other words, having a mechanism to regulate the energy of impacting ions.

Methods

Here, we choose one of the most widely studied coatings – AlCrN – to investigate the effect of synchronized bias. On two single element targets (Al, Cr), both arcs are simultaneously periodically pulsed and a substrate bias (from 30V up to 240V) is either constant or also pulsed in respect to the arc pulses (e.g. by Al pulse, we mean that arc current of Al cathode is at its maximum level). This offers us three basic modes we have focused on: (i) with a constant substrate bias, (ii) with bias applied during the Al pulse and leaving the substrate at a floating potential during Cr pulse and (iii) vice-versa applying the bias only during Cr pulse.

Results

By simply choosing the mode other than (i), we can change the coating microstructure, thus the properties – e.g., grain size, lattice orientation, residual stress, etc. We also investigated the effect of synchronized bias in a cutting test, where we observed an influence of a mode choice on cutting edge wear.

Conclusion

In summary, this study shows new possibilities of cathodic arc evaporation enabling to fine-tune coating microstructure to obtain desired properties and further more cutting performance.

to be submitted to Technical Symposium PP Plasma and Vapor Deposition Processes, and section PP1 PVD Coatings and Technologies (oral contribution)

11:20am **PP1-1-MoM-5 Industrial-Scale PVD Deposition of Aluminium Oxide***, **Ivan Kolev [ikolev@hauzer.nl]**,* IHI Hauzer Techno Coating B.V., Netherlands*; Philipp Immich, Daniel Barnholt, Julia Janowitz, Louis Tegelaers,* IHI Hauzer Techno Coating B.V.,, Netherlands*; Rolf Schäfer,* Robeko GmbH & Co. KG, Germany*; Tobias Radny,* Robeko GmbH & Co., KG, Germany

Aluminium oxide (Al_2O_3) is a well-known material with versatile properties, such as high hardness, electrical insulation, chemical inertness, and thermal stability. These properties make alumina also a desired thin film in various industrial applications. Its hardness and thermal stability are very beneficial for coatings on inserts. Other emerging application field is the sensor coatings, where the need ofhighly insulating films makes aluminium oxide a primary choice. Its optical transparency in combination with high hardness and chemical resistance find application in protective coatings.

Despite these multiple applications, efficient industrial-scale deposition of alumina thin films still has its challenges. RF sputtering from compound targets can produce stoichiometric high-quality coatings. However, its notoriously low deposition rate makes it unsuitable for large-scale mass production. Dual magnetron sputtering (DMS), from the other hand, can provide industrially meaningful deposition rates from metallic targets and successfully to circumvent the problem with the disappearing anode. However, it requires a very fast and solid regulation, allowing for long-term stable operation at narrow operating range. Special attention needs to be paid for arc handling on the target and substrate and its influence on the regulating algorithm.

In this talk, the contemporary state of the art for industrial DMS deposition of aluminium oxide for tool and sensor application is presented. Different ways of regulating are discussed and compared. The properties of low- and high-temperature deposited alumina films are reported. Future technology improvements are also discussed.

11:40am **PP1-1-MoM-6 Control of Microstructure and Phase of Sputter-Deposited Tantalum Thin Films for Inkjet Device Applications***, Brittney Burant [brittney.burant@hp.com],* HP Inc, USA

Tantalum (Ta) has long been used in thermal inkjet devices and plays a crucial role in the ink ejection cycle. It forms the bubble nucleation surface that transfers heat from the resistor to the ink, and also acts as a cavitation barrier that mechanically and chemically protects the resistor from damage during bubble collapse. Ta has a bulk stable α-phase with BCC structure, however, the metastable β-phase has historically been used in inkjet devices. Microstructure and phase control of the thin film is important for promoting cohesive bubble nucleation during ink firing cycles and ensuring the device functions reliably through its lifetime.

When pursuing new product architectures with reduced die separation ratios, it was found that sputter-deposited Ta films began to exhibit mixed phases, compromising the integrity of the cavitation barrier. Much research has been done to characterize the phase selection of Ta, however not much is understood about the underlying mechanisms of β-phase initiation and many studies report contradictory process parameters for phase selection. Through our work, we were able to demonstrate that substrate pre-treatment was promoting mixed phase formation during deposition, independent of other deposition parameters. We further aim to show that both substrate roughening and native oxide of the passivation surface plays a key role in initiating β-phase film growth on the substrate, by modifying the pre-sputter etch conditions and characterizing the surface and subsequent Ta phase.

12:00pm **PP1-1-MoM-7 Dc Magnetron Sputtering Yield Amplification of C, Si, and Ge Doped with W, Cu, Ta, or Mo***, Julio Cruz [juliocruz@ens.cnyn.unam.mx],* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; Rebecca Giffard,* Universidad de Guadalajara, Mexico*; Stephen Muhl, Marco Martínez,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; Roberto Sanginés, Roberto Machorro,* Centro de Nanociencias y Nanotecnología. Universidad Nacional Autónoma de México*; Efraín Chávez,* Instituto de Física. Universidad Nacional Autónoma de México

S. Berg in 1991 discovered the phenomenon called Sputtering Yield Amplification, SYA. The phenomenon is related to doping a sputtering target with atoms of different atomic mass than the target material. Such doping changes the collision cascade on the surface of the target, consequently increasing the number of ejected atoms from the target. In this work, we present a way of generating SYA of C and Si with two different types of co-sputtering experiments, in both by adding the doping element as small pieces on the surface racetrack. First, we increased the amount of W on C, Ge, and Si targets. Second, we increased the working gas pressure, i.e., the number of collisions in the gas phase, using a Si target and doping it with Cu, Mo, and, Ta. Then we studied the number of dopant atoms returning to the target racetrack surface and its spatial distribution. To determine their effect on the cascade of collisions and, consequently, the change in the target sputtering yield. With the Perfilometry and Rutherford Backscattering Spectrometry techniques, we measure the thickness of the deposited films and the total number of atoms deposited on the substrate. With Optical Emission Spectroscopy we analyze the intensity of the emission lines of neutral and ionized species in the sputtering plasma. Furthermore, with SIMTRA code we theoretically estimated the spatial distribution of atoms that were redeposited on the target. The results showed Si and C SYA doped with W. Somewhat similar results have been reported earlier. Furthermore, significant Si SYA doped with Cu, Mo, and Ta. These results may be interesting for materials that have both lower sputtering yield and important applications in the thin films industry.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP1-2-MoA

PVD Coatings and Technologies II

Moderators: Dr. Christian Kalscheuer, IOT, RWTH Aachen, Germany, **Dr. 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 [lshonroy@techcet.com]***, 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 [martin.rudolph@iom-leipzig.de]***, 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 [jefflee@mail.mcut.edu.tw]***, 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, AlCrNbSiTiCx 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 composiitons, 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 in 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 AlCrNbSiTiCx 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 [jlin@swri.org]***, 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 TiO_2/Al/TiO_2 Multilayer Thin Films**, ***Anand Joshi [anandyjoshi@gmail.com]***, *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 Buckypaper Hybrids: Co-N Phase Diagram Screening and Thin Film Porosity Enhancement**, ***Saraf Khan [sarafumeed.fr@gmail.com]***, 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 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 CoxN are formed on the carbon nanotube surface.

4:00pm **PP1-2-MoA-8 Optimizing Bi Stoichiometry in $Bi_{0.5}Na_{0.5}TiO_3$ Thin Films Deposited via Low-Pressure RF Magnetron Sputtering in Ar Plasma***, Zikriya Khan [Zikriya.Khan@student.umons.ac.be],* 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 $Bi_{0.5}Na_{0.5}TiO_3$. 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 $Bi_{0.5}Na_{0.5}TiO_3$ (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: "$Bi_{0.5}Na_{0.5}TiO_3$", "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 [shealseyjacobo15@gmail.com], 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 [Rakesh.singh@ferrotec.com],* 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 SiNx films at low temperature by reactive RF diode sputtering.

Target power density, substrate bias, reactive gas ($Ar+N_2$) composition, and working pressure are some of the parameters that significantly influence the composition and optical properties of the films. SiNx 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 [u.suri@iwm.rwth-aachen.de], 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 [liu@iot.rwth-aachen.de],* 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.

Plasma and Vapor Deposition Processes
Room Palm 3-4 - Session PP6-MoA

Greybox Models for Wear Prediction

Moderators: Philipp Immich, IHI Hauzer Techno Coating B.V., Netherlands, **Prof. Dr. Ludvik Martinu**, Polytechnique Montréal, Canada

1:40pm **PP6-MoA-1 Greybox Models for the Qualification of Coated Tools for High-Performance Cutting***, **Kirsten Bobzin [info@iot.rwth-aachen.de]**, Christian Kalscheuer, Muhammad Tayyab, Xiaoyang Liu,* RWTH Aachen University, Germany **INVITED**

The real application behaviour of coated cutting tools cannot be satisfactorily described mathematically. The incipient failure, wear progression and remaining service life cannot be predicted. However, there is a solid basic knowledge in machining technology and materials engineering, which is being described more and more fundamentally and atomistically in the form of white box models. This includes numerical simulations, which are becoming increasingly computationally and time intensive as the level of detail increases. However, the highly non-linear interactions of reality can never be fully described due to idealized assumptions. In contrast, black box models of machine learning can model complex correlations with a sufficient database and are capable of learning. However, physical interactions are then often not understood and their robustness in relation to changing boundary conditions remains uncertain.

As a new research approach, the existing deterministic white box models are to be combined with new data-driven black box models in grey box models. The robust but inaccurate predictions from white box models will be converged into a precise target window using data-driven and adaptive black box models. Already existing machine learning algorithms form the solution space for this. The gap that currently exists between stationary material properties before and after use, i.e. the unsteady system behaviour of coated tools during machining, is being researched and closed. This should enable knowledge-based selection and qualification of coated tools for more efficient machining processes in the future.

The large amounts of data collected but largely unused in research are seen as key. On the materials engineering side, the coated tools are initially analysed in their manufacturing state. However, the focus here is much more on time-dependent changes due to thermal, mechanical, and chemical loads during machining. The stress collective in the machining process is increasingly being monitored in situ in the form of forces, temperatures, images, or noises. The aim is to be able to trace changes in the in-situ measurement data back to the damage progress of the tools. Initially heterogeneous data formats from the machining process and from materials analysis need to be combined. As much real data as possible is systematically recorded, qualified, and correlated. The valid interpretation of the results requires a holistic view of the entire service life and interdisciplinary cooperation.

2:20pm **PP6-MoA-3 A Grey-Box Modell for Predicting Friction Coefficients of Coated Cutting Tools for Improved Wear Modelling***, **Jan Wolf [jan.wolf@ifw.uni-stuttgart.de]**,* University of Stuttgart - Institute for Machine Tools, Germany*; Nithin Kumar Bandaru, Martin Dienwiebel,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; Hans-Christian Möhring,* University of Stuttgart - Institute for Machine Tools, Germany

Wear of cutting tools is known to affect the surface integrity of the workpiece and contributes significantly to machine downtime. It has been shown that the wear rate increases dramatically once the coating is worn through. Predicting the wear of the coating is therefore a good indicator for the remaining useful life. Although white-box models based on Finite Element Analysis exist and showed good wear prediction capabilities for uncoated tools, transferring this approach to only model wear of coatings is challenging. One of the main factors for precise wear modelling is to use a precise friction model which captures the frictional behavior of the coating and the workpiece material under process conditions in cutting. Based on the design of a custom pin-on disk test setup in a vertical turning machine build for elevated temperatures and sliding velocity for matching the conditions in machining, a friction model is determined for a TiN/AlTiN coated cutting tool. The non-linear friction behavior is then determined via a regression approach by training machine learning algorithms. A custom-made- python interface for the seamless incorporation of typical AI libraries and their models is presented for the software DEFORM 2D. The interface of the tool and the chip is discretized due to employed friction windows, for which the determined regression approach predicts the friction coefficient based on the calculated state variables of the FEA. Thus, this work presents a novel Grey-Box approach for locally predicting friction coefficients along the surface of coated cutting tools, which is the basis for an improved wear modelling of cutting tool coatings.

2:40pm **PP6-MoA-4 Coating-Dependant Thermomechanical Loading of Cutting Tools for Greybox Models***, Thomas Bergs, Markus Meurer, **Mustapha Abouridouane [m.abouridouane@mti.rwth-aachen.de]**,* Manufacturing Technology Institute (MTI) - RWTH Aachen University, Germany*; Kirsten Bobzin, Christian Kalscheuer, Muhammad Tayyab,* Surface Engineering Institute - RWTH Aachen University, Germany

For economically efficient cutting processes, cutting tool life can be extended through physical vapor deposition (PVD) coatings. However, imprecise tool life prediction models limit the cost-effective qualification of PVD coated tools. Analytical or simulation-based whitebox models mostly ignore coating effect on tool wear and cannot fully capture nonlinear interactions in cutting processes due to necessary simplifications of boundary conditions. In contrast, data-driven blackbox models can represent complex correlations but often lack an understanding of physical causality and robustness under variable conditions. To overcome these limitations, greybox models can be developed by coupling whitebox and blackbox models to create a balanced predictive framework. Such models require an inclusive dataset containing information on coating properties, realistic thermomechanical tool loading, process data and tool wear behavior. The current investigation focuses on determination of coating-dependent thermomechanical loading of cutting tools, required for development of greybox models. Monolayer TiAlCrSiN and bilayer TiAlCrSiN/TiAlCrSiON coatings were deposited on cemented carbide substrates and characterized. In order to assess thermomechanical tool loading, analogy tests representing orthogonal cutting were carried out on heat-treated C45 and 42CrMo4 steels. The process forces and tool temperatures were measured by dynamometer and high-speed infrared camera, respectively. Moreover, the heat flow into the tool was determined by placing a pyrometer directly under the rake face of the cutting inserts. The experimental data from coating properties and cutting tests contributed to the extension and validation of finite element chip formation simulation for coated tools. Thermomechanical stress distributions on coated tools with high spatial and temporal resolution were computed using the validated simulation model. The experimental as well as simulative data was combined to understand the effect of coating and workpiece material combinations on the process forces, tool temperatures as well as the resulting friction and tool wear behavior. The study contributes towards extension of existing numerical whitebox models for consideration of coating as well as determination of more accurate thermomechanical loading on PVD coated tools. The resulting high-resolution spatial and temporal thermomechanical tool loading data can be instrumental to the development of greybox models for tool life prediction.

3:00pm **PP6-MoA-5 Bridging the Gap Between Milling and Tribological Wear Mechanisms: Comparative Analysis of Coated Carbide Tools***, **Amod Kashyap [amod.kashyap@kit.edu]**,* Institute for Applied Materials (IAM-ZM), Micro-Tribology Centre (µTC), Karlsruhe Institute of Technology, Germany*; Amirmohammad Jamali,* Institute of Production Science (wbk), Karlsruhe Institute of Technology, Germany*; Johannes Schneider,* Institute for Applied Materials (IAM-ZM), Micro-Tribology Centre (µTC), Karlsruhe Institute of Technology, Germany*; Michael Stueber,* Institute for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology, Germany*; Volker Schulze,* Institute of Production Science (wbk), Karlsruhe Institute of Technology, Germany

Milling tools used in metal manufacturing face severe challenges such as complex wear scenarios, heat generation and dissipation, and vibration, which lead to reduced tool life, poor surface quality, and higher operational costs. To address these issues, advanced coatings are applied to enhance their performance and longevity by reducing wear and friction, enabling higher cutting speeds and improved efficiency, and minimizing the formation of built-up edges. Coatings based on Titanium Nitride (TiN) and Aluminum Titanium Nitride (AlTiN) provide excellent heat resistance and hardness, crucial for maintaining tool integrity under high-temperature conditions.

The wear mechanisms of a milling tool vary depending on cutting parameters, and extensive research has been conducted on tool wear in coated milling tools with large-scale milling machines. Traditionally, researchers have attempted to evaluate coating performance using laboratory-based tribological setups. However, tribological tests do not accurately replicate the actual milling process. In this study, the authors aim to correlate tool wear in milling machines with wear observed in tribological model experiments. Milling tests were conducted with coated cemented carbide tools on C45 steel, and tribological tests involved coated cemented carbide cylinders against C45 discs. In-house TiN and AlTiN model coatings, deposited by pulsed-DC and high-power impulse magnetron sputtering techniques, were applied in these experiments. Tribological test parameters were optimized to replicate similar wear mechanisms on both the milling tools and coated cylinders, allowing for a detailed study of wear development through tribological testing only. Scanning electron and focussed ion beam microscopy including energy dispersive X-ray analysis were employed to analyse oxidation, adhesion, and diffusion wear on the coated carbide tools and cylinders. Additionally, the in-house-developed coatings were also compared with industrial coatings, enabling a comprehensive examination of wear mechanisms across different coatings.

3:20pm **PP6-MoA-6 Prediction of Tool Wear Depending on the Coating Architecture for Coated Cemented Carbide Tools by Machine Learning***,* *Benjamin Bergmann,* Institute of Production Engineering and Machine Tools - Leibniz University Hannover, Germany*; Christian Kalscheuer,* Surface Engineering Institute - RWTH Aachen University, Germany*; Berend Denkena,* Institute of Production Engineering and Machine Tools - Leibniz University Hannover, Germany*; Kirsten Bobzin, Xiaoyang Liu,* Surface Engineering Institute - RWTH Aachen University, Germany*; **Nico Junge [junge@ifw.uni-hannover.de]**,* Institute of Production Engineering and Machine Tools - Leibniz University Hannover, Germany

Cutting tools based on cemented carbide are usually coated by physical vapor deposition. In machining operations, the specific characteristics of the process parameters and the machined material determine the different wear behavior. However, the utilization of diverse coating properties enables the targeted enhancement of wear resistance. Furthermore, the coatings are adjusted to the individual substrate. It could be shown, that the interaction between the substrate and the interlayer thickness and coating architecture exhibit a significant influence on the tool wear behavior. Due to the high complexity for predicting the influence of the interlayer on the wear behavior wear models are not available. Therefore, machine learning was used to predict the tool wear based on coating properties, considering the complex interaction between process parameters, tool and material.

In this study PVD coated cutting tools with three different interlayer thicknesses were prepared. This method is used to analyze different substrate-coating systems while preserving the properties of the functional layer of the tool. The initial coating properties such as residual stress, hardness and thermal conductivity were measured and served as input parameters for the ML- model. Afterward experimental wear investigations in turning different steels and process parameters were conducted. The wear data and the process parameters were also used as the input for the machine learning model. Different machine learning models such as support vector regression (SVR) and multilayer perceptron (MLP) were tested regarding the wear prediction. It can be shown, that the used models can predict the wear form and the size of wear for the turning operation depending on the operating time and the different coating properties, such as the interlayer thickness.

4:00pm **PP6-MoA-8 Greybox Modeling the Run-in and Wear Behavior of Milling Tools Coated with Arc-Evaporated TiAlN Based on Operando, in Situ and Ex Situ Analyses***,* ***Wolfgang Tillmann [wolfgang.tillmann@udo.edu]**, Finn Rümenapf, Nelson FIlipe Lopes Dias, Simon Jaquet, Rafael Garcia Carballo, Dirk Biermann, Nils Denkmann, Jörg Debus,* TU Dortmund University, Germany **INVITED**

In modern machine manufacturing, a controlled cutting process is crucial for high workpiece quality and production efficiency. The dynamic stability of milling processes depends, e.g., on the cutting parameter values and the system behavior of the machine tool including the cutting tool. Milling tools are subjected to significantly more wear during dynamically unstable processes. To enhance wear resistance, cathodic arc evaporated TiAlN thin films are widely used. Throughout the cutting process, varying tribological loads alter the transient system behavior of the coated tools, which in turn impacts run-in behavior, tool wear, and lifetime. In this regard, the system behavior under varying dynamic load profiles remains largely unknown during the cutting process, thus complicating efforts to predict dynamic stability and tool wear accurately.

These challenges are addressed by using a greybox model approach designed to characterize the transient system behavior of TiAlN-coated tools. In a greybox model, experimental data of the steady-state and transient system behavior are exploited to reveal the wear initiation and development with respect to the dynamic run-in behavior. The experiments focus on the milling process of normalized C45 steel, utilizing tools coated with arc-evaporated TiAlN thin films. For the input of the greybox model a comprehensive dataset is produced, including *operando* cutting force measurements, *in situ* Raman spectroscopy, and *ex situ* analyses of chemical composition, hardness, and adhesion of the coatings pre- and post-cutting. A supervised machine learning model is used to enhance signal clarity and reliability of *in situ* input data. Furthermore, artificial neural networks with k-means clustering provide correlations between thin film properties, wear behavior and cutting performance. The combination of these AI-driven insights with physical and material-specific causalities allows the greybox model to predict tool wear progression and failure onset of the arc-evaporated TiAlN-coated milling tools.

Initial greybox model approaches demonstrate that the run-in behavior of the coated tools is influenced by the initial droplet distribution of the TiAlN, which in turn is affected by the choice of target material. This underlines the importance of considering the entire process, from coating deposition to tool performance. Additionally, a preliminary clustering of measurement data reveals meaningful patterns related to wear and stability. These first results highlight the potential of greybox models in describing the transient system behavior and predicting the lifetime of TiAlN-coated tools.

4:40pm **PP6-MoA-10 Determination of Residual Stress and Crystallite Size for TiAlN-Coated Milling Tools Using Laser-Spectroscopy-Based Grey-Box Modeling***,* ***Nils Denkmann [nils.denkmann@tu-dortmund.de]**,* Department of Physics, TU Dortmund University, 44227 Dortmund, Germany*; Nelson Filipe Lopes Dias, Finn Rümenapf,* Institute of Materials Engineering, TU Dortmund University, 44227 Dortmund, Germany*; Simon Jaquet, Rafael Garcia Carballo, Dirk Biermann,* Institute of Machining Technology, TU Dortmund University, 44227 Dortmund, Germany*; Wolfgang Tillmann,* Institute of Materials Engineering, TU Dortmund University, 44227 Dortmund, Germany*; Jörg Debus,* Department of Physics, TU Dortmund University, 44227 Dortmund, Germany

TiAlN thin films are widely used in machining processes due to their high hardness and high wear resistance. However, continuous and intermittent thermo-mechanical loads during machining impair the structural properties of the thin film, e.g., the phase composition and the residual stress state. Such an impact alters the wear resistance of the thin film as well as the constitution of the tools, which ultimately leads to a drastic increase in tool wear. For a comprehensive understanding of the wear of coated milling tools, it is crucial to gain insight into the microscopic structural-chemical properties that determine early-predictively the degradation of the coating.

We use laser scattering spectroscopy combined with AI supported data analysis to determine changes in the residual stress and crystallite size of TiAlN coatings applied to milling tools for C45 steel machining. By utilizing confocal Raman scattering with micrometer spatial resolution, we measure the longitudinal and transversal optical and acoustic lattice vibrations, whose spectral line features grant access to the residual stress and crystallite size of TiAlN.

The *k*-means clustered changes in the residual stress and crystallite size h of TiAlN are correlated for initial and different material removal volumes of the TiAlN-coated tool. In the initial state and after minor material removal, the residual stress changes are given by (1.2 ± 0.6) GPa, while h fluctuates around 50 nm. In case of high material removal, the residual stress switches from compressive to positive tensile stress ranges with decreasing h. The sign switching in the residual stress is attributed to a temperature-induced spinodal segregation in fcc-TiN and fcc-AlN. This phase transformation appears to be present at h below about 30 nm. As the wear is significantly lower than for the uncoated reference tool, it can be assumed that the spinodal segregation has a wear-reducing effect.

In addition to that, a possible wear initiation for the TiAlN thin films is determined by the frequency of missing TiAlN Raman scattering signals at local tool surface positions. The *k*-means cluster analysis of the scattering spectra shows that with increasing material removal volume a non-specific background is formed in 5 % and 11 % of the cases, respectively.

Raman spectroscopy combined with grey-box modeling reveals possible wear initiations for the TiAlN thin films and outlines that the observed wear mitigation is related to the formation of self-organized nanostructures, so that structural-chemical changes at the tool surface may be used to develop robust and early-predictive criteria for wear.

5:00pm **PP6-MoA-11 Predicting Solid Particle Erosion of Metals: A Machine Learning Approach**

***Stephen Brown* [stephen.brown@polymtl.ca]**, *Foutse Khomh,* Polytechnique Montréal, Canada; *Juan Manuel Mendez,* MDS Coating Technologies, Canada; *Marjorie Cavarroc,* Safran Tech, France; *Ludvik Martinu, Jolanta Ewa Klemberg-Sapieha,* Polytechnique Montréal, Canada

Solid particle erosion (SPE) is a tribological phenomenon in which a surface is impacted by a stream of particles, causing a gradual removal of the material. It is a critical challenge in aerospace, where compressor blades and other components are exposed to harsh particle-laden environments. Despite decades of research, accurately predicting SPE under diverse conditions remains difficult due to the non-linear relationships between erosion rates, material properties, and environmental factors. While several white-box models exist for the prediction of erosion, they rely on the use of empirically determined values that are sensitive to changes in erosion conditions and material properties, and are not easily adaptable to different erosion environments.

Machine learning (ML) offers a powerful alternative for handling variability and extracting insights from diverse datasets. This study compiles a database of over 1,000 erosion tests on metals based on the erosion literature and internal experiments, encompassing material and particle properties, experimental conditions, and article metadata. Using ML models such as XGBoost, Neural Networks, and Random Forests, erosion rates were predicted, achieving mean absolute errors (MAE) of 15-16% for the unseen test data. Model performance was further validated against interlaboratory test results from the ASTM G76 standard, with accurate predictions being made in two of three cases. The influence of different variables on erosion predictions was analyzed using feature importance metrics and partial dependence plots. Key features like particle velocity and impact angle showed expected effects, while the importance of target features such as density and Poisson's ratio was sometimes overstated due to their ability to act as classifiers for outlier materials.

These results demonstrate the potential of data-driven approaches to improve wear modeling by quantitatively predicting erosion rates across a wide range of conditions, while also highlighting the challenges arising from issues such as data sparsity and feature correlation.

5:20pm **PP6-MoA-12 Characterization of AlCrVY(O)N Thin Film Properties and Thermo-Mechanical Load Profiles in Machining AISI 304 Stainless Steel Using Greybox Modelling Approaches**

***Erik Krumme* [erik.krumme@tu-dortmund.de]**, Institute of Machining Technology (ISF), TU Dortmund University, Germany; *Finn Rümenapf,* Chair of Materials Technology (LWT), TU Dortmund University, Germany; *Kai Donnerbauer,* Chair of Materials Test Engineering (WPT), TU Dortmund University, Germany; *Jannis Saelzer,* Institute of Machining Technology (ISF), TU Dortmund University, Germany; *Nelson Filipe Lopes Dias,* Chair of Materials Technology (LWT), TU Dortmund University, Germany; *Pascal Volke, Andreas Zabel,* Institute of Machining Technology (ISF), TU Dortmund University, Germany; *Wolfgang Tillmann,* Chair of Materials Technology (LWT), TU Dortmund University, Germany; *Frank Walther,* Chair of Materials Test Engineering (WPT), TU Dortmund University, Germany

The thermo-mechanical load collective prevailing in machining significantly determines the wear of coated carbide tools and therefore also has an influence on the productivity and sustainability of many industrial value chains. The tool wear can be described and predicted by developing greybox models, whereby it is known that the temperatures occurring in the chip formation zone have a greater impact on wear than the mechanical tool loads. AlCrVY(O)N thin films thus show significant promise for reducing tool wear due to lower friction and enhanced thermal stability at elevated temperatures compared to conventional thin films. Based on the complex coupling of friction, temperature and wear, the need for further development of such systems is substantial. To initiate greybox modeling of wear behavior, these thin-film systems were tested in whitebox approaches, i.e. when machining AISI 304 during an orthogonal turning process. As a benchmark, the thin films were compared to TiAlN and AlCrN thin films as well as uncoated cemented carbide tools. The thin film properties of AlCrVY(O)N on the cemented carbide inserts were evaluated and correlated with the cutting performance. The test set-up used, enables a comprehensive examination of the thermo-mechanical load collective concerning the measurement of the process forces and rake face temperatures. A variation of the cutting parameters was carried out to investigate the performance of the thin films under different levels of load. The tool wear identified was evaluated using blackbox approaches. In particular, a neural network for image segmentation was trained and applied to optical micrographs of the used tools. As a result, an automated evaluation of the tools was possible and new criteria for quantifying tool wear were developed. In order to improve the prediction of the transient tool wear behavior in form of cracks in the thin film and cutting edge failures, a further machine learning approach was chosen. For this purpose an autoencoder was developed and trained, which first analyzes the experimentally determined force measurement signals ex situ and can subsequently identify process windows of interest with regards to the tool wear behavior. The fundamental investigations show that the applied thin films on the inserts generally have a homogeneous chemical composition and a high hardness around 35 GPa. In the operational tests the temperatures on the rake face were reduced by using the AlCrVY(O)N thin films compared to TiAlN. Despite the low level of wear due to the short cutting time, image segmentation was validated as a suitable method for wear quantification.

Plasma and Vapor Deposition Processes
Room Town & Country C - Session PP5-TuM

Microfabrication Techniques with Lasers and Plasmas

Moderators: Dr. Carles Corbella, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA, **Dr. Valentina Dinca**, National Institute for Laser, Plasma, and Radiation Physics, Romania

8:00am **PP5-TuM-1 Synthesis of 2D Transition Metal Dichalcogenides Using Advanced ALD Cycle Schemes***, **Ageeth Bol [aabol@umich.edu]**,* University of Michigan, Ann Arbor, USA **INVITED**

2D materials have been the focus of intense research in the last decade due to their unique physical properties. This presentation will highlight our recent progress on the large-area synthesis of two-dimensional transition metal chalcogenides for nanoelectronics using advanced plasma-enhanced atomic layer deposition cycle schemes. First, I will show how we can use advanced cycle schemes to deposit wafer-scale polycrystalline MoS_2 thin films at very low temperatures down to 100 °C. We have identified the critical role of hydrogen during the plasma step in controlling the composition and properties of molybdenum sulfide films. By increasing the H_2/H_2S ratio or adding an extra hydrogen plasma step to our ALD process, we can deposit pure polycrystalline MoS2 films at temperatures as low as 100 °C. To the best of our knowledge, this represents the lowest temperature for crystalline MoS_2 films prepared by any chemical gas-phase method.[1]

The most dominant methods for preparing MoS_2 via ALD is to alternately expose a substrate to a metalorganic precursor and a hydrogen sulfide (H_2S) or a plasma containing H_2S. H_2S is a corrosive, toxic, and flammable gas that is heavier than air, which makes it hazardous and expensive to store, install, and transport. Alternative sulfur precursors in the solid or liquid phase would be beneficial in terms of cost and safety and would require the installation of no additional hardware for most ALD reactors. In the second half of this contribution, the widely researched ALD process using bis(tert-butylimido)bis(dimethylamino)molybdenum(IV) ($(^tBuN)_2(NMe_2)_2Mo$) and H_2S plasma is compared to a novel ALD process using $(^tBuN)_2(NMe_2)_2Mo$, hydrogen plasma, and di-tert-butyl disulfide (TBDS), which is an inexpensive, liquid-phase sulfur precursor.

8:40am **PP5-TuM-3 Nanocalorimetry for Plasma-Assisted Process Metrology in Semiconductor Microfabrication***, J. Trey Diulus,* National Institute of Standards and Technology (NIST), USA*; **Carles Corbella [carles.corbellaroca@nist.gov]**,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA*; Feng Yi, David LaVan, Berc Kalanyan, Mark McLean,* National Institute of Standards and Technology (NIST), USA*; Lakshmi Ravi Narayan,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA*; William A. Osborn, James E. Maslar, Andrei Kolmakov,* National Institute of Standards and Technology (NIST), USA

New methods to monitor plasma processes in microelectronics industry, such as deposition, etching, and surface modification, require fine control of plasma parameters, basic plasma-surface interactions, and structural/chemical resolution. These challenges can be solved by implementing nanocalorimeter devices, which usually consist of a 100 nm-thin self-sustained silicon nitride membrane with lithographically defined metallic structure as a resistive temperature sensor and heater. The lateral sizes of the sensor can range from micrometer to millimeter scales. The small size/thermal mass, functionalization versatility, and low wafer-scale fabrication cost of nanocalorimeters, enable their facile integration into any reactor chamber to meet specific plasma process requirements. Here, we report on pilot tests of NIST-microfabricated nanocalorimeters aimed to detect reactive radicals generated by hydrogen cold plasma at typical conditions for semiconductor manufacturing (75 W RF, 10-30 Pa). The setup consists of a parallel arrangement of one gold-coated active sensor and a second alumina-coated reference sensor. Au layer serves as a catalyst with known hydrogen recombination coefficient. Hence, the difference in heat of recombination reactions is detected comparatively by activated and reference nanocalorimeters. The inert, reference sensor enables discrimination against the incoming UV-vis radiation, and fluxes of ions and electrons, which constitute the major parasitic signals. The setup was successfully tested, and parameters such as sensitivity in radical detection (5×10^{20} $m^{-2}s^{-1}$) and in radical density (10^{18} m^{-3}), and response time (sub-100 ms), are discussed within the framework of standard plasma diagnostic techniques. In conclusion, fast-scanning nanocalorimetry constitutes a promising platform for plasma process monitoring, whose flexibility enables its possible integration into other optical or electrical metrologies.

9:00am **PP5-TuM-4 Pulsed Laser Deposition for Energy Materials***, **Thomas Lippert [thomas.lippert@psi.ch]**,* Paul Scherrer Institute, Switzerland **INVITED**

One of the material systems which we study are oxynitrides that are applied as photoanodes in photo-electrochemical water splitting. Shortcomings of this material class are a fast decay in activity over the first few electrochemical cycles and a decay on the long term. While the long-term decay is possibly related to a degradation of the material, i.e., a loss of nitrogen, the fast decay is not really understood, and therefore also no approach can be envisioned how to overcome this problem. We studied the fast decay of the material (and first approaches how to prevent this) by using thin films as model system. We could detect a surface modification, i.e., a change in density, by NR in the range of 3 nm, while XAS was utilized to analyze changes in oxidation state (order) for the different elements. A change of oxidation state of the A cation was detected, while the B cation (here for $LaTiO_xN_y$), which is normally assumed to be the active site, undergoes local disordering. This surface modification reduces the overall water splitting activity, but we could identify a co-catalyst, which supresses these modifications. We could also identify critical steps in the water splitting mechanisms, where during surface modifications the formation of NO_x competes with the oxygen evolution. Without highly defined, high quality PLD films it would have not been possible to utilize the large facilities, and therefore to identify (mitigate) the origins of activity decay of these oxynitrides for water splitting.

Fundamental understanding material properties and reactions of energy materials can often be very well studied by large facility techniques, e.g., at synchrotrons or neutron sources, as unique information can be obtained in this way. A number of these methods require the application of well-defined samples, controlling crystallinity, roughness to interface quality. These requirements can often be fulfilled by thin films. We apply pulsed laser deposition (PLD) to create these thin films to utilize complementary techniques, ranging from neutron reflectometry (NR) to grazing incidence X-ray absorption spectroscopy (GIXAS).

9:40am **PP5-TuM-6 Honeycomb Structured Pdms Microtopography Modulates in Vitro Cell Behaviour and Bacteria Growth***, **Valentina Dinca [valentina.dinca@inflpr.ro]**,* National Institute for Laser, Plasma, and Radiation Physics, Romania

Nowadays, the reduction of complications following breast implant surgery together with the enhancement of implant integration and performance through the modulation of the foreign body response (FBR) still represents a fundamental challenge. Therefore, influencing FBR by tailoring the material's physical characteristics can provide a significant outcome in implantology. While polydimethylsiloxane (PDMS) patterning on 2D substrates is a relatively established and available procedure, micropatterning multiscaled bioactive interfaces on a controlled large area has been more challenging. Therefore, in the present work, novel PDMS-based shell interfaces featuring honeycomb-like wells microtextures were designed and their effectiveness towards creating a pro-healing environment was investigated. The microtextures were achieved through replication on a large-scale using moulds obtained by an innovative laser-based 3D fabrication assisted by a grayscale masks process. By comparison to the smooth substrate, the honeycomb topography altered the fibroblasts' behaviour in terms of adhesion and morphology and reduced the macrophages' inflammatory response. Additionally, the microstructured surface hindered the macrophage fusion process, and decreased the retention of Gram-positive and Gram-negative microbial strains. Overall, our study presents a novel approach for an attenuated in vitro FBR to silicone through the development of honeycomb like topography of prosthetic interfaces.

10:00am **PP5-TuM-7 Sputtering onto Liquids : From Nanoparticle Suspensions to Functional Polymer Composites***, **Stephanos Konstantinidis [stephanos.konstantinidis@umons.ac.be]**, France - Emmanuelle Bol, Valentine Jauquet, Jeremy Odent, Anastasiya Sergievskaya,* University of Mons, Belgium

Magnetron sputter deposition of metal atoms onto vacuum compatible liquids allows producing colloidal solutions of small metal nanoparticles (NPs) without any additional reducing or stabilizing reagents [1]. This presentation aims at presenting the results during which the process parameters were varied to study how the properties of the as-formed metal NPs are impacted. Parameters such as pressure, sputter power, and sputtering regime, e.g., DC or HiPIMS, were varied as well as the characteristics of the host liquid chemistry and viscosity. To monitor in space and time the behaviour of the NPs inside the liquid, in situ UV-Vis absorption spectrophotometry was implemented [2]. The temperature of the liquid was measured as well.

Our data show that the formation of a cloud of particles underneath the oil surface is usually observed while films form in the case of high viscosity liquids [3]. The effect of sputtering time and power, argon pressure, type of sputtering plasma (dcMS vs HiPIMS) were also studied taking castor oil, a vegetable liquid, as substrate. In this case, few - nm - in - diameter Au-NPs have a higher stability in the oil than Ag-NPs but secondary growth processes take place. Interestingly, HiPIMS promotes the formation of NPs larger than those obtained in dcMS mode [4]. Most recent experiments highllight the possibility of elaborating hydrogel / nanoparticle composites in a two step process by choosing an appropriate polymerizable host liquid [5]. Preliminary measures confirm that the as-obtained Ag-NPs / hydrogel composite can be used to detect mercury cations in aqueous solutions through color change.

Our data highlight that sputtering onto liquid allows for the synthesis of a few nm in diameter NPs but the plasma and liquid parameters matter. Ultimately, by chooseing carefully the liquid host, it is possible to elaborate polymer / NP functional composites.

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[4] A. Sergievskaya, A. O'Reilly, H. Alem, J. De Winter, D. Cornil, J. Cornil, S. Konstantinidis, Front. Nanotechnol. 3 (2021) 57.

[5] V. Jauquet, Master Thesis, University of Mons (June 2023).

10:20am **PP5-TuM-8 Rapid Single Step Atmospheric Pressure Plasma Jet Deposition of a SERS Active Surface***,* ***Oliver S. J. Hagger [oliver.hagger.21@ucl.ac.uk]****, M. Emre Sener,* University College London, UK*; Imran Khan,* Defence Science Technology Laboratory, UK*; Francis Lockwood Estrin, Ivan P. Parkin, Daren J. Caruana,* University College London, UK

This research introduces an innovative approach for the rapid and efficient deposition of silver and gold using atmospheric pressure plasma jets (APPJs) to produce Surface-Enhanced Raman Spectroscopy (SERS) substrates and conductive tracks. Central to this method is the utilisation of plasma, which enables precise and uniform deposition of zerovalent metallic nanoparticles on a variety of substrates, including glass, ceramics, and metallic objects.

The APPJ technique takes advantage of the unique properties of non-thermal plasma, facilitating the reduction of metal ions to zerovalent metals in a single step. The highly energised electrons in the plasma allow intricate redox chemistry to occur. The flexibility of the APPJ method extends to a wide range of materials, including silver, gold, and binary metal mixtures. Furthermore, by mounting an APPJ on a 5-axis manifold enables metallic deposition on topologically complex surfaces, which has significant applications in analytical chemistry and materials science.

SERS substrates can be produced using an APPJ by depositing silver or gold directly onto topologically complex, multi-material surfaces without the need for post-plasma treatment. The APPJ prints metallic islands with diameters of 150 ± 25 µm and heights of approximately 370 nm, spaced 500 µm apart, forming the fundamental structure of the SERS substrates. With a production time of only 5 seconds per SERS substrate, our method offers a significantly faster alternative compared to other manufacturing techniques.

Our APPJ SERS substrates have undergone rigorous testing with various analytes, demonstrating performance on par with commercially available products. The substrates exhibit an impressive detection limit of 154 ppb when tested with 4-mercaptobenzoic acid.

Plasma-prepared substrates show significant gains with respect to the economical use of materials and the rapidity of the synthesis of the substrates. We showcase using the atmospheric pressure plasma jet method for synthesis and deposition as an integral part of an analytical device. This approach presents a key advantage for academic and industrial applications.

10:40am **PP5-TuM-9 Synergies Between Laser Technology and Thin Films for Advanced Functionalities***,* ***Sylvain Le Coultre [sylvain.lecoultre@bfh.ch]****,* BFH-ALPS, Switzerland

In our ALPS Institute, laser technology and thin-film deposition are combined with the objective to unlock novel functionalities in nanofabrication. As a first example, by leveraging precise and partial laser ablation within multilayer systems, we achieve high-resolution decorative effects with nanometric precision. Laser structuring on thin-film materials enables tuning of material properties, as seen on carbon allotropes. Additionally, laser processing can be employed to generate nanoparticles by ablating a target, which can then be embedded in coatings to form nanocomposites with enhanced mechanical, optical, or catalytic properties. This presentation will explore a few specific applications and case studies that highlight the advantages of integrating laser processing with thin-film technologies.

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP2-1-WeM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

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

8:00am **PP2-1-WeM-1 Energetics and Chemistry of Cathodic Arc Ti-N Plasma: A Combinatorial Investigation Using Experimental Probes and Fluid Mechanical Modelling**, ***Nikolaos Giochalas [nikolaos.giochalas@liu.se]***, Linköping Univ., IFM, Nanostructured Materials Div., Sweden; *Grzegorz Greczynski,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *Ferenc Tasnadi,* Linköping Univ., IFM, Theoretical Physics Div., Sweden; *Lina Rogström, Magnus Odén,* Linköping Univ., IFM, Nanostructured Materials Div., Sweden

Cathodic Arc Deposition, a commonly used PVD process of growing hard coatings, involves high fluxes of ions and electrons in a dense, expanding plasma. The composition of the arc plasma may vary significantly within the deposition chamber, and the source-to-substrate distance impacts the coating growth conditions. This study investigates the Ti-N plasma generated by a 100 mm, dc-operated arc source at 20 V and 120 A, in an 1 Pa N_2 ambient within a cylindrical, lab-scale HV chamber. A combinatorial approach of experimental probes and finite element fluid mechanical modelling is used to understand the varying plasma composition in terms of ions, neutrals, and radicals, and their corresponding fluxes. The measured and simulated ion species are Ti^{1+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, TiN^{1+}, TiN^{2+}, N_2^{1+}, and N^{1+}. The dominant ion species in every probed spatial configuration is Ti^{2+}, while Ti^{1+} follows closely and equalizes the energetic footprint of Ti^{2+} when the distance from the source is increased. Atomic Nitrogen ions maintain a significant presence throughout the plasma volume, largely due to a sustained emission from the nitrided Ti-source surface, N_2 dissociation and charge exchange collisions. In general, the plasma density and average charge state follow a decreasing trend for distances larger than 35 cm from the source, where the presence of Ti^{3+} and Ti^{4+} is suppressed. At the same time, TiN-ions retain their presence, leading to different growth conditions at the substrate, depending on the chosen distance from the source.

8:20am **PP2-1-WeM-2 Exploring the Microstructure and Mechanical Properties of TiZrMbTaMoN Highentropy Alloy Nitride Coating: Effect of Nitrogen Content**, ***Sen-You Hou [housenyou23@gmail.com]***, National Tsing Hua University, Taiwan, China; *Po-Yu Chen,* National Tsing Hua University, Taiwan; *Bih-Show Lou,* Chang Gung University,Taiwan; *Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

The highpower impulse magnetron sputtering (HiPIMS) generates highdensity plasma through higher instantaneous pulse currents, resulting in thin films with fewer defects, higher density, and densermicrostructure. In this work, a combination of HiPIMS and radio frequency power supply system was used to deposit TiZrNbTaMoN highentropy alloy (HEA) thin films with varying nitrogen contents on Si wafer,AISI304 and 420 stainless steel substrates. The cross-sectional morphology, composition, and crystal structure of thin films were analyzed using scanning electron microscopy, electron probe microanalyzer, X-ray diffraction, andtransmission electron microscope, respectively. Subsequently, potentiodynamic polarization corrosion tests were conducted on the HEA thin films in 3.5 wt.% NaCl aqueous solution using an electrochemical workstation to evaluate their corrosion resistance. We found that TiZrNbTaMoN HEA nitride coatings exhibited a hardness of up to 29 GPa, along with outstanding corrosion resistance.The effect of nitrogen content on the phase, mechanical properties, and corrosion resistance of TiZrNbTaMoN HEA thin films was discussed in this work.The potential applications for the TiZrNbTaMoN HEA thin filmsin the machining industries were proposed.

8:40am **PP2-1-WeM-3 Insights into the Carbon HiPIMS Discharge: Ionized Flux Fraction and Ion Energy Distribution**, ***Tetsuhide Shimizu [simizu-tetuhide@tmu.ac.jp]***, *Ryo Sakamoto, Erdong Chen,* Tokyo Metropolitan University, Japan; *Caroline Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *Peter Klein,* Masaryk University, Czechia; *Daniel Lundin,* Linköping University, Sweden

Magnetron sputtering-based physical vapor deposition (PVD) has gained considerable attention for the synthesis of functional carbon and carbide coatings, such as tetrahedral amorphous carbon (ta-C), due to its scalability, cost-effectiveness, and uniform film deposition capabilities. In this context, enhancing the ionization degree of carbon using high-power impulse magnetron sputtering (HiPIMS) presents a promising opportunity to expand its applicability. Therefore, substantial progress has been made toward increasing carbon ionization in HiPIMS discharge, through techniques such as adding neon (Ne) gas and employing bipolar pulse schemes. However, the ionization fraction of carbon achieved by HiPIMS remains significantly lower than other techniques, e.g. filtered cathodic vacuum arc (FCVA) and pulsed laser deposition (PLD), presenting significant challenges to its adoption as an alternative approach. Despite these limitations, effectively utilizing the carbon ions generated in HiPIMS discharges requires a detailed quantitative understanding of the ionization fraction, their transport to the substrate, and their role in film growth. In this study, we aim to quantitatively investigate the ionized flux fraction and ion energy distributions in HiPIMS carbon discharges using argon (Ar) as the working gas, correlating these metrics with key process parameters. To achieve this, plasma diagnostics were performed using a magnetically shielded charge selective quartz crystal microbalance (ionmeter), time-of-flight (TOF) mass spectrometry, and time-resolved optical emission spectroscopy, with particular focus on the effects of the peak discharge current density, working gas pressure, and magnetic field. Our results demonstrate that the ionized flux fraction of carbon increases with higher peak current density, lower working pressure, and weaker magnetic fields. The maximum ionized flux fraction of ~12% was observed at a peak current density of 3.1 A/cm^2 under the weakest magnetic field configuration at a working pressure of 0.6 Pa. Furthermore, the ion energy distribution functions (IEDFs) revealed a distinct high-energy tail exceeding 100 eV, a feature not commonly observed in conventional HiPIMS discharges involving metal targets. Using time-resolved optical emission imaging, we also investigated the kinetic mechanisms underlying the acceleration of these high-energy carbon ions. This study highlights the importance of process parameter control in achieving efficient carbon ionization and transport, which is essential for advancing HiPIMS as a viable technique for carbon coating technologies.

9:00am **PP2-1-WeM-4 Reactive Mode Transition in Multi-Pulse HiPIMS Discharge of Vanadium in Ar/O2 Gas Mixtures**, ***Erdong Chen [chen-erdong@ed.tmu.ac.jp]***, *Tetsuhide Shimizu,* Tokyo Metropolitan University, Japan; *Caroline Hain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *Stephanos Konstantinidis,* University of Mons, Belgium; *Daniel Lundin,* Linkoping University, Sweden

Vanadium dioxide (VO2) is a thermochromic material that undergoes a metal-insulator transition (MIT) at approximately 68°C, resulting in significant alterations in optical and electrical properties. However, the formation of single-phase VO2 films is challenging in reactive sputtering due to the wide range of vanadium-oxygen (V-O) stoichiometries [1], leading to a limited process window. Based on the relationship between the oxidation state on the target surface and peak current in reactive high-power impulse magnetron sputtering (R-HiPIMS) systems [2], hysteresis examinations were performed to assess peak current evolution in response to variations in oxygen gas flow, aiming to identify an optimal process window for VO2 fabrication. An abrupt decline in peak current was observed upon increasing the O2 gas flow to 1 standard cubic centimeter per minute (sccm), accompanied by a relatively large hysteresis window, which hindered process stabilization and suggested the formation of vanadium pentoxide (V2O5) on the target surface. To address these challenges, we employed a novel approach utilizing very short, multi-pulse sequences in the R-HiPIMS process. This method eliminated the abrupt drop in peak current and reduced the hysteresis window by 36.6%, facilitating improved control over the VO2 deposition process. Additionally, multi-pulse HiPIMS (m-HiPIMS) enhanced both the ionization flux fraction and deposition rate while effectively managing arcing phenomena. Further analysis revealed characteristic variations in peak current (Ipk) as a function of O2 gas flow, with distinct peak current values and waveforms for each micro-pulse. Pulse on time and the number of micro pulses were also investigated to find a suitable process condition for VO2 deposition using multi-pulse mode R-HiPIMS. Comprehensive investigations into these micro-pulses were conducted using mass spectrometry to correlate findings with the surface chemistry of the vanadium target. The growth and properties of the deposited films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystallinity of VOx films and their electrical and optical performance were evaluated.

9:20am **PP2-1-WeM-5 HiPIMS goes Ferroelectric: Improving the Remnant Polarization and Leakage in Ferroelectric AlScN for Memory Applications**,
Federica Messi, Jyotish Patidar, Nathan Rodkey, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; Morgan Trassin,* ETH Zurich, Switzerland*; **Sebastian Siol [sebastian.siol@empa.ch]**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The increasing demands of big data and AI necessitate breakthroughs in energy-efficient computing and data storage. Ferroelectric nitrides, such as aluminum scandium nitride (AlScN), show great potential for non-volatile memory technologies due to their high remnant polarization, temperature stability, and compatibility with current semiconductor manufacturing processes.

The performance of ferroelectric nitrides is directly linked with their structural properties. The remnant polarization can be improved by increasing the c-axis orientation of the film, whereas the leakage current density can be improved by optimizing the microstructure. Point defects however negatively affect the breakdown behavior of the material, which represents a major challenge in the deposition of ferroelectric thin films.

Metal-ion synchronized high-power impulse magnetron sputtering (MIS-HiPIMS) can be used to accelerate film-forming metal ions onto the growing film, resulting in enhanced crystalline quality, improved c-axis texture, and a compact microstructure. Building on our recent successful demonstration of MIS-HiPIMS for piezoelectric thin films [1] we leverage the unique advantages of the technique for the deposition of ferroelectric AlScN with excellent performance.

Through a combinatorial study, we investigate the influence of HiPIMS on the ferroelectric properties of $Al_{1-x}Sc_xN$ films while correlating these properties with crystallinity and Sc composition. Our optimized deposition process successfully yields $Al_{1-x}Sc_xN$ films on Si substrates with performance that is otherwise only achieved using epitaxial growth.[2] Compared with previous reports using conventional sputtering the HiPIMS films show significantly enhanced remanent polarization with values of > 170 $\mu C/cm^2$ while maintaining comparable coercive fields of 5.0 MV/cm. Notably, our findings reveal that the remanent polarization remains stable even with increasing scandium concentrations. At the same time the leakage current densities are among the lowest reported to date.[3] These results can be explained by the excellent c-axis texture enabled by HiPIMS. In the future HiPIMS could enable dense ferroelectric films with low thickness to reduce the switching potential. To our knowledge this is the first report of ferroelectric switching in HiPIMS-deposited nitride thin films. Overall, the results are more than promising and highlight the potential of HiPIMS for the development of defect-sensitive electronic thin films.

[1] Patidar et al. Physical Review Materials 8 (9), 095001, 2024

[2] Deng et al. Journal of the American Ceramic Society, **107**, (3), 2023

[3] Yazawa et al. arXiv preprint arXiv:2407.14037, 2024

9:40am **PP2-1-WeM-6 Controlling Film Growth by Changing the Target Thickness**,
***Diederik Depla [Diederik.Depla@ugent.be]**, Farzaneh Ahangarani Farahani, Andreas Debrabandere,* Ghent University, Belgium

This paper summarizes a series of experiments demonstrating the significance of energetic species during DC magnetron sputter deposition. The first example focuses on the phase composition of tungsten (W) films, which can consist of a mixture of a-W and b-W crystals. Various mechanisms have been proposed to explain phase selection, including substrate heating due to plasma exposure and residual gas pressure. However, a broad parameter scan rules out these trends and shows that the phase composition can be quantitatively correlated with the flux of reflected neutrals with energies exceeding the displacement energy threshold. To establish this correlation, the phase composition is quantitatively determined using X-ray diffraction (XRD) analysis and combined with test particle Monte Carlo simulations to evaluate the energy of the reflected neutrals. The energy of these neutrals is defined by binary collisions between argon (Ar) and tungsten (W) atoms and the initial energy of the argon ions, which is set by the discharge voltage. Increasing the target thickness results in a lower magnetic field strength and, consequently, a higher discharge voltage. This effect allows the phase composition to be tuned by just adjusting the target thickness. The role of target thickness is further illustrated in a study on the percolation film thickness during the growth of silver (Ag) thin films. In-situ four-point probe resistance measurements are used to investigate the initial nucleation of these films. A power-law correlation between the percolation thickness and the deposition flux is observed, with the correlation exponent adjustable through variations in target thickness. Both studies highlight that reporting only the discharge power during experiments omits essential information critical for other researchers.

F. Ahangarani Farahani, D. Depla. “Phase Composition of Sputter Deposited Tungsten Thin Films.” *Surface and Coatings Technology*, vol. 494 (2024) 131447

11:00am **PP2-1-WeM-10 Effect of Nitrogen Content on the Microstructure, Mechanical, and Anti Corrosion Properties of AlCrNbSiTiN High Entropy Alloy Films Fabricated by High Power Impulse Magnetron Sputtering**,
***Sheng-Jui Tseng [pprayray0915@gmail.com]**,* National Taipei University of Technology, Taiwan*; Chia-Lin Li,* Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; Yung-Chin Yung,* National Taipei University of Technology, Taiwan*; Bih-Show Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taiwan*; Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) films, especially the HEA nitride coatings, have attracted much attention from industries and researchers due to their unique mechanical properties and corrosion resistance. In this work, the AlCrNbSiTiN HEA coatings were fabricated on Si wafers, AISI 420 and 304 stainless steel plates by high power impulse magnetron sputtering. To investigate the impact of equimolar AlCrNbSiTi target poisoning ratios (ranging from 10 to 90 %) and the nitrogen contents on the phase, microstructure, mechanical, and anti corrosion properties of AlCrNbSiTiN coatings, a plasma emission monitoring (PEM) feedback control system was employed during sputtering. A systematic analysis of the microstructure and mechanical properties was conducted. The chemical compositions of HEA coatings were investigated by a field emission (FE) electron probe microanalyzer. FE-scanning electron microscopy and transmission electron microscopy were used to examine the microstructure of HEA films. Additionally, X-ray diffraction was employed to assess grain size, lattice constants, and crystallinity. A series of mechanical property tests, including hardness, adhesion, wear, and residual stress measurements were performed. The potentiodynamic polarization test of coatings in the 0.5 M H2SO4 aqueous solution was examined. It is anticipated that the AlCrNbSiTi HEA film exhibited an amorphous structure. With increased nitrogen contents and target poisoning ratios, the AlCrNbSiTiN HEA nitride films transformed into a face-centered cubic structure. The HEA nitride films are projected to show enhanced hardness and elastic modulus, primarily due to the formation of a saturated metal nitride phase and solid solution strengthening from multiple elements. Based on the experimental results, the effects of target poisoning and nitrogen contents on the phase, microstructure, mechanical properties, and corrosion resistance of AlCrNbSiTiN coatings were discussed in this study.

11:20am **PP2-1-WeM-11 Effects of High-Power Impulse Plasma Source (HiPIPS) Parameters on the Properties of Aluminum Thin Films Synthesized at Atmospheric Pressure**,
***Brianna Hoff [brianna.hoff@mines.sdsmt.edu]**, Forest Thompson, Nathan Madden, Grant Crawford,* South Dakota School of Mines and Technology, USA

High vacuum is required for conventional physical vapor deposition (PVD) techniques which restricts the application space that benefits from the dimensional stability, functionality, and chemically benign processing afforded by PVD thin films. Motivated by this limitation, a high-power impulse plasma source (HiPIPS) has been developed for surface engineering at atmospheric pressure. HiPIPS technology utilizes high-voltage, low duty cycle DC pulses to generate a plasma discharge between a consumable feedstock (cathode) and a conductive plasma jet nozzle (anode). The plasma is forced out of the nozzle by high flow rates of process gas where it subsequently interacts with a substrate which may be biased to increase the kinetic energy of ionized species. The HiPIPS design enables high plasma density to be achieved while maintaining low average power. In this study, processing-microstructure-property relationships are reported for the HiPIPS deposition of metallic aluminum (Al) films. Argon (Ar) was used as the working gas, and Al thin films were deposited at atmospheric pressure by utilizing Al alloy electrodes. HiPIPS system design variables and plasma discharge characteristics were correlated with the mechanical, compositional, and microstructural properties of the Al films. Film characterization was conducted via adhesion testing, energy dispersive x-ray spectroscopy, transmission electron microscopy, and atomic force microscopy. In this presentation, HiPIPS parameters which lead to desirable film qualities are discussed.

11:40am **PP2-1-WeM-12 Enhancing CrAl Ionization in HiPIMS Using Auxiliary Targets: Insights from Time-Averaged OES**, ***Kai-Shawn Tang [a0966877063@gmail.com]****, Ying-Xiang Lin, Chih-Yen Lin, Yi-Hui Lee, Wan-Yu Wu,* National United University, Taiwan

Recently, High-Power Pulsed Magnetron Sputtering (HiPIMS) technology, due to its high ionization rate, has enabled increased ion bombardment during film growth, resulting in dense and smooth films. Previous studies using Bipulse-HiPIMS to deposit Ag-Cu and Ti-Cu films showed that, compared to unipolar mode, Ag-Cu co-sputtering significantly increased the ionization of Ag, while Ti-Cu co-sputtering greatly enhanced the ionization of Cu. These findings suggest that, in the Bipulse-HiPIMS process, the selection and configuration of targets, as well as the tuning of each target's parameters, are closely related to the ionization rate of plasma species.

CrAlN possesses excellent oxidation resistance; however, ternary metal nitride films are no longer sufficient to meet current demands. Therefore, we further investigated quaternary metal nitride films, doping with elements such as Cr, Ti, and Zr to enhance mechanical properties and oxidation resistance. This study uses Bipulse-HiPIMS co-sputtering, with CrAl as the main target at a fixed power of 1.5 kW and Cr, Ti, and Zr as auxiliary targets. Since Cr has a relatively high second ionization energy (16.49 eV), whereas Ti and Zr have second ionization energies of 13.58 eV and 13.13 eV respectively, Ti and Zr are expected to ionize more readily than Cr. The Bipulse-HiPIMS technique aims to assist the ionization of the less readily ionized material (Cr) by more easily ionized materials. Time-averaged OES was used to measure the effect of different target materials on the plasma spectrum during the process.

The auxiliary target power was increased from 0.2 kW to 0.8 kW, observing plasma conditions on the CrAl target. It was found that plasma intensity was lowest in single-target mode, while the addition of an auxiliary target significantly enhanced plasma intensity. The study showed that as auxiliary target power increased, the intensities of Cr^+, Ar^+, N_2^+, N_2^{2+}, and Cr^0 in the plasma also increased. Next, with the auxiliary target power fixed at 0.5 kW, the auxiliary target's duty cycle was varied from 3% to 15%. Under different duty cycle conditions, it was observed that lower duty cycles led to increased Cr^+ and Al^+ intensities, with minimal differences in N_2^+ and N_2^{2+}, while Ar^+ intensity increased with higher duty cycles. The effect of different auxiliary targets is also demonstrated.

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

HiPIMS, Pulsed Plasmas and Energetic Deposition II

Moderators: Dr. Tetsushide Shimizu, Tokyo Metropolitan University, Japan, **Dr. 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 Investigation of Surface Bond Structure and Colour Variations in Thin Films Deposited via Aca and Hipims Techniques***, **Milena Pazzi [milena.pazzi@unimore.it]**, Giovanni Bolelli,* Universita degli Studi di Modena e Reggio Emilia, Italy*; Andreas Fuchs, Daniel Barnholt, Philipp Immich,* Hauzer Technocoating, Netherlands*; Luca Lusvarghi,* Universita degli Studi di Modena e Reggio Emilia, Italy

Understanding surface bond structures and how they affect material properties is crucial for optimizing the optical and functional qualities of thin films for decorative and functional applications. Specifically, the objective of this research is to investigate the reasons behind color changes and physical property differences among coatings based on metal carbonitrides. We tested samples obtained by High-Power Impulse Magnetron Sputtering (HiPIMS) and Advanced Controlled Arc (ACA), two advanced techniques frequently used to deposit this type of coatings.

In order to investigate both chemical and structural issues, several analytical techniques will be employed. The bonding structures and the chemical composition of the coatings will be characterized by Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). By combining high-resolution Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS), we will be able to thoroughly analyze both surface and cross-sectional morphologies, giving us important insights on the compositional uniformity and microstructural integrity of the films. Additionally, mechanical performance will be studied by nanoindentation to evaluate hardness and scratch tests to assess adhesive strength. The exact color values in the CIE L* a* b* color space are measured using a colorimeter on the samples right after each batch.

By determining the parameters influencing these differences, we seek to improve the knowledge of the process-structure-properties relation in metal carbonitride films. The study's findings are expected to provide useful insights into the customisation of optical and mechanical properties in industrial applications that require precise control over both the appearance and performance of thin films.

3:00pm **PP2-2-WeA-4 On Unipolar and Bipolar Hipims Pulse Configurations to Enhance Energy and Ion Flux to Insulating Substrates***, **Mina Farahani [farahani@ntis.zcu.cz]**, Tomáš Kozák, Jiří Čapek,* University of West Bohemia - NTIS, Czechia

High-power impulse magnetron sputtering (HiPIMS) is an advanced technique for thin film deposition, delivering high target power in short pulses to achieve greater ionization than conventional DC magnetron sputtering. Despite this increase in ionization, many ions still have relatively low energy, so substrate biasing is often used to boost energy transfer to the growing film. For insulating substrates, where direct biasing is impossible, bipolar HiPIMS (alternating negative and positive pulses with a floating substrate) offers a partial solution. However, rapid charging of insulated substrates limits energy transfer. This study aims to optimize bipolar HiPIMS pulse configurations to explore the potential enhancement of energy transfer even for insulating substrates.

Experiments were conducted using a magnetron and a Ti target powered by a DC source and driven by a bipolar HiPIMS pulsing unit. Various pulse configurations (unipolar HiPIMS, bipolar HiPIMS, chopped unipolar, and chopped bipolar HiPIMS) were applied under unbalanced magnetic fields (Fig. 1) with the same average power. In-situ ion mass and energy spectroscopy (MS) analyses were carried out, and the total energy flux to a substrate was measured using a passive thermal probe at a floating and ground potential. Moreover, the depositions on insulating substrates or films with various capacitances were simulated by connecting a defined external capacitor between the probe and the ground. Finally, Ti films were deposited on a floating substrate holder for structural analysis.

Unlike standard HiPIMS, bipolar HiPIMS introduces a high-energy peak in the IEDF; with multi-pulse configurations, this peak broadens and the high-energy tail is enhanced. Additionally, time-resolved measurements provide valuable insights, like the evolution of energetic ion flux to the film. Both MS and thermal probe measurements show enhancement of ion and energy fluxes to the substrate for chopped configurations (Fig. 2). Moreover, heat flux varies with capacitance: with a low capacitance, ion acceleration occurs only at the start of each positive pulse before the film surface is fully charged, so the effect on the energy delivered to the film is small. With a high capacitance, ion acceleration is effective throughout the positive pulse regardless of its length, as is the case for a grounded substrate. For medium capacitance, chopping the positive pulse boosts the energy delivered to the film as the substrate discharges during pulse pauses. These effects were also manifested in the structure and stress of the deposited films.

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.

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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.

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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.

Plasma and Vapor Deposition Processes
Room Palm 3-4 - Session PP3-WeA

ALD, CVD Coating Technologies

Moderators: Dr. Hiroki Kondo, Kyushu University, Japan, **Dr. Frederic Mercier**, University of Grenoble Alpes, France

2:00pm **PP3-WeA-1 Electrical Conductivity as a New Parameter for SAMs-Free Area-Selective Atomic Layer Deposition, from Principles to Photoconversion Devices*, David Horwat [david.horwat@univ-lorraine.fr]*,** Institut Jean Lamour/Université de Lorraine, France **INVITED**

Area-selective atomic layer deposition (AS-ALD) has gained a lot of attention in recent years due to the possibility of achieving accurate patterns in nanoscales features, especially for complex 2D or 3D nanostructures [1], which makes this technique compatible with the continuous downscaling in electronics devices. AS-ALD is usually achieved by deactivation of part of the surface by self-assembly monolayer (SAMs) of certain molecules [2]. Here we propose a different approach that consists in modulating a property of the substrate to achieve localized growth of different materials, its electrical conductivity. This concept is demonstrated by selective growth of high quality metallic Cu, and semiconducting Cu_2O or absence of deposition, depending on the value of the electrical conductivity and substrate temperature. We will present our understanding of the process and will highlight some of its potentials. It is for instance possible to interface n and p semiconductors or semiconductors and metals with local control in order to fabricate demonstrator devices [3-5] of potential interest for photoconversion purposes.

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3:00pm **PP3-WeA-4 Selective Generation of Nanoparticles in Plasma-Enhanced CVD and Deposition of Carbon Films with Low Compressive Stress*, Kazunori Koga [koga@ed.kyushu-u.ac.jp]*,** Kyushu University, Japan **INVITED**

The stress of diamond-like carbon (DLC) films has been a significant issue in enhancing the performance of protective coatings used in dry etching masks, automotive parts, and battery electrodes. Traditionally, metal nanoparticles have been incorporated into the films to reduce stress. However, this approach often leads to metal contamination, which deteriorates the performance of semiconductor devices. In this study, inspired by the incorporation of metal nanoparticles, we aimed to alleviate stress by incorporating carbon nanoparticles (CNPs) into DLC films. As a first step, we successfully controlled the size of the nanoparticles using plasma chemical vapor deposition (CVD). Subsequently, we managed to control the amount of CNPs deposited on substrates using capacitively coupled plasma CVD, a technique widely employed for large-area deposition. Transmission electron microscopy (TEM) images revealed that the deposited CNPs could be classified into two size groups: the smaller group with a mean size of approximately 2.9 nm, and the larger group with a mean size of around 16 nm. We successfully controlled the amount of CNPs on the films with discharge duration. We shortened the discharge time to prevent the nanoparticles from piling up on the substrate, resulting in sparse deposition on the film surface. The amount of nanoparticles deposited was expressed as a percentage of nanoparticles per unit area of the film, defined as the coverage (Cp) of CNPs. Based on these results, we fabricated a-C:H/CNP/a-C:H sandwich-like films using the plasma CVD. A mixture of Ar and CH_4 gases was introduced from the top of the chamber at flow rates of 19 sccm and 2.6 sccm, respectively, maintaining a total pressure of 0.3 Torr. These conditions were consistent with those used for CNP deposition. The mass density of the deposited a-C:H films was 1.88 g/cm^3. We observed that the film stress decreased with increasing Cp, from 1.59 GPa at Cp = 0% to 1.02 GPa at Cp = 8.9%, with a similar value at Cp = 15.9%. This represents a reduction rate of 35.8%. These results indicate that incorporating a small amount of CNPs can effectively reduce film stress. Moreover, we successfully expressed the stress reduction rate in terms of Cp using experimental results for different sandwich film thicknesses.

4:00pm **PP3-WeA-7 Direct ALD Deposition by μDALP™. Precision Coatings for Next Gen Devices*, Mira Baraket [mira.baraket@mail.com]*,** ATLANT 3D Nanosystems, Denmark

Advancements in the microelectronics sector demand the ability to create high-quality films with nanoscale accuracy to pattern complex features on substrates. Area-selective deposition (ASD) meets this demand by enabling the selective formation of films on specific surface regions while preventing deposition elsewhere[1]. Atomic Layer Deposition (ALD), a well-established technique in the semiconductor field has been widely investigated for ASD applications. However, this method often requires initial surface treatments, surface functionalization, or alterations to the process[2].

ATLANT 3D has introduced an innovative technology named microreactor Direct Atomic Layer Processing - μDALP™, enabling precise localized thin film deposition with accuracy down to a few hundred microns, incorporating all conventional ALD advantages (Fig. 1 (a)). This technology leverages a specialized design of micronozzles to spatially separate precursors and reactants, facilitating rapid film deposition at atmospheric conditions (Fig. 1(b))[3]. The μDALP™ technology stands out for its vertical atomic monolayer precision, achieving an accuracy of 0.2 nm. It is especially effective for selective patterning across diverse surfaces, including microfluidic channels, optical gratings, and nanostructured interfaces, showcasing its versatility and precision. Moreover, this technology enables fast and cost-effective prototyping of devices, facilitating a level of design creativity and optimization that is challenging by traditional thin film deposition approaches.

ATLANT 3D's technology has been successfully utilized to innovate in fields such as optics and photonics, quantum devices, microelectromechanical systems (MEMS), RF electronics, cutting-edge memory technologies, advanced packaging, and energy storage, showcasing its wide-ranging application potential. In this talk we will explain the significant contributions of our μDALP™ technology to the evolution and expansion of thin-film manufacturing and discuss the wide array of opportunities it presents across different sectors.

Fig. 1. (a)Top view of aligned Si trenches (aligned horizontally) coated with a perpendicular line of TiO_2 (low magnification SEM). (b) Microfluidic precursor delivery concept: Schematic view of the delivery nozzle in frontal view (top) and in cross-section (lower panel).

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4:20pm **PP3-WeA-8 Temperature Influence on the Chemical Vapor Deposition of Nitrogen-Doped SiC Polycrystalline Films for Brain-Implantable Devices***,* *Michalis Gavalas,* SIMaP, CNRS, University Grenoble Alpes, France*; Konstantinos Zekentes,* Microelectronics Group/IESL-FORTH, University of Crete, Hellas, Greece*;* ***Frederic Mercier [frederic.mercier@grenoble-inp.fr]****,* SIMaP, CNRS, University Grenoble Alpes, France

Silicon carbide (SiC) is a wide-gap semiconductor, with high chemical stability, that is proposed as a functional material for biomedical applications [1,2]. Epitaxial and polycrystalline SiC has been proposed for neural recording and stimulation electrode devices [3,4]. Unlike the epitaxial case, polycrystalline 3C-SiC is advantageous as it can grow on various substrates (silicon, silica, diamond, sapphire etc) and at lower temperatures. However, the state of the art for the polycrystalline SiC based neural interfaces is still poor. Dense layers of poly-SiC with low resistivity and low stress combined with the good chemical stability of SiC are required for the fabrication of neural interfaces [3,4]. Towards this aim, polycrystalline nitrogen doped 3C-SiC thin films, are grown on 2 inches Si wafers by low-pressure chemical vapor deposition (LPCVD) technique with the aim to be used as support and active material in microelectronic devices and for neural interfaces. The effect of deposition temperature on the structural, mechanical and electrical properties is investigated. Growth rate is varying from 1 µm/h to 14 µm/h, along with the deposition temperature. We show that we can control simultaneously the structural and electrical properties of polycrystalline SiC by changing the deposition temperature. Films with resistivity as low as (10.0 ± 0.5) mΩ·cm, low residual stress of (245 ± 13) MPa and RMS surface roughness of (159 ± 54) nm are achieved. Furthermore, the chemical stability of SiC in physiological fluids is investigated and we show that polycrystalline SiC can be a suitable material for neural interfaces applications.

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Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP8-1-ThM

Commemorative Session for Papken Hovsepian I

Moderators: Prof. Arutiun P. Ehiasarian, Sheffield Hallam University, UK, **Philipp Immich**, IHI Hauzer Techno Coating B.V., Netherlands

8:00am **PP8-1-ThM-1 How Industry and Research Are Connected to Accelerate Development***, **Philipp Immich [pimmich@hauzer.nl]**,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

The relationship between Sheffield Hallam University and Hauzer has been long-standing, beginning with Dieter Münz, former CEO of Hauzer, becoming a professor at Sheffield in 1993. When Papken Hovsepian joined Hallam, the collaboration between become even more intense. Papken played a crucial role in the early discussions for the first EU projects focused on HIPIMS development.

In 2003, Hauzer conducted initial tests with Advanced Energy's power supply and AC Converters, marking the first empirical steps in HIPIMS alongside Papken. The EU INNOVATIAL project, which started in 2004, focused on HIPIMS development in collaboration with Sheffield Hallam University (SHU), which later licensed HIPIMS etching to Hauzer. Hauzer's involvement in significant European projects like Alticut and Nanocoat further strengthened this partnership. The first HIPIMS trials at Hauzer led to groundbreaking research and publications, particularly on superlattice coatings, a major focus of Papken's work.

The collaboration with Papken and later Arutiun Ehiasarian (Harry) was instrumental in Hauzer's success, resulting in numerous patents, including HIPIMS Bias and ARC handling. The initial impulse for the ABS conference days in 1995 was triggered by Dieter Münz, later involving strong participation from Papken in the HIPIMS Conference. Papken's motto was always about bringing industry and research together to learn from each other and accelerate developments.

In 2023, Hauzer celebrated its 40th anniversary by hosting the HIPIMS community for the 13th HIPIMS conference in Venlo for the second time since 2008, unfortunately a testament to the enduring relationship with Papken and his contributions.

Papken's legacy is deeply cherished by the Hauzer family, and his impact on the HIPIMS community and beyond will always be remembered. Thank you, Papken, for your invaluable contributions and for being an integral part of our history.

8:40am **PP8-1-ThM-3 Invited Paper***, **Ivan Petrov [petrov@illinois.edu]**,* University of Illinois at Urbana-Champaign, USA **INVITED**

9:20am **PP8-1-ThM-5 Invited Paper***, **Francisco Javier Perez Trujillo [fjperez@quim.ucm.es]**,* Universidad Complutense de Madrid, Spain **INVITED**

10:20am **PP8-1-ThM-8 Recent Progress in Coating Materials Design: Thermal Stability vs Chemical Stability***, Amir Navidi, Deborah Neuss, Soheil Karimi, Marcus Hans,* Materials Chemistry, RWTH Aachen University, Germany*; Daniel Primetzhofer,* Materials Physics, Dep. of Physics and Astronomy, Uppsala University, Sweden*; **Jochen M. Schneider [schneider@mch.rwth-aachen.de]**,* Materials Chemistry, RWTH Aachen University, Germany **INVITED**

The roles of chemical, structural and interfacial complexity for the design of thermally stable and chemically stable protective coating materials is discussed. In this talk the thermal stability of nitride thin films of varying chemical complexity is compared. Furthermore, the oxidation behavior of monolithic transition metal diboride based coating systems are compared to coating architectures containing multiple interfaces. The role of thermal stability for the oxidation behaviour of the above mentioned coating systems will be discussed.

11:00am **PP8-1-ThM-10 HiPIMS and Magnetron Sputtered Carbon-Based Nanocomposites***, **Sven Ulrich [sven.ulrich@imf.fzk.de]**,* Forschungszentrum Karlsruhe, Germany **INVITED**

Carbon-based nanocomposites with adjustable multifunctional properties are suitable candidates for both tribological applications and energy technologies. Reactive DC magnetron sputtering and HiPIMS are selected as coating processes, using a metallic transition metal target, argon as the working gas and methane as the reactive gas. As shown in plasma diagnostic investigations, in contrast to DC magnetron sputtering, HiPIMS exhibits a high ion content of the film-forming particles and the energy deposited by ion bombardment during film growth can be precisely adjusted. The cpnstitution and microstructure were determined by a combination of several analytical methods: EPMA, ERDA, Raman spectroscopy at four different wavelengths, XRD, TEM and HRTEM were used to determine the composition and correlate it with the mechanical properties. It is shown that by varying the methane reactive gas flow, single-phase transition metal carbide coatings as well as nanocomposites consisting of nanocrystalline transition metal carbide grains in a hydrogenated amorphous carbon network can be produced. Thus, by choosing the optimized process parameters (switching function), multilayers can be produced from these two components.

Keywords: HiPIMS, Magnetron sputtering, carbon-based nanocomposites

11:40am **PP8-1-ThM-12 Superlattice Coatings: Unleashing Superior Properties Through Architected Nanolayers***, **Paul Mayrhofer [paul.mayrhofer@tuwien.ac.at]**,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Inspired by Helmersson, Hovsepian, and Münz's pioneering work on transition metal nitride superlattices, this concept has been a part of my research since 2003, particularly influenced by Papken Hovsepian's application-driven advancements. Here, we explore how nanolamellar microstructures can simultaneously enhance the hardness and fracture toughness of hard coatings. Superlattices, formed by alternating nanometer-thick layers, present opportunities to engineer mechanical properties superior to their individual constituents.

Careful interface design enables superlattices to achieve exceptional hardness, toughness, and thermal stability, essential for extreme environments. This concept applies effectively to nitrides, carbides, borides, and their mixtures. Mechanisms like dislocation blocking, coherent interface strengthening, and stress modulation contribute to this superior performance. The "epitaxial stabilization effect" further plays a key role, where pseudomorphic forces of the stabilizing layer act on the surface of the other layer during nucleation and growth, causing it to crystallize in its metastable but more similar structure rather than its thermodynamically stable but different structure. As a result, in addition to coherency stresses (due to lattice mismatches) and modulus mismatches, phases as well as stoichiometries that may exhibit higher inherent ductility, according to their decreased G/B ratio and increased Cauchy pressure, become accessible (like shown for superlattices containing MoN_z, WN_z, SiN_z, or AlN layers).

Upon loading, dislocation nucleation and interface-triggered phase transformations dissipate energy, enhancing fracture toughness. For instance, TiN/WN superlattices achieve hardness (36.7±0.8 GPa) and fracture toughness (4.6±0.2 MPa·$m^{0.5}$) with optimized layer thicknesses (Λ = 8.1–10.2 nm). This work examines the influence of layer thickness, interface quality, and architecture on mechanical behavior, emphasizing the critical balance between toughness and hardness, alongside high-temperature stability. The findings underscore the potential of superlattice designs for protective coatings, high-performance tools, and structural components under severe thermal and mechanical loads.

In memorial of Papken Hosepian.

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP8-2-ThA

Commemorative Session for Papken Hovsepian II

Moderators: Prof. Arutiun P. Ehiasarian, Sheffield Hallam University, UK, **Philipp Immich**, IHI Hauzer Techno Coating B.V., Netherlands

1:20pm **PP8-2-ThA-1 PVD Based Solutions for Mankind Through Applied Research*, Ton Hurkmans [ton.hurkmans@ionbond.com],*** IHI Ionbond Group, Germany **INVITED**

During our Ph.D. studies as well as early work at Bodycote and then later at Ionbond, we had a lot of positive interaction with Prof. Dr. Papken Hovsepian. Our shared passion was a desire to use thin film vacuum coating technology to improve products that are being used by people on a daily basis.

Applied research requires insight on both the technology and the market opportunities. It's basically a reversed engineering from macro-scale back to atomic levels, i.e. to translate desired product properties into coating properties and finding a way to synthesize such coating properties. Sheffield Hallam University and Ionbond have worked on many such examples and during the presentation we will elaborate on some of them.

At Bodycote commercial products were introduced and sold, known under tradenames like Supercote 11 (TiAlCrYN), Supercote 30 (TiAlN/VN), and Supercote 55 (CrN/NbN). In parallel we collaborated on multiple EU funded development projects, with names like Newchrome (replacement of electroplating), HIDAM (cutting tools), NitraCote (duplex treatments), ALTICUT (high end machining operations), Colour PVD (PVD coating with post-anodizing), HIPIMS (first EU project on HIPIMS), INNOVATIAL (coatings for jet engines), CORRAL (atomic layers against corrosion), and Monaco (the use of OEM within industry 4.0). There were also joined developments where the manufacturer or end user participated as well.

All the hard work also resulted in joined scientific papers and patents.

2:00pm **PP8-2-ThA-3 Managing Relative Abundance of Ions and Neutrals: A New Plasma Performance Metric in Modern Surface Engineering*, Ganesh Kamath [ganesh.kamath@asml.com],*** ASML, USA **INVITED**

Modern engineering components made up of metals/alloys, plastics and glass have to meet very stringent multifunctional quality specifications and must survive under longer operating conditions. The advent of innovative industrial scale ionized plasma technologies have successfully demonstrated the ability to process those components and fullfill such demands. More specifically, these plasma technologies are being used to produce and control desired amount of ions ($Metal^+/Gas^+$) and neutrals to bombard onto engineering component surfaces to create new multifunctional homogeneous/inhomogeneous nanostructured surface. The metal ions havethe most important influence on coating properties and structure. The modification of the surface of the substrate-to-be-coated by metal ion etching is important for improvement of coating adhesion, while assistance of the coating deposition process by metal ion bombardment plays the leading role in formation of nanostructured coatings with unique properties, usually outside of the thermodynamic equilibrium. Thus relative abundance of ions and neutrals are considered as new plasma performance metric in today's advanced surface engineering application.

One of the first technologies which used metal ion bombardment as a tool for improvement of magnetron sputtering coatings was arc-bond sputtering (ABS) technology introduced by W.D. Munz in 1991 and later perfected in the collaborative works by W.D. Munz and P. Hovsepian and their coworkers. In this technology the initial coating sublayer was deposited by cathodic arc followed by magnetron sputtering deposition which dramatically improved adhesion of the magnetron sputtering coating to the substrate. The ABS technology was utilized in large industrial-scale coating machines by Hauzer company. The filtered cathodic arc technology developed in 1980s-1990s allows to get rid of macroparticles and produce 100% ionized metal vapor plasma flow. It was developed to industrial scale applications by Large Area Filtered Arc Deposition (LAFAD) systems. The LAFAD process is capable of deposition the thermodynamically non-equilibrium coatings such as hydrogen-free diamond-like carbon (DLC) coatings and DLC-based nanocomposite coatings, both as a single layer and as nano-multilayers with high adhesion and cohesion properties. The productivity of the LAFAD process allowed its application for deposition of multilayer erosion resistant coatings for turbomachinery with coating thickness >100 µm.

2:40pm **PP8-2-ThA-5 Invited Paper*, Pawel Ozimek [pawel.ozimek@trumpf.com],*** Trumpf, USA **INVITED**

3:20pm **PP8-2-ThA-7 Carbon Based Surface Solutions – from a Glorious Legacy to Recent Advances*, Vishal Khetan [Vishal.Khetan@oerlikon.com],*** Oerlikon Surface Solution AG, Switzerland **INVITED**

Tribology and Surface Engineering, as enabling technologies, have been continuously advancing global manufacturing sectors in terms of fuel economy (reduced friction and wear), improved productivities and product reliability, functionalisation of machine components, providing alternative manufacturing processes due to environment legislations, and electrification of vehicles, etc. Along with the new generation manufacturing and climate change energy challenges surface engineering will phase in a new era of research and innovation. Carbon based surface solutions using technologies such as physical/chemical vapour deposition (PVD, CVD) deliver new and sustainable pathway in multiple manufacturing industries such as automotive, medical, packaging and aerospace can be addressed and introduced to a broader industry perspective.

While developing new carbon coatings and bringing them to industry as solutions, we always stand on the shoulders of giants like Prof. Papken Hovsepian. His work in the field of thin film technology was an inspiration for many and through this talk we illustrate how his work has channelled beautiful scientific ideas which turn into products serving various industrial application especially in the field of carbon-based surface coatings. Further, in co-relation to his work, we would be discussing scientific background, tribological and industrial relevance various carbon based surface solutions offered by Oerlikon Surface Solutions AG ranging from amorphous hydrogenated carbon to hydrogen free carbon coatings via PACVD,S3p (Scalable pulsed power plasma), Cathodic Arc evaporation and PICVD(Plasma induced chemical vapour deposition) with special focus on new upcoming carbon based solutions such as BALINIT® MAYURA, upcoming nanocrystalline diamond coating using PICVD technology.

4:00pm **PP8-2-ThA-9 Invited Paper*, Arutian P. Ehiasarian [a.ehiasarian@shu.ac.uk],*** Sheffield Hallam University, UK **INVITED**

Plasma and Vapor Deposition Processes
Room Golden State Ballroom - Session PP-ThP
Plasma and Vapor Deposition Processes Poster Session

PP-ThP-1 Optimizing Thin Film Deposition with Ion Energy and Flux Measurements in Pulsed Plasmas with Plasma Diagnostics, ***Angus McCarter [angus.mccarter@impedans.com]***, *Thomas Gilmore, Anshu Verma,* Chase House, City Junction Business Park, Ireland

In the field of metallic coatings and thin film deposition, precise control of deposition processes has become crucial. These processes are heavily dependent on the chemical/physical processes occurring on the substrate surface. Like any other surface in contact with plasma, a sheath usually develops on the substrate which pulls down the ions out of bulk plasma necessary to complete the process on the substrate. Furthermore, external RF/DC/tailored waveform biases are applied to the substrate to modify the ion behaviors. As it can affect the chemical composition, microstructure and the associated electrical properties of the thin films during plasma assisted deposition processes. Therefore, the characterization of only bulk plasma is not sufficient in providing insights necessary to understand the plasma surface interactions. A high-speed monitoring of the ion energy distribution function and ion flux can lead to enhanced understanding of the plasma surface interactions and improved process performance.

We will highlight the successful measurements done by the Semion RFEA diagnostic under different chamber and bias conditions. Such applications enabling accurate and precise control of deposition process on different materials and various plasma chemistries. It measures the ion energies hitting a surface, the ion flux, negative ions and bias voltage at any position inside a plasma chamber using an array of integrated sensors. On the other hand, the Semion pDC system measures these parameters in real time over an energy range up to 2000 eV (process dependent). It can do sub-microsecond time resolved measurements, for studying pulsed ICPs, or pulsed DC biases, as well as floating and grounded substrate conditions. The Semion Pulsed DC system is the key instrument used to measure the temporal evolution of the ion energy and flux at different times through the pulse period of a pulsed DC plasma process.These measurements are essential for establishing the correlation between the plasma inputs and the ion energy/flux which, in-turn, determines the effectiveness of the surface treatment.

PP-ThP-2 Influence of the Substrate on the Growth of Aluminium Oxide Films by Atomic Layer Deposition for Food Packaging Applications, *Hugo Patureau,* SIMaP, CNRS, University Grenoble Alpes, France*; Thierry Encinas,* CMTC, Grenoble INP, University Grenoble Alpes, France*; Alexandre Crisci,* ***Frederic Mercier [frederic.mercier@grenoble-inp.fr]***, SIMaP, CNRS, University Grenoble Alpes, France*; Erwan Gicquel,* CILKOA, France*; Arnaud Mantoux, Elisabeth Blanquet,* SIMAP, CNRS, University Grenoble Alpes, France

With the gradual ban on single use plastics, cellulosic products have emerged as suitable candidates to replace plastics in the packaging industry. Cellulose is biodegradable, recyclable and possesses good mechanical properties. To be viable for packaging, especially in the food industry, cellulose surfaces need to be functionalised to obtain additional properties, such as wettability, oxygen/water barriers and mechanical resistance in humid conditions.

In this context, we have investigated the synthesis of aluminium oxide films by an industrial Atomic Layer Deposition (ALD) process on cellulosic substrates using the precursors trimethylaluminium (TMA) and water. While the reactivity of these precursors on silicon are well established, the same cannot be said of cellulosic substrates due to their complex structure and their affinity with water. In this presentation, a study on the growth of ALD Al2O3 on silicon and cellulose is conducted. X-ray fluorescence (XRF) and Inductively coupled plasma mass spectrometry (ICP-MS) on cellulose is developed and implemented to quantify the amount of aluminium deposited. The saturation curves are established on silicon and cellulose, as well as the effect of the synthesis temperature. A comparison of both substrates is made and specific growth mechanisms of aluminium oxide by ALD on cellulosic substrates is discussed.

PP-ThP-3 Minimizing Secondary Electron Yield in Amorphous Carbon Thin Films: A Study on Power Density, Discharge Modes, and Hydrogen Incorporation, ***Valentine PETIT [valentine.petit@cern.ch]***, *Yorick Delaup, Alessia Pascali, Pedro Costa Pinto, Marcel Himmerlich, Christos Kouzios,* European Organization for Nuclear Research, Switzerland

Amorphous carbon thin films with low Secondary Electron Yield (SEY) are critical for applications where electron multipacting limits achievable performance. Such films are effective to mitigate electron cloud formation within the vacuum beam lines of particle accelerators such as the Large Hadron Collider and Super Proton Synchrotron at CERN. They are now also being implemented in the new Electron Ion Collider under construction at Brookhaven National Laboratory.

Research over the last decade has highlighted the significant role of hydrogen presence in the plasma discharge during deposition. Hydrogen incorporation in the films has been shown to increase the SEY, posing a key challenge in coating the extensive beam pipes for particle accelerators.

In this study, we examine the effects of power density and discharge mode, i.e. Direct Current (DC) and High-Power Impulse Magnetron Sputtering (HiPIMS), on the SEY of amorphous carbon films. These films were produced by sputtering in an Ar atmosphere with 1.3% D_2 to simulate hydrogen-like impurities typically arising from outgassing in the beam pipes and the deposition system. The D_2 consumption during the coating process was monitored by mass spectrometry and is correlated with the SEY, while X-ray Photoelectron Spectroscopy was used to characterize the films. Our findings indicate that higher deposition powers result in films with reduced deuterium incorporation and lower SEY. Additionally, for the same average power density, films deposited in HiPIMS mode exhibit lower SEY compared to those deposited in DC mode. The results are discussed in the context of hydrogen incorporation mechanisms in carbon films, with a view toward optimizing coating system design and process parameters

PP-ThP-4 Accurate Reporting of Time-of-Flight Measurements with Gated Mass Spectrometry, ***Nathan Rodkey [nathan.rodkey@empa.ch]***, *Jyotish Patidar, Sebastian Siol,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

The quality of high-power impulse magnetron sputtering (HiPIMS) deposited films can often be improved through the effective use of metal-ion synchronization (MIS). However, effective synchronization requires precise measurements of the time-of-flight (ToF) of ions, such that an accelerating bias can be properly synchronized. These measurements are commonly done using time- and energy- resolved mass spectrometry but require calibrations of the transit time of ions inside of the mass spectrometer to accurately report the ToF. The transit time can be calculated by estimating the travel length in varying parts of the spectrometer (e.g. from orifice to detector) and accounting for the interactions of ions with varying electrostatic optics (such as the extractor, energy filter, mass filter, and dynode).The errors associated with these estimations can lead to nonphysical values in a HiPIMS process, such as negative ToFs, or metal ions arriving to the substrate before process gas ions. As a result, many groups emphasize that their calibrations are estimations, or relevant only at sufficiently large time steps. Here we report a practical approach to determine the transit time in the spectrometer experimentally, which was already successfully employed for multiple projects in our group**.**We use a bipolar HiPIMS power supply to synchronize a gating pulse to the front end of a HiDEN Analytical EQP-300 mass spectrometer. The orifice of the mass-spec (50 µm) was placed at a 12 cm working distance. ToF was then measured by applying a +70 V bias to repel ions, and a 5 µs gating pulse of -30 V to accept them. To prevent interference of the driven front end (kept at +70 V) with the HiPIMS plasma, a grounded shield is placed in front of the mass-spec head with a 1-2 mm opening. The gate was synchronized to the HiPIMS pulse by providing a trigger signal, and data was collected at 5 µs intervals by adjusting the time delay of this pulse. The time-of-flights of Ar^+, N^+, Al^+ , Cu^+ and W^+ ions measured in this way are compared to those calculated using mass spectrometry flight tube equations.

PP-ThP-5 Focused Magnetron Sputtering: A Comprehensive Study of Magnetron Power Effects on AlCrN Coatings Under Industrial Conditions, ***Martin Ucik [m.ucik@platit.com]***, Masaryk University, Czechia

Introduction

Traditional coating methods, such as Cathodic Arc Evaporation (CAE), face challenges due to microscopic defects and other limitations. Focused Magnetic Field Magnetron Sputtering (F-MS) has emerged as a transformative solution, achieving a high ionized metal flux fraction even for large-scale targets [1]. Compared to conventional magnetron sputtering (DCMS), F-MS demonstrates a six-fold increase in power density [2]. This advantage, combined with effective cooling and prolonged duty cycles, establishes F-MS as a groundbreaking technology. Its integration into PLATIT's PVD coating unit, Pi411, represents a significant advancement in hard protective coatings for industrial applications.

Methods

F-MS operates by moving a reduced-size magnetron longitudinally inside a tubular target (Ø110 × 510 mm). This design enables high-power sputtering of up to 30 kW and allows the deposition of dense coatings at a growth rate of 2 µm/h using a 3-fold carousel rotation system.

Results

Coatings of (Al,Cr)N deposited via F-MS exhibited stoichiometric composition, smooth surfaces, and controlled defect levels. Mechanical property tests, plasma diagnostics, and cutting tests demonstrated strong interrelationships and benefits associated with higher power levels. Notably, cutting tests confirmed the superior performance of (Al,Cr)N coatings compared to state-of-the-art CAE coatings.

Conclusion

F-MS technology represents a significant breakthrough in the coating industry, addressing the limitations of traditional methods. Its ability to achieve high plasma power densities and a high degree of ionization for large-scale targets holds immense potential to advance industrial coating practices by enhancing efficiency and enabling new applications.

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PP-ThP-6 Design and Evaluation of a Laboratory-Scale Thermal ALD Reactor: Case Study with Aluminum Oxide and Zinc Oxide.*, Jackeline Navarro-Rodriguez [jackeline.navarro@uabc.edu.mx],* *David Mateos-Anzaldo, Jesus Martinez-Castelo, Rogelio Ramos-Irigoyen, Oscar Perez-Landeros, Mario Curiel-Alvarez, Benjamin Valdez-Salas,* UNIVERSIDAD AUTONOMA DE BAJA CALIFORNIA, Mexico*; Eduardo Martinez-Guerra,* CIMAV-Monterrey, Mexico*; Hugo Tiznado-Vázquez,* UNAM, Mexico*; Nicola Nedev,* UNIVERSIDAD AUTONOMA DE BAJA CALIFORNIA, Mexico

Atomic layer deposition (ALD) is a crucial technique in microelectronics for thin film deposition due to its precise thickness control at the atomic scale, although its sustainability remains a challenge due to its high cost. This work presents the results of a customized, cost-effective and efficient thermal ALD system designed to deposit semiconducting and insulating thin films such as aluminum oxide (Al_2O_3) and zinc oxide (ZnO) films, using trimethylaluminum (TMA) and diethylzinc (DEZ) as precursors, respectively. The oxidizing agent used was hydrogen peroxide (H_2O_2).

Thin films of Al_2O_3 and ZnO were deposited on silicon and corning glass substrates at a temperature of 200°C. Ellipsometry measurements were carried out to determine the thickness, optical constants, band gap and transparency.

The results obtained indicate the presence of a thin film deposited on silicon with 1160 cycles, with a growth rate of 1 Å/cycle which is equivalent to a thickness of ~116.4 nm, as well as a refractive index of 1.76, an extinction coefficient of 0. In addition, the zinc oxide film deposited on corning glass present approximately 80% of transparency in visible region.

The system stands out for its optimized design, easy handling and low cost, which makes it a viable option for academic research and applications in electronics and nanotechnology.

PP-ThP-7 Energy Flux Diagnostics in High Power Impulse Magnetron Sputtering*, **Caroline Adam [c.adam@physik.uni-kiel.de]**,* Kiel University, Germany*; Holger Kersten,* Kiel University, Kiel Nano, Germany

High power impulse magnetron sputtering (HiPIMS) has shown significant potential for thin film deposition. This potential is evident through the enhancement of film quality, specifically in terms of increased density [1] and adhesion [2] along with the diminished requirement for high substrate temperatures [3]. To achieve the optimal deposition process, it is crucial to develop a comprehensive understanding of the plasma-surface interaction at the substrate. This includes, in particular, analyzing the energy flux (transferred power from the plasma to the surface) and its composition. The energy flux is investigated by using a passive thermal probe (PTP) [4], a so-called non-conventional diagnostic, measuring the integral energy flux to the substrate. Insights into the composition of the energy flux are gained by applying a bias voltage to the thermal probe [4] and using a novel combination of PTP with a retarding field analyzer (RFA) [5]. This allows to measure simultaneously the ion energy distribution (IED) and to perform energy-resolved energy flux measurements. In addition, the neutral energy flux component can be quantified by repelling all charge carriers by the grid potentials. Since the energy resolution and sensitivity of the RFA is limited, the measurements of the IED are completed by energy-resolved mass spectrometry, both time-averaged and time-resolved [6].

These diagnostics have been applied to compare HiPIMS and DC magnetron sputtering processes with same gas pressure and average power sputtering a planar copper target in argon atmosphere. In total, the mean energy flux to the substrate is lower in HIPIMS operation. Hence, temperature sensitive substrates are better protected. Normalizing the energy flux to the deposition rate, which is lower in HiPIMS as well, gives a higher value for the energy flux per adatom in HiPIMS, which can be attributed to the higher kinetic energy of sputtered particles. The dependence of the energy flux on the excitation mode (DC, HiPIMS), the HiPIMS pulse parameters, as well as on power and pressure is investigated. The advantages and limitations of the diagnostics used are discussed.

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

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Plasma and Vapor Deposition Processes
Room Palm 1-2 - Session PP4-FrM

Deposition Technologies for Carbon-based Coatings

Moderators: Dr. Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, **Dr. Biplab Paul**, PLATIT AG, Switzerland

8:20am **PP4-FrM-2 Insights Into Solid Lubrication Processes of DLC Films Thanks to Analytical Tribology***, **Julien Fontaine [julien.fontaine@ec-lyon.fr]**, Antoine Normant, Jules Galipaud, Frédéric Dubreuil,* LTDS, CNRS / Ecole Centrale de Lyon, France **INVITED**

Diamond-Like Carbon coatings may behave as very good solid lubricants, providing a good combination of tribological environment and coating composition is ensured. For instance, highly hydrogenated amorphous carbon (a-C:H) films may lead to super low friction regime ($\mu < 0.01$) under ultra-high vacuum, at least for a limited time. What are the tribological phenomena that allow for such performance, and what brings an end to this unique regime?To answer such questions, a traditional approach consist in performing some surface analysis after the experiments, inside and outside the wear tracks. These analyses are frequently morphological, structural or chemical, sometimes mechanical. While these informations are paramount for the understanding of the surface degradations during sliding, they don't provide information about the respective roles of these degradation on the evolution of the tribological response of the contact.In this work, we use a high resolution environment-controlled tribometer, based on a six axes force sensor, to probe the tribological response of a steel pin / a-C:H film contact, either by crossing existing wear tracks or by shifting the tracks to slide on pristine surfaces. This original approach helps understanding the respective role of surface modifications on the a-C:H coated flat or on the facing steel pin on the achievement of superlow friction. These experiments are combined with more traditional analytical means, like in situ XPS, AES and REELS analyses or ex situ SEM or AFM observations.The growth of a carbon-rich tribofilm on the steel counterpart appears necessary, but not sufficient to reach superlow friction. Changes on the topography and chemistry of the a-C:H film seems also paramount, with a smoothening of the a-C:H asperities and an increase of the sp^2 Carbon content. The respective role of these phenomena on the solid lubrication process of a-C:H film will be discussed.

9:00am **PP4-FrM-4 Diamond Like Carbon (DLC) Ablators for Fusion Energy***, **Nicolas Vargas [nicolas.vargas@ga.com]**, Kuo-Chun Chen, Priya Raman, Martin Hoppe, Fred Elsner,* General Atomics, USA

On December 5, 2022, after 4 decades of technical improvements, NIF reached "ignition" for the first time, achieving a 150% energy yield and with it unlocking the promise of unlimited energy supply for human society.This historical achievement was enabled by the many esoteric and ultra-high precision Inertial Confinement Fusion (ICF) components General Atomics manufactures and assembles into complex target assemblies, which are subsequently fielded, on national facilities such as the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (LLNL).Each target assembly has an ablator capsule at its center. HDC (high-density carbon), a form of nanocrystalline diamond, is the current choice for the ablator in these experiments. However, as NIF laser power scales up, Diamond Like Carbon (DLC) ablators are looking increasingly attractive.

Diamond Like Carbon (DLC) material has captured the interest of the laser fusion community due to its unique properties. DLC's amorphous microstructure, high density, and ability to be doped makes it an attractive choice for ablator material. At General Atomics, we developed a Hollow Cathode Radio Frequency Plasma Assisted Chemical Vapor Deposition (HC-RF PACVD) system to deposit DLC coatings on both flat and spherical substrates.

Our DLC capability, with precisely tuned hydrocarbon and carrier gas compositions, enables the deposition of thick, dense, and smooth Diamond-Like Carbon coatings for experiments in Inertial Fusion Technology. In this presentation, we will provide an overview of our major results to create free-standing DLC capsules, including the fabrication, characterization and post processing techniques.

This work performed under the auspices of General Atomics under Internal Research and Development.

9:20am **PP4-FrM-5 Multifunctional Nanocomposite Coatings: Aerosol Assisted Plasma Deposition***, **alexis aussonne [alexis.aussonne@lcc-toulouse.fr]**,* LCC, Laplace, France

Amorphous carbon thin coatings are widely used to protect surfaces due to their high hardness and their chemical resistance[1]. They can be deposited by various PVD methods such as ion beams[2], magnetron sputtering[3] or by PECVD[4] by injection a gaseous precursor into a plasma. PECVD allow to control the structure of the carbon coating by choosing the precursor. However, the continuous injection of gas does not allow to work with complex precursors such as mixtures, solutions containing reactive molecules or colloidal solutions.

An alternative way to inject the precursor in the plasma chamber would be by directly injecting a liquid as an aerosol in a pulsed manner. This would allow to work with liquids of a much more complex composition and thus reaching interesting coatings. Furthermore, by injecting colloids it is possible to deposit various nanocomposite[5] coating encapsulating various kind of nanoparticles (metallic, oxide, sulfide).

Herein we report the carbon deposition by a low pressure RF plasma with pulsed injection of a pentane aerosol. Carbon layers were characterized by Raman and Infrared spectroscopies. Additionally, colloidal solutions of MoS2 nanoparticles stabilized in pentane were injected to deposit nanocomposite thin films.

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9:40am **PP4-FrM-6 Amorphous Carbon Thin Films for Electron Multipacting Mitigation in the Large Hadron Collider Vacuum System***, **Valentine PETIT [valentine.petit@cern.ch]**, Pedro Costa Pinto, Mathias Gegg, Christos Kouzios, Giovanni Marinaro, Andrea Rocchi, Guillaume Rosaz,* European Organization for Nuclear Research, Switzerland

In modern particle accelerators with high intensity and positively charged beams, electron multipacting due to the exponential multiplication of electrons in the vacuum beam pipes results in the build-up of so-called electron clouds. In the Large Hadron Collider (LHC) at CERN, electron clouds lead to beam quality degradation, pressure rises and heat loads to the cryogenic sections hosting the superconducting magnets. Electron clouds are recognized as a critical limitation to reach the very high beam intensity required for the High-Luminosity upgrade of the LHC (HL-LHC).

To tackle this phenomenon, several mitigation approaches have been developed in the last decades, including clearing electrodes, confinement of electrons by solenoids or lowering of the Secondary Electron Yield (SEY) of the beam pipe surface, the quantity governing the multiplication of electrons. This last approach has been successfully implemented by coating the beam pipes with amorphous carbon thin films, which exhibit an SEY close to unity.

This contribution presents the development and prototyping phases towards the implementation of a coating technology to deposit amorphous carbon along several kilometers of narrow beam lines in-situ, i.e., without removing the superconducting magnets from their positions in the LHC tunnel, located 100 meters underground. The films are deposited by sputtering, using a tandem of 4 mobile targets, powered in HiPIMS mode, that are displaced along the beamlines. We report on the design of the coating system, on the characterization of the coatings, particularly under electron irradiation at 15 K, and on the optimization of the process parameters, considering the constraints for upscaling the technology to kilometers of vacuum pipes within the geometrical constraints of the LHC cryo-magnets.

10:20am **PP4-FrM-8 With Carbon Coatings towards CO_2 Neutrality - Industrialization in Electrochemical and Tribological Applications***, Martin Kopte [kopte.martin@vonardenne.com],* VON ARDENNE GmbH, Dresden, Germany **INVITED**

To date the global mining of fossil fuels continues to increase. As those resources are an integral part of almost any production value chain the CO2-equivalent of products needs to be accounted for in a clean balance sheet in every single production step and all the materials involved. The medium-term self-amortization of the CO2-equivalent of "active" products, that e.g. can replace fossil energy sources, is a desirable goal towards CO2-neutrality. Whereas "passive" products are required to be fabricated in the most efficient and sustainable manner, to keep the footprint as low as possible.

With PVD methods products can be refined to greatly increase in performance efficiency, self-amortization rate and sustainability. Typically, the additional effort of coating is already justified by the functionalization of the product itself. More and more the coating technologies must withstand a thorough review not only for the sake of cost effectiveness but also in terms of its contribution to the CO2-equivalent.

Carbon – inherently a good material choice – comes in wide variety of modifications with adjustable properties (e.g. electrical and mechanical) and hence can not only be used in a wide spectrum of electrochemical and tribological applications and thus targeting the scope of sustainable carbon-dioxide-free energy and energy saving solutions.

Paving the way to CO2-efficient industrialization of PVD-carbon coating equipment involves a careful consideration of many variables. This work touches on the challenges when it comes to the best choice of optimized materials, processes, methods etc. for engineering and scaling of competitive and efficient coating tools.

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