Plasma and Vapor Deposition Processes
Room Palm 5-6 - Session PP6-MoM

Microfabrication Techniques with Lasers and Plasmas

Moderators: Carles Corbella, George Washington University, USA, **Uros Cvelbar**, Jozef Stefan Institute, Slovenia

10:00am **PP6-MoM-1 Laser Bioprinting: From the Breast Tumor Microenvironment to Migration in Wound Healing Assays**, ***Doug Chrisey (douglasbchrisey@gmail.com)***, Tulane University, USA **INVITED**

Laser bioprinting can be both additive (depositing cells) and subtractive (etching) and both have power to study the micro-physiological behavior of heterogeneous tissue constructs *in vitro*. The use of a UV laser in both these scenarios is shown to be very powerful and this presentation will show results over this wide range of applications. The most enriched cell types in the breast tumor microenvironment are cancer cells, cancer-associated fibroblasts, and tumor-associated macrophages. To recapitulate the cellular dynamics of the breast tumor microenvironment *in vitro*, the most abundant cell types need to be incorporated. Laser direct write bioprinting offers a precise, gentle, and reproducible method to print disparate cell types in user-defined geometries. Herein, we develop novel laser direct write cell printing protocols – first as a customizable generalized framework, which is then adapted to print homotypic and heterotypic cancer-stromal arrays, and human macrophages. We demonstrate the ability to fabricate *in vitro*heterocellular constructs for studying cell-cell signaling in healthy and diseased microenvironments, as well as the capability to print human immune cells with high fidelity to pave the way for bioprinting immunocompetent tissue models going forward. Traditional *in vitro* scratch assays lack standardization due to poor control over wound geometry and fail to account for cell proliferation. Here, we developed a novel scratch assay that enables precise control over wound geometry using CAD/CAM laser photoablation and takes cell proliferation into consideration using a simple reaction- diffusion based mathematical model. We demonstrated that diffusivity in precisely photoablated cell layers serves as a more accurate measure of cell motility than the rate of gap closure. Further, we biologically validated this assay using cells harvested from patients and patient-derived xenografts to gain insights into the influence of the presence stromal cells on metaplastic and non-metaplastic triple negative breast cancer metastasis.

10:40am **PP6-MoM-3 Plasma-Assisted Nanofabrication of Advanced Nanoplasmonic Surfaces for SERS Applications**, ***Uros Cvelbar (uros.cvelbar@ijs.si)***, Jozef Stefan Institute, Slovenia **INVITED**

In the realm of plasmonic detection, pivotal for applications such as food and water quality monitoring, theranostics, and virus and toxin analysis, Surface Enhanced Raman Scattering (SERS) stands out as a powerful technique. Employing vibrational spectroscopy and surface nanoengineering, SERS leverages metallic nanoparticles to enhance signals through the confinement effect of the electromagnetic field, creating intense 'hot spots' near nanoscale metal surfaces. The morphology and arrangement of plasmonic nanomaterials crucially influence the formation of hot spot networks. This presentation focuses on our recent research in the plasma-assisted fabrication of advanced nanoplasmonic surfaces, showcasing nanocarbon structures, metal-oxide nanotrees, and coupled nanogold. Utilizing various plasma setups, including low-pressure and atmospheric pressure, we demonstrate their versatility, reliability, and fast, one-step processing. These surfaces excel in detecting cancerogenic toxins at ppb levels, ultrafast recognition of trace chemicals, and even bacterial DNA detection with nanogram sample amounts. The talk underscores the significant potential of plasma-assisted nanofabrication in advancing nanoplasmonic surfaces for a broad spectrum of analytical applications.

References:

[1] Shvalya, V., Filipič, G., Zavašnik, J., Abdulhalim, I., & Cvelbar, U. (2020). Applied Physics Reviews, 7(3), 031307. [2] M. Santhosh, N., Shvalya, V., Modic, M., Hojnik, N., Zavašnik, J., Olenik, J., Košiček, M., Filipič, G., Abdulhalim, I. & Cvelbar, U. (2021). Small, 17(49), 2103677. [3] Shvalya, V., Vasudevan, A., Modic, M., Abutoama, M., Skubic, C., Nadižar, N., Zavašnik, J., Vengus, D., Zidanšek, A., Abdulhalim, I., Rozman, D. & Cvelbar, U. (2022). Nano Letters, 22 (23), 9757-9765.

11:20am **PP6-MoM-5 Enhancing Tribological Performance of Carbon-Based Coatings Through Pulsed Lasertexturation**, ***Constant Boris Rieille (constant.rieille@bfh.ch)***, *S. LeCoultre,* Berner Fachhochschule BFH, Switzerland

This presentation aims to explore laser-textured carbon-based coatings and their improved tribological properties for different applications against various materials, including brass, titanium, aluminum and steel. The study involves a comprehensive comparative analysis with benchmark carbon coatings from the market, focusing on the performance of these coatings in diverse conditions.

Moreover, our research delves deeper into the tribolayer that forms on counterpart surfaces and employs advanced analytical techniques such as Raman spectroscopy and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (SEM+EDX) to gain insights into the intricate mechanisms at play.The contribution of topographical variations and structural changes to the carbon coating will be discussed.

We will also introduce a novel model to elucidate why laser textured carbon layers exhibit superior tribological performance compared to their untextured coatings and compare as well different possible mechanism for carbon transformation depending on laser pulse length between nano and femtosecond.

At the end of the presentation, we aim to present an innovative method for producing a high-performance coating that can be used for tribological applications in the cutting tool, watchmaking, and micromechanics industries.

11:40am **PP6-MoM-6 Designing Chiral Micropatterns via Ion Beam Colloidal Lithography**, *S. Portal,* ***Carles Corbella (ccorberoc@gwu.edu)***, George Washington University, USA*; O. Arteaga,* University of Barcelona, Spain*; A. Martin, T. Mandal,* New York University, USA*; V. Dinca,* National Institute for Laser, Plasma, and Radiation Physics, Romania*; B. Kahr,* New York University, USA

Optically anisotropic materials were fabricated via colloidal lithography and characterized by scanning electronic microscopy (SEM), confocal microscopy, and polarimetry. First, a mask consisting of hexagonal compact arrays of silica sub-micron particles (500-600 nm in diameter) was produced via Langmuir-Blodgett self-assembly. After that, the deposited mask pattern was transferred onto the underlying substrate by means of ion beam etching using an electron-cyclotron-resonance (ECR) plasma source. Monocrystalline silicon and commercial glass were used as substrates. In the etching processes, screw-like shaped pillars were carved into the substrates by irradiating their surfaces at oblique incidence and varying stepwise the azimuthal angle. Different chiral structures were obtained depending on the rotation direction of the azimuthal angle steps. Finally, thin gold films were deposited on top of the pillars to enhance the material optical properties through plasmon resonance effect. Polarimetric measurements were realized at normal and oblique incidences to assess the anisotropy of the samples. The etching directions have an influence on the value of the linear birefringence and linear dichroism. A dependence of the birefringent parameters on the angle of incidence of the light was found: an amplification of the chiroptical response of the material was observed at increasing angle of incidence. This fast, cost-effective technique is promising for the preparation of large micropatterned surfaces aimed at photonic and biological applications.

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

PVD Coating Technologies I

Moderators: Christian Kalscheuer, RWTH Aachen University, Germany, **Vladimir Pankov**, National Research Council of Canada

8:00am **PP1-1-TuM-1 Discharges Modes Relevant to Plasma-Based Coatings: an Analysis of Their Physics and Economics*, Andre Anders (andre.anders@iom-leipzig.de),*** Leibniz Inst. of Surface Eng. (IOM), Germany **INVITED**

Physical Vapor deposition (PVD) has matured over the last decades, where plasma processes have been added to control the microstructure of thin films and coatings. The different processes make use of different discharge modes, such as magnetically enhanced glow (magnetron discharge) and arc discharges, where the latter has the most prominent and very different sub-modes of thermionic and cathodic arcs.However, these are not the only ones.The overview connects the discharge physics of the different modes – resulting in plasmas of quite different properties – to the film microstructure, control options, but also considers the economics (especially energy considerations) associated with the different approaches.

8:40am **PP1-1-TuM-3 Design of an Innovative Cathodic Arc Source with High Deposition Rate and Low Macroparticles Generation*, Raül Bonet (raul.bonet@eurecat.org),*** Eurecat Technological Center of Catalonia, Spain*; L. Carreras,* Tratamientos Térmicos Carreras S.A, Spain*; J. Orrit-Prat, J. Caro,* Eurecat Technological Center of Catalonia, Spain

Within the group of PVD techniques, the cathodic arc evaporation technique stands out for its performance, which is characterized by a nearly 100% ionized, high energy plasma. Its versatility, lower economic cost compared to other deposition techniques and easy industrial scaling has led to a massive industrial implementation for the preparation of coatings and thin layers of different nature. One of the disadvantages of the cathodic arc technique is the generation of macroparticles because of the electric arc discharge on the cathode surface. This fact can be an important technological limitation for those cases where a good surface finish, low friction coefficient or good wear and corrosion resistance is required. Traditionally, this problem has been solved by applying magnetic filters that separate the macroparticles from the plasma ions. However, this solution involves a considerable reduction in the deposition rate, which makes its industrial implementation difficult. On the other hand, in order to reduce the coating process costs, cathodic arc sources that allow a high deposition rate are required.

In this work, an innovative cathodic arc source has been designed to achieve a deposition rate of up to 20 microns/hour, with a reduction of 80 % of macroparticles. In order to increase the deposition rate, a high-current pulsed source (100-500 A, 10-20000 Hz) has been used to generate the arc discharge between the anode and cathode. On the other hand, to reduce the generation of macroparticles, an optimized magnetic field configuration around the cathode has been obtained by means of Finite Elements Method (FEM) simulation, which allows to induce a fast and homogeneous movement of the electric arc on the cathode surface. Standard transition metal nitride (CrN, AlTiN) hard coatings obtained using this source exhibit excellent surface finish and improved mechanical properties in terms of adhesion and hardness.

9:00am **PP1-1-TuM-4 TaB_X Thin Film Synthesis from an Industrial-Sized DC Vacuum Arc Source*, Igor Zhirkov (igor.zhirkov@liu.se),*** *A. Petruhins, A. Shamshirgar,* Materials Design Division, IFM, Linköping University, Sweden*; S. Kolozsvári, P. Polcik,* PLANSEE Composite Materials GmbH, Germany*; J. Rosen,* Materials Design Division, IFM, Linköping University, Sweden

Thin films of transition metal borides are gaining increasing attention due to their physical and chemical characteristics. Most publications in this area focus on TiB_2, synthesized through various sputtering techniques, targeting applications as protective hard layers. Tantalum diboride, TaB_2, is another system with interesting properties, especially for high temperatures, but is much less explored. The elastic modulus of TaB_2 is ~ 2 times lower than that of TiB_2, but displays similar high hardness, combining high strength with high resistance to elastic and plastic deformation. Deposition of TaB_2 coatings with the industrially relevant physical vapor deposition (PVD) process DC vacuum arc is virtually absent in the literature. Still, DC arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This motivates development and investigation of arc processes for TaB_2 synthesis. In the present work, we investigate DC arc plasma generation and deposition of TaB_x, and compare to previously investigated TiB_x. We use an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. Process stability and cathode dependent features of arcing is evaluated, and plasma analysis with respect to charge-state resolved ion energy is performed, showing a high ionization degree, and ion energies extending well above 100 eV. It is well known that plasma generation from compound cathodes gives a mass-dependent angular distribution for the elements of the compound, which is confirmed for the here investigated borides. This, in turn, is one of the factors contributing to a resulting film composition diverging from the cathode composition. The plasma characterization and macroparticle generation is correlated to deposited thin films; their composition, structure and properties. Altogether, the results show that DC vacuum arc is an industrially relevant technique for deposition of metal diborides.

9:20am **PP1-1-TuM-5 Plasma Enhanced Magnetron Sputtering and Its Applications in Industry*, Jianliang Lin (jlin@swri.org),*** Southwest Research Institute, USA **INVITED**

Plasma enhanced magnetron sputtering (PEMS) technology is an advanced version of the conventional magnetron sputtering technique. The PEMS technique draws electrons off of hot filaments installed in a sputtering system when electrons have gained enough energy to exceed the work function of the filaments. The electrons collide with neutral atoms and generate a large number of ions through impact ionization. As a result, a global hot filament assisted plasma is formed in the entire chamber which is independent of the magnetron discharge plasma.The hot filaments also provide additional thermal energy without using external heating elements. Plasma diagnostics showed that the majority of the ions in the PEMS plasma exhibited low energies of less than 5 eV. However, a significant increase in the ion flux can be achieved by increasing the hot filament discharge current. The extra ion fluxes provide enhanced ion bombardment on the substrates, which is beneficial for improving the structure and properties of coatings. The PEMS plasma can be utilized to perform different surface engineering tasks, e.g. plasma cleaning/etching, plasma nitriding, and coating depositions. It can be easily combined with other magnetron sputtering techniques, e.g. DC, RF, pulsed DC, and high power impulse magnetron sputtering (HiPIMS) to enhance ion fluxes and thermal energies. In this presentation, the principle and characteristics of the PEMS technology will be introduced. Technical examples of PEMS coatings for different industry applications will be reviewed, for example, solid particle erosion resistant coatings for aerospace and Oil&Gas, duplex coatings for die casting dies, low friction nanocomposite coatings for combustion engine piston rings, protective coatings for high temperature sCO_2 environment, etc.

10:00am **PP1-1-TuM-7 Sustainable and Economical Production of High-Quality HIPIMS Coatings*, Stephan Bolz (stephan.bolz@cemecon.de),*** *B. Mesic, O. Lemmer, C. Schiffers,* CemeCon AG, Germany

Constant improvement of ceramic coatings for cutting tools aiming at best wear resistance under conventional and extreme conditions is driven by the development of new workpiece materials with improved properties. Economical machining of such materials requires ever denser and harder coatings with better adhesion to the tool substrate. In addition to the required coating properties, however, the economical production of these coatings plays a more important role since some time. Shorter coating processes, reduced handling and lower energy consumption are the right keywords to well describe the current situation.

Considering these aspects, high-performance coating technologies, such as HiPIMS, are becoming more and more interesting for the market. Thanks to HiPIMS dense, hard, adhesive, and droplet-free layers can be deposited in highest quality with high energy efficiency at high deposition rates. Furthermore, well-chosen HiPIMS pulse parameters combined with an appropriate bias synchronization can avoid high residual stress of coatings for sharp edged cutting tools.

In our presentation we show that optimization of HiPIMS pulse parameters leads to a significant increase in metal ionization, accompanied by improved coating properties of an (Al,Ti,Si)N layer. The improved coating properties include above all a denser microstructure and a smoother surface, which allows to skip time consuming and energy-intensive post-treatment steps. Brilliant shine and best optical appearance are related with low friction and perfect chip removal during use. This combination of layer properties is a guarantee for a perfect surface finish of the workpiece.

10:20am **PP1-1-TuM-8 Increasing the Metal Ion Flux Fraction in Industrial Conditions**, ***Peter Klein (pklein@mail.muni.cz)***, *J. Hnilica,* Masaryk University, Czechia*; V. Sochora,* SHM s.r.o., Czechia*; P. Vašina,* Masaryk University, Czechia

The field of coating technologies progressively changes. Before, PVD technologies were utilized to produce a coating with a single superior quality such as very high hardness, high ductility, or very low roughness. Nowadays, due to increasingly sophisticated applications, a combination of superior properties is required. Generally, high-quality coatings require high ion flux to be formed, which is easily achievable by arc–based techniques, but those are prone to have high roughness of produced films. This work reports on high ionized metal flux fraction (IMFF) in industrial DC magnetron conditions.

A biased QCM was employed in the industrial magnetron deposition system to quantify the metal ion contribution to the forming film. The used deposition system can utilize up to four cylindrical rotating electrodes, each measuring 50 cm in length and 10 cm in diameter. For the titanium magnetron cathode, up to 40 kW DC power can be supplied over the 90 cm^2 racetrack, providing a current density of around 0.8 $A.cm^{-2}$. Such a high current density is rather similar to pulsed power techniques and unsurprisingly, up to 30% of IMFF can be obtained purely in the DC operation. A striking difference from laboratory DC magnetron discharges, where the literature states the IMFF can reach only up to 2%.

The IMFF can be further enhanced in the described system through the utilization of a lateral glow discharge (LGD). Lateral glow discharge uses one of the arc electrodes as an electron source. Produced electrons from the arc cathode are drawn to the opposite arc electrode, forming an area over the magnetron cathode where the collision with the sputtered metal occurs. This increases IMFF by a further 10%, which makes this a comparable system to HiPIMS. Unlike HiPIMS, the introduction of LGD into the DC magnetron sputtering process does not affect the deposition rate. Despite LGD being arc-based technology, it does not create macroparticles, but It has to be noted that the LGD requires multi-electrode configuration to run.

10:40am **PP1-1-TuM-9 Unraveling the Dynamics of Reactive Magnetron Sputtering: Insights into Feedback Control, Metastable Conditions, and Long-term Stability**, ***Josja Van Bever (Josja.VanBever@UGent.be)***, *K. Strijckmans, D. Depla,* Ghent University, Belgium

High-quality coatings with optimized stoichiometry in reactive magnetron sputtering are essential for numerous industrial applications. This demands meticulous control of process conditions within the transition region between metallic and poisoned modes, achieved through feedback control or high pumping speeds [1]. Despite advancements, a comprehensive understanding of the convergence and steady-state conditions in feedback control for this context is still elusive.

In this study, we present *precise feedback* measurements, focusing on the intricate dynamics within the aluminum-oxygen system. Our investigations unveil two distinct metastable states dependent on the system's history. We establish a clear connection between these states and the *double hysteresis* phenomenon, as predicted by the Reactive Sputtering Deposition (RSD) model [2-4] and substantiated by prior research on IV-characteristic data analysis [5]. This linkage is achieved through careful manipulation of discharge current density and process parameters associated with target poisoning mechanisms.

Delving into the *long-term stability* of the double hysteresis in feedback control, we compare it with stable transition conditions achieved through high-pumping speeds. Our discussion encompasses various factors influencing *long-term stability, including target erosion effects [6], chamber wall gettering, anode effects [7]*, and fluctuations induced by the chosen process control. *A new type of feedback input signal is introduced* to compensate for plasma and chamber wall effects.

Furthermore, we explore diverse feedback convergence strategies, shedding light on the path toward an optimal approach that considers the stability of each set of transition conditions. This understanding provides a valuable guideline for industry professionals seeking to employ feedback control reproducibly and efficiently.

Our research significantly contributes to the body of knowledge in reactive magnetron sputtering, providing insights into the intricate interplay between feedback control, metastable conditions, and long-term stability. These findings promise to elevate the precision and reliability of thin film deposition processes, with implications for a wide range of technological applications.

References are found in the supplementary material.

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

PVD Coating Technologies II

Moderators: Christian Kalscheuer, RWTH Aachen University, Germany, **Vladimir Pankov**, National Research Council of Canada

1:40pm **PP1-2-TuA-1 Use of van der Waals Layers and Ultrahigh Vacuum Environment to Control Composition and Crystallinity in Sputter-Deposited Thin Films**, ***Suneel Kodambaka (kodambaka@vt.edu)***, Virginia Tech, USA; *K. Tanaka, A. Deshpande, P. Arias, A. Aleman, H. Zaid, M. Liao,* University of California at Los Angeles, USA; *C. Ciobanu,* Colorado School of Mines, US; *M. Goorsky,* University of California at Los Angeles, USA **INVITED**

Compositional control in sputter-deposited thin films is typically achieved via changing the deposition parameters, such as partial pressure of the reactive gases, substrate temperature, deposition fluxes, and the target composition. Common approaches to improve crystallinity, to increase grain size and the grain orientation in thin solid films typically involve the use of single-crystalline substrates, high substrate temperatures combined with low deposition fluxes, and energetic ion beams.

In this talk, I will present approaches involving the use of ultra-low (e.g., 0.002%) partial pressures of the reactive gases and van der Waals (vdW) layers as buffer layers to grow thin films of desired composition and enhanced crystallinity. Using Ta-C and Mo-S as model materials systems, we demonstrate compositional tunability and improved crystallinity. We also shown that Ta_2C thin films grown on $Ta_2C(0001)$ covered with hexagonal boron nitride (hBN), a vdW-bonded material, are more highly oriented than those films grown directly on bare $Ta_2C(0001)$ under identical deposition conditions. That is, heteroepitaxial growth across a vdW layer seemingly yields better crystalline quality than homoepitaxy. We observe similar highly-oriented growth of face-centered cubic Pd, body centered cubic Mo, and hexagonal MoS_2 thin films on hBN-covered substrates. Our results provide new insights into the factors underlying the growth of highly-oriented thin films.

2:40pm **PP1-2-TuA-4 Generating Spokes in Direct Current Magnetron Sputtering Discharges by an Azimuthal Strong-to-Weak Magnetic Field Strength Transition**, ***Martin Rudolph (martin.rudolph@iom-leipzig.de)***, *W. Diyatmika,* Leibniz Institute of Surface Engineering (IOM), Germany; *O. Rattunde, E. Schuengel,* Evatec AG, Switzerland; *D. Kalanov,* Leibniz Institute of Surface Engineering (IOM), Germany; *J. Patscheider,* Evatec AG, Switzerland; *A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany

Spokes in magnetron discharges are zones of enhanced excitation and ionization that can be suspected to influence the ion ejection from the plasma toward a substrate and by that influence a deposited thin film morphology. Here, we show that spokes can be generated at a desired location by introducing a step in the magnetic field strength along the racetrack. For the experiments we use a magnetron with a 300 mm Al target operated in direct current mode. Two magnetic field strength transitions are obtained when splitting the racetrack into a section with a weak parallel magnetic field strength above the racetrack of ≈ 40 mT, and a strong magnetic field strength section with ≈ 90 mT. Using a gated intensified charge-coupled device (ICCD) camera, we observe the generation of spokes where drifting electrons transit from the strong to the weak magnetic field. The generated spokes move against the electron Hall drift into the strong magnetic field section, thereby creating a region of high spoke activity. The observation can be explained by an accelerating electron drift velocity as the magnetic field strength weakens. At the transition from the weak to the strong magnetic field, we observe a region of enhanced light emission that we attribute to the accumulation of electrons due to a lower drift velocity in a strong magnetic field. The observed effect is similar to a cross-corner effect known from rectangular magnetrons and we confirm here that this effect is primarily due to the change in the magnetic field strength and not caused by the geometry of the racetrack.

3:00pm **PP1-2-TuA-5 the Surface Temperature of a 2” Water-Cooled Ti Target Measured During DC Magnetron Sputtering**, ***Stephen Muhl (muhl@unam.mx)***, *J. Cruz, A. Garzon,* Universidad Nacional Autonoma de Mexico

The lateral temperature of a 2” diameter water-cooled titanium target was measured using an electrically floating fine, 0.005” wire, type K chromel-alumel thermocouple. The temperature measurements were performed as a function of the DC plasma power (power densities of 1.0, 2.2 and 4.1 W/cm2) and Ar gas pressures of 10 to 60 sccm. Typically, the temperature difference between the centre of the target and inside the racetrack was more than 200 oC, the racetrack temperature increased almost linearly with the applied power to a maximum value of ~840 oC.

The target temperature was also investigated as a function of the N_2 gas concentration in the Ar gas mixture (1 to 20%), and these measurements are compared with the elemental composition of the deposits produced.

4:00pm **PP1-2-TuA-8 Black Metal Thin Films Deposited on Cooled Substrates by Sputtering**, ***Midori Kawamura (kawamumd@mail.kitami-it.ac.jp)***, *H. Iino, H. Mori, Y. Otomo, T. Kiba, Y. Abe,* Kitami Institute of Technology, Japan; *M. Ueda,* Hokkaido University, Japan; *M. Micusik,* Slovak Academy of Sciences, Slovakia; *M. Hruska, M. Novotny, P. Fitl,* University of Chemistry and Technology, Czechia

Black metal thin films with a porous structure being broadband light absorber are attractive for various applications such as photothermic conversion and photodetection. Recently, they are expected to be applied to gas sensors, due to their large surface area. In addition to vacuum evaporation, sputtering has also been reported as a method for preparation of black metal thin films[1)]. It has been well known that porous films can be obtained at low substrate temperature and high Ar gas pressure based on the structure zone model by Thornton. We have attempted to prepare black Al, Ag and Au thin films by sputtering on the substrate cooled with liquid nitrogen to suppress surface diffusion of atoms. The sputtering power and Ar gas pressure were also changed to obtain the films with porous structure. An RF magnetron sputtering system, in which the substrate can be cooled by liquid nitrogen, was mainly used for the deposition. The films were deposited on glass and Si substrates at room temperature, -80°C, and -170°C with Ar gas pressure of 6.5 - 33.3 Pa and sputtering power of 100 - 150 W at background pressure below 3.3×10^{-5} Pa. The deposited films were characterized by four point probe, SEM, AFM, XRD, XPS, and spectrophotometer.The Al films obtained at low temperature were black in color. However, metallic luster was observed from the backside of glass substrate. It means that a porous layer was formed after a thin dense layer was formed on the substrate. It was also found that black films formed by deposition at high Ar gas pressures and high RF powers. The light absorption of the films obtained was as high as 80% for the black Al films. The samples had a columnar structure and (100) crystal orientation.In conclusion, our results show that black metal films can be obtained by sputtering at low temperatures, high gas pressures and high RF powers. As shown in the figure, conditions which we explored for Al deposition are beyond the SZM. We are currently engaged in experiments with new deposition conditions, such as sputtering in Kr gas and DC power discharge, and results of these experiments will be presented as well.

Acknowledgement This work was supported by JST SICORP Grant Number JPMJSC2108, Japan, the Ministry of Education, Youth and Sports of the Czech Republic project No. 8F21008, and project No. JP22420 from the International Visegrad Fund.

Reference [1]J. More-Chevalier *el al.*, RSC Advances,10, 20765-20771 (2020).

[2] J. A. Thornton, J. Vac. Sci. Technol. 11, 666–670 (1974)

4:20pm **PP1-2-TuA-9 Advanced Process Control for PVD Coating Technologies in Production Lines**, ***Thomas Schütte (schuette@plasus.de)***, *J. Urbach, P. Neiß, M. Radloff,* PLASUS GmbH, Germany

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 which gather comprehensive in-situ data of the process conditions as well as product properties.

Spectroscopic plasma process monitoring is a standard measurement technique to acquire data from the actual coating process in real-time. Also, time-resolved electrical measurements of generator power, voltage and current provide valuable process information especially in pulsed plasma applications. In addition, in-situ broadband photometric measurements can reveal important properties of the growing coating such as film thickness or color values.

This presentation will introduce the combined in-situ data acquisition from spectroscopic plasma monitoring, electrical measurements and photometric thin film measurements in demanding coating processes like metallic and reactive sputtering, HIPIMS, PECVD and microwave driven processes. By combining information from the different measurement techniques in a single system and evaluating the comprehensive data in real-time process control becomes more accurate and reliable and in turn enhances production stability and improves product quality.

Examples from various coating applications in industry and R&D are presented, including tribological, optical and architectural glass coating processes.

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

CVD Coating Technologies

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

8:00am **PP3-WeM-1 Area-Selective Deposition of DLC Using Optoelectronic-Controlled Plasma CVD Method***, Susumu Takabayashi (stak@ariake-nct.ac.jp),* National Institue of Technology, Ariake College, Japan **INVITED**

Diamond-like carbon (DLC) is an amorphous carbonaceous material composed of sp^2 carbon, sp^3 carbon and hydrogen. We propose a controlled DLC film synthesis by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD). PA-PECVD is a DC discharge plasma with the aid of photoelectrons from the substrate on which a deep UV light irradiates. The current flows only in the UV-irradiated area and the starting voltage of the glow discharge, called photoemission-asssietd glow discharge (PAGD), becomes stable owing to plenty of photoelectrons as initial electrons. The discharge before starting PAGD occurs is photoemission-assisted Townsend discharge (PATD). The current in PATD is around 10,000 time larger than that in conventional Townsend discharge. The substrate is not subject to the sheath electric field, so minute and precise synthesis with a rate of nm/min. is realized in PATD. With PATD, we actually succeeded to fabricate a graphene field effect transistor (GFET) with a DLC top-gate dielectric and synthesize oxygen and nitrogen-doped DLC films on the order of nm thickness. With PA-PECVD, we are developing and exploring application of DLC in nano-electronics and science.

9:00am **PP3-WeM-4 Microstructure and Mechanical Properties of TiZrN and TiZrCN Coatings Grown by Chemical Vapor Deposition***, Akihiro Murakami (amurakam@mmc.co.jp), M. Okude,* Mitsubishi Materials Corporation, Japan

Chemical Vapor Deposition (CVD) method has been used for the industrial production of wear resistant coatings on cutting tools and TiCN coatingshave been widely used for several decades because of its excellent hardness, good thermal and chemical stability. New CVD coatings that is superior to TiCN are continuously explored, and it is reported that ZrN and ZrCN has advantageous properties as wear resistant coatings. However, there are few reports on TiZrN and TiZrCN coatings.

In this work, TiZrN coatings were deposited from $TiCl_4$-$ZrCl_4$-N_2-H_2 precursors at 1050°C (HT-TiZrN). And TiZrCN coatings were produced from two precursor systems: TiCl--$_4$-$ZrCl_4$-N_2-CH_4-H_2 precursors at 1050°C (HT-TiZrCN) and $TiCl_4$-$ZrCl_4$-CH_3CN-N_2-H_2 precursors at 900°C (MT-TiZrCN). All coatings were deposited on TiCN coated cemented carbide.

We investigated microstructure, crystal orientation and hardness. HT-TiZrN has granular structure and lower hardness than conventional TiCN. HT-TiZrCN has columnar-like-structure, and its hardness is close to conventional TiCN. On the other hand, MT-TiZrCN has columnar structure, (211) crystal orientation and higher hardness than TiCN. In addition, Electron Back Scattered Diffraction (EBSD) analysis revealed partial epitaxial growth of TiZrCN on TiCN.

These coatings were evaluated by turning tests of alloy steel (AISI:4140). As a result, cutting performance of MT-TiZrCN coatings was superior to conventional TiCN. It seems that higher hardness of MT-TiZrCN enhances the cutting performance.

11:00am **PP3-WeM-10 New Perspectives of Atmospheric Pressure Dielectric Barrier Discharges for the Deposition of Thin Films : From Uncontrolled Amorphous Plasma-Polymer Layers to Chemically Patterned and Crystalline (in)Organic Coatings***, François Reniers (freniers@ulb.ac.be),* Université libre de Bruxelles, Belgium **INVITED**

For more than a century, atmospheric pressure dielectric barrier discharges (DBDs) have been used industrially for gas conversion, the Siemens ozone process dates from 1857 [1], and for surface treatment. Deposition of coatings remained confidential, due to the poor control of the quality of the films. Indeed, the very small mean free path at atmospheric pressure leads to species with very low energies, and random processes due to moving filaments often occur.

We show that, nowadays, starting with organic precursors, DBD can lead to chemically well controlled and tunable thin films, with a variety of properties (hydrophobic/hydrophilic). We establish correlations between the gas phase chemistry (analyzed by mass spectrometry) and the coating chemistry (characterized by XPS and IR spectrometry)[2]. The effect of the nature of the carrier gas (Ar or He) on the roughness and chemistry of the deposited coating is evidenced and explained[3]. With the improvement of the understanding of the plasma chemistry, amorphous inorganic coatings (SiOx, TiO_2) can now be easily deposited. By controlling the substrate temperature and the plasma parameters, pure and dense crystalline TiO_2 can now be deposited by APDBDs [4]. By modifying the gas composition, introducing ammonia into the plasma, N-doped TiO2, photocatalytic (and antiviral) under visible light can now be synthesized in one single step [[].

Very recently, one could immobilize streamers in a DBD and use them to deposit, in one simple step, locally chemically patterned organic films. The local chemistry (analyzed by µXPS) is depending on the gap between the electrodes, the power impulsion mode (continuous vs pulsed), the precursor flow. A physico-chemical interpretation is proposed [6,7].

Finally, injecting a precursor for inorganic coating in such discharges with immobilized filaments, in appropriate substrate and plasma streamer conditions, crystalline spots, with multi-micron length crystal needles were for the first time synthesized.

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11:40am **PP3-WeM-12 Novel Metal Boride Coatings in the System Zr-Hf-Ti-B by LPCVD***, Mandy Höhn (mandy.hoehn@ikts.fraunhofer.de), M. Krug, S. Höhn, B. Matthey,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

The synthesis of metal diboride thin films is recently attracting large interest. Boron forms binary compounds with most metals. These materials in general are high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness.

In this work the preparation of mixed metal boride coatings with Me = Zr, Hf, Ti by chemical vapor deposition (CVD) is described. A low-pressure CVD (LPCVD) process using the metal tetrachlorides $MeCl_4$ (Me = Zr, Hf or/and Ti) as precursors as well as BCl_3, H_2 and Ar is applied. At a deposition temperature of 850°C and a deposition pressure of 6 kPa boride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour.

Layers were deposited in the binary systems $HfTiB_2$, $ZrTiB_2$ and $HfZrB_2$ as well as in the ternary system $HfZrTiB_2$. The deposited diboride layers show crystalline structures with a high hardness of up to 38 GPa. Depending on the precursor ratio layers with single phase diboride composition or a mixture of different metal diborides were obtained. Phase composition and structure were examined using SEM, EDX and EBSD-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 300 MPa and 800 MPa.

A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In cutting tests a high performance of the CVD diboride coatings was observed. $HfZrTiB_2$ coated inserts showed a higher lifetime in comparison with state-of-the-art CVD-TiB_2 coatings in face-milling of TiAl6V4.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-1-WeM

Deposition Technologies for Carbon-based Coatings I

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

8:00am **PP4-1-WeM-1 Molecular Dynamics Study of Interfacial Phenomena in Diamond-Like Carbon Films***, **Kwang-Ryeol Lee (krlee@kist.re.kr)**,* Korea Institute of Science and Technology (KIST), Republic of Korea*; X. Li,* Chinese University of Mining and Technology, China **INVITED**

Due to the experimental limitations in precisely characterizing the complicated evolution of a-C film deposition and their physical and chemical properties, molecular dynamics simulation has been widely employed for atomistic understanding of the structural evolution and investigating structure-property relationship. Especially, much attention has been drawn to reactive molecular dynamics simulation technology that can include the chemical reaction during the atomic scale structure evolution. We compared various reactive force field (ReaxFF) models in terms of the structural properties of the simulated a-C films prepared by atom-by-atom deposition approach. By linking the structural properties of the film with the difference in the parameter sets of the ReaxFF models, we reveal that the carbon triple bond stabilization energy in the ReaxFF model, v_{trip}, significantly affects the growth dynamics and structural evolution of the simulate a-C films. Tribological behavior of amorphous carbon surface was extensively investigated in atomic or molecular scale by the reactive molecular dynamics simulation. Simulational study of friction in hydrogenated surface of a-C revealed that hydrogenating the a-C surface only improved the friction property drastically while not deteriorating the intrinsic properties of a-C films. The analysis of interfacial structure demonstrated that being different with a-C:H cases, the competitive relationship between the stress state of H atoms and interfacial passivation caused by H and C-C structural transformation accounted for the evolution of friction coefficient with surface H content. This disclosed the friction mechanism of a-C with surface hydrogenated modification and provides an approach to functionalize the carbon-based films with combined tribological and mechanical properties for specific applications. The reactive molecular dynamics simulation resulted in fundamental understanding of low-friction mechanism. We comparatively investigated the friction property and structural information of contacting interface under different passivated or graphitized states. For the passivation mechanism, the low friction behavior attributes to the reduction of both the real contact area and shearing strength of graphitized sliding interface due to the passivation of a-C dangling bonds. However, the graphitization mechanism strongly depends on the size and layer number of graphitized structure, causing the transition of sliding interface from a-C/a-C, a-C/G to G/G, which is followed by the low-friction mechanism evolved from passivation synergistic effect between graphitization and passivation to graphitization mechanism.

8:40am **PP4-1-WeM-3 Study of ta-C Thick Film Deposition Using FCVA-Based Hybrid Coating System***, **Jongkuk Kim (kjongk@kims.re.kr)**, J. Kim, J. Jang, Y. Jang,* Korea Institute of Materials Science, Republic of Korea

Tetrahedral amorphous carbon (ta-C) coating film has a high sp^3 content and excellent wear resistance and heat resistance even without hydrogen, so it is used in various industrial fields such as cutting tools, automobiles and molds.

In the vacuum arc process using a carbon target, coating is difficult for a long time due to the unstable movement of the arc spot inside the carbon target, resulting in poor thickness and an enlarged coating area. In addition, the Ta-C coating film deposited by this method has high internal stress, making it difficult to increase its thickness.

We controlled the electric and magnetic fields to stabilize the arc spot movement of the carbon cathode for a long period of time, allowing the carbon arc target to be used stably for up to 24 hours at a discharge current of 160 A.

The designed hybrid coating system consists of 1) anode-layer ion source (ALIS) for the etching processes, 2) an unbalanced magnetron sputter (UBM) for the interlayer deposition, 3) a filtered cathodic vacuum arc (FCVA) source for the ta-C film deposition, and 4) pulsed bias power.

To apply the designed hybrid coating process, a system consisting of a single ALIS, two UBMs, and eight FCVAs with a maximum deposition area of 900 mm in diameter and 500 mm in height was built to deposit a 7 μm coating film on a piston ring used in an automobile engine.

We have also built a smaller machine with similar capabilities that can deposit rainbow coatings (up to 0.7 um) and black coatings (0.7-3 um) on non-ferrous cutting tools for a variety of applications, depending on their thickness.

9:00am **PP4-1-WeM-4 Diamond-Like Films of Tetrahedral Amorphous Carbon Deposited by Anodic Arc Evaporation of Graphite***, **Bert Scheffel (bert.scheffel@fep.fraunhofer.de)**, O. Zywitzki,* Fraunhofer FEP, Germany

A physical vapor deposition process using anodic arc evaporation in combination with a hollow cathode arc discharge was applied to the evaporation of graphite for deposition of hydrogen-free carbon layers. The diamond-like carbon (DLC) films deposited on 100Cr6 steel substrates were investigated by nanoindentation, Raman spectrometry, FE-SEM, AFM and spectroscopic ellipsometry. The relationships between the process parameters and the coating properties are discussed. Coatings deposited without bias voltage at substrate temperatures < 200°C are very hard (61-75 GPa) with also very high Young's modulus (588-685 GPa). The evaluation of the Raman spectra indicated a high proportion of tetrahedral sp3 bonds in the range of 70-88 %. The coatings proved to be completely droplet-free and have a very low surface roughness as confirmed by FE-SEM and AFM. The deposition rates in the range of 4-18 nm/s are exceptionally high for such ta-C coatings, which is a good prerequisite for industrial applications.

9:20am **PP4-1-WeM-5 Constitution and Properties of TiC1-x:H/a-C:H Nanocomposite Thin Films Prepared by HiPIMS Processes at Low and Elevated Temperature***, **Sven Ulrich (sven.ulrich@kit.edu)**, C. Poltorak,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Sternschulte, J. Grau,* Technical University of Applied Sciences Augsburg, Germany*; J. Julin, T. Sajavaara,* RADIATE, University of Jyväskylä, Finland*; A. Bergmaier,* University of the Bundeswehr Munich, Germany*; K. Seemann, M. Dürrschnabel, M. Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Carbon-based nanocomposites with tunable multifunctional properties are suitable candidates for diverse fields of applications like tribology or biological, medical and energy technologies. Reactive HiPIMS is selected as a coating process with a Ti-target, an average target power of 5 kW, 50 µs pulse length, 550 µs cycle duration, working gas pressure of 0.3 Pa, 300 sccm Ar working gas flow and up to 40 sccm CH_4 reactive gas flow as well as 200°C and 400°C substrate temperatures. HiPIMS show a high ion fraction of the film-forming particles and the deposited energy by ion bombardment during film growth can be adjusted precisely. The constitution and microstructure war determined by a combination of several analytical techniques: EPMA, ERDA, Raman spectroscopy, XRD, TEM and HRTEM. It is shown that by varying the methane reactive gas flow, the following structures can be adjusted: Ti, TiC_{1-x}:H and TiC:H single layer coatings as well as TiC:H/a-C:H nanocomposites. A clear correlation is identified between the constitution and microstructure with the mechanical properties.

9:40am **PP4-1-WeM-6 Effect of Deposition Temperature and Nitrogen Concentration on Highly Conductive a-C:H:N Films Obtained by Means of DC PACVD***, **Manuel Schachinger (manuel.schachinger@fh-wels.at)**,* University of Applied Sciences Upper Austria*; F. Delfin,* University of Applied Sciences Upper Austria, Argentina*; C. Forsich, D. Heim,* University of Applied Sciences Upper Austria*; B. Rübig, T. Müller, C. Dipolt,* Rubig GmbH & Co KG, Austria

a-C:H films are known for their distinct properties such as excellent wear resistance, chemical inertness and a low coefficient of friction. However, these films are typically highly electrically insulating materials. In view of the constantly increasing demands on technical components, it is critical to further expand the areas of application of a-C:H coatings by combining their desired and well-established material properties with low electrical resistivity. One way to decrease the specific electrical resistance of DLC films substantially is via the utilization of high-temperature DC PACVD. For further optimization of the electrical properties, nitrogen doping may be applied. In this work, a-C:H:N films were deposited at 450°C and 550 °C via DC PACVD on steel and titanium substrates, employing C_2H_2 and an additional N_2 flow. This resulted in an N_2 concentration of 0-63 vol. -% in the gas mixture. Subsequently, film characterization was carried out via nanoindentation, density measurement, calotest, the van der Pauw method, GDOES and Raman spectroscopy. Nanoindentation showed that hardness was increased at higher deposition temperatures and continued to increase with nitrogen gas concentrations up to a certain point. Thereafter, at trend inversion was observed. Density was higher for 550°C deposition compared to the 450°C process and increased for both temperatures with higher N_2 gas concentrations up to 31 vol. -%.

Thereafter, a trend reversal was observed, pointing towards an increased fraction of terminating structures such as C-H or CN triple bonds and a lower fraction of C-C sp^3 bonding in the material. Coating thickness decreased from 40 µm to 14 µm at 450°C and from 32 µm to 12 µm at 550°C with increasing nitrogen flow following an exponential function. Specific resistivity reached an average minimum of 1688 µΩ cm at 31 vol. -% N_2 for 550°C, which approximates the conductivity of compressed graphite powders. In addition, it decreased by several decades at 450°C, reaching an average minimum of 45 000 µΩ cm. GDOES analysis showed that nitrogen concentrations in the films were markedly low ranging from 0,08 to 1,3 at. -% on average. Raman analysis indicates that nitrogen incorporation induces disordering effects in the film structure, combined with a rise in the number and size of aromatic clusters. In summary, the addition of nitrogen as a process gas successfully enhanced the properties of the film, resulting in materials that exhibited higher hardness than martensitic steels with an electrical resistivity equivalent to that of compressed graphite powders.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-2-WeA

Deposition Technologies for Carbon-based Coatings II

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

2:00pm **PP4-2-WeA-1 DLC-Coating Against the Backdrop of High Economic Requirements***, **Jens Emmerlich (jens.emmerlich@de.bosch.com)**, D. Tiedemann,* Robert Bosch Manufacturing Solutions GmbH, Germany*; V. Gupta,* Robert Bosch Manufacturing Solutions GmbH, India*; K. Boebel,* Robert Bosch Manufacturing Solutions GmbH, Germany **INVITED**

In the pursuit of economic viability, this study delves into the strategic utilization of Diamond-Like Carbon (DLC) coatings, emphasizing the distinctive advantages offered by diverse deposition sources. Microwave and cathodic arc deposition, magnetron sputtering as well as High-Power Impulse Magnetron Sputtering (HiPIMS) emerge as pivotal techniques, each contributing unique attributes to the economic landscape. Microwave and cathodic arc deposition showcase efficiency in scalability and uniformity, optimizing the cost-effectiveness of large-scale applications. Sputtering, on the other hand, proves adept at achieving precision and controlled film properties, catering to industries with specific coating requirements. The innovative approach of HiPIMS introduces enhanced adhesion and superior film density, paving the way for extended component lifespan and reduced maintenance costs. Beyond these, the infusion of artificial intelligence (AI) emerges as a pivotal factor in predicting coating parameters and thus orchestrating cost reduction and minimizing scrap rates. By leveraging AI algorithms, the deposition process is optimized with unprecedented precision, ensuring an ideal balance between coating thickness, quality, and resource utilization. This study delves into the economic benefits derived from the application of DLC coatings in combination with AI, shedding light on their potential to enhance durability, reduce maintenance costs, and contribute to overall operational efficiency. As industries strive to navigate the intricacies of a competitive economic environment, the integration of DLC coatings emerges as a strategic imperative for achieving both performance excellence and economic viability.

2:40pm **PP4-2-WeA-3 Comparison of Performance Parameters of Carbon Coatings by Different PVD Methods***, **Martin Kopte (Kopte.Martin@vonardenne.com)**, J. Walther, B. Gebhardt, H. Proehl,* VON ARDENNE GmbH, Germany

PVD based carbon coatings show superior electrochemical resistance enabling durable coatings for metallic bipolar plates in PEM fuel cells etc. High durability and high conductivity (low interfacial contact resistance – ICR) of bipolar plates are essential, nevertheless only a cost-efficient coating method will have the chance for industrialization. Therefore, we only investigated PVD methods which allow scaling of the bipolar plate coating volume to MW and GW powers per year, which are electron-beam based PVD, as the method for highest productivity and deposition rate, and plasma based PVD which is high power magnetron sputtering and (pulsed) cathodic laser arc in our case. The electrical conductivity or ICR and corrosion performance of all those carbon coatings have been optimized to compete with gold coatings at fuel cell operation voltage. Anyway, the limits of the electrochemical corrosion performance of different carbon coatings at high electrochemical potentials occurring for split seconds on the cathode side of the bipolar plate during start/stop of a fuel cell can be crucial for the overall layer stack performance and durability. Depending on the deposition method and parameters, the properties of the carbon layer stack can highly differ from each other which leads to a different corrosion performance at such a high electrochemical potential.

3:00pm **PP4-2-WeA-4 Carbon-Based Coatings with Tailorable Properties as a Function of sp^3:sp^2 Hybridization***, **Biplab Paul (b.paul@platit.com)**, G. Wahli, J. Kluson, H. Bolvardi, A. Lümkemann,* PLATIT AG, Switzerland

Carbon-based coatings offer a variety of exceptional properties, including mechanical (hardness, elastic modulus, friction coefficient), physical (optical, electrical), chemical (chemical inertness), and biomedical (biocompatibility) properties. However, to exploit the entire range of functionalities from this class of coatings we need appropriate technologies to make the coatings preferentially engineered. For example, carbon-based coatings can be engineered to be graphite like or diamond like by preferentially tuning the ratio of sp^3/sp^2 hybridization in the coatings. The monolithic tetrahedrally-bonded coatings (ta-C), with 100% sp^3 content, provide the highest hardness, while amorphous carbon (a-C) coatings with $sp^3/sp^2 < 1$ provide softer coatings with low coefficient of friction (COF), useful for many frictionless mechanical applications. PLATIT's advanced coating units, integrating sputtering, arc and PECVD techniques, provides the unique scope to grow a plethora of diamond like coatings (DLC) with varying functionalities, categorized as DLC1 (metal doped a-C:H with $sp^2 >$ 50%, i.e., $sp^3/sp^2 < 1$), DLC2 (Si doped a-C:H), and DLC3 (hydrogen free ta-C with $sp^3 >$ 50%, i.e., $sp^3/sp^2 > 1$). The DLC1 coatings are grown by sputtering from metal targets (e.g. Ti, Cr, etc.) in acetylene atmosphere, offering the scratch proof aesthetic black coatings, useful for decorative and biomedical applications. The DLC2 coatings are grown by PECVD technique, offering the hard coatings (Hardness = 30-35 GPa, Lc2 = 30 N), useful for cutting tools and for various mechanical and electronic components. The DLC2 coatings being grown by PECVD technique, they offer the coating possibilities on difficult parts with complex geometries and miniaturized dimension (e.g., microtools). The DLC3 coatings are done by sputtering from carbon target at low temperature, providing hardness (H) > 40 GPa, and scratch resistance with Lc2 > 30 N, while COF < 0.2. With such high hardness and low COF values the DLC3 coatings offer the best coating solution for machining nonferrous materials. The physical properties of carbon-based coatings can be directly corelated to their color, which is defined by L*a*b* values. Figure 1 shows the L* values of carbon-based coatings as a function of hardness. The high L* values for DLC3 coatings indicate their higher transparency than other DLC coatings. This is attributed to the higher degree of sp^3 hybridization in DLC3 coatings as compared to that of DLC1 and DLC2 coatings.

3:20pm **PP4-2-WeA-5 Atmospheric Pressure Plasma Functionalization of Diamond Particles for Use as Quantum Sensors***, G. McGuire,* Rivis, Inc., USA*; M. Torelli, **Nickolas Nunn (nnunn@adamasnano.com)**, O. Shenderova,* Adámas Nanotechnologies, Inc., USA **INVITED**

Negatively charged nitrogen vacancy centers (NV^-) in diamond have unique properties making them excellent candidates for nanoscale magnetic and electric field sensors, as quantum bits as well as other applications. As quantum sensors they promise comparable sensitivity at room temperature to commonly used magnetic field sensors that must be cooled to liquid helium temperature, for example. NV centers may occur as neutral NV^0 or negatively charged NV^-, however, it is only NV^- that exhibits this magnetic sensitivity. With growing interest in the use of quantum sensor it is necessary to ensure predictable and reliable performance which requires uniform NV^- formation. However, the stability of NV^- centers is strongly influenced by the surface functionalization of diamond particles. Both nitridation and fluorination have been shown to help stabilize NV^- centers especially for shallow NV centers which provide greater sensitivity. Uniform functionalization of particles in batches is necessary for cost effective production. This has been investigated using an atmospheric pressure plasma system. Results of treatment in fluorine and nitrogen-based plasmas will be reviewed. Fluorescence spectroscopy was used as a means to determine the presence of NV^0 and NV^- following treatment and the impact of the treatment will be discussed.

4:00pm **PP4-2-WeA-7 Quantification of the sp^3 Content in DLC Films Deposited by HiPIMS Using EELS and NEXAFS***, **João Carlos Oliveira (joao.oliveira@dem.uc.pt)**,* University of Coimbra, Portugal*; A. Vahidi,* University of Coimbra, Pakistan*; R. Serra,* University of Coimbra, Portugal

Diamond-like carbon (DLC) films are a class of amorphous carbon materials with unique properties, including high hardness, low coefficient of friction (CoF), high wear resistance and chemical inertness, biocompatibility, and excellent electrical insulation. Therefore, these films have been commonly used in various industries, such as aerospace, automotive, biomedical, and microelectronics.

The advent of High-Power Impulse Magnetron Sputtering (HiPIMS) in the last two decades opened a new route for magnetron-sputtered coating. In HiPIMS, a large fraction of the sputtered atoms is ionized due to the several orders of magnitude higher plasma densities than in DCMS. Although HiPIMS has been successfully implemented for many metals, it is much less effective for DLC coatings deposition since C has significantly higher ionization energy and lower ionization cross-section than typical metals.

In previous works, the authors have shown that adding Ne to the plasma significantly improves the properties of DLC films deposited by Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS. Replacing half of the Ar process gas by Ne allowed for the deposition of denser films, with hardness up to 25 GPa, while still retaining a low CoF. Furthermore, the specific wear rate (SWR) of the DLC films decreased by close to 50 %, both in linearand reciprocating slidingagainst steel counterparts, being comparable with state-of-the-art hard DLC deposited by CAD and PLD.

The main objectives of the present work were to quantitively evaluate the sp^3 content in DLC films deposited by DOMS, to identify the relevant film formation mechanisms and to better understand process-properties relationships resulting from the addition of Ne to the plasma. DLC films were deposited by DOMS both in pure Ar and in mixed Ar + Ne plasmas. Quantitative evaluation of the sp^3 content in the films was performed by Electron Energy Loss Spectroscopy (EELS) and Near Edge X-ray Absorption Fine Structure (NEXAFS). Additionally, for comparison purposes, Raman spectroscopy was also used for qualitative assessments of the film's sp^3 content. Although hydrogen was not purposefully incorporated in the DLC films deposited in this work, the hydrogen content was measured by Elastic Recoil Detection Analysis (ERDA) in combination with Rutherford Backscattering Analysis (RBS). T. The surface morphology of the DLC films was characterized by Scanning Electron Microscopy (SEM) while their microstructure was investigated by High-Resolution Transmission Electron Microscopy (HRTEM).

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

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

9:00am **PP2-1-ThM-4 Metal-Ion Synchronized HiPIMS of AlN and AlScN for Piezoelectric Applications***, J. Patidar,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S. Bette,* aixACCT systems GmbH, Aachen, Germany*; O. Pshyk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R. Kessels,* aixACCT Systems GmbH, Aachen, Germany*; **Sebastian Siol (sebastian.siol@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Ionized physical vapor deposition (PVD) techniques, such as High Power Impulse Magnetron Sputtering (HiPIMS), offer unique opportunities to control the microstructure of thin film materials by accelerating ions onto the growing film using substrate-bias potentials. At moderate acceleration potentials, the increase in ad-atom mobility often leads to improved crystalline quality and texture. This, in turn, enables the deposition of high-quality thin films at low deposition temperatures. However, gas-ion incorporation can limit the feasibility of such synthesis approaches for defect-sensitive materials. In recent years, HiPIMS processes with a synchronized pulsed substrate bias have been developed with the goal to selectively manipulate the kinetic energy and momentum transfer of the film-forming species, particularly the metal ions. These processes hold remarkable potential to significantly reduce the defect concentration and stress in HiPIMS-deposited films, potentially unlocking a host of new applications for the technique.

In this presentation, I will showcase our latest work on the development of reactive metal-ion synchronized HiPIMS processes for the growth of piezoelectric AlN and AlScN thin films. It will be shown how highly textured, c-axis oriented AlN and AlScN films can be grown using reactive metal-ion synchronized HiPIMS. Here, even unconventionally moderate substrate bias potentials of up to only -30 V already lead to significant improvements in the films' properties. Most strikingly, the application of a substrate bias facilitates the deposition at oblique deposition angles and on structured substrates, while also significantly reducing the fraction of undesirable misoriented grains. A detailed characterization of the piezoelectric coefficients of the materials show values comparable to the current state-of-the-art. In addition, for AlScN in particular, the phase formation and stress state can be tailored by applying different biasing schemes and combinations of different sputter modes (i.e., HiPIMS or DCMS, or hybrid). Importantly, it will be shown that the applicability of these types of processes can be significantly extended, even on insulating substrate materials.

The goal of this presentation is to demonstrate the tremendous potential of synchronized HiPIMS processes for the deposition of defect-sensitive materials, especially in applications where tailoring microstructure and texture of the thin film materials is important.

9:40am **PP2-1-ThM-6 Optimization of Deposition Parameters of Titanium Oxide Films by Taguchi Method***, **Shih-Yang Hsu (pupuyang0120@gmail.com)**,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan*; B. Lou,* Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan*; J. Lee,* Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan*; Y. Yang,* Department of Materials and Mineral Resources Engineering, Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan

Titanium dioxide thin film exhibits excellent photocatalyst effect, antibacterial ability, and optical performance, which makes it widely studied and applied in related applications. Due to its antibacterial and transparent performance, the TiO_2 film can be deposited on touch screens and touch panels to prevent the infection of microorganisms. This work used a superimposed high power impulse magnetron sputtering and mid-frequency (HiPIMS-MF) sputtering system to deposit TiO_2 films on 304 and 420 stainless steel, silicon wafers, and glass slide substrates. Through the Taguchi method, nine batches of TiO_2 thin films were grown under different deposition processing parameters, including the HiPIMS frequency, HiPIMS duty cycle, working pressure, and substrate bias. The cross-sectional morphology of the film was observed with a field emission scanning electron microscope. the phase structure of the film was analyzed with an X-ray diffraction analyzer, and the hardness and adhesion of thin films were measured with a nanoindentation instrument and a scratch tester. The antibacterial and transmittance properties of TiO_2 thin films were examined. The Taguchi method was employed to investigate the optimal deposition conditions using signal-to-noise ratio and analysis of variance (ANOVA), discussing and optimizing the impact of process parameters on the antibacterial and transmittance properties of TiO_2 thin films.

10:20am **PP2-1-ThM-8 Phase Transformation of Boron Carbon Nitride Coatings Deposited by High-Power Impulse Magnetron Sputtering***, H. Nagakura, H. Komiya,* Tokyo Metropolitan University, Japan*; Y. Touta,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; I. Fernandez,* Nano4Energy, Spain*; R. Boyd, U. Helmersson, D. Lundin,* Linköping University, Sweden*; **Tetsuhide Shimizu (simizu-tetuhide@tmu.ac.jp)**,* Tokyo Metropolitan University, Japan

To realize the growth of cubic boron nitride (c-BN) towards a full-scale industrial application of this coating materials, this work has been aimed to understand the discharge physics and growth kinetics in reactive high-power impulse magnetron sputtering (HiPIMS) of B_4C target in Ar/N_2 gas mixtures. One of the most significant challenges to industrialize the c-BN coating is the significant degradation of film adhesion due to the high residual stresses during the cubic phase formation. While the key to nucleate c-BN phase is a formation of “nano-arches” by ion bombardment on turbostratic BN phase (t-BN), the bombardment by the gas ions, such as Ar^+ ions, leads the entrapment of the gas atoms into the crystal lattice, causing the increase in residual stress. On the other hand, time-transient discharge of HiPIMS makes the time separation of ion arrivals to the substrate and it enables the tuning of incident ions and the independent control of its kinetic energy by the use of synchronized pulsed substrate biasing technology. This would realize the selective ion bombardment of film forming species, expecting to result in efficient momentum transfer without introducing film stresses through the rare gas incorporation. In addition, this great feature of HiPIMS discharge allows us to systematically isolate the influencing factors and will dramatically advance the understanding of nucleation physics of c-BN. In this study, the impact of ion acceleration schemes, including DC bias, synchronized pulsed bias and bipolar pulse configurations and its process parameters, such as the pulse duration, delay time and the substrate bias potential are thoroughly investigated, based on the mass-spectroscopy study of reactive HiPIMS discharge of B_4C target in Ar/N_2 gas mixture. In addition to the great importance of bias potential, the obtained results clearly show the effect of the synchronized pulse duration and the time delay on the chemical bonding states of B-C-N films and its mechanical properties, owing to the time domain of accelerated ions during film growth. By focusing on the average momentum transfer per deposited atoms at each biasing conditions, role of mass and flux of incident ions on the formation of c-BN bonding state are discussed.

10:40am **PP2-1-ThM-9 Thick and Smooth Nanostructured Cr Coatings with Enhanced HiPIMS Ionization***, **Ricardo Serra (ricardo.serra@dem.uc.pt)**,* University of Coimbra, Portugal*; S. Adebayo,* University of Coimbra, Nigeria*; J. Oliveira,* university of coimbra, Portugal

In sputtering deposition processes the atomic shadowing effect, originated from the preferential deposition of obliquely incident atoms on higher surface points of any substrate, drives the formation of open columnar anisotropic microstructures, with columns interspersed with voids or underdense regions. The effect increases the surface roughness as the film thickness increases and undermine their performance, also limiting the maximum achievable thickness of films. Energetic ion bombardment during film growth counteracts the atomic shadowing effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and triggering re-deposition processes. However, film surface bombardment with highly energetic particles forms higher density of defects, disrupting the crystalline structure of the films and adding compressive internal stress.

In a previous work was shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment.

Thick chromium films were prepared by DOMS, with different levels of ionization to test and study the influence on the film growth conditions and respective coating properties, like structure and surface morphology. An electrostatic flat probe mounted at the substrate location was used to characterize the saturated current density of positive charges bombarding the substrate during film growth, evaluating the flux of positive ions bombarding the growing film. Film hardness decreases with increase of thickness, however, Young's Modulus values remain close to Cr bulk value. The films have [110] preferential orientation depending on the bombarding conditions.

The authors would like to acknowledge the Portuguese Foundation for Science and Technology for funding of this work through project IoShad PTDC/CTM-REF/1464/2021.

11:00am **PP2-1-ThM-10 Implementation of HiPIMS Technology in Different Industrial Sectors***, **IVAN FERNANDEZ (IVAN.FERNANDEZ@NANO4ENERGY.EU)**,* NANO4ENERGY SL, Spain

After 20 years of continuous development by several research groups and companies it is now clear that real industrial breakthroughs for the high-power impulse magnetron sputtering (HiPIMS) technology are happening. HiPIMS is a state-of-the-art tool for applying high demanding metal and ceramic coatings with superior properties for applications such as: metal fabrication process (machining, stamping, molding or other tools), functional decorative, trench filling in semiconductor industry, or tribological (H-free DLC coatings with reduced friction, high hardness and enhanced thermal stability). Despite the great perspective and the positive forecasts for HiPIMS-technology since its' discovery in 1999, it has taken more than 15 years for the real industrial breakthrough to start. For example, the deposition rate of HiPIMS is still considered to be rather low compared with conventional magnetron sputtering and even more so when compared to cathodic arc-deposition. Another issue is the complexity of use due to the large number of adjustable process parameters. It is not only the HiPIMS power supply, which itself has more controllable parameters than any traditional power supply, what contributes to this great deposition technology. It is also the process regulation (monitoring), the magnetron system (magnetic configurations), the gas flow, the pumping speed, etc.

Apart from the traditional use of HiPIMS which is being currently implemented by the industry, it has been recently demonstrated that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse (Bipolar HiPIMS) gives rise to the generation of high fluxes of energetic ions. This solution allows unprecedented benefits for the coating industry, such as the energetic deposition onto insulating or grounded substrates, improved coverage on 3D parts or components, or even substrate etching. Also, Dual Magnetron HiPIMS operation is implemented more often in combination with multiple magnetron sources for the large production of high-end decorative coatings. A few examples of implementation of HiPIMS technology in industrial systems as well as the experimental results obtained in different configurations will be presented in this talk.

11:20am **PP2-1-ThM-11 Impact of Energetic Film-Forming Particles in Ion Beam Sputter Deposition of Epitaxial Ga_2O_3 Thin Films***, **Dmitry Kalanov (dmitry.kalanov@iom-leipzig.de)**, Y. Unutulmazsoy, J. Gerlach, A. Lotnyk, J. Bauer, A. Anders, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides intrinsic heating and kinetic assistance to the growing film by energetic particles arriving at the substrate surface, which affect various thin film properties such as density, microstructure, and forming phase. In IBSD, the kinetic energy distributions of film-forming particles can be controlled by changing process parameters, including the sputtering geometry, the flux, and the energy of primary ions. This is especially important for the growth of epitaxial thin films since it is necessary to find the optimal energetic assistance while minimizing the damage to the crystal lattice.

In this study, reactive IBSD is used for deposition of epitaxial Ga_2O_3 thin films on Al_2O_3(0001) substrates.The influence of process parameters such as substrate temperature, kinetic ion energy, ion beam current, sputtering geometry, oxygen pressure, and deposition time on the properties of the epitaxial films is investigated. The kinetic energy distributions of ions in the film-forming flux are measured by using a combined mass and energy analyzer and the resulting films are characterized regarding growth rate, roughness, crystalline structure, and microstructure. The impact of energetic bombardment by film-forming particles on the thin film structure is analyzed, and a significant change in crystalline quality is observed above the threshold in the average energy of film-forming particles (around 40 eV for the sputtered Ga^+ ions).

11:40am **PP2-1-ThM-12 Quantification of the Negative Oxygen Ion Yield***, **Diederik Depla (diederik.depla@ugent.be)**,* Ghent University, Belgium

Many thin film applications are based on oxides. The optimization of the oxide properties is an on-going process and requires a deep understanding of the deposition process. A typical feature of reactive (magnetron) sputter deposition is the presence of negative oxygen ions. The presence of negative ions in gas discharges was already postulated in the very first paper on sputtering by Grove.

In a magnetron oxygen containing discharge, two groups of ions can be identified based on their energy. Low energy ions are generated in the bulk of the discharge. The high energy ions are emitted from the oxide or oxidized target surface. As these ions are generated at the cathode, they are accelerated by the electrical field towards the growing film. Depending on the discharge voltage and the powering method, their energy is typically several tenths to hundreds electron volt. As such the ions can have a strong impact on the film properties. Nevertheless, despite the many illustrative studies on the impact of negative oxygen ions, quantification is often lacking as the negative ion yield is only known for a few oxides. A compilation of several literature sources permits not only the prediction of the negative ion yield, but also a comparison amongst different oxides.

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP2-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

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

2:00pm **PP2-2-ThA-3 Strategies for Low Temperature Reactive Deposition of Crystalline TiO_2 Thin Films**, ***Tomas Kubart (tomas.kubart@angstrom.uu.se)***, Uppsala University, Department of Electrical Engineering, Sweden **INVITED**

Titanium dioxide thin films have a multitude of different applications. While the amorphous TiO_2 has excellent optical properties and very good conductivity, the presence of defects leads to an increased recombination. For this reason, crystalline thin films of TiO_2 are desirable for photocatalysis as exemplified by plasmonic photoconversion devices for production of chemical molecules or oleophobic surface treatment by photofixation of SO_2 on anatase surfaces. In general, there is a great interest in deposition techniques that enable phase control of oxide thin films with TiO_2 being the prominent example.

This contribution deals with reactive HiPIMS deposition of TiO_2 thin films. First, experiments with a relatively long target-to-substrate distance are presented. It is shown that in the absence of substrate heating, all deposited films are X-Ray amorphous. Despite that, films prepared by an optimized HiPIMS process exhibit up to 3 times higher photocatalytic activity evaluated by photodegradation of stearic acid, as compared to reference pulsed DC films prepared using the same setup. High oxygen partial pressure is required to achieve the enhanced photocatalytic performance. Increased ion energy, however, has a detrimental effect on the photoactivity. The deposition conditions have also pronounced impact on the crystallization kinetics of the thin films as illustrated by in-situ GIWAXS studies.

When the target-to-substrate distance is reduced, the crystallinity of the as-deposited films is greatly improved. Growth of anatase as well as rutile can be achieved by changing the total deposition pressure. Even here, the HiPIMS process facilitates crystallization of the films as compared to pulsed DC. The deposition, however, results in a pronounced unintentional heating of the substrate. The heat input to the substrate is characterized and results from alternative experiments are presented.

In summary, the HiPIMS deposited films clearly outperforms the ones prepared by pulsed DC. Although the exact growth conditions are dependent on the deposition geometry and specifics of the deposition setup, some general trends can support the process development.

2:40pm **PP2-2-ThA-5 Plasma Dynamics of Individual HiPIMS Pulses Investigated by High-Frame-Rate Camera**, ***Matjaz Panjan (matjaz.panjan@ijs.si)***, Jozef Stefan Institute, Slovenia

Plasma of high-power impulse magnetron sputtering (HiPIMS) discharges is not azimuthally homogenous instead it is concentrated in dense angular regions called spokes [1]. These regions are organized in periodic or quasi-periodic patterns, typically have triangular shape and rotate with velocities of several km/s. Spokes are also present in other types of magnetron discharges. They have been observed in DC magnetron sputtering [2] and RF magnetron sputtering discharges [3].

In this work, we studied the dynamics of HiPIMS plasma with microsecond time resolution using a high-frame-rate camera. The individual pulses were investigated for different Ar pressures (0.25-2 Pa) and peak currents (10-400 A). The experiments show three distinct stages in the plasma dynamics and self-organization with increasing discharge current. From the pulse onset and up to currents of 25-50 A the dynamics is similar to one observed in DCMS discharges. Spokes rotate in the -**E**×**B** direction with velocities from 4 km/s to 15 km/s and exhibit elongated triangular shape. The growth rate in discharge current strongly influences the spoke velocity – spokes rotate faster for higher growth rates. This DCMS-like stage is followed by a chaotic plasma reorganization with the formation of irregular patterns and complex spoke propagation. As current increases above approximately 50 A, plasma starts to form regular patterns with triangular spoke shape. During this stage, spokes rotate in the **E**×**B** direction with velocities from 6 km/s to 9 km/s. The spoke velocity depends on the pressure but is practically independent of the discharge current. Spokes rotate faster at lower pressures than at higher pressures. Remarkably similar plasma evolution is observed for pulses with comparable discharge current waveforms.

[1] A. P. Ehiasarian *et al.Appl. Phys. Lett.,* **100** (2012) 114101

[2] M. Panjan *et al.Plasma Sources Sci. Technol.*, **24** (2015) 065010

[3] M. Panjan *J. Appl. Phys.*, **125** (2019) 203303

3:00pm **PP2-2-ThA-6 PowerFlex 500CG: A New HiPIMS Machine for Microtools Coating**, ***Tommaso Ceccatelli Martellini (tommaso.ceccatellimartellini@protectim.com)***, Protec Surface Technologies, USA; *G. Coletta,* Protec Surface Technologies, Italy

A new PVD platform for the deposition of ultra-smooth hard coatings on microtools is introduced: the PowerFlex 500CG. This PVD machine is based on HiPIMS technology and allows the reliable deposition of multiple industrial coatings (TiSiN-based, AlCrN-based or sputter taC) for demanding applications such as high precision machining of hardened steel (HRC60), TiAlV or Al-alloys. The current cutting applications require coatings with extremely high smoothness, durability, and thermal resistance as well as tailored stress and toughness. The performance of the PowerFlex 500CG machine will be described in this paper, including its new etching protocol allowing in-situ microtool edge preparation or a stable reactive sputtering process to improve deposition rate. Finally, a comparison with the industrial benchmark coatings for high precision machining is presented.

3:20pm **PP2-2-ThA-7 Toward Decoupling the Effects of Kinetic and Potential Ion Energies: Ion Flux Dependent Structural Properties of Thin (V,Al)N Films Deposited by Pulsed Filtered Cathodic Arc**, ***Yeliz Unutulmazsoy (yeliz.unutulmazsoy@iom-leipzig.de)***, *D. Kalanov, K. Oh,* Leibniz Institute of Surface Engineering (IOM), Germany; *S. Karimi Aghda,* RWTH Aachen University, Germany; *J. Gerlach, N. Braun,* Leibniz Institute of Surface Engineering (IOM), Germany; *F. Munnik,* Helmholtz-Zentrum Dresden - Rossendorf, Germany; *A. Lotnyk,* Leibniz Institute of Surface Engineering (IOM), Germany; *J. Schneider,* RWTH Aachen University, Germany; *A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany

Multiply charged ions formed in pulsed filtered cathodic arc process carry significant kinetic and potential energy which contributes to the formation of dense, adherent and macroparticle-free thin films. While the impact of kinetic ion energy on thin film formation during energetic processes such as cathodic arc deposition is well explored, the effects of ion potential energy are less known. We aimed to decouple the contribution of ion kinetic and potential energy regarding the structural effects on the forming thin films. To reach that goal, different arc source configurations are utilized in the filtered cathodic arc experiment including biasing the plasma in relation to the grounded substrate and applying an external magnetic field at the source. Charge-state-resolved energy distribution functions of ions measured at the substrate positions revealed the differences in plasma properties between the arc source configurations, and applying external magnetic field is found to be the primary tool to increase the ratio of multiply charged ions. Thin films of metastable cubic (V,Al)N films are deposited using different electrical configurations and characterized in detail. The resulting thin films demonstrate the possibility to deposit crystalline films without substrate heating due to “atomic scale heating” stemming from the high flux of multiply charged ions, namely the ions carrying significant kinetic and potential energy, in the case of an external magnetic field. However, additional complexity added by the high flux needs further research to distinguish the sole effects of ion flux and ion potential energy on the structure of a forming thin film.

4:20pm **PP2-2-ThA-10 Tough Plasmonic Titanium Nitride Films Deposited by High Power Impulse Magnetron Sputtering**, *E. Muir,* Sheffield Hallam University, UK; *R. Bower, P. Petrov,* Imperial College of Science, Technology and Medicine, UK; ***Arutiun P. Ehiasarian (A.Ehiasarian@shu.ac.uk)***, Sheffield Hallam University, UK

TiN is one of the most plasmonically active and environmentally robust materials with photocatalytic function. However thin films suffer from high optical losses due to a high uptake of C and O impurities at grain boundaries. Densification of the microstructure through High Power Impulse Magnetron Sputtering (HIPIMS) deposition improves the optical properties, however the influence of plasma chemistry is not known. This study utilises constant-current HIPIMS as a technology to achieve high pulse-to-pulse reproducibility and overall operational stability in the discharge in a wide operating window. Time-resolved optical emission spectroscopy reveals a gas-rich ignition phase with duration of 30 µs which develops into a metal-rich phase where the metal component is continuously pumped over 70 µs while the plasma density remains constant. A steady metal-dominated state is reached for pulse durations above 100 µs. Films deposited during the ignition stage were markedly different than those deposited when the discharge develops into the “pumping” and “steady state” regimes, for a constant peak and average power. Differences are observed in the crystallographic texture shifting from a strong (111) to a stronger (200) component confirmed by XRD pole figures, and H_{IT}^3/E_{IT}^2 ratio (toughness) increasing dramatically from 0.2 to 0.3 GPa for a nano-hardness increase from H_{IT} = 33 to 34 GPa. The changes are correlated with the grain morphology observed by AFM. All films were deposited without heating or substrate bias and exhibited excellent plasmonic properties with a single wavelength of electric permittivity near zero and low optical losses represented by the imaginary component of the electric permittivity as determined from modelling of ellipsometry data. The antimicrobial properties of the films will be discussed.

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

Plasma and Vapor Deposition Processes (Symposium PP) Poster Session

PP-ThP-5 Recyclable Thin Coatings Deposited by Means of Plasma-Assisted Techniques on Polymer Foils for Food Packaging Applications, ***Francisco A. Delfin (Francisco.Delfin@fh-wels.at)****, C. Forsich, M. Schachinger, S. Augl,* University of Applied Sciences Upper Austria*; S. Brühl,* National University of Technology, Regional Faculty of Concepción del Uruguay (UTN – FRCU), Argentina*; C. Burgstaller, D. Heim,* University of Applied Sciences Upper Austria

The prevalent pollutant in our lands and oceans today is plastic litter. Emphasizing waste recycling is crucial to counter this environmentally harmful issue. Nonetheless, the recycling process faces challenges when items such as food packaging consist of multiple layers of diverse polymers co-extruded together to ensure adequate barrier properties. A solution to this problem lies in applying thin coatings using plasma-assisted techniques on single-layer polymer foils, which can provide similar resistance to water and oxygen permeation. Considering the nanometric thickness of these coatings, it is feasible to recycle them without significant problems.

In this study, thin coatings deposited on polymer foils using two plasma-assisted techniques are compared: Plasma-Assisted Chemical Vapor Deposition (PA-CVD), employing a bipolar DC pulsed discharge, and Magnetron Sputtering Physical Vapor Deposition (MS-PVD). Carbon and silicon-based coatings were obtained with PA-CVD using acetylene C_2H_2 and hexamethyldisiloxane (HMDSO) as precursors, respectively. MS-PVD was used to deposit carbon, silicon, and aluminium coatings. Polypropylene (PP), Low Density Polyethylene (LDPE) and Polyethylene Terephthalate (PET) with a thickness of approximately 20 µm were used as substrate. The effect of coating thickness (directly correlated to deposition time) and chemical composition on the barrier properties was examined. Characterization included Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Surface Free Energy (SFE), Water Vapor Transmission Rate (WVTR) and Oxygen Transmission Rate (OTR).

The FTIR spectra of the Si-coated films exhibited a characteristic band at around 1075 cm^{-1}, corresponding to the asymmetric stretching vibrations of Si–O–Si. Carbon based coatings displayed a broad band at around 1600 cm^{-1} related to C=C bonding vibrations. Raman spectra of carbon coatings showed the typical D and G bands which are characteristic of amorphous carbon. SFE was about 45 mN/m for carbon- and about 20 mN/m for silicon-based coatings, while that of the untreated polymers is in average 30 mN/m. SEM cross-sections allowed for an estimation of coating thickness between 50 and 150 nm, which is considered to be neglected in conventional recycling processes. Depending on thickness and chemical composition, barrier properties improved by 20 to 50%, with Al-PVD coating showing the best performance with an improvement of up to 10 times.

PP-ThP-6 Design and Manufacturing of Low-Cost Atomic Layer Deposition System to obtain Semiconductor and Dielectric Thin Films, *J. Navarro-Rodríguez, F. Mateos-Anzaldo,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico*;* ***Jesús Román Martínez-Castelo (jesus.roman.martinez.castelo@uabc.edu.mx)****,* Facultad de Ingeniería, Mexicali-Universidad Autónoma de Baja California, Mexico*; A. Pérez-Sánchez, J. Ruiz-Ochoa,* Facultad de Ciencias de la Ingeniería y Tecnología, Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; A. Gaytán-Pérez,* Facultad de Ciencias de la Ingeniería y Tecnología-Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; H. Tiznado-Vázquez,* Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México*; N. Nedev,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

This work describes the design and manufacturing of a lab-made ALD system. In the system, the chamber reactor was designed using SolidWorks software and machined with a lathe. The chamber is of aluminum and has an internal diameter of 3.5 inches, with two entries for precursors with a diameter of 1/64 inch, and one exit with a diameter of 1/2 inch. To dose the precursor and the oxidant, two 3-way diaphragm valves were used. This type of valves allow a continuous flow of nitrogen as carrier gas and permit formation of high- and low-pressure zones, which allow a high-speed deposit. To heat the system, a flat circular resistance controlled by a PID was used. The control of all the system is carried out using a graphical interface of LabView.

PP-ThP-7 Neon Addition to the Plasma for Enhanced Ionization in the Deposition of Cr films by HiPIMS-DOMS, ***João Carlos Oliveira (joao.oliveira@dem.uc.pt)****,* University of Coimbra, Portugal*; S. Adebayo,* University of Coimbra, Nigeria*; R. Serra,* University of Coimbra, Portugal

In magnetron sputtering-based deposition processes, particles that arrive at oblique angles relative to the growing film's surface promote the atomic shadowing effect which, ultimately, results in porous and underdense columnar microstructures. Energetic particles bombardment helps to prevent this effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and/or triggering re-deposition processes. However, bombarding the film's surface with highly energetic particles comes with a heavy cost: the formation of a high density of defects, which disrupts the crystalline structure of the films, and the creation of compressive stresses.

In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material[1]. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. The most straightforward route to achieve high ionization of the sputtered species in HiPIMS is to increase the peak power. However, this also increases the average energy of the sputtered species and brings about energetic bombardment. Partially replacing Ar by Ne in the process gas promotes an increased mean electron energy which increases plasma ionization, as the ionization energy of Ne (21.56 Ne) is significantly higher than that of Ar (15.75 eV). In this work, partial substitution of Ar by Ne in the DOMS process gas was investigated as a mean to increase the ionization degree of the sputtered species without increasing their average energy.

In this work, Cr thin films were deposited by DOMS in pure Ar and mixed Ar + Ne plasmas up to 60 % Ne. Adding Ne to the plasma resulted in 25 % increase in the ions saturation current density (ISCD) as measured by an electrostatic flat probe placed at the substrate location. All the deposited films have a dense and compact columnar microstructure with an almost complete [110] out of the plane preferential orientation. The lattice parameter of the Cr films increased with increasing Ne content in the plasma while their surface roughness decreased from 6 to 3 nm. The hardness and young's modulus of the Cr films were evaluated by nanoindentation.

PP-ThP-9 Mechanical Properties Thermal Stabilities of Multilayered AlCrBN/AlTiSiN Hard Coatings, ***Chung-En Chang (abcd0214milk@gmail.com)****, T. Tsai, H. Feng, M. Yang, Y. Chang,* National Formosa University, Taiwan

AlCrN and AlTiN coatings have been applied widely in cutting tools and mold dies because of good mechanical properties, tribological properties and oxidation resistance as resulting from the incorporation of Al into CrN and TiN. The AlCrN coating possesses good oxidation resistance even at 1000 °C while the AlTiN has high hardness at high temperature. To make further improvement of these two coatings, multilayer coatings with alternate AlTiN and AlCrN layers have been designed. In addition, it is known that adding Si and B to coatings can effectively enhance their mechanical properties. Through combining the characteristics of Si and B, multicomponent and multilayer AlCrBN/AlTiSiN coatings were prepared using an electro-magnetic controlled cathodic arc ion plating method, and their thermal stabilities at high temperature up to 900 °C and 1000 °C were studied to align with the requirements of high-temperature applications. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). In this study, multilayered AlCrBN/AlTiSiN coatings were deposited using cathodic arc evaporation with periodic layering structures. Nanoindentation measurements and SEM/TEM observations revealed that when the samples were subjected to vacuum annealing at 900 ºC, the addition of Si and B not only suppressed the unfavorable formation of h-Cr_2N and w-AlN phases that would deteriorated mechanical properties, but also resulted in the phenomenon of increased coating hardness due to the formation of nanometer-sized c-TiN and c-AlN after the phase decomposition of the coating. In comparison, the hardness of AlCrN coatings decreased continuously with increasing temperature due to the absence of inhibiting h-Cr_2N formation. And, strengthening mechanisms from the phase decomposition was not observed in this AlCrN at high temperature. The AlCrBN/AlTiSiN coatings exhibited the capability to maintain or even enhance their mechanical properties at high temperature. In addition to the improved oxidation resistance, secondary hardening mechanism at high temperature could contribute to the successful application of such coatings in high-temperature environments.

PP-ThP-10 CVD Equipment: Yesterday, Today and Tomorrow*, **Anne Zhang (anne.zhang@ihi-bernex.com)**, H. Strakov,* IHI Bernex AG, Switzerland

Bernex coating systems are used worldwide to produce coatings on metal / ceramic compounds for the purpose of reducing wear and/or friction, providing corrosion and oxidation protection,or obtainingother specific surface characteristics. The CVD coating processes are based on chemical reactions on hot surfaces between reactant gases, which directly yield the solid coating material. One of the advantages of CVD resides in the ability to coat a wide range of materials with complex shapes, even porous and hollow ones, and is also suitable for coating internal surfaces. Applications include industrial components, aerospace, cutting inserts, forming/molding/extrusion tools, etc.

Bernex coating systems cover various CVD technologies, including Chemical vapor aluminizing (CVA), Chemical vapor infiltration (CVI) and CVD with solid metalorganic precursors (MOCVD). These systems are highly modular and provide significant process flexibility. Based on customer requirements, the systems can be pre-configured upon purchase, or extended at any time. This not only includes hardware and software components, but also comprises external units and accessories.

Coatings developed by Bernex will be presented, along with new process modules and general improvements on hardware and software modules. An insight of future developmentswill also be provided.

PP-ThP-12 Synthesis and Characterization TiAlZrTaNbN Coatings Obtained by High-power Impulse Magnetron Sputtering*, I. Gonzalez Avila, J. Gónzalez Lozano, O. Piamba Tulcan, **Jhon Jairo Olaya Florez (jjolaya@unal.edu.co)**,* Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia

TiAlZrTaNbN coatings were obtained by High-Power Impulse Magnetron Sputtering and deposited on superalloys and Ti alloy substrates. The effect of working pressure and bias voltage on hardness, corrosion and wear resistance was investigated and correlated with the microstructure of the samples. The microstructure, morphology and chemical composition of the coatings were analyzed by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy. The sample porosity and corrosion resistance were studied by electrochemical methods. The mechanical properties were evaluated by means of nanoindentation, and the tribological properties was studied with pin-on-disk technique. The pulse power and current peak have been affected by working pressure which modified significantly the films properties. The relationship between growth conditions, microstructure, wear and corrosion resistance is presented and discussed in this work. Finally, the effect of substrate-coating system and the deposition parameters are highlighted in order to further enhance HiPIMS coatings properties.

PP-ThP-13 Residual Stress Analysis in 30 µm thick High-Speed PVD Coatings*, K. Bobzin,* surface Engineering Institute - RWTH Aachen University, Germany*; C. Kalscheuer, **Max Philip Moebius (moebius@iot.rwth-aachen.de)**, P. Hassanzadegan Aghdam,* Surface Engineering Institute - RWTH Aachen University, Germany

Several studies focus on the impact of residual stress in coatings, predominantly synthesized by conventional physical vapor deposition (PVD) techniques like Arc PVD and Magnetron Sputtering (MS). High-Speed PVD (HS-PVD) is a PVD variant based on hollow cathode gas flow sputtering. It enables the deposition of thick PVD coatings s >20 µm in contrast to Arc or MS-PVD, where coating thickness is limited due to compressive residual stress. Therefore, the effect of the residual stress on coating and compound properties of several HS-PVD coatings was analyzed for the first time in this study.

The aim is to evaluate the influence of diverse substrate materials, different coating systems, and process parameters on the residual stress state in HS-PVD coatings. Herein different coatings systems like AlCrN and AlCrO, were deposited at different process parameters such as reactive gas flow, deposition time, and bias voltage. The residual stress of oxide coatings with s ≈ 30 µm, deposited on WC-CO and steel X40CrMoV5-1, was analyzed using X-ray diffraction (XRD) and the $\sin^2\psi$ method. For the nitride coatings, in addition to the XRD method, the residual stresses were measured by the focused ion beam-digital image correlation (FIB-DIC) ring-core method to investigate different measuring methods.

With increasing coating thickness, a reduced compressive residual stress is determined by both analysis methods. AlCrN and AlCrO coating systems show higher adhesion strength with increasing thickness. Moreover, AlCrO coatings deposited on WC–Co indicate higher residual stresses than coatings deposited on steel substrate.

Using HS-PVD, the deposition of thicker coatings with simultaneously higher adhesion strength is possible, which is typically a limitation of Arc and MS-PVD. Additionally, lower residual compressive stresses are unexpectedly observed at higher coating thickness. This indicates an outstanding research demand to investigate, how an increased coating thickness in HS-PVD leads to reduced residual stresses.

PP-ThP-14 Corrosion and Tribocorrosion Behavior of DlC/CNx/CrC/Cr Multilayers Deposited by Hipims in Synthetic Seawater*, **Martin Flores (martin.fmartinez@academicos.udg.mx)**, L. Flores, L. López,* Universidad de Guadalajara, Mexico*; A. González,* Unversidad Autónoma de Tamaulipas, Mexico

Diamond-like carbon (DLC), CNx and CrC coatings have a wide range of potential applications to reduce the sliding friction and improve wear and corrosion resistance of bearings and other components. AISI 4317 steel is used in bearings of crane grabs for the transport of minerals with sulfur and fluor content in port facilities. These steels suffer from tribocorrosion and corrosion promoted by chloride ions at the port and the ions from the minerals. The multilayers were deposited by High Power Impulse Magnetron Sputtering (HIPIMS). The ion etching using Ar ions cleans the substrate and the metal ion etching (Ar^+ and Cr^+) promotes a good adhesion of the film. In this work the metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target, the ion energy distribution function was studied for each plasma used to deposit the multilayers. This work reports the results of the potentiodynamic polarizations to evaluate the corrosion and the measurements of open circuit potential during the tribocorrosión tests. Synthetic seawater was used as electrolyte. The structure of Cr and CrC layers was studied by XRD. Raman spectroscopy was used to study the sp2 and sp3 bonds of DLC and CNx. The results show an improvement in the corrosion and tribocorrosion resistance of the samples coated with the multilayer.

PP-ThP-15 Stable Hybrid HiPIMS/RF Sputtering Process on a Single Magnetron for arc-free Deposition of Compact Oxide Films*, A. Fromm,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; C. Adam,* Fraunhofer Institute for Mechanics of Materials IWM, MELEC GmbH, Kiel University, Germany*; F. Meyer,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; **Günter Mark (guenter.mark@melec.de)**, J. Löffler,* MELEC GmbH, Germany*; M. Thomas, M. Wirth, F. Burmeister,* Fraunhofer Institute for Mechanics of Materials IWM, Germany

Thin, insulating coatings are required for electronics, sensors and medical technology. Most of them are deposited by reactive magnetron sputtering and involve an RF or MF excitation of the plasma (radio/mid frequency). However, this often results in sub-stoichiometric layers with process-induced, but undesired residual porosity. With HiPIMS (high power impulse magnetron sputtering), significant advantages over conventional sputtering processes can be achieved, such as the production of coatings with high adhesion and almost bulk density. However, the deposition rates are lower when compared to an RF or MF process with the same average power. In addition, process stabilization is not trivial due to high peak currents and short pulse durations. Instabilities are induced by arcing between insulating areas on the target, leading to droplet formation, which significantly reduces the achievable film quality [2]. To overcome these difficulties, we have for the first time investigated the combination of an RF and HiPIMS excitation in a single magnetron.

Therefore, a HiPIMS generator from Melec company was combined with a RF-Generator and connected to a single magnetron. To avoid back reflections, a special RF-Filter was used.Al_2O_3 layers were deposited in a hybrid RF/HiPIMS process using a metallic Al target and O_2 as reactive gas, with variations in power and pulse parameters.

A stable reactive hybrid RF/HiPIMS process on a single magnetron, with higher process stability when compared to a simple HiPIMS process, has been demonstrated for the deposition of Al_2O_3 layers. The number of arcing events could be significantly reduced. A higher deposition rate with higher nano hardness of the deposited coatings could be achieved [5].

A proof of principle for a combination of RF and HiPIMS excitation in one source has been established and opens up a new route for the 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 relationship of average HiPIMS and RF power. For a pulsed superposition of RF and HiPIMS, further developments of ultrafast impedance matching techniques are also necessary.

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Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP5-FrM
Plasma Surface Interactions and Diagnostics

Moderator: Arutiun P. Ehiasarian, Sheffield Hallam University, UK

8:00am **PP5-FrM-1 The Role of Plasma in Plasma Enhanced Atomic Layer Deposition***, **Scott Walton (scott.walton@nrl.navy.mil)**, D. Boris, M. Johnson, V. Wheeler,* US Naval Research Laboratory, USA*; M. Sales, P. Litwin,* NRC, USA*; J. Woodward,* US Naval Research Laboratory, USA*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center, USA*; J. Hite, D. Pennachio, M. Mastro,* US Naval Research Laboratory, USA **INVITED**

Plasma-enhanced atomic layer deposition (PE-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. The plasma-based advantages come at the cost of a complex array of process variables that can drastically impact the growth modes and resulting film properties. Accordingly, understanding the process-structure-property relationship is both critical and challenging. We approach this problem by combining plasma diagnostics and material characterization techniques. Plasma diagnostics are used to inform the choice of process conditions for PE-ALD systems including VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the plasma used in commercial and research PE-ALD tools. In particular, we assess the spatial variation of plasma parameters, flux and energy of ions reaching the substrate surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of operating powers, gas pressures, and gas input flow fractions typically used to grow nitride, oxide, and fluoride films. Changes in plasma parameters are then linked with changes in growth modes and film properties using both ex situ and in situ characterization techniques. Select example systems including AlF_3, InN, TiO_2 and Ga_2O_3, will be discussed. This work supported by the Naval Research Laboratory base program.

8:40am **PP5-FrM-3 Navigating the Complexity of Microwave Plasma-Assisted ALD During AlN and TiN Fabrication***, **Caroline Hain (caroline.hain@empa.ch)**, K. Maćkosz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; C. Guerra,* Swiss Cluster AG, Switzerland*; T. Nelis,* BFH, Bern University of Applied Sciences, Switzerland*; J. Michler, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Plasma-based atomic layer deposition (ALD) techniques are becoming increasingly relevant, offering extended control over process parameters such as temperature range, precursor/co-reactant chemistries and surface reactions. This freedom allows for a wider choice of substrates and thin film materials, as well as the ability to precisely tailor material properties critical to specific applications. Nevertheless, the complexity introduced by plasma necessitates a more detailed understanding of the deposition environment. This study aims to characterise *in situ* the surface reactions occurring during electron cyclotron resonance (ECR) microwave plasma-assisted ALD and their influence on the deposited films, in this case using the examples of aluminium nitride (AlN) and titanium nitride (TiN). Trimethylaluminium (TMA) and tetrakis(dimethylamido)titanium (TDMATi) were used as precursors for AlN and TiN, respectively, with plasma-activated nitrogen serving as co-reactant. Two types of time-of-flight mass spectrometers (ToFMS) were used to identify neutral and ionic species produced during the sequential ALD cycles. Optical emission spectroscopy (OES) was utilized to identify the nitrogen species produced during the nitrogen plasma step, while Langmuir probe measurements determined the plasma spatial potential, density, and electron temperature as a function of microwave power and distance from the source. Finally, the chemical composition, thickness, density, and structure, as well as surface uniformity of deposited AlN and TiN thin films were investigated via a combination of scanning and transmission electron microscopy (SEM/TEM), X-ray reflectometry (XRR) and ellipsometry. This work offers insights on the complexity of plasma-assisted ALD processes and paves the way for informed optimisation and application-based customisation of deposited thin films.

9:00am **PP5-FrM-4 Advanced Ion Energy Measurement Tools to Understand the Effect of Ion Energy on Film Properties***, **Thomas Gilmore (thomas.gilmore@Impedans.com)**,* Impedans, Ireland

In any plasma assisted deposition process, ion surface interactions can influence the film properties significantly. Ion energies determine if deposition, sputtering or implantation occurs, while ion flux determines the rate of this processing. The ion/neutral ratio impacts the thin film properties. Measuring these values for various chamber conditions can not only aid in process development, but also facilitate process transfer, as these ion parameters are the direct process drivers.

We, at Impedans Ltd, offer solutions to the requirements of ion energy and flux measurements. Our collection of sensors includes the Semion, Quantum and Vertex RFEAs for wafer level measurements. In this talk we will demonstrate the role of energetic ions in plasmas and how they affect the properties of materials etched or deposited in plasma processing. We will show how to use measured ion flux, ion energies and ion-neutral fractions to optimize industrial plasma-assisted processes. The *Semion RFEA* 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 [1-3] over a region of 300 mm large size wafer with down to 44 ns time resolution. On the other hand, the *Quantum system* is an energy resolving gridded quartz crystal microbalance (QCM), used to measure the ion-neutral fraction hitting a surface inside a plasma reactor. This instrument also measures the etching/deposition rate, ion energy, ion flux and bias voltage [4, 5]. The Vertex RFEA design has a variable aspect ratio (AR), controlled using a potential difference between its grids. A variable AR controls the ion angular spread passing through the sensor for detection. The Vertex product produces a plot of ion energy distribution versus AR [6].

We will highlight the successful measurements done by our RFEA product range in selected applications (like pulsed source and /or bias, tailored waveform biasing, etc) enabling better control of film properties of different materials and various plasma chemistries.

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9:20am **PP5-FrM-5 Plasma Polymerization Processes***, **Dirk Hegemann (dirk.hegemann@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Plasma polymer films are deposited via reactive intermediate species as formed in a low temperature plasma. Over the last decades, the understanding of the mechanisms behind plasma polymerization processes has steadily been improved, which will be discussed. Basically, the highly non-equilibrium conditions provide an average energy per molecule in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Due to the related energy distribution, the probability for the activation mechanism to produce film-forming species can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach to optimize plasma polymerization processes for surface functionalization is demonstrated on the basis of siloxanes, hydrocarbons, and further gaseous mixtures.

Hexamethyldisiloxane (HMDSO) has been well studied in the past revealing insights into the plasma chemical reaction pathway, which can thus be used as a model monomer following Arrhenius-like behaviour. Nano-scaled controlled film deposition is obtained considering the flux of film-forming radicals, etchants, and energetic species. Thus, dense to porous, hydrophilic to hydrophobic films can be generated. Such films are investigated for the chemical modification of catalytic substrates, as durable barrier layers and bioactive surfaces.

Furthermore hydrocarbon molecules are mixed with reactive gases such as CO_2 or NH_3 to investigate the penetration of radicals into complex 3D structures, which is studied using cavity techniques. Various applications in technical and biomedical fields will be presented.

Finally, an outlook is given about the applicability of the presented approach for plasma gas conversion based on comparable plasma chemical processes.

Plasma and Vapor Deposition Processes
Room Town & Country B - Session PP7-FrM

Modeling and Data-Driven Methods for Process Design, Analysis and Control

Moderator: Petr Zikán, PlasmaSolve s.r.o., Czechia

10:20am **PP7-FrM-8 Insights on Plasma Processing from Multi-Scale Physical and Data-Driven Modeling***, L. Vialetto,* Stanford University, USA*; T. Gergs,* Kiel University, Germany*; I. Chaerony Siffa,* Leibniz Institute for Plasma Science and Technology (INP), Germany*; C. Stüwe,* Kiel University, Germany*; T. Mussenbrock,* Ruhr University Bochum, Germany*; M. Becker,* Leibniz Institute for Plasma Science and Technology (INP), Germany*; **Jan Trieschmann (jt@tf.uni-kiel.de)**,* Kiel University, Germany **INVITED**

The theoretical description of plasma processing provides a formidable task that has been addressed by analytical modeling and numerical simulation for decades. Although the continuous increase in compute power has enabled simulation studies of the gas discharge physics in great detail, many open questions remain. This is reasoned by the extremely complex dynamics of multi-component plasmas facing solid surfaces, involving a large number of processes in the plasma and in the solid, as well as their plasma-surface interaction. The time and length scales of these physico-chemical processes span many orders of magnitude. Well separated scales often allow for the description of a given phenomenon on its respective scales, paired with a hierarchical coupling. This coupling is often rather static and realized via oversimplifying assumptions (e.g., tabulated coefficients), and may be biased-by-experience. Advantage can be taken from more unbiased data-driven approaches, which are derived from high fidelity data obtained from physical models at the lower scales. Moreover, the description of certain physical mechanisms may be substituted by data-driven sub-models (e.g., electric field calculation or transport parameters from a kinetic description). Correspondingly, a hierarchy of physical and data-driven models may be derived, linking global process quantities (e.g., pressure, voltage, current) to microscopic process quantities (e.g., thin film composition, electrical properties).

This approach is exemplified by the investigation of a low-pressure partially-magnetized capacitively coupled radio frequency discharge for the sputter deposition of silicon oxide thin films. The model is implemented in the OpenFOAM framework, extended by a Particle In Cell/Monte Carlo Collisions (PIC/MCC) implementation and coupled to a system of fluid equations for the neutral background. The surface evolution is described by a system of rate equations, which takes into account physical sputtering, chemisorption, physisorption, and surface diffusion of adatoms. The dynamics of physical sputtering are included using an artificial neural network model trained on surface kinetics data with varying stoichiometry from Monte Carlo simulations. It is argued that the versatility of the implementation also allows to use this model in a broader range of applications, such as plasma etching.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 138690629 – TRR 87 and – Project-ID 434434223 – SFB 1461.

11:00am **PP7-FrM-10 Utilizing Digital Twin Technology for Automated Coating Recipe Development***, **Petr Zikan (zikan@plasmasolve.com)**, A. Obrusnik,* PlasmaSolve s.r.o., Czechia

Recent developments in the field of coating technology have seen a rise in the adoption of process modeling and digital twin tools. The primary motivation for this shift is the extended duration and unpredictability of process transfers and scaling in coating applications. Moreover, these technologies are now beginning to contribute to energy reduction in coating processes.

In our previous work, we introduced a Digital Twin model for coaters, integrated into the MatSight framework by PlasmaSolve. This model demonstrated high accuracy in predicting the composition and key performance characteristics (such as hardness and residual stress) of coatings, utilizing a dataset of only eight characterized samples for training. This achievement was made possible by a hybrid process model that merges simulations of physical processes and chemistry with machine learning techniques. By incorporating knowledge of the coater's physical limitations, the model significantly reduced the need for extensive training experiments.

This contribution advances our research by tackling an inverse problem: using the Digital Twin model to create a coating recipe based on defined material specifications. These specifications include the number of layers, the thickness and composition of each layer, and the target hardness/residual stress for the complete stack. The model generates a recipe file compatible with coater operations, allowing for immediate implementation and validation of model predictions.

Furthermore, we illustrate how the Digital Twin model can be seamlessly integrated with other PVD simulation tools, offering a comprehensive view of the coating process. A case in point is the integration with the MatSight Coating Uniformity App, which enhances understanding of the coating's thickness distribution and the variations in ion bombardment and composition across a 3D object.

11:20am **PP7-FrM-11 Open-Source Plasma Modelling for Thin-Film Technologies with the Simulation Tool PICLas***, **Paul Nizenkov (nizenkov@boltzplatz.eu)**, A. Mirza, S. Copplestone, J. Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany

Simulating technical plasmas or highly rarefied gases in vacuum chambers presents a significant challenge due to the complexity of processes such as electron kinetics and strong non-equilibrium effects. To address these challenges, gas kinetic approaches are often employed. These approaches describe the medium not as a continuum, but as a stream of particles, including atoms, ions, and electrons.

This talk introduces PICLas, an open-source simulation tool originally developed for the simulation of space systems such as atmospheric re-entry & electric propulsion and now applied in various technical fields for simulating plasma processes. PICLas is based on gas kinetic approaches, utilizing particle methods like Particle in Cell (PIC) and Direct Simulation Monte Carlo (DSMC). A distinctive feature of PICLas is its modular structure, which allows the software to be used either as a pure DSMC or pure PIC solver. Combining these methods opens up exciting possibilities, such as simulating collisional plasmas.

The development of an intelligent graphical user interface aims to make this complex modeling more accessible to technical developers. This interface leverages modern web-based technologies and other open-source projects for cost-effective development. The talk will demonstrate how these technologies, combined with PICLas, can streamline the pre-processing, simulation setup, and post-processing in numerical simulation projects. Furthermore, the talk shall present different application examples, where the code has been tested and validated for thin-film technologies.

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