## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B2-1-MoM

## CVD Coatings and Technologies I
**Moderator: Raphael Boichot**, Grenoble-INP/CNRS, France

10:20am **B2-1-MoM-2 Diamond Coatings for Cutting Tool Applications***, **Manfred Weigand (manfred.weigand@cemecon.de)**, M. Woda, W. Puetz, M. Wegh, C. Schiffers, W. Koelker, O. Lemmer,* CemeCon AG, Germany

Thin film Diamond as pure sp3 bonded crystalline carbon is able to significantly improve cutting tool performance in hard to machine applications. These coatings are typically deposited by the means of hot filament CVD processes on an industrial scale nowadays.

When applying diamond thin films to cutting tools with a cemented carbide substrate and with complex geometries, a large set of work piece materials can be machined including carbon fiber reinforced plastics (CFRP), zirconium oxides, aluminum silicon alloys, graphite or even cemented carbide. This work presents some of the latest results of various case studies revealing the benefits of CVD diamond coatings upon cutting operations on these very demanding work piece materials.

10:40am **B2-1-MoM-3 Deposition of Hard Carbon Films by High Power Pulse Magnetron Sputtering (Virtual Presentation)***, **Takayuki Ohta (tohta@meijo-u.ac.jp)**,* Meijo University, Japan*; A. Oda,* Chiba institute of Technology, Japan*; H. Kousaka,* Gifu University, Japan **INVITED**

Diamond-like carbon (DLC) films, which is an amorphous carbon including both graphite (sp2 bond) and diamond (sp3 bond) structures, has widely used for hard mask for plasma etching and hard coating of the sliding parts. The DLC film containing rich sp3 bond realizes high hardness or low friction coefficient. A bombardment of carbon ions with incident energy of 100 eV into the film is essential to increase the sp3 bond in the DLC film. However, it is difficult to produce the high energy ions in conventional direct current magnetron sputtering (dcMS). High power impulse magnetron sputtering (HiPIMS) is attractive method to obtain large ion flux or high energy ions because the peak power density of HiPIMS is about 100 times larger than that of dcMS under same average power density. A DLC film on Si substrate deposited by HiPIMS shows the hardness of 20 GPa without negative substrate bias voltage[1]. A DLC film on plastic substrate has also deposited by HiPIMS without negative substrate bias voltage. The energy distributions of argon ion ($Ar^+$) and carbon ion ($C^+$) were measured using energy-resolved mass spectrometry in HiPIMS discharge in order to investigate the relationship between hardness and ion flux. The total ion flux of HiPIMS was about 100 times larger than that of dcMS under same average power density. The distribution of $Ar^+$ was composed of low energy component and high energy component whereas $C^+$ was mainly composed of high energy component. High energy component of both $Ar^+$ and $C^+$ simultaneously increased with increasing target voltage in comparison with low energy component of $Ar^+$. The difference in IEDF is explained by the difference in production process of ions.

The hydrogen-free Si-DLC film was deposited by dual magnetron sputtering method using carbon and silicon targets. The friction coefficient measured with the ball on disc test decreased to be 0.074 with increasing the Si content in the DLC film. At this experimental condition, the hardness was 18.4 GPa measured by the nano-indenter. Si-C bond increased with increasing the Si content from C1s spectra of XPS analysis. The relation among sp3 fraction, hardness, and behaviors of ions will be discussed.

reference

[1] K. Iga et al., Thin Solid films, 672, 104 (2019).

11:20am **B2-1-MoM-5 $Ti_3SiC_2$-SiC Multilayer Thin Films Deposited by High Temperature Reactive Chemical Vapor Deposition***, **Jorge Sánchez Espinoza (jorge.sanchez@grenoble-inp.fr)**, F. Trabelsi, E. Blanquet, F. Mercier,* SIMAP, Grenoble-INP, CNRS, France

MAX phases have a unique combination of ceramic and metallic properties that make them excellent candidate materials for high temperature applications. They are particularly interesting for their excellent thermal stability up to 1500 °C, their exceptional thermal shock resistance and their damage tolerance. In addition to their good mechanical properties at elevated temperatures and high stiffness, they exhibit optical, electrical and thermal properties similar to metals.

In this work, we report on the preparation of multilayer ceramic coatings based on MAX Phases by Reactive Chemical Vapor Deposition (R-CVD), able to withstand high temperature (T>1000°C) under air while maintaining their structural and functional properties. Computational Fluid Dynamics calculations, thermodynamic and diffusion considerations were developed for the selection and the design of the multilayer experiments.

R-CVD depositions were conducted in a vertical quartz cold-wall CVD reactor in the system $TiCl_x$ - $H_2$ - $SiH_4$ - $C_3H_8$ - $H_2$ between 1100-1300 °C in order to form multi-layer coatings that consist of stacks of titanium silicon carbide (MAX phase layer $Ti_3SiC_2$) and silicon carbide (SiC).

The surface morphology and cross-sectional microstructure of as-grown $Ti_3SiC_2$–SiC layers were characterized by Scanning Electron Microscopy (SEM), and X-Ray Diffraction analysis to identify the different solid phases. High temperature oxidation tests, nano-indentation and emissivity measurements were carried out with the aim of evaluating the potential of this material for high temperatures applications.

11:40am **B2-1-MoM-6 Chemical Vapor Deposition of W(C,N): Process Parameter – Microstructure – Mechanical and Tribological Property Relationships***, **Katalin Bőőr (katalin.boor@kemi.uu.se)**,* Uppsala University, Angstrom Laboratory, Sweden*; L. von Fieandt, E. Lindahl,* Sandvik Coromant, Sweden*; M. Fallqvist,* Karlstad University, Sweden*; O. Bäcke,* Chalmers University of Technology, Sweden*; R. Lindblad,* Uppsala University, Sweden*; M. Halvarsson,* Chalmers University of Technology, Sweden*; M. Boman,* Uppsala University, Sweden

There is a constant need to improve the performance of metal cutting tools. A materials research approach is the chemical vapor deposition (CVD) of coatings on the tool insert to enhance some of its properties or to introduce new functionalities. Hexagonal WC is the hard component of cemented tungsten carbide and is expected to have a good performance as a coating as well. Tungsten based coatings deposited by chemical vapor deposition are, however, so far relatively unexplored. The deposition from the gas phase can introduce new microstructures and textures, leading to enhanced mechanical properties. Moreover, the coating is expected to be under a compressive stress after post-deposition cooling if the substrate contains Co and the coating only the hexagonal WC phase. This differs from a tensile stress causing cracks in many conventional CVD coatings on cemented carbide.

The aim of this research was to deposit a new CVD coating, tungsten carbonitride (W(C,N)), which is a solid solution of hexagonal WC and WN, onto cemented carbide. Hexagonal WC and WN are line phases and are difficult to obtain by CVD due to the discrepancy in the reactivity of W-halide and C-precursors or a stable cubic $WN_{1-x}$ phase, respectively. For the W(C,N) synthesis $WF_6$, $CH_3CN$ and $H_2$ were used and they proved to have a balanced reactivity for W, C and N incorporation in ratios that enabled the formation of the hexagonal phase.

First, the current understanding on the growth mechanism will be presented. The results are based on a kinetic study and the influence of the process parameters on the coating microstructure and composition. Correlations between the grain size, morphology and orientation will be shown. The coating microstructure was characterized by scanning electron microscopy (SEM), the composition by elastic recoil detection analysis (ERDA) and the texture by X-ray and electron backscatter diffraction (XRD and EBSD). Transmission electron microscopy (TEM) was used to investigate a preferred prismatic texture and the type of defects introduced during the growth. Hard X-ray Photoelectron Spectroscopy (HAXPES) was used to investigate the reason behind a (C+N)-rich composition.

Further, the possibilities to tailor the microstructure and grain orientation of the coatings will be discussed. Nanoindentation measurements, diamond scratch and abrasion tests showed that the coatings were hard or superhard and their mechanical and tribological properties were dependent on the above properties.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B4-1-MoM

### Properties and Characterization of Hard Coatings and Surfaces I

**Moderators: Naureen Ghafoor**, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

10:00am **B4-1-MoM-1 Cathodic Arc Deposition of Chromium Based Coatings***, **Johan Nyman (johan.nyman@liu.se)**, H. Högberg,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Chromium is a widely used metal in coating industry with applications as decorative coating and for wear resistant purposes. The dominating Cr coating technique has been and still is electroplating. As health- and environmental concerns of electroplating is receiving ever increased attention, a need arises to develop alternative methods of synthesizing equally well-performing coatings. The multitude of application areas for electroplated Cr means that no universal solution exists to replace it. We investigate cathodic arc deposition of metallic Cr as well as Cr-based coatings alloyed with C and/or N with the purpose to tailor the properties of the coating between metallic and ceramic, seeking a combination of hardness and toughness. Thus, focus is put on determining synthesis-composition-structure relationships and their connection to the resulting mechanical properties of the coatings. We employ nanoindentation to analyze the mechanical properties of the coatings. From applied depositions conditions, transitions between metallic and ceramic properties are identified by determining chemical compositions by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA), bonding structure by X-ray Photoelectron Spectroscopy (XPS), resistivity by four-point probe measurements and phase distribution by X-ray diffraction (XRD) θ/2θ scans.

For Cr-C coatings, ToF-ERDA measurements show an increase in C content from 2 at.% at a $C_2H_2$ partial pressure of 0.1 Pa to 40 at.% at a $C_2H_2$ partial pressure of 0.3 Pa, corresponding to a composition of $Cr_3C_2$. The increase in C content is accompanied by a decrease in deposition rate from 130 to 30 nm/min. In θ/2θ XRD scans, Cr 110, 200, 211 and 220 peaks are clearly visible at C contents below 2 at.% , but where the peak intensities are suppressed with increasing C content. At a C content of 40 at.% there are no discernable peaks, indicating growth of X-ray amorphous coatings. Four-point probe measurements confirm the metallic properties at C contents below 2 at.% where resistivity values are close to values for pure metal Cr coatings with 20 µΩ*cm. At a C content of 7 at.% the resistivity has risen to 35 µΩ*cm and at 40 at.% it is 120 µΩ*cm . Nanoindentation reveals an increase in hardness from about 8 GPa for metallic Cr to 12 GPa already at 2 at.% C, indicating that a window exists for combining beneficial properties from that of a metal and a ceramic. Results from coatings alloyed with N will also be presented.

10:40am **B4-1-MoM-3 Grain Boundary Segregation Engineering in AlCrN Hard Coatings by CrN precipitation***, **Tobias Ziegelwanger (tobias.ziegelwanger@unileoben.ac.at)**, N. Jaeger, C. Mitterer, R. Daniel, J. Keckes, M. Meindlhumer,* Montanuniversität Leoben, Austria

As the modern day race for higher efficiency and machining speed in metal cutting industry asks for steady improvement of both hardness and toughness, this contribution has investigated grain boundary segregation engineering as a viable tool for hard coatings. Wurtzite (w-) AlCrN was chosen as a material of interest due to its favourable decomposition route and precipitation of cubic (c-) CrN. This behaviour was manipulated by alloying with Si in varying content.

A gradient coating $(Al_{0.8}Cr_{0.2})_{1-x}Si_xN$ was deposited by cathodic arc evaporation and annealed at several dedicated temperatures of up to 1100 °C. The Si content was increased with the increasing film thickness. The coating was characterized, in as-deposited and annealed states, by cross sectional X-ray nanodiffraction (CSnanoXRD), in small angle X-ray scattering (SAXS) as well as wide angle X-ray scattering (WAXS) geometries, at the synchrotron source PETRA III at the German Synchrotron (DESY) [Fig1.]. Therein, the formation of a w-AlCrN phase as well as the precipitation of c-CrN was indicated. Furthermore, the formation of periodic nanolayers within the coating in as-deposited state was observed. Their periodicities of 12 and 25 nm, depending on the Si content, were retrieved by the SAXS data.

The collected data from the gradient coating was used for the design of two multilayered coatings each consisting of alternating layers with compositions of $Al_{0,8}Cr_{0,2}N$ and $(Al_{0,7}Cr_{0,3})_{0,9}Si_{0,1}N$ in different layer thicknesses. Additionally, reference coatings of the sublayer materials were deposited as well. The mechanical properties of these four coatings were investigated by in-situ cantilever bending experiments and fracture surface analysis. The multilayered coatings displayed an increase in fracture stress of up to 20% and stable levels of fracture toughness after annealing at 1050°C. A maximum fracture stress of 4.7 GPa and fracture toughness values of 2.7 $MPam^{1/2}$ were measured.

In total it could be shown that the addition of Si to the AlCrN coating enhances its mechanical performance by change of fracture mode. However, the fracture stress did not preserve after heating at 1050°C. The multilayered coatings performed in as-deposited state between the two reference coatings, but exhibited the improved fracture stress after the heat treatment.

11:00am **B4-1-MoM-4 Influence of Deposition Pressure and Gas Mixture on the Microstructure, Phase Composition and Thermal Stability of Arc Evaporated TiSiN Coatings***, **Yvonne Moritz (yvonne.moritz@unileoben.ac.at)** [1] , C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* Ceratizit Austria GmbH, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

Owing to their advantageous properties including excellent hardness and high oxidation stability, arc evaporated TiSiN coatings are frequently used as protective hard coatings for various machining applications in the metal cutting industry. By varying the deposition conditions, microstructural changes and thus also changes of the mechanical or thermal properties can be obtained. Within this work, the influence of a varying $N_2$ deposition pressure and the addition of Ar to the deposition atmosphere on the microstructure and thermal stability of TiSiN coatings was studied in detail. Scanning electron microscopy and high-resolution scanning transmission electron microscopy investigations revealed a feather-like and fine-grained structure as well as the presence of an amorphous $SiN_x$ phase for all TiSiN coatings. However, at higher $N_2$ deposition pressures also several larger grains appear. Further investigation of powdered TiSiN coatings by X-ray diffraction (XRD) revealed a significant decrease in lattice parameter for an increasing $N_2$ deposition pressure, while maintaining an identical chemical composition. These changes in lattice parameter can either be attributed to the formation of a TiSiN solid solution and/or to the formation of vacancies during the deposition process. In addition, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the thermal stability of the coatings. Continuous monitoring of the lattice parameter over the whole temperature range by sequential Rietveld refinement revealed non-linear changes of the lattice parameter upon heating, resulting in a significantly larger lattice parameter for all powdered coatings after annealing. This change in lattice parameter becomes even more pronounced at higher $N_2$ deposition pressure. It can be assumed that this observation is an effect of Si diffusion out of the crystalline lattice during the annealing process and/or annihilation of vacancies. In order to differentiate between these two effects positron annihilation measurements were performed to evaluate if significantly different vacancy concentrations can be detected for the TiSiN samples deposited at varying $N_2$ pressure or in $Ar/N_2$ atmosphere. The presented combination of sophisticated characterization techniques contributed to gain a deeper insight into the microstructure and phase composition of TiSiN coatings synthesized with varying deposition conditions in the as-deposited state as well as at elevated temperatures.

[1] **Graduate Student Award Finalist**

11:20am **B4-1-MoM-5 Grain Boundary Segregation Alters the Fracture Mechanism of an AlCrN Thin Film**, *Michael Meindlhumer (michael.meindlhumer@unileoben.ac.at), T. Ziegelwanger,* Montanuniversität Leoben, Austria*; J. Zalesak,* Austrian Academy of Sciences, Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; L. Löfler, S. Spor, N. Jäger,* Montanuniversität Leoben, Austria*; A. Stark,* Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Geesthacht, Germany*; H. Hruby,* voestalpine eifeler Vacotec GmbH, Düsseldorf, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; J. Schneider,* RWTH Aachen University, Germany*; C. Mitterer, R. Daniel, J. Keckes,* Montanuniversität Leoben, Austria

Despite having superior hardness and indentation modulus, thin films deposited by physical vapour deposition often lack sufficient fracture strength and toughness, which is related to intercrystalline fracture occurring predominantly along columnar grain boundaries of low cohesive energy. In this study, an $Al_{0.9}Cr_{0.1}N$ thin film was deposited by cathodic arc evaporation and thoroughly investigated. In as-deposited state, a chemical composition modulation within the wurtzite AlCrN grains was detected by transmission electron microscopy and atom probe tomography, where the Al content depleted down to ~0.83, while the Cr-content nearly doubled up to ~0.17 without interrupting the crystallographic structure. These composition modulations exhibited a periodicity of ~35 nm. A heat treatment monitored by *in situ* high-energy high-temperature grazing incidence transmission X-ray diffraction was performed on the $Al_{0.9}Cr_{0.1}N$ film. The heat treatment caused dissolution and promoted the formation of globular cubic (c) Cr(Al)N and elongated c-CrN precipitates with sizes of ~5-30 nm at the position of the former Al-content minima within the grains and at the grain boundaries, respectively, resolved by transmission electron microscopy and atom probe tomography. Additionally, some precipitations of c-Cr were found, which were attributed to macrodefects originating from the arc evaporation process. The X-ray data obtained during the heat treatment partly illuminated the segregation and formation of precipitates along the interlayer interfaces. *In situ* micromechanical testing before and after the heat treatment revealed simultaneous enhancement of Young's modulus, fracture stress and fracture toughness, most prominent enhancing fracture stress from 3.4±0.4 GPa to 5.1±0.4 GPa. Together with the strengthening of the film's mechanical properties, the fracture morphology altered from (typical) intercrystalline to transcrystalline fracture, proving enhanced grain boundary cohesion. The experimental results represent a new and cost-effective way to increase mechanical properties and thus reliability of transition metal nitride thin films.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B2-2-MoA

### CVD Coatings and Technologies II

**Moderator: Raphael Boichot**, Grenoble-INP/CNRS, France

1:40pm **B2-2-MoA-1 Synthesis of Rare Earth Silicate Coatings by CVD***,* ***Arthur Derrien (derrien@lcts.u-bordeaux.fr)****, L. Lager, J. Roger, J. Danet, S. Jacques,* LCTS, CNRS, Univ. Bordeaux, France

Rare earth silicates (RESiO) are increasingly studied due to their optical and electrical properties. They are also chemically inert and have numerous crystalline structures allowing their properties to be adjusted depending on the required application. They are used in various fields such as lasers, sensors, microelectronic components or solid oxide fuel cells.

These applications require a good control of the process during the synthesis of these materials, sometime used as coatings. The methods conventionally used to produce these films, such as sol-gel or PVD, have disadvantages in terms of thickness control, homogeneity and conformity on parts presenting complex geometry. Thus, the production of these thin films by CVD can overcome these disadvantages to obtain coatings with controlled composition and desired crystalline phase, in order to have homogeneous and conformal thin films, by avoiding, for example, the shading phenomena linked to PVD processes oncomplex shaped parts.

Since the crystallized phases of these materials are formed at relatively high temperatures (>1000°C), the most suitable gaseous precursors for the deposition of RESiO are halogen-containing reagents, especially $SiCl_4$ and $RECl_3$, because of their thermal stability. While $SiCl_4$ is liquid at room temperature, rare earth chlorides are solid up to more than 700 °C, complicating their transport to the reaction zone and the control of their flow. The control of the composition, and therefore of the crystalline phase of the produced coating is difficult.

The case of yttrium silicates is studied here. After setting up an in-situ weighing system, the evaporation of $YCl_3$ could be studied over a pressure/temperature range matching with the CVD deposition conditions that were previously determined by a thermodynamic approach. In this way, the flow rate of chlorinated precursors could be controlled up to 1150 °C in order to lead to the formation of yttrium silicate coatings on alumina substrates. The obtained coatings were characterized using different techniques: Raman spectroscopy, X-ray diffraction, EDS and SEM.

2:00pm **B2-2-MoA-2 Doped Alumina Coatings***,* ***Zhenyu Liu (zhenyu.liu@kennametal.com)****,* Latrobe, USA

In order to enhance the performance of the conventional alumina coating and meet the needs for high performance and high-speed cutting applications, the definite demands in the improvement of thermal resistance and wear resistance are necessary. Therefore, it is the technique need to develop novel CVD alternative alumina coatings with novel structures or coating architectures. By using doping elements, such as Ti, Zr and/or other group IV elements, the doped alumina with excellent wear resistance and tool life can be achieved.

The doping process will create not only novel grain crystalline structures but also alternative coating structures. We have developed different doping procedures including Ti, Zr, Hf-doping and the co-doping. The previous research showed that dopant such as Ti can modify the surface energy of formed oxide crystalline planes. One good support on this hypothesis and practice is that the Ti-doped $CeO_2$ particles showing round shape, in contrast to the un-doped $CeO_2$ having polyhedron crystal structures. the dopant atoms may distribute at single atom level in the oxide metal ion column and enrich at the grain boundary. According to the Goldschmidt's Rules on Thionic substitution, the ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 15%. (Free substitution can occur if ionic size difference less than 15%; Limited substitution can occur if ionic size difference is 15~30%; little or nonsubstitution can occur if ionic size difference is greater than 30%.) In the systematical doped alumina coatings, the ionic radius of $Al^{3+}$ is ~0.675 Å, $Ti^{4+}$ is ~0.745 Å; $Zr^{4+}$ is ~0.80 Å and $Hf^{4+}$ is ~0.79 Å. The ion size differences from the group IV B is less than 15%, then they should be substituted freely by one another.

At the same time, the dopant atoms can segregate and enrich at the grain boundary. The grain boundary engineering can provide enhanced grain interaction and dopant atoms can function as the pinning atoms or provide pinning effect for grain boundary, leading to enhancement of the thermomechanical properties. It is already accepted that the dopants will markedly strengthen the alpha-$Al_2O_3$ interface against mechanical deformation.

Keywords: CVD, $Al_2O_3$, thin films, nucleation, crystal growth

2:20pm **B2-2-MoA-3 Stress Control of AlN-based Multilayer Coatings with Amorphous Intermediate Layers***, V. Tabouret, R. Reboud, A. Crisci,* ***Frederic Mercier (frederic.mercier@grenoble-inp.fr)****,* SIMAP, Grenoble-INP, CNRS, France

Aluminium nitride (AlN) possesses attractive properties like piezoelectricity, high thermal conductivity, low thermal expansion coefficient, high temperature stability, chemical barrier capabilities and ability to develop stable alumina scales at high temperature. Stress control of AlN-based coatings is therefore of high importance for emergence of new applications.

We report in this presentation the possibility to tune the stress in AlN-based multilayers by introducing amorphous intermediate layers. AlN-based multilayer coatings are grown by metal-organic chemical vapor deposition (MOCVD) on 300 µm thick silicium (100) wafer at 900°C. Trimethylaluminium, ammonia and propane were used as Al, N and C precursors. Alternative injection of precursors enables the growth of polycrystalline/amorphous multilayers and the control of the stress in the coatings. In situ curvature, ellipsometry and reflectance measurements are performed simultaneously during growth.

Based on in-situ measurements and ex-situ precession electron diffraction techniques, we demonstrate that the growth of virtually stress free AlN is possible with the introduction of amorphous layers in the multilayer structure.

2:40pm **B2-2-MoA-4 Circumventing Thermodynamic Constraints – A Selective Kinetic Growth of Low Thermal Expansion $Al_2TiO_5$-coatings by Chemical Vapour Deposition***,* ***Sebastian Öhman (sebastian.ohman@kemi.uu.se)****,* Uppsala University, Angstrom Laboratory, Sweden

Most materials expand upon heating. Yet, a few are known to behave the opposite way around. Almost exclusively, these may be found among multicomponent transition metal oxides sharing a diverse range of properties. However, their potential applications have remained scarce due to the difficulties faced in their synthesis and their general metastable characters, which typically limits their thermal stabilities.

This talk will present a novel chemical vapour deposition method to prepare such multicomponent phases at low temperatures and with increased stabilities. Specifically, I will demonstrate how aluminium titanate ($Al_2TiO_5$), a renowned low-to-negative thermal expansion material with favourable heat-resistant properties, can be synthesized at much lower temperatures than predicted by thermodynamics. Examinations of the Al-Ti-O system led us to discover new types of structurally related intergrowth phases, having enlarged unit cells, leading to improved thermal stabilities of these materials. The cause and origin of these intergrowth phases will be discussed based on detailed Raman spectroscopic measurements and in-situ TEM analyses studying their crystallization behaviours.

Materials possessing a low-to-negative thermal expansion are an attractive candidate to improve the thermal resistance of multi-layered coating designs used in applications such as microelectronics, optical engineering, energy harvesting and wear resistance. Thus, this talk aims to not only present a method to fabricate materials for these specific purposes, but also to open the potential of fabricating new multicomponent oxide coatings within other material systems.

3:00pm **B2-2-MoA-5 Atomic Layer Deposition of BN Based on Polymer Derived Ceramics Route: Fabrication of Functional and Protective Coating***,* ***Catherine Marichy (catherine.marichy@univ-lyon1.fr)****, W. Hao, A. Hossain, C. Journet,* University Lyon, France **INVITED**

The scientific interest for hexagonal boron nitride (h-BN) material, especially as thin film and nano-/hetero-structures, is growing owing to its potential use in various domains such as microelectronic, spatial, lubricant, energy and environment. Atomic Layer Deposition (ALD) is a technique of choice for fabrication of such thin films and complex nanostructured material.(*1*, *2*) Despite some limitations of temperature and crystalline quality, ALD already demonstrates suited to fabricate BN layers that can successfully be integrated into electronic devices.(*3*) Based on polymer derived ceramics chemistry, we developed a two-step ALD process of BN that permits access to various BN thin films and complex nano-/hetero-structures. It consists of the growth layer by layer of a preceramic BN films, onto various substrates, at low temperature, and then to its densification into pure BN by annealing process.(*4*)

Herein, the potential of the ALD process based on PDCs route for BN thin films will be discussed. Indeed, BN thin films were successfully deposited in a controlled manner on various inorganic and organic substrates/templates. The application of the developed process for fabricating protective coating towards oxidation and functional quality crystalline BN nano/heterostructures will be presented.


1. *Advanced Materials*. **19**, 3425–3438 (2007).

1. *Advanced Materials*. **24**, 1017–1032 (2012).

1. *et al.*, *Scientific Reports*. **7** (2017), doi:10.1038/srep40091.

1. *ChemNanoMat*. **3**, 656–663 (2017).


## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B4-2-MoA

## Properties and Characterization of Hard Coatings and Surfaces II

**Moderators: Naureen Ghafoor**, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

1:40pm **B4-2-MoA-1 Microstructural Simulations on Thin Films***, Vinzenz Guski (Vinzenz.Guski@imwf.uni-stuttgart.de), W. Verestek, S. Schmauder,* Universität Stuttgart, Germany **INVITED**

Due to their outstanding mechanical properties, hard coatings possess a wide range of applications as protective layers. However, an experimental determination of the properties of such thin coatings is not only difficult but also cost- and time intensive. In this regard, numerical methods, such as finite element method (FEM), have the ability to reduce the experimental effort, significantly. Usually, for characterisation of hard coatings indentation tests are performed to determine the hardness, the Young’s modulus or the adhesive behaviour. With the aid of FE simulations, additional important effects such as residual stresses or the microstructure on the material properties can be investigated.

In the presented work FE simulations of indentation tests using a Vickers pyramid were carried out to investigate the mechanical behaviour of hard coatings in depth. During a sensitivity study, FE models with different coating microstructures, such as equiaxed or columnar grains with different grains size distributions, and coating thicknesses were established and analysed. Besides, the effect of residual stress on the mechanical behaviour are addressed. The performed simulations were validated by indentation test data and cross sections of the coatings. Finally, these simulation results deliver a property-microstructure-relation of the investigated hard coatings and can provide suggestions for optimization.

2:20pm **B4-2-MoA-3 Ab Initio Supported the Development of Tin/Mon Superlattice Thin Films With Improved Hardness and Toughness***, Zecui Gao (zecui.gao@tuwien.ac.at), J. Buchinger, N. Koutná, T. Wojcik, R. Hahn, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Motivated by superior strength and toughness indicators predicted for $TiN/MoN_{0.5}$ superlattices by ab initio calculations, we synthesize a series of $TiN/MoN_y$ superlattice (SL) thin films by DC reactive magnetron sputtering to extract the superlattice effect on hardness and fracture toughness. The SLs crystallise with a single-phase centred cubic (fcc, rock salt) structure. The $MoN_y$ layers are stabilised in their fcc structure by the coherent growth with TiN layers and low $N_2$-partial pressure, ensuring a close to $MoN_{0.5}$ stoichiometry, favouring fcc. Both hardness and toughness, reveal a distinct dependence on the bilayer period L, featuring a hardness peak of 34.8 ± 1.6 GPa for L = 9.5 nm. The fracture toughness ($K_{IQ}$) shows a significant enhancement compared to TiN ($K_{IQ}$ ~ 2.2 MPa√m) and $Mo_2N$ ($K_{IQ}$ ~ 2.7 MPa√m) coatings, peaking with ~ 4.1 ± 0.3 MPa√m also at L = 9.5 nm.

2:40pm **B4-2-MoA-4 Effect of Substrate Bias on the Residual Stress Depth Profile and the Mechanical Properties of Ti-Al-N Coatings Prepared by Cathodic Arc Deposition***, Luis Varela (luis-bernardo.varela-jimenez@polymtl.ca), K. Tsoutas, A. Miletic, E. Bousser,* Polytechnique Montréal, Canada*; J. Mendez,* MDS Coating Technologies Corporation, Canada*; J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Ti-Al-N coatings were prepared by the Cathodic Arc Deposition (CAD) onto Inconel 718 substrates. The substrate bias voltage during deposition was varied, and we evaluated its effect on the residual stress (RS) distribution throughout the thickness of the coatings. Structural characterization and RS measurements were performed by classical X-ray Diffraction and synchrotron X-ray radiation measurements. Mechanical properties, namely the hardness and Young’s modulus, were measured by depth-sensing indentation. The results indicate a higher compressive RS at the film surface (several GPa) that decays to a lower compressive stress value (hundreds of MPa) at the film/substrate interface. Hardness values significantly increased from 23 GPa to 31 GPa upon substrate bias increase, with a slight reduction of the Young’s modulus. Similarly, the average compressive RS increased from 1.0 to 4.7 GPa for coatings deposited at bias voltages of 0V and -100V, respectively. As well, scanning electron microscopy morphological analysis of the cross-sections revealed a pronounced width reduction of the columns with the increase of the bias. The present findings provide a better insight into the impact of the substrate bias voltage on RS, film microstructure, and the mechanical properties of arc evaporated Ti-Al-N coatings. This allows one to select the most suitable coatings for specific mechanical solicitations in different industrial applications.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B4-3-TuM

### Properties and Characterization of Hard Coatings and Surfaces III

**Moderators: Naureen Ghafoor**, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

8:00am **B4-3-TuM-1 Thermal Stability of Nanotwinned Metallic Thin Films (Virtual Presentation)***, **Fan-Yi Ouyang (fyouyang@ess.nthu.edu.tw)**,* National Tsing Hua University, Taiwan **INVITED**

The vertically integrated systems, three-dimensional integrated circuit (3D-IC), are regarded as a solution to the demand of both the trend of miniaturization for electronic devices and the better performance. Metal-to-metal direct bonding technology has been considered as a promising method to connect different chips in 3D-IC packaging. Twinning structure has been regarded as an important strengthening mechanism because of its special properties, including low electrical resistivity, great thermal stability, high strain rate sensitivity, and increased mechanical strength, which is a good candidate for application in electronic application. In this talk, the key deposition parameters to fabricate nanotwinned structure in FCC metallic Ag and Cu thin films by sputtering system is reviewed and we found the substrate bias and deposition temperature are the most critical one. In addition, their corresponding thermal stability are investigated by annealing at 150 to 500 ℃ under ordinary vacuum environment. The results show that the thermal stabilities of the nanotwinned metallic thin films are significantly affected by interlayer and defects in the films. Highly (111) preferred orientation (over 95% surface area) of metallic thin films can be found and they can maintain a columnar structure with high-density nanotwins with twin spacing around 10 nm after annealing at 450 ℃. However, the (200) anisotropic abnormal grain growth can also be found in the highly (111)-oriented nanotwinned metallic thin film after the annealing process at over 250 ℃, and the columnar structures with high-density nanotwins are consumed. The mechanism of abnormal grain growth in highly (111)-oriented nanotwinned metallic thin films will be discussed. This study successfully established the roadmap on the microstructure and properties of nanotwinned metallic thin films for different industrial applications.

8:40am **B4-3-TuM-3 Phase Stability and Mechanical Characteristics of Sputtering (Mo, Hf)N Coatings***, **Shu-Yu Hsu (stuu96753@gmail.com)**, Y. Chang,* National United University, Taiwan*; F. Wu,* Dept. of Materials Science and Engineering, National United University, Taiwan

This work focused on microstructure and mechanical property evolution of (Mo, Hf)N coatings in terms of input power modulation and annealing temperature. The influence of input power and annealing on composition, phase, hardness, modulus, and tribological behavior was discussed. The MoN,HfN, and (Mo, Hf)N films were fabricated through radio frequency reactive magnetron sputtering at a fixed Ar/$N_2$ inlet gas ratio of 12/8 sccm/sccm. For MoN and HfN films, the input power on Mo and Hf targets were both set at 150W. As for (Mo, Hf)N coatings, the input power modulation was set as 150W and 25 to 200W. The vacuum annealing was performed at 500 and 650$^o$C for 1 hr, followed by the furnace-cooling to room temperature. The structure of MoN film exhibited B1-MoN, γ-$Mo_2N$, and $MoN_2$ phases, while the HfN film existed δ-HfN and c-$Hf_3N_4$ phases. The Hfcontents in(Mo, Hf)N coatings increased linearly from 0 to 12.8 at.% with input power rose. When Hf was below 5.6 at.%, a polycrystalline microstructure with δ-HfN, B1-MoN, β-$Mo_2N$, γ-$Mo_2N$ and $MoN_2$ phases were identified. According to nano-indentation, scratch and wear test results, the best combination in mechanical characteristics of (Mo, Hf)N film were observed when input power ratio of Mo/Hf was set as 150/100W. The coating exhibited a highest hardness of 22.5 GPa and presented a least wear damage. The vacuum annealing effect onmultiphase feature and grain recrystallizing was discussed. The dense structure, excellent adhesion and superior tribological behavior of the nitride films owing to multiphase strengthening and solid-solutioning were anticipated.

Keywords: Microstructure; (Mo, Hf)N; Input power; Annealing; tribological behavior

9:00am **B4-3-TuM-4 Evidencing Different Dislocation Types in Magnetron-sputtered Epitaxial TiN Thin Films on MgO***, **Janella Salamania (janella.salamania@liu.se)**, D. Sangiovanni,* Linköping University, IFM, Sweden*; L. Johnson, I. Schramm, K. Calamba,* Sandvik Coromant, Sweden*; T. Hsu,* Linköping University, IFM, Sweden*; B. Bakhit,* Linköping University, IFM, Thin Film Physics Division, Sweden*; R. Boyd, F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, IFM, Sweden

Although the growth and microstructure of titanium nitride coatings have been extensively studied, the presence and atomic structures of different dislocation types in TiN films remains overlooked. Here, a series of highly crystalline heteroepitaxial (001)-oriented TiN (B1) films has been grown on high-purity MgO substrates by DC reactive magnetron-sputtering from pure Ti targets at 800°C in a mixed Ar/$N_2$ atmosphere. Using a combination of high-resolution aberration-corrected scanning transmission electron microscopy (STEM), fast Fourier transform (FFT) filtering, atomic segmentation and localization, we present evidence of different dislocation types, including partials, in as-deposited TiN films. Besides the perfect edge dislocation types, Shockley partials, Frank partials, and Lomer sessile configurations exist. We support our experimental findings by performing classical molecular dynamics (MD) and density functional theory (DFT) calculations of these defect configurations to gain detailed insights about the dislocation core structures and properties. Our results suggest that a variety of dislocations should be considered when interpreting and evaluating the properties of TiN films.

9:20am **B4-3-TuM-5 TiN/$Zr_{0.34}Al_{0.66}$N Multilayer Films: Growth Temperature Dependence on Structure and Mechanical Properties***, **Marcus Lorentzon (marcus.lorentzon@liu.se)**, N. Ghafoor, J. Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

TiN/ZrAlN multilayer are shown to exhibit high hardness and thermal stability when grown as cubic(c)-TiN and high Al containing $Zr_{0.43}Al_{0.57}$N nanocomposite layers with segregated domains of c-ZrN and wurtzite(w)-AlN [1]. We extend these investigations to tune the phase and resulting interface structure of nanocomposite layer as a function of growth temperature and ZrAlN layer thickness.

1µm thick TiN/$Zr_{0.34}Al_{0.66}$N multilayer films were deposited at RT, 200°C, 350°C, 500°C, 800°C and 900°C with equal layer thicknesses of 2-10nm using ion assisted reactive DC magnetron sputtering from elemental Ti and compound $Zr_{0.5}Al_{0.5}$ targets on single crystal MgO(001) and Si(001) substrates with a substrate bias of -30V.

Preliminary analysis shows strong effect of growth temperature on overall texture of the multilayers, driven by change in the morphology of ZrAlN layers and interface structure. Regardless of texture, all multilayers exhibit sharp interfaces, analyzed from appearance of higher order multilayer reflections in X-ray reflectivity profiles. In agreement with previous study [2], $Zr_{0.34}Al_{0.66}$N layers exhibit nanocomposite formation with segregated domains of thermodynamically stable c-ZrN and w-AlN binary compounds. On the other hand, RT grown $Zr_{0.34}Al_{0.66}$N layers exhibit single cubic phase with the lattice match with TiN layers. XRD shows single common peak from the layered structure indicative of TiN/$Zr_{0.34}Al_{0.66}$N superlattice formation. Large residual stress observed in low temperature grown superlattice films also indicates interface coherency strain generated due to superlattice formation. We will present details of superlattice structure at different temperatures and layer thicknesses, as well as stress generations and nanoindentation response of TiN/$Zr_{0.34}Al_{0.66}$N films analyzed by x-ray diffraction, x-ray reflectivity, elastic recoil detection analysis, Rutherford backscattering spectrometry, nanoindentation, and transmission electron microscopy.

[1] K. Yalamanchili, F. Wang, H. Aboulfadl et. al., "Growth and thermal stability of TiN/ZrAlN: Effect of internal interfaces", Acta Mater 121 (2016) 396-406, https://doi.org/10.1016/j.actamat.2016.07.006

[2] N. Ghafoor, I. Petrov, D. Holec, et. al., "Self-structuring in Zr1-xAlxN films as a function of composition and growth temperature, Sci Rep 8, 16327 (2018). https://doi.org/10.1038/s41598-018-34279-w

9:40am **B4-3-TuM-6 Physicochemical Properties of Single Phased Tantalum Nitride Thin Films***, **Aurélie Achille (aurelie.achille@icmcb.cnrs.fr)**, A. Poulon-Quintin, F. Mauvy, D. Michau, S. Fourcade,* CNRS, Univ. Bordeaux, ICMCB, France*; C. Labrugere,* CNRS, Univ. Bordeaux, PLACAMAT, France*; M. Cavarroc,* SAFRAN Paris-Saclay – SAFRAN Tech, France

Stoichiometric Tantalum Nitrides (TaN) exist as a face-centred cubic phase, which is a metastable high temperature phase and as a stable hexagonal phase. Using reactive RF Magnetron Sputtering and reactive High Power

Impulse Magnetron Sputtering (HiPIMS) both phases are obtained with different microstructures. This talk will be focus on the metastable cubic phase. First, the structural and optical properties are presented. Evolution of the electrical conductivity with the temperature will be presented. Using cyclic voltammetry measurements, the electrochemical properties (corrosion current and potential) will be analysed as a function of the operating temperature up to 120°. All the presented results will be discussed based on the microstructure differences (depending on the sputtering method used).

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B4-4-TuA

## Properties and Characterization of Hard Coatings and Surfaces IV

**Moderators: Naureen Ghafoor**, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

4:40pm **B4-4-TuA-10 Synthesis by CVD and Properties of Polycrystalline Silicon Coatings for Structural Applications***, **Axel Le Doze (ledoze@lcts.u-bordeaux.fr)**, G. Couégnat, J. Danet, F. Rebillat, G. Chollon,* LCTS, CNRS, Univ. Bordeaux, CEA, SAFRAN CERAMICS, France

Environmental barrier coatings (EBCs) are used to limit the oxidation/corrosion of ceramic matrix composites. The silicon bond coat (BC) is a key component of the EBC system. In use, the silicon BC oxidizes to form a silica layer (TGO) at the EBC/BC interface. For high temperature applications, excessive creep may lead to unacceptable deformation of the system and impede its use as coating for rotating parts with high centrifugal loads. It is therefore crucial to control the creep behavior of the BC. Currently developed by plasma spraying, the silicon BC is composed of micrometric grains. Tailoring the silicon microstructure could be an efficient way to adjust the creep behavior of the BC. Chemical vapor deposition (CVD) is a process that allows the coating microstructure to be varied.

In this work, the CVD of polycrystalline silicon from $SiHCl_3/H_2$ was explored in details and a selection of coatings were prepared on various substrates for testing. A microbalance and FTIR spectrometer were coupled to the reactor to monitor deposition kinetics and the composition of the exhaust gas. The morphology and microstructure of the deposits were investigated by SEM (grain size, surface roughness) and EBSD (grain size and orientation, texture), and the creep properties by high temperature flexural tests (3-point bending). The oxidation/corrosion kinetics of the deposits were also evaluated *post mortem* after annealing in a corrosion furnace at controlled $H_2O$ pressure and gas flow.

Several microstructures were obtained by varying the CVD conditions (temperature, pressure, total gas flow, $H_2/SiHCl_3$ ratio) and thermal annealing. Distinctive responses of the silicon coatings to mechanical stresses have been measured, illustrating different deformation mechanisms (intra-granular dislocations, diffusion at grain boundaries). This work confirms that the creep behavior of polycrystalline silicon is strongly dependent on the microstructure (grain size/orientation, nature and proportion of grain boundaries). The oxidation/corrosion tests show that oxidation kinetics are relatively independent of the microstructure.

In conclusion, a wide variety of microstructures can be obtained by CVD and thermal annealing. They result in creep behavior that can vary considerably, but similar corrosion rate. The thermomechanical properties of CVD Si can be readily modulated without compromising its corrosion resistance.

5:00pm **B4-4-TuA-11 Erosion Resistance of Thin Films Under Solid Particle Flows and Temperature***, **Kai Treutler (treutler@isaf.tu-clausthal.de)**, J. Hamje,* Clausthal University of Technology, Germany*; T. Bick,* Clausthal University of Technology, Clausthal, Germany*; V. Wesling,* Clausthal University of Technology, Germany

Components such as turbine blades are often provided with protective coatings to protect them from wear. These are usually ceramic or metallic coatings that can be applied using the PVD process, for example. While hard ceramic coatings are very effective for sliding wear, soft coatings with a metallic character are better for impact wear. The aim of the investigations presented is the characterization of metallic-ceramic coatings under particle jet wear at elevated temperatures. The presented coatings offer the advantage that they can be converted to a ceramic state with the aid of heat treatment. If the heat treatment is carried out by means of a laser beam, the coating properties can be influenced locally and adapted according to the stress. The wear behaviour of f.e. Ti-Si-C and Ti-Si-B coating systems will be presented below at angles of incidence of 30°, 45° and 60° and an abrasive mass flow rate of 9 g/min. For this purpose, the surfaces were irradiated at room temperature and 200°C with a mixture of clay dust and quartz powder, and the abrasion was determined gravimetrically.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B5-1-WeM

## Hard and Multifunctional Nanostructured Coatings I
**Moderator: Tomas Kozak**, University of West Bohemia, Czechia

8:20am **B5-1-WeM-2 Enhanced Thermal Stability of (Ti,Al)N Coatings by Oxygen Incorporation**, ***Damian M. Holzapfel (holzapfel@mch.rwth-aachen.de)*** [1], RWTH Aachen University, Germany; *D. Music,* Malmö University, Sweden; *M. Hans,* RWTH Aachen University, Germany; *S. Wolff-Goodrich,* Max-Planck-Institut für Eisenforschung GmbH, Germany; *D. Holec,* Montanuniversität Leoben, Austria; *D. Bogdanovski,* RWTH Aachen University, Germany; *M. Arndt,* Oerlikon Balzers Coating Germany GmbH, Germany; *A. Eriksson, K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *D. Primetzhofer,* Uppsala University, Sweden; *C. Liebscher,* Max-Planck-Institut für Eisenforschung GmbH, Germany; *J. Schneider,* RWTH Aachen University, Germany

Thermal stability of protective coatings is one of the performance-defining properties for advanced cutting and forming applications as well as for energy conversion. To investigate the effect of oxygen incorporation on the high-temperature behavior of (Ti,Al)N, metastable cubic (Ti,Al)N and (Ti,Al)($O_xN_{1-x}$) coatings are synthesized using reactive arc evaporation. X-ray diffraction of (Ti,Al)N and (Ti,Al)($O_xN_{1-x}$) coatings reveals that spinodal decomposition is initiated at approximately 800°C, while the subsequent formation of wurtzite solid solution is clearly delayed from 1000°C to 1300°C for (Ti,Al)($O_xN_{1-x}$) compared to (Ti,Al)N. This thermal stability enhancement can be rationalized based on calculated vacancy formation energies in combination with spatially-resolved composition analysis and calorimetric data: Energy dispersive X-ray spectroscopy and atom probe tomography data indicate a lower O solubility in wurtzite solid solution compared to cubic (Ti,Al)(O,N). Hence, it is evident that for the growth of the wurtzite, AlN-rich phase in (Ti,Al)N, only mobility of Ti and Al is required, while for (Ti,Al)(O,N), in addition to mobile metal atoms, also non-metal mobility is required. Prerequisite for mobility on the non-metal sublattice is the formation of non-metal vacancies which require larger temperatures than for the metal sublattice due to significantly larger magnitudes of formation energies for the non-metal vacancies compared to the metal vacancies. This notion is consistent with calorimetry data which indicate that the combined energy necessary to form and grow the wurtzite phase is larger by a factor of approximately two in (Ti,Al)(O,N) than in (Ti,Al)N, causing the here reported thermal stability increase.

8:40am **B5-1-WeM-3 Metastable Single- or Dual-Phase Structures in Magnetron Sputtered W-Zr Thin-Film Alloys: Properties and Thermal Behavior**, *M. Cervena, S. Haviar, R. Cerstvy, J. Rezek,* ***Petr Zeman (zemanp@kfy.zcu.cz)***, University of West Bohemia, Czechia

Metastable solid materials such as amorphous or nanocrystalline alloys, supersaturated solid solutions, high-temperature or high-pressure phases persisting at normal conditions, have been of great interest due to a possibility to explore novel structures with unknown properties. These materials are kinetically determined and can be therefore synthesize only by non-equilibrium processes. Magnetron sputtering is thus a suitable technique for their preparation as thin films.

The present study focuses on preparation of thin-film alloys from the W-Zr system by non-reactive magnetron sputtering and systematic investigation of their structure, properties, and thermal behavior at elevated temperature. The films were sputter-deposited in argon gas using two unbalanced magnetrons equipped with a W and Zr target, respectively. The elemental composition of the films was controlled in a very wide composition range (0-100 at.% Zr), by varying the deposition rate from the individual targets.

Using magnetron sputtering, we were able to prepare W-Zr thin-film alloys with several metastable structures in respect to the equilibrium phase diagram [1]. Up to 24 at.% Zr, the structure of W-rich films is characterized by a supersaturated bcc α-W(Zr) solid solution with a highly oriented structure, columnar dense microstructure, enhanced hardness and very low residual stress. In a wide range between 33 and 83 at.% Zr, an amorphous structure with features indicating metallic glass behavior is observed. These films exhibit a very smooth surface, a moderate compressive stress, and a constant electrical resistivity. Above 83 at.% Zr, high-temperature bcc β-Zr(W) and high-pressure hcp ω-Zr(W) phases with an enhanced hardness are prepared in Zr-rich films. Moreover, a very interesting dual-phase structure with crystalline columnar submicrometer-sized conical domains surrounded by a metallic glass is spontaneously formed at 28 at.% Zr [2].

Preliminary results on the thermal behavior indicate that the stability of the metastable α-W(Zr) solid solution in the W-rich films reaches at least 1000°C and its oxidation resistance is improved by an Zr addition. The stability of the amorphous of W-Zr films with metallic glass behavior depends on their elemental composition and can be as high as 1400°C. Moreover, the oxidation of these films to 600°C leads to a homogenously oxidized amorphous structure with twice higher hardness than in the as-deposited state.

[1] M. Červená, R. Čerstvý, T. Dvořák, J. Rezek, P. Zeman, J. Alloy. Compd. 888 (2021) 161558.

[2] P. Zeman, S. Haviar, M. Červená, Vacuum 187 (2021) 110099.

9:00am **B5-1-WeM-4 A Conformable SiAlN/Mo Thermal Barrier Layer for Titanium Alloys Deposited by Magnetron Sputtering**, *Z. Gao,* The University of Manchester, UK; ***Justyna Kulczyk-Malecka (j.kulczyk-malecka@mmu.ac.uk)***, *P. Kelly,* Manchester Metropolitan University, UK; *P. Xiao,* The University of Manchester, UK

Titanium and its alloys are widely used in the aeronautical and automotive industries, as well as in bio-medical implants due to their low density, high specific strength, and excellent corrosion resistance at lower temperature ranges. Nevertheless, at temperatures above 500ºC Ti alloys exhibit a rapid oxidation, which leads to the formation of a less protective brittle oxide scale that limits its application. To mitigate the formation of a detrimental oxide scale, a protective bilayer coating consisting of an amorphous SiAlN top layer and a Mo interlayer were deposited onto Ti alloys using pulsed DC reactive magnetron sputtering. Coated Ti samples were then exposed to oxidative corrosion in air at 800°C for up to 200 hr and the degradation and thermal barrier ability of the bilayer nitride coatings were studied and correlated with the coating thickness and the presence of the Mo interlayer.

It was found that the thermal barrier nature of the bilayer coating stack is attributed to the interfacial reaction between the Ti substrate and the Mo interlayer and the formation of mechanical twinning within the interfacial reaction product, i.e. a $TiN_{0.26}$ conformable interlayer, which accommodates the thermal mismatch strain between the coating and the substrate upon thermal cycling. The degradation mechanism of SiAlN/Mo coatings is determined by the depletion of the coating induced by interfacial diffusion and reaction between the elements composing the coating and the Ti substrate. The morphology of as-deposited and oxidised samples was characterised using imaging techniques, such as SEM and TEM, the physiochemical properties of the coating were investigated using XPS and EDS and residual stresses in the SiAlN coatings were obtained using a FIB milling-stress driven buckling method. This work, therefore, provides a new coating stack design for aeronautical applications displaying exceptional environmental protection for Ti at high temperatures through the interfacial reaction mechanism, which controls the coating degradation.

9:20am **B5-1-WeM-5 Thermal Decomposition of Hard Coatings - Insights from Nanometer-Scale Characterization**, ***Marcus Hans (hans@mch.rwth-aachen.de)***, RWTH Aachen University, Germany; *Z. Czigány,* Centre for Energy Research, Hungary; *D. Neuß, J. Sälker, H. Rueß, J. Krause, P. Ondračka,* RWTH Aachen University, Germany; *D. Music,* Malmö University, Sweden; *S. Evertz, D. Holzapfel,* RWTH Aachen University, Germany; *G. Nayak, D. Holec,* Montanuniversität Leoben, Austria; *D. Primetzhofer,* Uppsala University, Sweden; *J. Schneider,* RWTH Aachen University, Germany **INVITED**

Three-dimensional atom probe tomography is a powerful technique to characterize the local chemical composition of materials. Since the spatial resolution at the nanometer scale is ideally suited to identify decomposition-relevant mechanisms, the thermal stability of (V,Al)N hard coatings is the focus of this talk.

Based on thermodynamic considerations of $d^2\Delta G/dx^2 < 0$, spinodal decomposition is predicted for NaCl-structured $V_{1-x}Al_xN$ with $x \geq 0.35$ by ab initio calculations. Consistent with these predictions, metastable single-phase cubic $(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films exhibit chemical modulations after annealing at 900°C, which implies spinodal decomposition into V- and Al-rich cubic nitride phases. However, the formation of thermodynamically stable wurtzite AlN occurs concurrently and the higher mobility of Al in (V,Al)N in comparison to (Ti,Al)N may be understood by the smaller lattice parameter difference of the cubic VN and AlN phases.

[1] **Graduate Student Award Finalist**

Systematic investigations by post-deposition vacuum annealing revealed the onset of spinodal decomposition after cyclic vacuum annealing at 700°C. Moreover, at this temperature, evidence for Al diffusion to grain boundaries and triple junctions is provided by correlation of transmission electron microscopy and atom probe tomography data. The formation of Al-rich regions can be understood by the more than 25% lower activation energy for bulk diffusion of aluminum compared to vanadium as obtained from ab initio calculations. The significantly larger equilibrium volume of wurtzite AlN compared to the cubic phase explains its initial formation exclusively at triple junctions and grain boundaries. Interestingly, the formation of the wurtzite phase at grain boundaries and triple junctions can be tracked by resistivity measurements, while X-ray diffraction and nanoindentation data do not support an unambiguous wurtzite phase formation claim for annealing temperatures < 900°C.

Hence, it is evident that previously reported formation temperatures of wurzite AlN in transition metal aluminum nitrides, determined by other characterization techniques than chemical and structural characterization at the nanometer scale and/or resistivity measurements, are overestimated.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B6-1-WeM

## Coating Design and Architectures I

**Moderator: Paul Heinz Mayrhofer**, Institute of Materials Science and Technology, TU Wien, Austria

11:00am **B6-1-WeM-10 Thermally Induced Phase Formation in Magnetron Sputtered Ru/Al Multilayers - Impact of Modulation Period on Transition Temperatures and Phase Sequence***, Vincent Ott (vincent.ott@kit.edu),* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; C. Schaefer,* Saarland University, Chair of Functional Materials, Germany*; T. Weingaertner, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; C. Pauly,* Saarland University, Chair of Functional Materials, Germany*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Intermetallic phases in the CsCl B2 structure like NiAl are in focus since long as engineering materials for high temperature applications. Besides good thermal conductivity, they offer high melting points and good oxidation resistance. A major disadvantage is its brittleness, which limits not only its processing at room temperature but also its potential applications. A promising candidate material with improved mechanical properties is the B2 RuAl phase.

Nanoscale multilayer coatings, which can exhibit self-propagating reactions, are a promising approach to synthesize coatings with a targeted microstructure that allows to tailor the material properties. We will show that the synthesis of B2 structured RuAl thin films is also possible by thermal activation close to equilibrium conditions without ignition of the exothermic self-propagating reaction by utilizing a imprinted nanoscale thin film architecture.It will be demonstrated for magnetron-sputtered Ru/Al multilayer thin films, that a specific phase formation sequenceis dependent of the modulation length and microstructure of the bilayers.Thus, by controlling the phase formation sequence, the microstructure of the resulting single-phase AlRu layer can be tuned. For a specific nanoscale layer design, the final phase AlRu can be formed directly from the deposited multilayer state via this approach, without the formation of intermediate intermetallic phases. This statement will be supported by in-situ HT-XRD, TEM, AES mapping and further analyses.

11:20am **B6-1-WeM-11 Structural Design of Diboride Thin Films (Virtual Presentation)***, Marian Mikula (mikula@fmph.uniba.sk), T. Fiantok,* Comenius University in Bratislava, Slovakia*; N. Koutná,* Linkoping University, Sweden*; V. Šroba,* Comenius University in Bratislava, Slovakia*; D. Sangiovanni,* Linkoping University, Sweden **INVITED**

Transition metal diborides from the group IIIB to VIIB ($TMB_2$) represent promising candidates for hard and protective films applicable in extreme temperature conditions and under high mechanical loads. This idea is motivated by the knowledge of their bulk equivalents which exhibit excellent mechanical properties, chemical inertness, high temperature stability and good oxidation resistance. Physical vapor deposition (PVD) techniques allow the growth of $TMB_2$ films with a specific nanocomposite character often formed by (sub)stoichiometric crystalline $\alpha$-$TMB_2$/$\omega$-$TMB_2$ nanofilaments embedded in an amorphous matrix. Although, these films are extremely hard, unfortunately, they are also inherently brittle, and the presence of an amorphous matrix provides an easy pathway for undesired oxidation at relatively low temperatures. For this reason, their application potential is currently very limited and suitable improvements to their weaknesses are intensively sought: (i) from a technological view, it is the use of progressive technologies (HiPPMS, HiTUS) and understanding the relationship between deposition parameters and specific diboride growth; (ii) from a structural point of view, it is the concept of alloying and multilayer architecture where a certain "tuning" of the films could lead to an improvement of the high-temperature behavior and a more ductile response to the mechanical load. Transport of Ions in Matter simulations and Time-resolved Mass Spectroscopy of deposition processes are very useful tools where we can better understand the growth of diboride films. Here, different angular distribution, ionization of target species, influence of Ar neutrals play an important role. Furthermore, using Density Functional Theory calculations we can predict the structural evolution of diboride systems, and their mechanical properties based on thermodynamic assumptions and valence electron concentrations. As we will show, the simplistic models used in DFT calculations at 0 kelvin are unable to predict formation of nanocomposite structures in diboride films, which are more complex in comparison to, e.g., single phase TM nitride films. In this lecture, several case studies of diboride films will be discussed, with the main focus on improving their mechanical and physical properties using a combination of theoretical predictions and experimental approaches.

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## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B5-2-WeA

### Hard and Multifunctional Nanostructured Coatings II

**Moderators: Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Tomas Kozak**, University of West Bohemia, Czechia

2:00pm **B5-2-WeA-1 Design of Coatings for Harsh Environments by Computation and Experiment (Virtual Presentation)**, ***Efstathios "Stathis" I. Meletis (meletis@uta.edu)***, University of Texas at Arlington, USA **INVITED**

One of the great challenges in engineering science is to protect a material at its surface from chemical reactions and mechanical degradation such as high temperature oxidation, impact and wear. Applying a hard coating, which bonds strongly to the surface of the material, prevents excessive abrasion and provides the needed shield towards mechanical impact. At high temperatures in an oxidative environment, however, many hard boride, carbide and nitride coatings quickly deteriorate due to thermal instability and chemical degradation. An overview is presented of our recent efforts under the materials genome initiative to develop a new class of protective ceramic coatings, coalescing computational investigation and experimental realization and characterization. The efforts focus on several transition metal quaternary (Zr,Hf,Si)BCN and ternary (Hf,Ta)SiN amorphous and nanocomposite coatings for severe environment applications. Compositional and structural atomistic simulations using density-functional theory and large-scale molecular dynamic calculations were conducted to explore thermal, oxidation and mechanical properties. A number of complementary experimental characterization techniques were used to study the thermal, mechanical and oxidation resistance of the coatings. Atomistic and local structure characterization and image simulations were conducted by using HRTEM to develop a comprehensive understanding of the synthesis-structure-property relationship in these high potential coating systems.

2:40pm **B5-2-WeA-3 Microstructure and Properties of PVD Synthesized Super-hard Ti-B-N Coatings**, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)***, *R. Hahn, A. Kirnbauer,* TU Wien, Institute of Materials Science and Technology, Austria; *P. Polcik ,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Ternary transition-metal boron nitride Ti-B-N has emerged as an outstanding material system in the field of protective coatings due to its high hardness and temperature stability. In particular, its large number of equilibrium and metastable phases offers numerous possible compositions for investigating and understanding structural effects and their influence on mechanical properties.

With prior interest in chemical compositions close to the TiN-TiB line in the corresponding equilateral concentration triangle, Ti-B-N coatings were prepared using a Ti-TiN-$TiB_2$ target containing 10 at.% B.

Focusing on the investigation of single-phase structured super-hard (H≥40 GPa) Ti-B-N coatings, the influence of various deposition conditions on the structure and mechanical properties during non-reactive DC magnetron sputtering - compared to nanocrystalline Ti-B-N - comprises this study. The results show - consistent with previous ab initio calculations - that up to 10 at.% B can be incorporated into the face-centered cubic (fcc) TiN lattice.

3:00pm **B5-2-WeA-4 Enhanced Mechanical Performance of Nanostructured B-Dopednitride Coatings Deposited by HiPIMS With Positive Pulses**, *P. Diaz-Rodriguez, A. Mendez, J. Santiago,* ***Ivan Fernandez (ivan.fernandez@nano4energy.eu)***, *A. Wennberg, J. Endrino,* Nano4Energy, Spain; *E. Chacon, A. Guzman, M. Panizo,* Universidad Politecnica de Madrid, Spain; *M. Monclus, J. Molina,* IMDEA Materiales, Spain

In recent years, due to the advancement of high-speed machining(HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance,anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured AlTiBN and AlCrBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The formation of nanocrystalline grains embedded in an amorphous boron-rich phase provides enhanced toughness and wear resistance[3]. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splittingwere used to evaluate toughness and thermal resistance of the coatings. Finally, micromilling tests were carried out to assess the performance of these nanostructured coatings in micromachining of stainless steel and titanium alloys.

[1] J. Musil,Surface and Coatings Technology 125 (2000 ) 322–330

[2]P. Mayrhofer et al.,Progress in Materials Science 51 (2006) 1032–1114

[3] A.Mendez et al., Surface and Coatings Technology 422 (2021) 127513

3:20pm **B5-2-WeA-5 Development of $TiB_2$ Coatings in a New Generation Industrial Reactor Based on Hybrid DC-pulsed and HIPIMS Magnetron Sputtering on HSS Steels – Tribological Study at Room, Medium and High Temperature**, *E. Arias,* Asociación de la Industria Navarra, Spain; ***Gonzalo Garcia fuentes (gfuentes@ain.es)***, Asociación de la industria Navarra, Spain; *H. Gabriel,* PVT Plasma und Vakuum Technik GmbH, Germany; *I. Fernández,* N4E, Spain; *J. Fernández Palacio,* Asociación de la Industria Navarra, Spain

Titanium di-boride ($TiB_2$) coatings exhibit excellent combination of hardness and low adhesion to cutting metal alloys such as these based on Ti, Al or Ni, and it has been used since a decade on cutting tools in the aerospace sector. $TiB_2$ is well known to exhibit low moderate toughness, which limits it applicability under complex 3D shaped cutting tools, or tools subject to very high loads. Pulsed DC sputtering as well as other conventional vapor deposition techniques are being developed to this purpose. In our approach, a hybrid industrial scale system equipped with 4 magnetron sputtering sources and a 600/350 mm Height/Diameter effective volume is chosen to implement TiB2 coating formulations. The system is equipped with pulsed DC and HIPIMS V+ PSUs. The target configuration is chosen in the unbalance mode while the BIAS pulse is synchronized with the HIPIMS PSU so to enhance the Me+ ion bombardment ratio. The HIPIMS V+ parameterization will be focus to provide an enhanced coating-to-substrate adhesion strength, but also microstructural strength to the $TiB_2$ matrix. Optical emission probes will provide valuable information about the concentration ratio of Me/Ar ionized species for different pulsing/power deposition conditions. The characterization of the coatings is carried out using glow discharge emission spectroscopy, x-ray diffraction, scanning electron microscopy and nanoindentation. The friction and wear is characterized using different conditions of temperature, and load. In particular, the surface contact interaction with Ti-alloys and Al-alloys will be discussed in terms of the galling of the testing materials for different conditions.

3:40pm **B5-2-WeA-6 Study the Effect of Nozzle Geometry on Spray Coating by Aerosol Deposition Method**, ***Bahareh Farahani (bahareh.farahani@csulb.edu)***, California State University, Long Beach, USA; *M. Jadidi,* Ryerson University, Canada; *S. Moghtadernejad,* California State University, Long Beach, USA

The Aerosol Deposition (AD) method, also known as Vacuum Cold Spraying (VCS), is an emerging spray coating technology to fabricate a dense thick/thin ceramic or metal layer on a substrate through the kinetic impaction and cumulative deposition of ultrafine solid particles under near-vacuum conditions [1]. AD is a Room Temperature Impact Consolidation (RTIC) mechanism that causes negligible oxidation or degradation to the feedstock powders making it a desirable candidate for applying coatings on lower-melting and temperature-sensitive substrates such as glass, metal, and polymers. This high-velocity deposition technique is a promising coating process for industrial applications, such as solid oxide fuel cells, solid-state lithium batteries, bio-component coatings, and surface protection [1]. One of the challenges of this method is achieving successful deposition of the particles with high coating quality. It should be noted that coating quality can be significantly improved by optimizing the particle impact velocity. As such, the focus of this project is to study the effect of nozzle geometry and operating parameters such as range of pressure ratios and standoff distance on particle impact velocity using the method of Computational Fluid Dynamics (CFD).

In this work, a de Laval nozzle with two axisymmetric geometries of 1) sharp and 2) rounded edge will be modeled to generate a supersonic gas flow to accelerate particles toward a substrate using CFD. To simulate the gas flow behavior in the jet stream leaving the nozzle, a realizable k-epsilon turbulence model will be used. Results will be validated by comparing the locations of the Mach disks in highly under-expanded free-jet conditions with the experimental data of nozzles with the same geometries. In addition, a Eulerian-Lagrangian based discrete-phase model will be used to study the particle trajectory and velocity upon impact with the substrate. The effect of drag coefficient and thermophoretic force on in-flight particles behavior will be also evaluated to improve the particles deposition formation upon impact. The simulation results will lead to understanding the effects of nozzle geometry and operating parameters on the particle impact velocity and distribution. This ultimately provides the baseline to design and optimize an AD system with enhanced coating quality.

[1] D. Hanft, J. Exner, M. Schubert, T. Stöcker, P. Fuierer, and R. Moos, "An overview of the Aerosol Deposition method: Process fundamentals and new trends in materials applications," *J. Ceram. Sci. Technol.*, vol. 6, no. 3, pp. 147–181, 2015, doi: 10.4416/JCST2015-00018.

4:00pm **B5-2-WeA-7 Thick Ceramic Coatings Deposited by Supercritical Fluid Chemical Deposition (SFCD)***, **Erwan Peigney (erwan.peigney@icmcb.cnrs.fr)**, G. Aubert,* ICMCB-CNRS, France*; M. Cavarroc,* SAFRAN, France*; A. Poulon-Quintin, C. Aymonier,* ICMCB-CNRS, France

Requirements for the elaboration of ceramic coatings are constantly evolving, especially when it comes to depositing high thicknesses on complex shaped substrates. In this way, traditional deposition methods do not fully meet the new challenges, notably directional processes such as PVD. Liquid-phase processes suffer also many limitations, including contamination issues and poor mass transport. Likewise, non-directional gas-phase processes such as CVD encounters precursor volatility constraints, which lead to mass transport-limited conditions, poor step coverage and non-uniformity for submicrometer-patterned substrates.

To overcome all these difficulties, new processes have shown great interest in recent decades. Among this, Supercritical Fluid Chemical Deposition technology (SFCD) stands out thanks to its advantages. Indeed, supercritical fluids have hybrid thermophysical properties, intermediate between liquids and gases, which are continuously adjustable with small variations of pressure and temperature. For instance, they exhibit gas-like viscosities and diffusivities while having liquid-like densities allowing the dissolution of a wide range of metallic precursors with substantial concentrations. SFCD process proposes to deposit thick inorganic films with uniform coverage of complex shaped substrate, complete filling of narrow high aspect ratio features, reduction in process temperatures and this with a high growth rate deposition.

The present work concerns the development of thick ceramic coatings on complex shaped metallic substrates using a cold-wall reactor filled with different mixture of fluids at sub- and supercritical conditions. Depending on the precursor selected, the fluid composition and the deposition parameters, the coating properties are tuned in terms of adhesion to the substrate, hardness, roughness and corrosion resistance. The material microstructure and crystallinity are also impacted. They are characterized through GIXRD, TEM, XPS and Raman spectroscopy.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B6-2-WeA

### Coating Design and Architectures II

**Moderator: Paul Heinz Mayrhofer**, Institute of Materials Science and Technology, TU Wien, Austria

2:00pm **B6-2-WeA-1 Industrial Antibacterial Decorative Coatings***, **Ivan Kolev (ikolev@hauzer.nl)**, P. Immich, A. Fuchs, H. Vercoulen, D. Doerwald,* IHI Hauzer Techno Coating B.V., Netherlands

Anywhere large numbers of people gather, touch-based contamination contributes to the spread of bacterial infections. Coatings with antibacterial effect could have an important public health benefit. This includes door handles, bathroom taps and other high-touch elements in public and private buildings. Already for decades these elements have commonly had a PVD decorative finish, which provides them with an attractive look and increased wear and corrosion resistance. The next generation decorative coating should also include antibacterial properties.

In this work, decorative antibacterial coatings on industrial scale are presented. The antimicrobial properties are realised by doping of the standard decorative coatings with Cu and Ag. To verify the efficacy, the coatings are tested for their kill rate against two of the most common bacteria *Escherichia coli* and *Staphylococcus aureus*. The testing shows excellent results – kill rate of up to 100% within one hour. The effect on the doping upon standard properties, such as colour, wear and corrosion resistance are also discussed

2:20pm **B6-2-WeA-2 Few Thoughts about Hard Coatings and Machining Industry***, **Aharon Inspektor (ainspekt@andrew.cmu.edu)**,* Carnegie Mellon University, USA

The development of cutting tools is a traditional proving ground for the design and testing of new materials, new coatings and new concepts in materials science. Recently we witnessed rapid development of innovative hard coatings with superior mechanical properties, thermal stability and chemical resistance. The new coatings are well suited for machining materials at significantly higher speeds and feed rates and play important role in machining industry. Nevertheless, "older" coatings such as TiN, TiCN and TiAlN are also still in use at many small and large machining centers. Why it is so? What is the reason for this wide range of hard coatings in the cutting tools industry? And how this affect development and introduction of novel coatings? In this paper we will discuss these questions, present selection criteria of hard coatings in the industry and examine how the Fourth Industrial Revolution will affect future hard coatings and machining landscape. We will start with "machining wear maps" that display the relationships between machining parameters and tool's wear: the starting point for tools' selection, and for the resultant wide range of hard coatings in the industry. Then we will examine how the Fourth Industrial Revolution, Industrial Internet of Things (IIOT) with multi-level connectivity of sensors, machines and systems, will likely changes this manufacturing landscape. We will conclude the talk by discussing the germane trends and ensuing future development of hard coatings for metal cutting industry.

2:40pm **B6-2-WeA-3 Effect of Coating Architecture on Stress Relief Mechanism of TiZrN Coatings on Si Substrate (Virtual Presentation)***, **Jia-Hong Huang (jhhuang@ess.nthu.edu.tw)**, M. Liu, Y. Chiu,* National Tsing Hua University, Taiwan **INVITED**

Hard coatings deposited by physical vapor deposition are usually subjected to high residual stress. To relieve the residual stress, it is commonly introducing a metal interlayer between coating and substrate or by further coating architecture design. However, the underlying stress relief mechanism of coatings with architecture has not been fully understood. The purpose of this study was to investigate the extent of stress relief achieved by employing different types of interlayers or coating architecture, and explain the stress relief mechanism in each coating architecture using a simple energy-balance model. Themodel was based on the concept that the relief of stored energies from both coating ($\Delta G_f$) and Si substrate ($\Delta G_{Si}$) was converted to the plastic work by the metal interlayer. TiZrN/TiN/Ti tri-layer coatings and TiZrN bi-layer coatings with Ti, TiZr and TiZr/Ti interlayers on Si substrate were chosen as the model systems, which were deposited using unbalanced magnetron sputtering. Laser curvature method and the average X-ray strain method combined with nanoindentation were used to measure the residual stress of the entire specimen and individual layers, respectively. For the TiZrN specimens with different interlayers, the results showed that increasing the metal interlayer thickness may not be an effective way on increasing stress relief efficiency in the coating. Since plastic deformation of the interlayer could only occur in part of the interlayer near the TiZrN/interlayer interface, increasing the interlayer thickness did not substantially increase the effective deformation thickness. Furthermore, plastic deformation became difficult for the metal interlayer with higher strength coefficient (k). Therefore, $\Delta G_f$ may decrease by using high-k interlayer with the same thickness. However, the high-k interlayer could act as a channel to transfer the stress to the Si substrate, if proper interlayer thickness was used. For the specimens with coating architecture, the results revealed that the extent of stress relief in TiZrN coating with TiN/Ti architected interlayer was larger than that with only a single Ti interlayer. The TiN transitional layer served as an energy channel that effectively transferred the stored energy in TiZrN to the Ti interlayer and alleviated the large stress difference at the original TiZrN/Ti interface, thereby increasing the plastic deformation capacity of the underlying interlayer; therefore, a larger fraction of residual stress in TiZrN was relieved.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B1-1-ThM

## PVD Coatings and Technologies I

**Moderator: Frank Kaulfuss**, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

8:20am **B1-1-ThM-2 Optimization of RF Magnetron Sputter Deposition of Ultrathick Boron Carbide Coatings***, **Alison Engwall (engwall1@llnl.gov)**,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; L. Bayu Aji, S. Shin, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Boron carbide is a material of interest as an ablative layer for inertial confinement fusion (ICF) applications due to its robust physical properties and uniform amorphous structure. However, growing boron carbide films to thicknesses of >50 µm, as needed for ICF, presents many challenges. Our approach to the optimization of two main process parameters (the target-to-substrate distance and Ar gas pressure) for the deposition of boron carbide coatings by RF magnetron sputtering is based on a combination of film characterization, plasma diagnostics, and modeling. Monte Carlo simulations of ballistic sputtering and gas-phase atomic transport are benchmarked by selected measurements of the deposition rate, residual film stress, and plasma parameters monitored with an electrostatic probe. We describe results of this study of parameter space and ultimately demonstrate the deposition of >50 µm-thick boron carbide coatings with close-to-zero residual stress.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

8:40am **B1-1-ThM-3 Hybrid Technologies for Wear Protective Coatings With Adaptive Behavior***, **Andrey Voevodin (andrey.voevodin@unt.edu)**,* University of North Texas, USA **INVITED**

Physical Vapor Deposition (PVD) technologies offer a suite of methods for surface engineering, where the broad range controls of the deposited flux chemical composition, density, ionization state and energy allow for the growth of wear reducing materials with complex compositions and structures tailored for an adaptive behavior in variable environments and temperatures.For example, the hybridization of magnetron sputtering and pulsed laser deposition had led possibility to embed transition metal dichalcogenides into hard ceramic matrices which had open a range of adaptive coating capable to operate over the broad range of environment humidity and temperature by self-changing the contact surface chemistry and structure in response to the environment change. The hybrid processes for the formation of adaptive wear protective coatings were further expanded to include combinations of PVD methods with other methods, e.g. laser texturing and electro-spark deposition, had led to additional avenues for realization of robust wear protective coatings with adaptive behavior to operate under high contact loads and speeds.The presentation reviews developments of adaptive wear protective coatings produced with hybrid PVD methods and places perspectives for future opportunities.

9:20am **B1-1-ThM-5 Cylindrical Magnetron Deposition of TiAlN Coatings with HiPIMS***, **Veronika Simova (veronika.simova@polymtl.ca)**, O. Zabeida, L. Varela Jimenez, J. Qian, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Rotating cylindrical magnetrons have several important benefits in comparison with widely used planar magnetrons, making them interesting for large-scale industrial applications. Due to their rotation, target erosion is uniform that results in a much higher target utilization (70% or more) and a high stability during reactive sputtering processes. Moreover, better cooling efficiency allows one to use higher power densities and, consequently, higher deposition rates can be achieved. This makes cylindrical magnetron sputtering (CMS) well adapted for HiPIMS.

In the present work, we investigated the use of CMS for the fabrication of $Ti_{0.5}Al_{0.5}N$ as a model hard coating extensively used for the protection against harsh environments such as those seen in aerospace and manufacturing. We studied the effect of pulsed-DC and HiPIMS deposition conditions (frequency of 0.91 kHz, duty cycle of 91% and 9.1%, respectively) on the microstructure, mechanical properties, residual stress and stress depth profiles. In addition, *in situ* real-time plasma monitoring by optical emission spectroscopy (OES) was applied for the study of the process and of the film growth conditions.

By applying the substrate bias, the coating hardness increased from 20 GPa (no bias) up to 30 GPa for a bias of -60 V without any additional heating. This increase in hardness is in good correlation with the increase in compressive stress from -0.9 GPa to -5.5 GPa and corresponding decrease in the grain size (from 16 nm to 9 nm). The stress depth profiles clearly show a steep gradient in compressive stress increasing from the substrate interface towards to the coating surface.

Substrate heating results in further enhancement of the mechanical properties, accompanied by a considerably lower compressive stress and its gradient. Consequently, when combining substrate heating with substrate biasing, hard TiAlN coatings with even lower compressive stress can be produced (-2.3 GPa).

The results clearly show that the substrate bias and heating can effectively be used to tune the mechanical properties and residual stress and stress depth profiles of TiAlN coatings.

9:40am **B1-1-ThM-6 Development of VC-based Early Transition Metal Carbide Superlattices via Compound Target Magnetron Sputtering***, **Barbara Schmid (barbara.schmid@tuwien.ac.at)**, N. Koutná, R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee Composite Materials, Germany*; E. Pitthan Filho, D. Primetzhofer,* Uppsala University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides are known to feature high thermal and mechanic stability as well as high melting points, sometimes above 3500 K, and can be regarded as ultra-high temperature ceramics (UHTC). The huge downsides to those materials is the high inherent brittleness.

Superlattice architecture describes the alternation of coherently grown nanolayers of two or more materials. By creating such superlattices, optical, magnetic, electronic, tribological, or mechanical properties can be influenced. The hardness but also the toughness of superlattice materials can be significantly higher than their monolithically grown components.

Therefore, we developed superlattice structures of selected transition metal carbides combined with VC as well as performed bilayer period variations between 2 and 50 nm.

The selected carbide combinations are based on density functional theory simulations, which revealed VC containing films as most promising candidates to have an improved toughness behavior due to the superlattice structure.

All coatings are developed via DC magnetron sputtering using the respective ceramic targets. Their characterization includes X-ray diffraction, scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy, elastic recoil detection analysis, nanoindentation and in-situ micromechanical investigations.

10:00am **B1-1-ThM-7 New Approach to Ceria-Based Electrolyte Deposition by Reactive Magnetron Sputtering***, **Kamel Ouari (kamel.ouari@utt.fr)**, E. Zgheib, S. Achache,* LASMIS, University of Technology of Troyes, France*; M. Arab Pour Yazdi, A. Billard, P. Briois,* FEMTO-ST, University of Technology of Belfort-Montbéliard, France*; F. Sanchette,* LASMIS, University of Technology of Troyes, France

Low-Temperature Solid Oxide Fuel Cells (LT-SOFC) represent a future technology for clean and efficient power generation from renewable sources. Low-temperature operation can make SOFC technology technically useful, i.e. less manufacturing cost and with more stable long-term performance. However, it also brings significant challenges in cell fabrication, especially in producing thin and dense electrolyte films with good mechanical and electrical properties. Magnetron sputtering is one of the advanced techniques used to develop micrometer coatings. Although it is a scalable industrial process, it also has drawbacks, such as low oxide deposition rates. Ceria-based electrolytes, Ce(Gd, Sm)O2, are one of the most promising alternatives to the conventional SOFC electrolyte, Yttria-Stabilised Zirconia (YSZ), due to their high ionic conductivity at low temperatures (< 600°C). Thus, in this work, optimized electrolytes for LT-SOFCs are deposited by reactive pulsed DC magnetron sputtering. The objective is to obtain dense coatings of a few micrometres with high deposition rates. Coatings were deposited using an DEPH 4 system (DEPHIS, Etupes, France) to prove their feasibility on a large scale. We report two new methods for depositing high-quality electrolyte layers by reactive magnetron sputtering, one involving sub-stoichiometric coating and the other stoichiometric without using any control systems (e.g. optical emission spectroscopy, target voltage, mass spectrometry, or other). The sub-stoichiometric films require ex-situ annealing to fully oxidize them. The deposition rates are in the order of that of the metal mode of the reactive deposition method. Moreover, the discharge voltage and overall pressure stabilize after a few minutes. Investigations are focused on growth, physico-electrochemical characterizations of Gd- and Sm-doped ceria as a function of deposition parameters (bias, O2 flow rate, etc.), and performance tests of LT-SOFCs with 2, 5 and 10 µm thick sputtered electrolytes.

10:20am **B1-1-ThM-8 Sputter-Deposited Zr-Cu Thin Film Metallic Glasses: Microstructure and Properties Control of as-Deposited Films and Impact of Ultra-Short Pulsed Laser Irradiation Treatments on the Film's Structure***, **Alejandro Borroto (alejandro.borroto@univ-lorraine.fr)**,* Institut Jean Lamour - Université de Lorraine, France*; M. Prudent,* Laboratoire Hubert Curien - Université de Lyon, France*; S. Bruyère,* Institut Jean Lamour - Université de Lorraine, France*; F. Bourquard,* Laboratoire Hubert Curien - Université de Lyon, France*; D. Pilloud, D. Horwat,* Institut Jean Lamour - Université de Lorraine, France*; M. Leroy,* IREIS, Groupe HEF, France*; P. Steyer,* MATEIS, INSA Lyon, Université de Lyon, France*; J. Colombier, F. Garrelie,* Laboratoire Hubert Curien - Université de Lyon, France*; J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

Owing to their amorphous structure, metallic glasses (MGs) have emerged as a new class of materials with remarkable properties compared with their crystalline counterpart. Using physical vapor deposition methods such as sputtering, MGs can be prepared in the form of thin film metallic glasses (TFMGs). Thus, the microstructural control inherent to the sputtering process can be exploited to tailor the properties of TFMGs. Meanwhile, laser irradiation is a well-established technique for surface functionalization, allowing the generation of ripples known as laser-induced periodic surface structures (LIPSS).However, a lack exists on the laser-induced surface functionalization of MGs, most of the studies are focused on the laser irradiation-crystalline material interaction.

Here, sputter-deposited Zr-Cu thin films, largely known for their good glass forming ability, are used as a model system and studied over a wide range of compositions. Our results are divided into two parts. First, we report on the influence that the energy of the sputtered atoms arriving at the substrate (controlled here through the deposition pressure) has on the structure, microstructure, and properties of the deposited films. We demonstrate that by increasing the deposition pressure, a composition-dependent transition from a denser to a columnar microstructure occurs. This microstructural transition directly affects the residual stress state as well as the electrical and optical properties of the deposited TFMGs. In particular, we show that there is a threshold in the deposition pressure below which the resistivity of the films remains constant. Second, we report on the laser-induced structural changes occurring at the surface and near-surface in Zr-Cu thin film metallic glasses. Hence, we study the influence that the alloy composition has on the crystallization process induced by laser irradiation. Transmission electron microscopy is used to study the evolution of the film's structure, microstructure, and composition after laser irradiation. In particular, we demonstrated the feasibility of laser treatment to obtain periodic surface structures of different geometries in TFMGs. Our results shed new light on the laser-amorphous material interaction process, opening a new avenue for future applications.

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

## HiPIMS, Pulsed Plasmas and Energetic Deposition I

**Moderators: Tiberiu Minea**, Université Paris-Saclay, France, **Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

8:00am **B8-1-ThM-1 the Role of He (23S1) Metastable Atoms to Generate High Current Density in Pulsed Magnetron Discharge***, **Abderzak FARSY (abderzak.el-farsy@universite-paris-saclay.fr)**,* Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France*; E. Morel,* SuperGrid Institute, France*; T. Minea,* Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France

Magnetically enhanced plasmas are used in various applications of low-temperature plasmas including magnetron sputtering and Hall-effect thrusters. In magnetron discharge technologies for sputtering applications, the use of the magnetic field allows the electron confinement yielding for the increase of the plasma density by 1-2 orders of magnitude and the increase of the deposition rate. High power impulse magnetron sputtering (HIPIMS) is a recent ionized physical vapor deposition where a pulsed power supply delivers a huge peak power during a short pulse to achieve a very high ionization degree (>50%) of the metallic sputtered vapor.

In this contribution, we focused on the time-resolved characterization of gas temperature and the density of He ($2^3S_1$, 19.82 eV) metastable atoms in the ionization region of magnetron plasma operated with a graphite target (2 inch in diameter) and a high current density range (10-20 $A/cm^2$) within a pulse of 50 µs. Those characterizations are combined with the electrical ones of the cathode voltage and the discharge current. The temporal evolution of He metastable atoms velocity distribution functions (AVDFs) was measured using Time Resolved Tunable Diode Laser Absorption spectroscopy (TR-TDLAS), see figure 1 in supplemental document. A diode laser, accorded to provide 30 pm wavelength range without mode hop and centered at $\lambda_0$=1082.909 nm, was used to probe the He $2^3S_1 – 2^3P_0$.

In our conditions, the measured TR-TDLAS profile is affected only by the Doppler broadening; all other mechanisms are negligible. Thus, from the analysis of TR-AVDFs, the gas temperature and He metastable atoms density are calculated (figure 2b in supplemental document), we assumed that the He ground state and the He metastable have the same temperature. The main result obtained by those diagnostics is that the He metastable atoms density reaches the maximum by a time-shift with the current maximum. The He metastable atoms density reaches the maximum at 20 µs whereas the discharge current at 31 µs. In the presentation, this behavior will be used to discuss the role of the He metastable atoms to generate the high current density. Since the measurements were carried out in the ionization region, the He metastable atoms density is affected by electron density and temperature and also by the gas rarefaction effect. Therefore, the effect of cathode voltage, the gas pressure and the discharge current will be presented and discussed.

8:20am **B8-1-ThM-2 Transport of Ions and Neutrals in HiPIMS Studied by Particle-Based Simulations***, **Tomas Kozak (kozakt@ntis.zcu.cz)**,* University of West Bohemia, Czechia

High-power impulse magnetron sputtering (HiPIMS) technique is being increasingly used for deposition of films due to its ability to deliver more energy into the growing film via target material ions. The sputtered target material atoms are ionized in the high-density plasma above the target. Some of these ions return onto the target due to the structure of the plasma potential above the target. To understand the effect of the pulse shape and other discharge parameters on the ion return probability is very important for the optimization of the ionized fraction, the energy and the total flux of film-forming atoms on the substrate.

A 3D computer simulation employing the direct simulation Monte Carlo (DSMC) method was developed to bridge the gap between existing volume-averaged (less detailed) and particle-in-cell (very detailed) models. The presented simulation can directly calculate the return probability and the related ionized fraction of the target material species on the substrate for a given (time-dependent) spatial distribution of the plasma potential which is estimated based on recent experimental studies. Moreover, the simulation provides time- and space-resolved densities of atoms and ions in the discharge plasma and their fluxes to various surfaces (including energy distributions). The calculated densities are in a good agreement with density maps obtained by optical methods. The ionized fraction on the substrate is found to strongly depend on the plasma potential drop across the ionization region above the target while the ion return probability changes only weakly (around the value of 0.9). This highlights the importance of accurate determination of the ion return probability. By comparing the simulation results with experimental data (such as, ionized fraction, deposition rate), other unknown discharge parameters can be determined.

The simulation also provides quantitative evaluation of the gas rarefaction effect which is found to significantly reduce the process gas density between the target and the substrate (during and after the HiPIMS pulse). Additionally, the effects of various collisional processes in the plasma or the effect of varying plasma potential (*e.g.*, due to spokes) can be studied by the simulations.

8:40am **B8-1-ThM-3 Kinetic Investigation of Electron Heating in HiPIMS Discharges***, **Bocong Zheng (bcong.zheng@gmail.com)**,* Fraunhofer USA*; Y. Fu,* Tsinghua University, China*; K. Wang, T. Schuelke,* Fraunhofer USA*; Q. Fan,* Michigan State University, USA **INVITED**

We provide a self-consistent and complete description of discharge characteristics of high power impulse magnetron sputtering (HiPIMS) through fully kinetic 1d3v particle-in-cell/Monte Carlo collision (PIC/MCC) simulations. As HiPIMS employs much higher transient power than conventional DC magnetron sputtering (DCMS), more physical processes need to be considered in its simulations, such as Coulomb collisions between charged species, sputtering winds, i.e. gas rarefaction due to momentum exchange between the sputtering species and the background gas, ionization of metal ions from the sputtering species, and secondary electron emission induced by these multi-charged metal ions. This study considers all of the above processes and on this basis provides a detailed description of the HiPIMS discharge characteristics, including discharge runaway, electron dynamics, and sputtering winds. Some important conclusions previously obtained from the global model are confirmed by this *ab initio* kinetic simulation. During the discharge runaway process, i.e., the transition from the low-current DCMS regime to the high-current HiPIMS regime, metal ions gradually replace gas ions as the dominant ones, and the electron energization transitions from sheath energization to Ohmic heating of the ionization region. These results are beneficial for the design and optimization of HiPIMS discharges in practical applications.

9:20am **B8-1-ThM-5 The Influence of the Magnetic Field on the Discharge Parameters of a High Power Impulse Magnetron Sputtering Discharge***,* 
***Martin Rudolph (martin.rudolph@iom-leipzig.de)****,* Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Intstitute of Technology, Sweden*; H. Hajihoseini,* University of Iceland*; . Raadu,* KTH Royal Institute of Technology, Sweden*; T. Minea,* Université Paris– Saclay, France*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linköping University, IFM, Sweden

The magnetic field of a magnetron is crucial for the working principle of magnetron sputtering. This becomes apparent in particular for high power impulse magnetron sputtering (HiPIMS), where changes in the magnetic field are known to strongly affect the discharge current and voltage waveforms. For examples, for discharges with the peak discharge current kept constant, the discharge voltage decreases with stronger magnetic fields. Simulating these discharges using the Ionization Region Model provides insights into the discharge physics. We reveal that the decreasing discharge voltage has the effect that a higher fraction of the input power is used for electron heating rather than for accelerating ions. This is because stronger magnetic field increases the fraction of the discharge voltage that drops over the ionization region which enhances Ohmic heating. As a result, the discharge voltage can be lower to reach the same peak discharge current. For discharges operated with the discharge voltage kept constant, the peak discharge current increases for stronger magnetic fields. The reason is again that a higher fraction of the input power is directed to the electrons, the discharge becomes more energy efficient. This increases the electron density which lowers the discharge impedance and enables the discharge to run at a higher discharge current. Indeed, we find a close link between the evolution of the electron density and that of the discharge current during the pulse. This suggests that the discharge current can be used as a handle to adjust the electron density of a HiPIMS discharge and by that, to adjust the probability that a sputtered atom is ionized in the ionization region.

9:40am **B8-1-ThM-6 Digitalisation Strategies for a Digital Twin of the Synthesis of Functional Materials by High Power Impulse Magnetron Sputtering and Other Plasma PVD Processes***,* 
***Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk)****, A. Arunachalam Sugumaran, P. Hovsepian,* Sheffield Hallam University, UK*; C. Davies, P. Hatto,* Ionbond UK

Optical emission spectroscopy (OES) was combined with process parameters to monitor all stages of both High Power Impulse Magnetron Sputtering (HIPIMS) and conventional magnetron sputtering processes to provide a robust method of determining process repeatability and a reliable means of process control for quality assurance purposes. Strategies for the in-situ real-time monitoring of coating thickness, composition, crystallographic and morphological development for a CrAlYN/CrN nanoscale multilayer film were developed.Equivalents to the ion-to-neutral ratio and metal-to-nitrogen ratios at the substrates were derived from readily available parameters including the optical emission intensities of Cr I, $N_2$ (C-B) and Ar I lines in combination with the plasma diffusivity estimated from the ratio of substrate and cathode current densities.The optically-derived equivalent parameters identified the deposition flux conditions which trigger the switch of dominant crystallographic texture from (111) to (220) observed in XRD pole figures and the development of coating morphology from faceted to dense for a range of magnetron magnetic field configurations.

The work paves the way to implementation of machine learning protocols for monitoring and control of these and other processing activities, including coatings development and the use of alternative deposition techniques.The work provides essential elements for the creation of a digital twin of the PVD process to both monitor and predict process outcomes such as film thickness, texture and morphology in real time.

10:00am **B8-1-ThM-7 Decrease of the Interfacial Adhesion to Polymers and Pharmaceuticals Through Modification of Steel Surfaces by PVD and CVD Techniques***,* 
*M. Lima,* University of Minho, Portugal*; R. Silva,* University of Aveiro, Portugal*; F. Ferreira,* University of Coimbra, Portugal*; F. Oliveira, R. Silva,* University of Aveiro, Portugal*; A. Cavaleiro,* ***Sandra Carvalho (sandra.carvalho@dem.uc.pt)****,* University of Coimbra, Portugal

The adhesion is a thermodynamic parameter that quantifies the interatomic and intermolecular interaction between two surfaces and involves chemical, physical, and rheological phenomena [1]. Many industrial processes are affected by adhesion phenomena occurring during the contact of two surfaces with different properties.

An example is the demolding stage of the injection molding process because small fractions of the polymers frequently remain adhered to the mold surface, producing defective polymeric parts (~2 % of the injected parts are rejected) and reducing the mold lifetime [2].

On the other hand, the production of pills and tablets in the pharmaceutical industry is limited by the interaction between the punch and the powder. Different factors such as chemical composition, excipients, particle sizes, melting and compression points of the pharmaceuticals, and the surface properties of the punch determine the success of the drug compaction. The compaction and surface finishing of the pills will directly influence the disintegration and drug dissolution leading to diverse and undesired drug absorption kinetics [3].

Solving adhesion problems in these specific industries will reduce the generation of waste and increase productivity.

There are different ways to optimize the demolding process, such as temperature and humidity optimization, applied demolding and molding forces, or modification of the steel surface using physical vapor deposition (PVD), plasma treatments, and chemical vapor deposition (CVD) methods.

This work will report the development of coatings deposited by atomic layer deposition as well as magnetron sputtering onto steel surfaces to reduce the adherence of both polymeric and pharmaceutical materials. Coatings with different chemical and physical properties presented different surface energy values and this parameter was related to the adhesion of the polymers or the pharmaceuticals to the surfaces. Additionally, the steel coated surfaces were characterized by different techniques (SEM, XRD, FTIR, XPS, nanoindentation, OCA) to disclose the adhesion mechanisms. The coated surfaces with the lowest surface energy showed in a simulated injection process (polymers) and a powder compression machine (pharmaceuticals), the most promising results.

References

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10:20am **B8-1-ThM-8 Target Erosion Effects During Hipims Deposition of Ultrathick Au-Ta Alloy Films***,* 
*J. Bae,* General Atomics, USA*; A. Engwall, L. Bayu Aji, S. Shin, A. Baker, J. Moody,* ***S. O. Kucheyev (kucheyev@llnl.gov)****,* Lawrence Livermore National Laboratory, USA

Gold-tantalum alloy films are of interest for biomedical and magnetically-assisted inertial confinement fusion (ICF) applications. Here, we systematically study properties of Au-Ta alloy films deposited by high-power impulse magnetron sputtering (HiPIMS) from alloyed targets. By varying substrate tilt, bias, and HiPIMS pulsing parameters, properties of Au-Ta films can be controlled in a very wide range, including residual stress from -2 to +0.5 GPa, density from 12 to 17 g/cm$^3$, and electrical resistivity from 50 to 4500 micro-Ohm cm. Emphasis of this presentation will be on understanding and controlling effects of target wear/erosion, which strongly influences film properties during the long runs required for depositing >10-micron-thick coatings for ICF hohlraums. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country C - Session B1-2-ThA

## PVD Coatings and Technologies II

**Moderator: Frank Kaulfuss**, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

1:20pm **B1-2-ThA-1 Ultra-Precision Optical Surface Processing by Reactive Atmospheric Plasmas and Low Energy Ion Beams (Virtual Presentation)**, ***Thomas Arnold (thomas.arnold@iom-leipzig.de)***, Leibniz Institute of Surface Engineering (IOM), Germany; *J. Bauer,* Leibniz Institute of Surface Engineering (IOM), Germany , Germany; *G. Boehm, H. Müller,* Leibniz Institut of Surface Engineering (IOM), Germany **INVITED**

High-performance optical elements such as lenses and mirrors require high accuracy regarding figure error, waviness, and roughness. Furthermore, the complexity of surface shapes increases and an increasing demand for individually and complex shaped optical elements like non-standard aspheres, acylinders, or freeform elements is observed. In particular, the use of free-form elements in optical systems offers new functions in illumination and imaging applications and leads to fewer optical surfaces and thus more compact system designs. Recent advances in manufacturing technology are giving optical system designers more and more freedom. However, once the machinability of complex shaped surfaces is proven, tolerances become more stringent. Especially for scientific devices, e.g. space- and earth-based spectrometers or telescopes, or for laser beam shaping applications, high precision of free-form optical surfaces is required.

Depending on the material to be machined different non-conventional processing methods have been developed that are based either on atmospheric pressure reactive plasma jet etching or ion beam etching to deterministically remove material from the surface or for finishing.

Fluorine plasma jet-based methods are usually applied on materials like optical glasses, silicon, SiC or ULE. Here the specific chemical interactions between reactive radicals formed in the plasma and the surface constituents must be taken into account to achieve predictable results with respect to form accuracy, roughness, and laser damage threshold. The presentation gives an overview over different plasma jet based processing chains for precise freeform optical lens generation and finishing.

Ion beam etching technology has been recently shown to be applicable to aluminium surfaces. Increasing demands on applications of high-performance mirror devices for visible and ultraviolet spectral range call for new processing schemes. Reactively driven ion beam machining using oxygen and nitrogen gases allows direct figure error correction up to 1 µm machining depth while preserving the initial roughness. Machining marks originating from preliminary surface shaping by single-point diamond turning often limit the applicability of mirror surfaces in the short-periodic spectral range. Ion beam planarization with the aid of a polymeric sacrificial layer is shown as a promising process route for surface smoothing, resulting in successfully reduction of the turning mark structures. A combination with ion beam direct surface smoothing to perform a subsequent improvement of the microroughness is presented.

2:00pm **B1-2-ThA-3 A Combinatorial Approach to Developing Sputter-Deposited Heavy-Metal Alloy Films for Inertial Confinement Fusion Applications**, ***Leonardus Bimo Bayu Aji (bayuaji1@llnl.gov)***, *A. Engwall,* Lawrence Livermore National Laboratory, USA; *J. Bae,* General Atomics, USA; *A. Baker, S. Shin, S. McCall, J. Moody, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Magnetically-assisted inertial confinement fusion (ICF) could push current National Ignition Facility (NIF) implosions closer to ignition. The application of a pulsed magnetic field to an ICF target requires the development ofnew hohlraums, which are sphero-cylindrical canswith wall thicknesses of over about 10 µm made from heavymetals. Magnetized ICF targets require heavy metal hohlraums with an electrical resistivity of over 100 µΩ cm at cryogenic temperatures of about 20 K. Such requirements cannot be met by the Au and depleted U hohlraums traditionally used for ICF. Here, we present results of our systematic study by combinatorial direct-current magnetron co-sputtering, aimed at developing a family of binary Au-Ta and Au-Bi films with the microstructure, stress, mechanical properties, and electronic transport favorable for ICF applications.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

2:20pm **B1-2-ThA-4 Machine Learning Based Model for Plasma Prediction in HPPMS Processes**, *K. Bobzin, C. Kalscheuer, M. Carlet,* ***Julia Janowitz (Janowitz@iot.rwth-aachen.de)***, Surface Engineering Institute - RWTH Aachen University, Germany

The coating development using Physical Vapor Deposition (PVD) is time intensive and expensive. The coating processes are usually developed and improved based on the operator's experience. In order to improve the understanding of the processes during coating deposition, methods of plasma diagnostics can be used in the coating process. However, this is also time intensive and requires the installation of special diagnostics. The aim of the current study is to build a model of PVD processes for prediction of the intensity of the plasma species during the coating process. Through this, a contribution to data based coating development can be achieved. Machine learning methods are used to build a model of the PVD process to predict the intensity distribution of the species in the plasma during coating deposition. Based on measured data of different coating processes, the models were trained and tested. Therefore, a broad database was established by measuring the ion intensities of the species in the plasma. The data was collected for chromium and aluminum based hard coatings using an industrial magnetron sputtering unit for coating deposition. The data was measured for hybrid processes of direct current (dcMS) and high power pulsed magnetron sputtering (HPPMS). Here, the gas flow of the reactive gases oxygen and nitrogen was varied. Ion intensities were measured using optical emission spectroscopy (OES) with six substrate side positioned collimators to measure the influence of all cathodes used. The data was measured time resolved during the coating process. The predictions of the intensities show similar trends for the measured intensities of the species within the coating chamber. The predicted intensity range is in good agreement with the measured data. The built models can be used for a more targeted process development. This can contribute to the application oriented adjustment of the coating processes and the coating properties. Within the scope of this study, it was possible to predict the intensities of the plasma species in the coating process for an industrial coating unit using hybrid processes dcMS/HPPMS.

2:40pm **B1-2-ThA-5 Oxidation Stability of Oxynitride CrAlON Hard Coatings**, *K. Bobzin, C. Kalscheuer,* Surface Engineering Institute - RWTH Aachen University, Germany; *G. Grundmeier, T. de los Arcos, S. Schwiderek,* Technical and Macromolecular Chemistry - University of Paderborn, Germany; ***Marco Carlet (carlet@iot.rwth-aachen.de)***, Surface Engineering Institute - RWTH Aachen University, Germany

Hard coatings like CrAlN deposited by physical vapor deposition are state of the art for wear and oxidation protection of cutting tools. High power pulsed magnetron sputtering (HPPMS) leads to a higher degree of ionization in plasma compared to direct current magnetron sputtering (dcMS). This enables the deposition of coatings with denser structures and smoother surfaces. Conducting a dcMS/HPPMS hybrid process combines the advantages of HPPMS with the high deposition rates of dcMS. Adding oxygen to CrAlN leads to the oxynitride coating system CrAlON. A reduced friction against steel was found for CrAlN coatings with an oxynitride CrAlON toplayer in previous studies. Since this decreases the thermal loadings on the coated cutting edge, it is beneficial during cutting. Nowadays, the interest of industry in oxynitride hard coatings is rising. However, the oxidation behavior of the quaternary oxynitride CrAlON has hardly been investigated yet. Therefore, the influence of the oxygen content in CrAlON hard coatings on the coating properties and on the oxidation stability was taken into account in the current study. The morphology of the coatings was investigated by scanning electron microscopy (SEM). The chemical composition of the bulk was measured by electron probe micro analysis and of the reaction layer by X-ray photoelectron spectroscopy. The phase composition of the coatings was investigated by X-ray diffraction (XRD) and the elastic-static properties by nanoindentation. Subsequently, the coated cemented carbide samples were heat treated at T = 900 °C and T = 1,000 °C for t = 0.5 h in ambient atmosphere. Finally, the heat treated samples were investigated by SEM and XRD again. A higher oxygen ratio of $y = O/(N+O)$ of the coatings increased the indentation hardness and the resistance against plastic deformation. A moderate oxygen ratio of y = 13.2 % of the oxynitride coating increased the aluminum content of the reaction layer to $x = Al/(Al+Cr)$ = 37.4 % compared to x = 27.3 % for the nitride coating and to x ≤ 30.2 % for the oxynitride coatings with higher oxygen contents of y ≥ 33.3 %. As shown by XRD, this enhanced the oxidation stability of the oxynitride coating with a moderate oxygen content of y = 13.2 % from T = 900 °C to T ≥ 1,000 °C.

## Hard Coatings and Vapor Deposition Technologies
## Room Pacific D - Session B3-ThA

### Deposition Technologies and Applications for Carbon-based Coatings

**Moderators: Konrad Fadenberger**, Robert Bosch GmbH, Germany, **Frank Papa**, GP Plasma, USA

1:20pm **B3-ThA-1 Smooth and Wear-resistant Carbon Coatings Deposited by S3p™**, ***Julien Kéraudy (julien.keraudy@oerlikon.com)***, *K. Siegfried, D. Martin, S. Guimond,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Diamond-like carbon (DLC) coatings, namely hydrogenated amorphous carbon (a-C:H) coatings deposited by a PECVD process emerged years ago as the ideal solution for applications where component parts are under high loads or subject to extreme friction, wear and contact pressures with other parts. However, there are nowadays many tribological systems, in which the abrasion resistance of a-C:H coatings is at the limit or even insufficient. With its higher hardness, tetrahedral amorphous carbon (ta-C) would provide more abrasion resistance, a longer lifetime and enable a better performance for the related components. However, the state-of-the-art arc-deposited ta-C coatings (filtered or not) are simply too rough for many applications. Possible solutions to improve surface quality are post-finishing methods such as brushing or polishing, which however have a significant impact on the processing costs.

Recently, high power impulse magnetron sputtering (HiPIMS) was reported to be a suitable method to deposit dense hydrogen-free amorphous carbon (a-C) coatings. In this work, we report on the coating growth and properties of smooth and hard carbon coatings produced by the S3p™ (Scalable Pulsed Power Plasma) method in an industrial deposition plant. S3p™ technology enables scalability of the pulse power density and pulse length in a wide range and expands significantly the choice of the deposition parameters and process stability as compared to conventional HiPIMS technology. Smooth and hard hydrogen-free carbon layers were produced using graphite targets in Ar ambient. The thermal stability of the coatings in air and their tribological behavior in dry and lubricated environments were investigated and compared to the results of standard a-C:H and ta-C coatings. Furthermore, the influence of adding a $C_2H_2$ precursor in an Ar ambient atmosphere on the film properties and S3p™ reactive process was investigated.

Finally, selected applications where carbon coatings deposited by S3p™ outperformed common DLC coatings will be presented.

1:40pm **B3-ThA-2 New Developments on Hydrogen Free Carbon Coatings for Automotive, Industrial and Tool Applications**, ***Philipp Immich (pimmich@hauzer.nl)***, *L. Tegelaers, G. Negrea, R. Jacobs, G. Fransen,* IHI Hauzer Techno Coating B.V., Netherlands

Nanostructured and amorphous coatings play an important role in today's automotive, industrial and tool applications. There are huge areas for application for these kinds of coatings – first of all the automotive market, but also traditional applications like cutting or forming tools.

Today the focus is on the growing customer demand for coating properties like higher temperature stability and increased wear resistance in combination with low viscosity lubricants and fuels. In the last years therefore development work shifted to the group of hydrogen free DLC coatings like a-C and ta-C coatings.

To industrialize these coatings different developments routs were carried out in the last years, to ensure an economic and reliable way of deposition. The equipment design and even the selection of most suitable process technology are however also strongly determined by the productivity and the coating properties. In this regard we will demonstrate by using the different Hauzer high energetic pulsed technologies HIPIMS as well as new developed pulsed arc, that coatings can be more tuned and tailormade towards dedicated properties. We will also show that these technologies can be easy upscaled on different machine sizes and deliver here reliable industrial processes with a good ratio of coating cost per coated part and performance.

2:00pm **B3-ThA-3** ***Carbon-Based Coatings for Forming and Protection of Stainless Steel Sheets***, ***Marcus Morstein (marcus.morstein@hightechzentrum.ch)***, Hightech Zentrum Aargau AG, Switzerland **INVITED**

Carbon-based coatings, because of their unique combination of low friction, low wear and chemical inertness, have a long-proven potential as coating materials. Both cutting and forming tools are coated with diamond-like carbon (DLC) coatings, as are components in the automotive sector, both for combustions engines and xEV components. Besides, its appealing dark black color renders DLC useful for decorative purposes.

For different applications different types of DLC coatings have been established, where hydrogen-stabilized DLC, despite its relatively low hardness, is the material of choice for components such as sliding or rolling bearings, or decorative coatings. On the high-performance end, tetrahedral amorphous carbon (*ta*-C) withstands tough conditions and provides superior hardness of up to about 60 GPa.

While the temperature- respectively, oxidation sensitivity limits the application range of carbon-based coatings, new applications keep being added and progress in deposition technology allows for (relatively) low-cost coating even of large-area parts with DLCs.

A recent example for the successful use of amorphous carbon as protective coating for stainless steel are metallic bipolar plates for proton-exchange membrane (PEM) fuel cells. These thin sheets of below 100 µm, often made from 316L (1.4404) steel, need to be protected from corrosion in order to achieve the desired stack lifetimes. For this purpose, chemically passive carbon-based coatings have been used with success.

Recently, precision forming processes have been developed for the economical mass production of these bipolar plates. In production-near tests, DLC coatings combined with an advanced surface treatment process for the steel tools have been shown to perform very well, compared to alternative PVD coatings

DLC coatings are also commonly applied as black color layer for e.g. household appliances. However, because of the imminent exposure to abrasive wear of those surfaces, the supporting properties of the otherwise soft stainless steel substrate need to be enhanced by mechanical of diffusion treatment.

Progress has been made in deposition technology, too. A novel hybrid deposition technique combining a microwave plasma with sputtering allows for the fabrication of high-hardness, non-hydrogenated diamond-like carbon coatings. The properties and morphology of the fabricated DLC films are comparedto those from pulsed-direct current magnetron sputtering (DCMS) or high-power impulse magnetron sputtering (HiPIMS), using techniques such as Raman spectroscopy, nanoindentation, X-ray reflectometry and scanning electron microscopy.

2:40pm **B3-ThA-5 DLC Coatings: Diamond Hardness & Graphite Lubrication Combined to Meet Industrial Application Requirements**, ***Hamid Bolvardi (h.bolvardi@platit.com)***, PLATIT AG, Switzerland; *J. Kluson, M. Jilek,* PLATIT a.s., Czechia; *R. Zemlicka, A. Lümkemann,* PLATIT AG, Switzerland

Dimond-like Carbon (DLC) coatings have unceasingly absorbed overwhelming interest from industry as well as academic research institutions within last years. High hardness and elastic modulus, chemical inertness, superior tribological properties and good corrosion resistance as well as high biocompatibility and resistance to bacterial colonization make DLC an engrossing coating system. Owed to the unique and broad range of properties, DLC coatings are constantly employed in new applications from cutting and forming tools to components; saw blades, end mills, micro-tools, punches, injection and extrusion molds and dies, automotive, decorative, medical applications are just some raised examples here. DLC coatings consist of a mixture of $sp^3$ (diamond) and $sp^2$ (graphite)bonds. The higher $sp^3$ bond fraction results in a higher density, hardness (at ambient and elevated temperature), thermal stability, oxidation resistance, higher residual stress and lower thermal conductivity. Hence, comprehending the correlation between DLC coating properties and industrial application requirements is a crucial prerequisite to a performance increase in industry. An attempt is made here to cover the range from DLC synthesis to its implementation in industrial applications and the obtained performance results thereof.

3:00pm **B3-ThA-6 Modeling of High Power Impulse Magnetron Sputtering Discharges With Graphite Target**, *H. Eliasson,* Linkoping University, Sweden*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Institute of Technology, Sweden*; H. Hajihoseini,* University of Twente, Netherlands*; M. Zanaska,* Linkoping University, Sweden*; M. Adriaans,* Eindhoven University of Technology, Netherlands*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; **Tiberiu Minea (tiberiu.minea@universite-paris-saclay.fr)**,* Universite Paris-Saclay, France*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linkoping University, Sweden

By using high power impulse magnetron sputtering (HiPIMS) to deposit tetrahedral amorphous carbon (ta-C) or diamond like carbon (DLC) thin films the aim is to increase the ionization fraction of the carbon atoms sputtered off the target, as it is known that energetic ion bombardment of the substrate is essential to deposit ta-C or DLC films with high $sp^3$ content. In fact the deposition of DLC films by HiPIMS has been explored extensively for deposition of DLC films. Here, the ionization region model (IRM) is applied to model a high power impulse magnetron sputtering (HiPIMS) discharge in argon with a graphite target. The model gives the temporal variation of the various species and the average electron energy, as well as internal discharge parameters such as the ionization probability, back-attraction probability, and the ionized flux fraction of the sputtered species. It is found that the discharge develops into working gas recycling and most of the discharge current at the cathode target surface is composed of $Ar^+$ ions, which constitute over 90 % of the discharge current, while the contribution of the $C^+$ ions is always small (<5 %), even for peak current densities close to 3 A/cm$^2$. For the target species, the time-averaged ionization probability $< \alpha_{t,pulse} >$ is low, or 13 - 27 %, the ion back-attraction probability during the pulse $\beta_{t,pulse}$ is high (> 92 %), and the ionized flux fraction is about 2 %. It is concluded that in the operation range studied here it is a challenge to ionize carbon atoms, that are sputtered off of a graphite target in a magnetron sputtering discharge, when depositing amorphous carbon films. It is concluded that it is a challenge to provide a high flux of ionized carbon from the HiPIMS process investigated here. This is due to a combination of a high ionization energy, a small ionization cross section and a low residence time of sputtered carbon in the ionization region. This requires fine-tuning of the process, for which the work suggests promising handles.

3:20pm **B3-ThA-7 Time Resolved Determination of Plasma Parameters, Ionization and Macroparticles in an Industrial Scale Ta-C Laser-Arc Coating System**, ***Mathis Klette (klette@physik.uni-kiel.de)**,* Kiel University, Germany*; M. Kopte, W. Fukarek,* VTD Vakuumtechnik Dresden GmbH, Germany*; H. Kersten,* Kiel University, Germany

The early 1990s marked the beginning of carbon laserarcs being used to deposit tetrahedral amorphous carbon (ta-C). Since then, many improvements to the process have been made [1,2]. Ta-C coatings provide the treated object with improved tribological and hardcoating properties, lowering friction and improving wear resistance. These properties make them ideal for automotive powertrain components, drill bits, cutting tools and other applications. While ta-C can be deposited using various techniques, the laserarc technology allows for a strong temporal and spatial control of the deposition process while providing high deposition rate and enabling up-scaling for industrial applications.

However, the up-scaling of deposition rate and process geometry has a profound impact on the physical process. In this contribution, we present measurements of a 100 µs pulsed 1-2 kA up-scaled carbon laserarc using various diagnostics to analyze this effect. A custom-tailored diagnostic setup enables Langmuir probe and Faraday cup measurements for electron and ion energy distribution functions, while spatially and time resolved optical emission spectroscopy yields ion species and densities. Of special interest is the characterization of C2+ ions which have been rarely observed so far.

The energy influx on the substrate is monitored by using calorimetric probes [3], while a force probe [4] and a high-speed camera analyze the neutral contributions and macro particles. This information can be used to estimate the individual contributions to the total energy influx and allows to optimize the particle filter.

Additionally, a second high-speed camera monitors the arc discharge at the cathode itself.

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3:40pm **B3-ThA-8 Fabrication of Hot Magnetron Carbon Targets for a High-Rate Films Deposition by Using Magnetron Sputtering Technique Under the Injection of Neon-Helium Gas Mixture**, ***Bartosz Wicher (Bartosz.Wicher.dokt@pw.edu.pl)**, R. Chodun,* Warsaw University of Technology, Poland*; Ł. Skowroński, M. Trzcinski,* Bydgoszcz University of Science and Technology, Poland*; K. Król,* Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, Poland*; A. Lachowski,* Institute of High Pressure Physics, Polish Academy of Sciences, Poland*; K. Nowakowska-Langier,* National Centre for Nuclear Research (NCBJ), Poland*; K. Zdunek,* Warsaw University of Technology, Poland

A study of temperature of magnetron glassy carbon targets was performed for the case of gas injection magnetron sputtering (GIMS) of diamond–like carbon (DLC) and amorphous C–SiC films, by using unique geometry of the cathode source with increased temperature (HT – hot target). Cathode material was hollowed out for this purpose, from the bottom to the max. depth of 5 mm, which allowed to achieve target temperatures ranging from 790 to 1350 °C during the deposition of h-free carbon films. For the latter, four sockets were drilled in carbon target and then filled up with silicon carbide powder. In the second experiment, temporal evolution and spatial distribution of C–SiC cathode surface temperature were controlled by initiation of discrete pulse plasma discharges with power energies (Ei) changing from 122 to 403 J, which resulted in the temperature range from 730 to 1200 °C. The role of sputtering, sublimation and thermalized electrons in the increase of atoms removal from targets with limited heat conduction was clarified on the basis of an almost 4–fold increase in film deposition rate (up to 74 nm/min), compared to the completely cold process. For both variants of film deposition, GIMS were operated by generating as short as 400–ms and 250–ms plasma pulses at the frequencies of 1 and 2 Hz, respectively, thereby limiting the capability to cool targets operation over the neon–helium gas mixture. By contributing through the heat dissipation effect of HT, GIMS regime proved therefore to be an accurate in terms of increasing optical bandgap within DLC films, from 2.3 to 3.1 eV, which is derived from ordering of $sp^2$–graphene domains. The chemical and phase state of C–SiC films deposited from HT, revealed in turn, ~ 15 % of Si–C bonds, terminated in the 30 %–rich $sp^3$ carbon matrix, which puts its positive attribution to enhanced mechanical response, by means of 30.1 GPa hardness result.

**Fig. 1.** IR-thermogram of the studied targets’ surface with its corresponding mean temperature; a, c) cold carbon and C–SiC targets, b, d) hot carbon and C–SiC targets, respectively.

**Acknowledgment**

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4:00pm **B3-ThA-9 Adjusting the Properties of ta-C by Doping with Metals and Non-metals**, ***Frank Kaulfuss (frank.kaulfuss@iws.fraunhofer.de)**, F. Hofmann, T. Kruelle, V. Weihnacht,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

Tetrahedral amorphous carbon coatings (ta-C) are characterized by their very high wear resistance and low friction under most conditions. However, the requirements in the various application areas differ significantly and there is a need for application-specific adaptations of the coatings in some cases.

Current investigations show that the Laser-Arc process can be used to produce doped carbon coatings via the evaporation of composite graphite cathodes. Cathodes with 5 at% dopant content were used for this purpose. Iron and molybdenum were investigated as metal dopants and boron and silicon as non-metal dopants. The processing conditions were kept identical for all doped cathodes, and an undoped ta-C reference was also prepared. It can be observed that the defect density of the resulting coatings are significantly lower than the reference, especially for boron and molybdenum doping. For example, a 5 µm thick boron-doped coating shows lower roughness than 1 µm ta-C. Significant differences are seen in the morphology of these coatings, with the defect density being significantly reduced. Excitation of boron in the plasma is similar to carbon, and amorphous coatings are formed with comparable hardness to the ta-C reference. In contrast, the very highly excited molybdenum reduces the hardness significantly. In the case of iron and molybdenum doping the coatings are then no longer completely amorphous, as crystalline clusters are formed. Under some lubricated tribological conditions, the ta-C:B and a-C:Mo show clear advantages over ta-C reference coatings with comparable hardnesses.

4:20pm **B3-ThA-10 Improved Tribological Properties of DLC Coatings by Pulsed Laser Hardening***, **Sylvain Le Coultre (sylvain.lecoultre@bfh.ch)**,* Berner Fachhochschule, Switzerland*; J. Matthey, C. Rieille,* HE-Arc, Switzerland*; B. Neuenschwander,* Berner Fachhochschule, Switzerland

For many applications in cutting tools or watchmaking industries, the need to develop new solutions in order to improve the lifetime and performances of the components requires new approaches and solutions. In a joint project between the (Berner Fachhochschule) BFH and the (Haute Ecole ARC) HE-ARC, promising results have been obtained with nanotextured graphite layers produced using a two step hybrid production technology. First, a graphite coating is deposited using magnetron sputtering technology. Second, the coating is treated at with high power pulsed laser at high repetition rate.

As pin-on-disc measurements show, laser nanotexturing not only lowers the friction coefficient of the graphite coating, but also eliminates the run-in phase and significantly reduces wear in dry conditions. In addition, the topography induced by the laser treatment generates an optical effect of iridescence which adds a decorative function.

These first result open possibilities to develop a new type of graphite coating modified by laser pulses for application on 2D or 3D products with sizes in the order of mm2 to a few cm2.

These are first results, further improvement are expected via appropriate texture patterns and doping of the carbon target. Under wet condition, microchannel with heights in the nanometer range between are expected to be beneficial for storing lubricant.

## Hard Coatings and Vapor Deposition Technologies
## Room Town & Country D - Session B8-2-ThA

## HiPIMS, Pulsed Plasmas and Energetic Deposition II
**Moderator: Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

1:20pm **B8-2-ThA-1 Diagnosing Bipolar HiPIMS Plasmas Using Laser Thomson Scattering (Virtual Presentation)***, **James Bradley (j.w.bradley@liv.ac.uk)**, M. Law,* University of Liverpool, UK **INVITED**

A laser Thomson scattering (LTS) experiment has been developed to measure the temporal and spatial evolution of the electron temperature $T_e$ and density $n_e$ in HiPIMS plasmas. The circular magnetron source furnished with a tungsten target has been operated in both unipolar and asymmetric bipolar pulsing modes. The LTS measurements made in the magnetic trap and on the centre-line are complemented by time-resolved Langmuir probe data as well as plasma optical emission measurements.

In conventional unipolar mode, during the HiPIMS pulse (on-time), the LTS measurements of $n_e$ are seen to peak at $6.9 \times 10^{19}$ $m^{-3}$, falling by two orders of magnitude some 300 µs into the afterglow. The value of $T_e$ is seen to rise and fall during the negative pulse on-time as the discharge moves from one dominated by argon to metal vapour. Langmuir probe measurements are in good agreement with the LTS data.

When the source is operated in asymmetric bipolar pulsing mode, the pulse on-time results on the discharge centreline are similar to the unipolar case, however during the positive pulse periods we see significant electron heating in which $T_e$ can rise to values comparable to the those measured in on-time. The on-set of the rises in $T_e$ are significantly delayed relative to the start of the positive pulse, with the delay time decreasing with the magnitude of the positive voltage. The local electron density on the centreline $n_e$ is seen to decay significantly more quickly in the afterglow than for the corresponding unipolar pulsing case. Optical emission intensities show the presence of W(I) lines well into the afterglow. The phenomenon of plasma electron heating in the positive pulse is believed to be due to the existence of a transient reverse discharge, in which the vessel walls become an effective cathode.

LTS measurements in the magnetic trap however, show no such anomalous electron heating in the positive pulse period. These observations are discussed in terms of electron cross-field transport from wall to different regions of the plasma.

2:00pm **B8-2-ThA-3 Time Resolved IEDF, EEDF and Q/M of a HiPIMS Discharge for Different Pulse Conditions, Pressures, and Probe Orientations***, Z. Jeckell,* University of Illinois at Urbana Champaign, USA*; D. Barlaz,* University of Illinois Urbana Champaign, USA*; W. Huber, T. Houlahan, I. Haehnlein,* Starfire Industries, USA*; **Brian Jurczyk (bjurczyk@starfireindustries.com)**,* Starfire Industries LLC, USA*; D. Ruzic,* University of Illinois Urbana Champaign, USA

**Zachary Jeckell[1], David Barlaz[1], David Kapelyan[1], Wolfgang Huber[2], Thomas Houlahan[2] Ian Haehnlein[2], Brian Jurczyk[2], David N[1]. Ruzic[1]**

[1] Department of Nuclear, Radiological, and Plasma Engineering, University of Illinois at Urbana-Champaign, Urbana, IL

[2] Starfire Industries, Champaign, IL 61820

This work investigates the temporal evolution of both the electron energies as well as the ion energies during a variety of high-power impulse magnetron sputtering conditions utilizing the positive voltage reversal, known as the Positive Kick, including pulse conditions and pressures ultimately to better understand the physics needed to tailor future depositions. This work was carried out using the HIDEN PSM probe which allows for time resolved ion energy and q/m measurements enabling differentiation between working gas ions and target ions, as well as identification of higher ionization states.Sputtered neutral distribution, low-energy sputtered ions, ionized process gases and accelerated ions from the near-magnetron magnetic trap influence the deposited film based off the modified Thornton-Anders diagram for HiPIMS plasmas. The differentiation between charged species showcases the time evolution of the $M_{magentictrap}^+/Ar_{magentictrap}^+$ and the $M_{bulkplasma}^+/Ar_{bulkplasma}^+$ ratios which are useful for optimizing pulse conditions to efficiently transport metal ions to the substrate and to aid in the selection of process recipes with suitable ratios. The IEDF measurements are paired with time resolved EEDF data acquired from a custom sampling circuit capable of discretizing increments of the duration of one HiPIMS pulse with the Positive Kick. Performed by sweeping voltages, an array for I-V-T are formed that allows for the EEDF to be calculated for all times t. Commentary on plasma potential evolution and expansion is given in relation to the measured IEDF at different on-axis and off-axis locations via linear motion feedthrough.

2:20pm **B8-2-ThA-4 Metal-Ion Synchronized Reactive HiPIMS of AlScN for Piezoelectric Applications***, **Jyotish Patidar (jyotish.patidar@empa.ch)**, K. Thorwarth, T. Amelal, S. Zhuk, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The growing demand for highly integrated piezoelectric micro-electro-mechanical systems motivates the development of novel piezoelectric thin films. AlN in wurtzite structure is a promising candidate for a number of piezoelectric applications due to its high temperature stability and linear frequency response. Isovalent alloying of AlN with Sc is a successful strategy to enhance its piezoelectric coefficient. The heterostructural nature of the alloy system, however leads to low miscibility and a high degree of structural frustration for high Sc concentrations. Consequently, to achieve highly textured AlScN films using conventional magnetron sputtering high deposition temperatures or epitaxial stabilization are needed.

In this work, we present the development of a metal-ion synchronized reactive high-power impulse magnetron sputtering (MIS-HiPIMS) approach for AlScN that could lead to advantages over the current state-of-the-art. HiPIMS is rarely employed for the synthesis of electro-ceramics or semiconductors, since the highly energetic synthesis environment often results in a large number of bulk defects. However, MIS-HiPIMS enables the control of the incident ions kinetic energy while simultaneously reducing the ion-implantation and consequently the bulk-defect concentration in the film. [1]

The MIS-HiPIMS approach presented here is based on reactive HiPIMS sputtering of Al combined with direct current (DC) sputtering of Sc in Ar/N atmosphere. The ion-energy-distribution at the substrate is recorded using a time and energy-sensitive quadrupole mass spectrometer. Subsequently, the negative substrate bias is synchronized on the Al-rich part of the pulse. The HiPIMS pulse pattern, as well as the timing of the synchronization is varied to tailor the microstructure and texture of the AlN thin films. In addition, the non-equilibrium solubility of Sc in AlN is investigated as a function of the incident ion kinetic energy. The materials are fully characterized with respect to their phase constitution, structure and composition using state-of-the-art techniques including high-resolution X-ray diffraction, Rutherford backscattering spectroscopy, elastic recoil detection analysis as well as hard X-ray photoelectron spectroscopy. For selected samples, the transverse piezoelectric coefficients $e_{31,f}$ are compared.

A successful demonstration of a MIS-HiPIMS process for highly textured AlScN could enable the deposition on temperature sensitive substrates, such as polymer foils, but also the functionalization of surfaces with high aspect ratios and would enable a variety of exciting new applications.

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

2:40pm **B8-2-ThA-5 Selective Metal Ion Irradiation Using Bipolar HiPIMS: A New Route to Tailor Film Nanostructure and the Resulting Mechanical Properties***, **Ivan Fernandez (IVAN.FERNANDEZ@NANO4ENERGY.EU)**,* NANO4ENERGY SLNE, Spain

Metal ion irradiation combining HiPIMS discharges and pulsed bias synchronization has been demonstrated in the recent years to be a powerful method to achieve an accurate control on film nanostructure and phase control for the deposition of Transition Metal (TM) Nitrides [1]. It allows the deposition of films with optimum mechanical properties as well as reduced accumulated stress compared to the films deposited with gas-ion bombardment in Direct Current Magnetron Sputtering (DCMS). The selective attraction of metal ions at the substrate position optimizes the metal ion energy and momentum required during film growth.

In this presentation we extend this concept of selective metal ion irradiation by combining Bipolar HiPIMS with conventional DC magnetron sputtering operation and DC biasing. The concept of Bipolar HiPIMS was introduced some years ago by different groups and consist in applying a positive pulse with controlled pulse width and amplitude voltage after the conventional HiPIMS negative pulse [2]. This positive pulse allows the accurate acceleration of the positive metal ions towards the substrate, thus, promoting improved film properties such as reduced stress, higher film densification, improved mechanical properties - such as hardness or wear resistance- or better coverage of 3D complex parts. Moreover, it has been recently demonstrated that using bipolar HiPIMS with a substrate at ground potential (comparable to negative biased) results in a similar ion current profile as in conventional HiPIMS with a synchronized pulsed bias with the same delay and timing as the positive pulse [3].

This new coating process has been used for the deposition of hard, dense Transition Metal (TM) Nitrides commonly used in the metalworking industry. This manuscript studies the influence of Nb and Cr ion irradiation on the mechanical properties of TiAlN films, as they show a high large difference in mass. The description of the process as well as the resulting properties (microstructure, hardness, stress and texture) will be presented in this paper.

**References**:

[1] G. Greczynski et al.,). "*Metal-ion subplantation: A game changer for controllingnanostructure and phase formation during film growth by physical vapor deposition*". J.Appl. Phys. 127, 180901 (2020).

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

[3] R. Viloan et al., "*Copper thin films deposited using different ion acceleration strategies in HiPIMS*" *Surface* & Coatings Technology 422 (2021) 127487

3:00pm **B8-2-ThA-6 Ion Beam Sputter Deposition of Gallium Oxide Thin Films***, D. Kalanov, Y. Unutulmazsoy, **André Anders (andre.anders@iom-leipzig.de)**, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides unique opportunities to control the sputtering and growth processes and to study the correlations between them. The process provides intrinsic heating to the growing film by energetic particles, which can be used to tune various thin film properties, such as microstructure (incl. film density) and crystalline phase.

Gallium oxide is a material of high technological interest because of its unique properties, such as a wide bandgap and a high breakdown field strength. It enables the use of the material, for instance, in ultra-high-power electronics. To fully exploit the potential of gallium oxide thin films, high crystalline quality is needed. The IBSD is a process proven to be capable of growing films of such quality. In contrast to magnetron sputtering, IBSD does not have the unwanted highly energetic (several 100 eV) negative ion component, which causes defects.

The present report covers a systematic study of ion beam sputter deposition of gallium oxide thin films by investigating the fundamental correlations between (i) process parameters (sputtering geometry, ion species, ion energy, oxygen partial pressure), (ii) properties of secondary, sputtered and scattered particle species, and (iii) thin films.

The properties of secondary particles are studied by measuring energy distributions of ions, sputtered and scattered from the target. It is shown that changes in the sputtering geometry and energy of primary ions give control over the high-energy tail of the distribution. The composition of the film-forming flux is compared between processes with primary $Ar^+$ and $O_2^+$ beams, by varying the background oxygen pressure. Thin films are deposited for the same process configurations, and characterized regarding growth rate, density, roughness, crystallinity, and chemical composition. Presented systematic analysis may help to improve the process for depositing films of high crystalline quality at different substrate conditions (elevated temperatures, various substrate materials).

3:20pm **B8-2-ThA-7 The Promise of Data-Driven Methods for Diagnostics and Control of Plasma Interactions with Surfaces***, **Ali Mesbah (mesbah@berkeley.edu)**,* University of California Berkeley, USA **INVITED**

Data-driven methods can create unprecedented opportunities for real-time diagnostics and control of low-temperature plasmas (LTPs), which are increasingly used for treatment of heat and pressure sensitive (bio)materials in surface etching/functionalization, environmental, and biomedical applications. Some of the main challenges in modeling and control of LTP applications arise from their inherent complexity and variability. Firstly, the dynamics of LTPs are highly nonlinear and spatio-temporally distributed, which are hard to model due to their mechanistic complexity. Secondly, the LTP effects on complex surfaces are generally poorly understood. And thirdly, LTPs exhibit run-to-run variations and time-varying dynamics, whereby LTP treatments may be carried out under similar conditions, but yield different results. In this talk, we will demonstrate the usefulness of learning-based diagnostic and predictive control approaches for LTP treatment of complex surfaces. We will discuss how advanced machine learning and optimization methods can be leveraged to learn the complex plasma and surface dynamics in real-time, toward safe and high-performance LTP treatment of complex surfaces.

4:00pm **B8-2-ThA-9 Colored Random Noise of Cathodic Arcs: What Is It? Should We Care?***, **Andre Anders (andre.anders@iom-leipzig.de)**, K. Oh, D. Kalanov,* Leibniz Institute of Surface Engineering (IOM), Germany

Cathodic arcs are well established as the plasma source of a high-rate deposition technology, delivering hard and corrosion-resistant coatings, which are often based on nitrides but also on oxides, carbides, and multilayers and nanocomposites thereof.Through clever configurations of magnetic field, gas supply locations and choice of substrate location, the effects of arc plasma fluctuations or "noise" are mitigated and/or utilized. The physical origin of such noise lies in non-stationary cathode spot processes.Cathode spots, the small locations of current concentration and plasma generation, are known to be greatly affected by the chemical and microstructural properties of the cathode surface.Therefore, it should be expected that not all noise is equal but dependent on the cathode material and surface conditions.One can quantify the type of noise through their power spectral density and define a colored random noise (CRN) index, which lies between 1 (white noise) and 2 (brown noise), and it can even be greater than 2 when events are coupled due to strong feedbacks.In this contribution we summarize the findings, primarily based on FFT (fast Fourier transform) analysis of streak images of cathode spot plasma in vacuum, in argon, nitrogen, and oxygen.We show that the CRN index of cathode spots in vacuum is slightly larger than 2, indicating a general random walk behavior but with feedback, which is likely due to the influence of spot plasma on the ignition of the next spots.Argon as a process gas has no discernable influence on the CRN index, whereas nitrogen and especially oxygen reduce the index.This seems to be related to "easier" ignition of spots in the presence of a compound layer.A compound layer makes it easier for spots to ignite relatively far away from the original spot, but also to repeatedly ignite at about the same position.In the latter case, the spot may appear macroscopically stationary.The spot processes are orders of magnitude faster than the deposition duration and therefore, from a deposition point of view, the fluctuating plasma flow is generally considered with its “noise-averaged” properties.

## Hard Coatings and Vapor Deposition Technologies
## Room Golden State Ballroom - Session BP-ThP

## Hard Coatings and Vapor Deposition Technologies (Symposium B) Poster Session

**BP-ThP-1 Influence of Various Tool Steels and Cemented Carbide on Growth of PVD Hard Coatings**, *K. Bobzin, C. Kalscheuer,* ***Marco Carlet (carlet@iot.rwth-aachen.de)****, D. Hoffmann,* RWTH Aachen University, Germany

In order to pursue lightweight construction, components are manufactured with high-strength materials. On the tool side, this leads to increased tool wear, e.g. on the punches of fine blanking tools. For this reason, high-strength and tough tool steels produced by powder metallurgy (PM) are increasingly used. Furthermore, PVD hard coatings are applied to increase tool life. In this study, the influence of the alloying elements as well as the manufacturing method of tool steels, whether powder or melt metallurgical (MM), is investigated on the coating growth and morphology. For this purpose, PVD hard coatings, particular the nanocomposite TiAlCrSiN, was deposited on various tool steels using an industrial coating unit. In the current study, PM and MM high speed steels (HSS) as well as MM cold work, hot work and plastic mold steel substrates were taken into account. In addition, cemented carbides were used as reference substrate material. Moreover, the influence of a TiAlN interlayer on the growth of the nanocomposite TiAlCrSiN toplayer is analyzed. The deposition of a CrAlN coating was investigated as reference to the nanocomposite. Confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) were used to analyze the coating topography. The coating morphology was examined by SEM and the crystal structure by X-ray diffraction (XRD). The indentation hardness and modulus were determined by nanoindentation. It can be seen that the coating growth of TiAlCrSiN is strongly dependent on the manufacturing process of the tool steel. On the PM HSS, the TiAlCrSiN coating exhibits a significantly rougher topography compared to all investigated melt metallurgical steel substrates and cemented carbide. Furthermore, it is evident in cross-sectional micrographs that the otherwise fine-crystalline, homogeneous morphology of the TiAlCrSiN coatings from the PM HSS substrate material exhibit cone-shaped grains. In addition to the nanocomposite TiAlCrSiN, the coating system CrAlN was deposited. Compared to the TiAlCrSiN nanocomposite, the CrAlN coating reveals no significant differences depending on the substrate materials. The findings can support the selection of suitable combinations of substrate materials and PVD hard coatings to improve tool life. In this work, it was shown that the coating growth of the PVD nanocomposite TiAlCrSiN is significantly dependent on the substrate material, in contrast to the ternary coating system CrAlN. Furthermore, the substrate influence of the coating growth cannot be suppressed by the prior application of an interlayer.

**BP-ThP-2 Influence of Deposition Parameters on Chemistry, Structure and Mechanical Properties of Vanadium Carbide Thin Films**, ***Barbara Schmid (barbara.schmid@tuwien.ac.at)****, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria*; E. Halwax,* TU Wien, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Cubic transition metal carbides generally exhibit high melting points as well as high hardness, which makes them especially interesting for the application as protective coatings. Vanadium carbide (VC) is not an exception to this trend with a melting point above 3000 K and up to 40 GPa in hardness.

However, the non-reactive synthesis of $VC_x$ via DC magnetron sputtering is rare. The variation of deposition parameters such as working gas pressure (here, Ar), gas flow and sputtering power density applied to a stoichiometric VC compound target can result in drastically different thin film materials.

Varying these deposition parameters allowed to synthesise $VC_x$ thin films with different chemistry, microstructure, as well as indentation hardness and modulus.

These material characteristics were investigated using electron probe microanalysis, X-ray diffraction, scanning and transmission electron microscopy, and nanoindentation. The obtained variation in lattice parameter and indentation modulus have been compared to density functional theory data for stoichiometric and non-stoichiometric $VC_x$. This allowed us to draw a clear picture of the deposition–structure–property relations for $VC_x$.

**BP-ThP-3 Influence of High-Power Pulse Magnetron Sputtering Tantalum Nitride Film Characteristics and Protection Behavior**, ***Yung-Chi Chang (vicky5062823@gmail.com)****, S. Hsu, C. Tu, D. Hong, F. Wu,* National United University, Taiwan

Nowadays quality requirements, such as higher hardness, wear resistance, sufficient toughness, adhesion strength and so ow, are focused for transition metal nitride, TMN, hard coating field. The selection of coating among various possible materials and related manufacturing processes is quite a challenge and requires careful consideration on the functions in the development systems. Among TMNs, with high hardness excellent tribological behavior, thermal and electrical performance, TaN. Has been chosen as a good protective layer for working components in versatile applications. In this study, and the enysfalline and metastable amorphous phase of tantalum nitride are fabricated using radio frequency, r.f., reactive magnetron sputtering technique. A multilayer film formed by alternating stacking of the above mentioned crystalline/amorphous layers is deposited through input power and gas inlet control. The adhesion of the tantalum nitride film is studied and compared with controlling parameters of interlayers with changes thickness, r.f. power, and high intensity power plasma. Compared with r.f., the single-layer film has a compact structure due to the higher energy of plasma power. The higher energy deposition, improves the crystallinity, and lead to a larger grain size. At the same time, the surface roughness of the film is reduced, and the hardness and Young's modulus are improved. The multilayer film is manufactured through the crystalline/amorphous stacking, the hardness and Young's modulus and wear resistance are superior than those of the single-layer film.

**Keywords :** HiPIMS, sputtering, TaN, multilayer

**BP-ThP-5 Rotating Spokes in Reactive HiPIMS Process Measured by Spatially Resolved OES**, ***Marta Šlapanská (slapanska@physics.muni.cz)****, M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as spokes, spontaneously appearing in E × B magnetised plasma discharges, such as Hall thruster and high power impulse magnetron sputtering (HiPIMS) discharge, have been thoroughly investigated mainly in the non-reactive atmosphere under many different experimental parameters. Among other things, it has been discovered that the presence of spokes enhanced the transport of sputtered species from the target to the substrate, leading to a much more energy-efficient HiPIMS process. Due to the reactive processes being widely used in industry, there is an effort to find out more information about spokes in reactive atmospheres and their effect on the deposition process and the transport of sputtered species at those conditions. The use of spatially resolved optical emission spectroscopy in a single-shot mode is one of the possibilities for a deeper understanding of the spokes.

In this contribution, the non-invasive spatial-resolved OES of the spoke was conducted in reactive HiPIMS discharge. The HiPIMS pulses were 100 µs long with a repetition rate of 5 Hz. The 3-inch titanium target, argon as working gas, and nitrogen as reactive gas were utilised. The constant total pressure was set to 1.0 Pa. Different reactive gas flows were applied to measure the properties of spokes in both metallic and poisoned modes.

The fast photodiode and the Langmuir probe were used to capture and determine the position of the passing spoke. The signals from the photodiode and the Langmuir probe were synchronised with the spectrometer and an ICCD camera. The ICCD camera possesses a dual-image-feature mode, which allows capturing two consecutive images with only a 1.5 µs delay between them. It enabled to determine the spoke propagation velocity. The single-shot measurements ensured that one waveform and one double image were acquired simultaneously from a single HiPIMS pulse for each spectrum. The spatial-resolved emissions of argon, nitrogen, and titanium atoms and ions spectral lines were investigated within the spoke passing by the probes.

**BP-ThP-6 Sputtered Amorphous Carbon Interlayers for Homogeneous Lithium Plating and Stripping in Solid-State Batteries**, *T. Amelal, M. Futscher, J. Patidar, A. Müller, A. Aribia, Y. Romanyuk,* ***Sebastian Siol (sebastian.siol@empa.ch)****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Recently, it was shown that the introduction of an amorphous Ag-C composite into solid-state batteries can lead to increased long-term stability.[1] However, the reason why the interlayer shows this advantageous behavior is not well understood.

We deposit thin carbon interlayers between current collector and solid electrolyte by two physical vapor (PVD) deposition techniques. By using direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) the kinetic energy of the incident ions can be tuned over a wide range. This allows us to independently vary the density, conductivity, and microstructure of the carbon interlayers.

We show the influence of different material properties of the carbon interlayer on lithium plating and stripping using copper as the current collector and lithium phosphorus oxynitride (LiPON) as the solid electrolyte. We find that the amorphous carbon interlayer reduces the overpotential for lithium plating and increases the critical current density for lithium plating and stripping up to 8 mA/cm$^2$. We further show that the initial lithium loss due to interphase formation and the critical current density strongly depends on the morphology and the electrical conductivity of the carbon interlayers. Finally, we investigate the role of Ag by introducing different amounts of Ag into the amorphous carbon interlayers. Our results shed light on the key factors that enable homogeneous lithium plating and thus the use of lithium metal in solid-state batteries.

[1] Y.-G. Lee et al. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. Nat. Energy 5, 299–308 (2020)

**BP-ThP-9 e-Poster Presentation: Effect of Precursor Interactions on Film Growth Rate and Properties in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Alloy Films***, Kinsey Canova (kcanova2@illinois.edu), S. Shrivastav, C. Romnes, D. Yun, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign, USA

$HfB_2$ coatings impart excellent surface hardness and low sliding friction, but the service life in air at moderate temperatures is reduced by the formation of boron oxide, which is lost to evaporation.Addition of Al is one possible route towards oxidation resistance, if the surface can form an $Al_2O_3$ surface layer that impedes further oxygen transport. (We report oxidation studies elsewhere in this conference.)

We use low temperature chemical vapor deposition (CVD) to grow $Hf_{1-x}Al_xB_2$ alloy films from two precursors, $Hf(BH_4)_4$ and $Me_3N$-$AlH_3$ (TMAA).We show that TMAA flux accelerates the reaction rate of the $Hf(BH_4)_4$, but that a flux of the TMAA byproducts, including $Me_3N$, inhibits the growth rate of $HfB_2$. In the former case, we will present evidence towards which chemistry is involved in the growth acceleration, whether it be precursor-precursor interaction or another precursor-byproduct interaction; high byproduct pressures for these experiments can be sustained within a deep trench or under slow pumping.These results imply a feedback loop in the film growth rate, where the accelerated deposition due to TMAA is opposed by a progressive increase in the $Me_3N$ inhibitor pressure, which may dampen the acceleration effect.

We uncouple these interactions using two distinct CVD chambers.The conventional CVD chamber is rapidly pumped, and the alloy growth rate is found to be a steady-state function of the precursor fluxes and substrate temperature (surface reaction rates).The other CVD chamber is unpumped (static), which allows the use of very high precursor pressures to amplify the effects of precursors and byproducts. We interpret these results in the context of accelerating and inhibiting interactions that we have measured in other chemistries, and we then show how the growth rate affects film stability, density, and composition.

**BP-ThP-13 Biocompatibility Evaluation of nc-TiC/a-C:H Nanocomposite Diamond-like Carbon Coatings: Effect of Carbon Content***, B. Lou,* Chang Gung University, Taiwan*; Y. Hsiao, L. Chang,* Ming Chi University of Technology, Taiwan*; M. Ger,* National Defense University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

The nc-TiC/a-C:H nanocomposite diamond like carbon (DLC) coating has been studied due to its good mechanical properties, corrosion resistance and biocompatibility. In this work, four nc-TiC/a-C:H coatings with different carbon contents were grown by a superimposed high power impulse magnetron sputtering (HiPIMS) and medium frequency (MF) coating system utilizing a plasma emission monitoring feedback control. The target poisoning ratio ranging from 80% to 95% and the gas flow rate of acetylene were controlled by a plasma emission monitoring (PEM) system. The chemical composition, crystallinity, hardness, wear resistance, adhesion and surface roughness values of coatings were investigated. Furthermore, the in vitro biocompatibility of MG 63 human osteoblast-like cells and the migration ability of HaCaT keratinocyte cell on selected DLC coatings were also evaluated, respectively. The sensitization test of DLC coatings was conducted by the in vivo animal test using the subcutaneous implantation of DLC coated 316L SS disks on the back of SD rats. The pathological changes and inflammation of tissues after the subcutaneous implantation were explored.

In this work, the hardness and elastic modulus of four DLC coatings fabricated from 80% to 95% target poisoning ratios were higher than 14 GPa and 120 GPa, respectively. The wear rates of four DLC coatings were all lower than $10^{-6}$mm$^3$/N/m with coefficient of friction values less than 0.25. Meanwhile, very good cell adhesion, free of toxicity, good cell migration (**Fig.1**) and proliferation ability, and free of sensitization in animal body were achieved for two nc-TiC/a-C:H DLC films (TiC80 and TiC90) deposited at 80% and 90% target poisoning ratios, which can be further deposited on the 3-dimensional surfaces of surgical instrument, such as surgical blades and xysters.

**Keywords:** nc-TiC/a-C:H nanocomposite diamond like carbon coating, HiPIMS, in vitro MG63 cell test, in vitro cell migration test, subcutaneous implantation in vivo animal test

**BP-ThP-14 TiN/TaN Superlattice Films Improved by Interfacial Dopings***, **Zecui Gao (zecui.gao@tuwien.ac.at)**, N. Koutná, J. Buchinger, T. Wojcika, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The superlattice architecture, characterized by different nanolayered materials that are alternatively and coherently stacked, allows to stabilize metastable phases and optimize typically antagonistic properties of ceramic coating materials, such as hardness and fracture toughness. As rocksalt-structured TiN and $Ta_{0.5}N$ (featuring metal vacancies) have significant elastic differences, they promise a pronounced superlattice (SL) effect. TiN/$Ta_xN$ films were thus deposited with a ~5 nm bilayer period by DC reactive magnetron sputtering. As expected, the SLs show a higher hardness (32.9 GPa) than monolithic TaxN (30.1 GPa) and TiN (28.5 GPa), with an intermediate indentation modulus of 425.0 GPa ($Ta_{0.5}N$ 379.9 GPa and TiN 529.7 GPa).

As established by previous studies, the improved hardness is partly due to the hindrance of dislocation movement across interfaces. Thus, we implement atomic quantities of Si/C/B in between all layers of TiN/$Ta_xN$ SLs to further enhance the interlayer boundaries. All of the doped superlattice coatings show exceptional hardness properties and improved epitaxial growth on MgO compared to the doping-free SL. Especially, the TiN/Si/$Ta_xN$ film produced the highest hardness of ~40.7 GPa, and the TiN/B/$Ta_xN$ film produced the highest fracture toughness of ~4.11 MPaÖm. Overall, they possess promising hardness and Fracture toughness compared favorably to their monolithic building blocks and TiN/$Ta_xN$ SL.

**BP-ThP-16 Fifty Shades of TiN: How Deposition Conditions Influence the Growth Morphology and Thereby Hardness and Especially Fracture Toughness***, **Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)**, R. Hahn, B. Hajas, A. Kirnbauer,* TU Wien, Austria

About fifty different TiN coatings were prepared by reactive and non-reactive magnetron sputtering, as well as by reactive cathodic arc evaporation. In addition to vary between these three individual deposition techniques, we also individually varied the substrate temperature, partial pressures, substrates (e.g., Si(100), MgO(100)(110)(111), sapphire), substrate-to-target distance, as well as bias potential. The fracture toughness of these individually prepared TiN coatings was evaluated from micromechanical bending tests (inside a FEGSEM) of free-standing cantilevers. The individual deposition techniques and conditions result in either pronounced columnar or rather dense growth morphologies, with open or compact column and grain boundary regions, or epitaxially grown single-crystals. Due to these variations in growth morphology, the hardness (obtained by nanoindentation) of TiN varied between 15.9 and 33.9 GPa and their fracture toughness between 0.6 and 2.9 MPa√m.

We will have a closer look on the overall correlation between growth morphologies, preferred orientation, residual stresses, and mechanical properties. But also, how a subsequent vacuum annealing treatment (to mimic application at elevated temperatures) influences these characteristics.

# Author Index

## Bold page numbers indicate presenter

# Author Index