

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

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

**Moderators:** Dr. Naureen Ghafoor, Linköping University, Sweden, Dr. Marcus Günther, Robert Bosch GmbH, Germany, Dr. Fan-Yi Ouyang, National Tsing Hua University, Taiwan

#### 10:00am B4-1-MoM-1 Effects of Al and Nd additions and Annealing on Microstructures and Mechanical Properties of CoCrNi Medium Entropy Alloy Films, *YI-LING WU, C. Hsueh*, National Taiwan University, Taiwan

CoCrNi medium entropy alloys have attracted great attention on account of the outstanding strength and ductility. It was reported that the moderate amount of Al addition could enhance the mechanical properties resulting from the solid solution strengthening and the phase change from FCC to BCC. Also, with the negative mixing enthalpies, doping rare earth elements could easily combine with the constituent elements in CoCrNi to form precipitates and result in precipitation hardening. To achieve multiple strengthenings, (CoCrNi)<sub>92.7-x</sub>Al<sub>7.3</sub>Nd<sub>x</sub> ( $x = 0, 0.2, 0.5, 1.0, 1.7, 2.6, 3.5$ ) medium entropy alloy films (MEAFs) were fabricated using magnetron co-sputtering deposition by controlling the sputtering power  $P_{Nd}$  applied on the Nd target in the present study. With the fixed sputtering deposition time of 40 min, the film thickness was  $\sim 1.86 \mu\text{m}$  for the Nd-free film, and it decreased initially to  $\sim 1.65 \text{ nm}$  with the increasing  $P_{Nd}$  and then increased to  $\sim 1.91 \text{ nm}$  with the further increase in  $P_{Nd}$  which could be explained by the larger atomic radius and atomic weight of Nd. The XRD revealed that the as-deposited MEAFs changed from FCC to a fully amorphous structure with the increasing Nd content. Using nanoindentation, the maximum hardness of 10.15 GPa was obtained at  $x=0.5$ , while the minimum hardness of 8.04 GPa was obtained at  $x=3.5$ . However, after annealing at 773K for 10 min, both XRD and TEM showed the presence of HCP and L12 phases in the films, and the hardness increased from 10.27 GPa at  $x=0$  to 11.45 GPa at  $x=3.5$ . Because of the fast cooling rate during sputtering deposition, precipitates could not readily be formed in the as-deposited Al- and Nd-doped CoCrNi MEAFs which, in turn, would result in limited strengthening. However, post-annealing of the films prompted the formation of dual-phase precipitates to result in multiple strengthenings.

#### 10:20am B4-1-MoM-2 Microstructures and Mechanical Properties of (CoCrNi)<sub>100-x-y</sub>Si<sub>x</sub>Nd<sub>y</sub> Medium Entropy Alloy Films, *Hui-Wen Peng, C. Hsueh*, National Taiwan University, Taiwan

A series of (CoCrNi)<sub>100-x-y</sub>Si<sub>x</sub>Nd<sub>y</sub> medium entropy alloy films (MEAFs) was deposited on p-type (100) silicon substrates by direct current (DC) and radio frequency (RF) magnetron co-sputtering of equiatomic CoCrNi alloy target, (CoCrNi)<sub>90</sub>Nd<sub>10</sub> alloy target and Si target. The powers applied on the CoCrNi and Si target were respectively fixed at DC 30 W and RF 20 W, while RF powers from 0 to 450 W were applied on the (CoCrNi)<sub>90</sub>Nd<sub>10</sub> target, respectively, to tailor the Nd content. All the films were deposited for 90 min without external substrate bias and heating. The chemical compositions of MEAFs determined by electron probe microanalyzer (EPMA) revealed that the Nd content of the films increased as sputtering power of the (CoCrNi)<sub>90</sub>Nd<sub>10</sub> target increased from 0 to 450 W. With the increasing Nd content, a transition from single FCC phase to the coexistence of FCC, HCP CoCrNi and NdNi<sub>5</sub> phases was observed in X-ray diffractometer (XRD) and transmission electron microscope (TEM) diffraction patterns. The scanning electron microscope (SEM) and TEM images showed the refined columnar grains due to the Nd addition, and the film thickness increased from 1.09 to 2.60  $\mu\text{m}$  with the increasing Nd content. The hardness ( $H$ ) and reduced modulus ( $E_r$ ) were characterized using the nanoindenter. The  $H$  showed the initial increase with Nd addition via the solid solution strengthening, reached the maxima at Si<sub>0.58</sub>Nd<sub>5.59</sub> film due to the grain refinement and precipitation strengthening. However, the hardness decreased at Si<sub>0.58</sub>Nd<sub>6.06</sub> film resulting from the inverse Hall-Petch effect.

#### 10:40am B4-1-MoM-3 Recent Developments Towards Reliable X-Ray Photoelectron Spectroscopy Analyses of Thin Films, *Grzegorz (Greg) Greczynski, L. Hultman*, Linköping Univ., IFM, Thin Film Physics Div., Sweden

The number of papers in peer-reviewed journals where X-ray photoelectron spectroscopy (XPS) analysis is employed increased by a factor of 40 during last 40 years, to the level of 12000 articles published in

2021 alone. This makes XPS the most common – and for many indispensable – method for characterization of surface chemistry. From a concern within the surface science community that this rapid increase in the number of XPS studies is accompanied by a decrease of work quality,[1] we reviewed efforts towards improving correct use of the technique for reliability of data. Several sources of errors have thus been identified, including an unreliable charge referencing of the binding energy (BE) scale,[2] unrecognized sputter damage,[3] and neglected effects of sample storage.[4] By performing experiments on large sets of thin film samples such as Group IVB-VIB transition metal borides, carbides, nitrides, and oxides, we demonstrated disconcerting failure of the most popular referencing method based on the C 1s peak of adventitious carbon.[2] We appeal that it should no longer be used, with science reproducibility at stake. Furthermore, the extent of spectral changes following Ar<sup>+</sup> etching, commonly applied to remove surface contaminants, was evaluated using reference spectra from *in-situ* capped samples.[3] We showed that changes greatly depend on the type of material system: from very subtle effects in the case of Group IVB TM carbides to a complete modification of spectral appearance for IVB-TM oxides. The effects of sample storage on XPS spectra were evaluated for commonly used storage environments such as office shelf, polypropylene wafer carrier, polystyrene box, cellulose/polyester wipers or sealed polyethylene bag.[4] Results revealed significant differences between the various storage types and provide guidance for planning all sorts of studies including those that employ Ar<sup>+</sup> ion etch prior to analyses. Examples illustrating each of the above issues will be discussed during the talk and several principled practices offered.

[1] G.H. Major, et al. *J. Vac. Sci. Technol. A* 38, 061204 (2020)

[2] G. Greczynski and L. Hultman, *Angew. Chem.Int. Ed.* 59 (2020) 5002

[3] G. Greczynski and L. Hultman, *Applied Surface Science* 542 (2021)148599

[4] G. Greczynski and L. Hultman, *Vacuum* 205 (2022) 111463

#### 11:20am B4-1-MoM-5 Effect of Nitrogen Flow Rate on the Microstructure and Mechanical Properties of (V,Mo)N Thin Films, *Yiqun Feng*, National Tsing Hua University, Taiwan; *T. Chung*, National Yang Ming Chiao Tung University, Taiwan; *J. Huang*, National Tsing Hua University, Taiwan

(V,Mo)N is considered to be a promising coating material for tribological applications, owing to having high hardness and ductility deriving from its extraordinary metal-nitrogen bonding environment [1]; however, the coating is lack of relevant mechanical properties and fracture toughness data. The objective of this study was to investigate the effect of nitrogen flow rate on the microstructure and mechanical properties of (V,Mo)N nanocrystalline thin films. Five compositions of (V,Mo)N thin films were deposited by dc-unbalanced magnetron sputtering with various nitrogen flow rate. The N/Metal ratios increased from 0.47 to 0.85 with increasing nitrogen flow rate from 1.2 to 6.0 sccm. The texture of the thin films changed from (200) to random texture with increasing nitrogen flow rate. (V,Mo)N thin film deposited at the lowest nitrogen flow rate (D12) was found to contain multiple phases by transmission electron microscopy, and single phase (V,Mo)N thin films were obtained as nitrogen flow rate was above 2.5 sccm. Specimen D12 possessed the largest hardness owing to the multiphase structure, where the Mo metal phase may retard the crack propagation, thereby increasing the film hardness. Fracture toughness ( $G_c$ ) of the thin films was evaluated using internal energy-induced cracking method [2]. The fracture morphology showed that the cracks initiated in the Si substrate and then propagated into the film, implying the high toughness of (V,Mo)N thin films. The resultant  $G_c$  of the (V,Mo)N thin films, ranging from 20.9 to 30.1 J/m<sup>2</sup>, linearly increased with increasing nitrogen

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content. The results showed  $G_c$  of the (V,Mo)N thin films was more significantly affected by nitrogen content than by texture. The higher  $G_c$  for the (V,Mo)N thin films than that of VN and TiN thin films is consistent with the theoretical predictions.

11:40am **B4-1-MoM-6 In Situ Stress Evolution in Ti/Pt Multilayers During Magnetron Sputter Deposition**, *Naureen Ghafoor, M. Lorentzon, S. Bairagi, P. Sandstrom, J. Birch*, Linköping Univ., IFM, Thin Film Physics Div., Sweden

Control of stress evolution during film growth is crucial in many coating applications and requires *in situ* analysis. One such product is a micron-thick free standing biocompatible Ti/Pt multilayer film used as diaphragms for implantable inner ear microphones [[1] [#\_ftn1] ]. For a given size and thickness the diaphragm compliance and hence, the deflection can only be maximized if the intrinsic stresses in the thin film structure are zero. In this work, we have measured intrinsic stresses based on dynamic wafer curvature measurement using multiple laser beam deflection optical Stress measurements. The instantaneous stress state at any stage of Ti and Pt layer's growth and the final stress of a micron-thick film allows for direct feedback of the effects of deposition parameters. We investigated the influence of process pressure, target-to-substrate distance, target power, and influence of applied bias to the substrate- while keeping a low temperature- on the residual stress in Ti single-layered and Ti/Pt multilayered films deposited on double-sided polished 150 mm thick Si(100) wafers using magnetron sputtering technique [[2] [#\_ftn2],[3] [#\_ftn3]]. The example of stress evolution during the growth of a Ti single layer compared to oscillating stress state during Ti/Pt multilayer is shown in the figure. An excellent finding here is that tuning the layer thickness ratios in Ti/Pt multilayers particularly at the onset of growth up to 100 nm can be used to engineer the final stress state between compressive and tensile. This is attributed to Ti growing as type I (low mobility) generating tensile stress while Pt grows as type II (high mobility) generating compressive stress, at room temperature. The residual stress is also compared with post-deposition XRD wafer curvature measurement technique and differences along with the structural characterization of the films will be presented at the conference.

[[1]] L. Prochazka, ..., F. Pfiffner, *Sensors* 4487, 19 (2019), <https://hearmore.cochlear.com/>

[[2]] D. E. Ibrahim, Master Thesis, LiU-IFM/LiTH-EX-A-20/3821-SE, (2020)-

[[3]] Prochazka, L. *N.Ghafoor, et al.* Novel Fabrication Technology for Clamped Micron-Thick Titanium Diaphragms Used for the Packaging of an Implantable MEMS Acoustic Transducer. *Micromachines* **13**, 74 (2021).

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country C - Session B2-MoA

#### CVD Coatings and Technologies

**Moderators:** Prof. Raphaël Boichot, Grenoble-INP/CNRS, France, Dr. Hiroki Kondo, Nagoya University, Japan

**1:40pm B2-MoA-1 Si and SiC-based CVD Coatings for High Temperature Structural Applications**, A. Le Doze, P. Drieux, Laboratoire des Composites Thermostructuraux - CNRS, France; S. Jacques, Laboratoire de Composites Thermostructuraux - CNRS, France; G. Couégnat, **Georges Chollon**, Laboratoire des Composites Thermostructuraux - CNRS, France **INVITED**  
Thermal chemical vapor deposition (CVD) is well suited to produce high-purity, high-crystallinity films compatible with high temperature structural applications. A good example of such structural coatings is the silicon carbide matrix of ceramic matrix composites (CMCs). However, in SiC/SiC composites, the role of the matrix in the overall mechanical behavior appears to be minor compared to that of the fibers or the interphase. Yet, intrinsically, the CVD coating can exhibit all these qualities. The key is to adjust the process parameters to obtain an appropriate composition and microstructure. The evaluation of the mechanical properties of the coating itself must also be performed using specific tests. These two aspects will be developed in the presentation through two examples.

The first one is a high-strength, gas-tight CVD SiC sheath, to complete the composite structure of a nuclear fuel claddings. Long, free standing SiC tubes were prepared at atmospheric pressure using  $\text{CH}_3\text{SiHCl}_2/\text{C}_3\text{H}_6/\text{H}_2$  mixtures, in a fast, original, and near net shape process. Sliding the heating system along the tubular substrate allowed the continuous deposition of long and thick CVD SiC sheaths. Their composition, microstructure and surface morphology were analyzed in details. C-ring specimens were cut from the tubes and submitted to high temperature compressive tests. The deposition rate, Si/C atomic ratio, crystalline state and surface roughness of the CVD-SiC tubes are related to the gas phase reactions. Their thermomechanical properties can be improved by adjusting the through-thickness composition gradient using a proper precursor mixture.

The second example is a CVD silicon coating used as the bond coat (BC) of an environmental barrier coating on a CMC. In use, the BC may oxidize, which can cause local stresses and eventually damages. Centrifugal loads can also generate some creep deformation of the rotating parts. It is thus crucial to control the creep behavior of the BC, and hence its microstructure, through the CVD process. The deposition of polycrystalline silicon from  $\text{SiHCl}_3/\text{H}_2$  was explored and a selection of coatings were prepared on fine carbon fiber substrates for testing. The morphology and microstructure of the deposits were investigated by SEM and EBSD, and the creep properties by 3-point bending. Several microstructures were obtained by various combinations of CVD conditions and thermal annealing. Different responses of the silicon coatings to mechanical stresses have been measured, illustrating different deformation mechanisms.

**2:20pm B2-MoA-3 Influence of Bilayer Periodicity on Microstructure, Residual Stress and Mechanical Properties of CVD TiN/TiB<sub>2</sub> Multilayer Coatings**, Michael Tkadletz, Montanuniversität Leoben, Austria; A. Lechner, B. Sartory, Materials Center Leoben Forschung GmbH, Austria; C. Czettel, CERATIZIT Austria GmbH, Austria; N. Schalk, Montanuniversität Leoben, Austria

Chemical vapor deposited (CVD) TiN and TiB<sub>2</sub> are quite different materials, but both are frequently utilized as wear resistant hard coatings. CVD TiN exhibits a comparatively large grain size in the  $\mu\text{m}$  range, tensile residual stress and a moderate hardness. CVD TiB<sub>2</sub> in contrast is usually characterized by a nanocrystalline microstructure and high compressive residual stress accompanied by a high hardness. In order to investigate the interaction of such different materials, CVD TiN and TiB<sub>2</sub> were combined in two multilayer coatings with different bilayer periodicities of  $\sim 100$  and  $\sim 200$  nm. Subsequently, the influence of the multilayer architecture on the evolving microstructure and grain size was investigated by means of scanning transmission electron microscopy, energy dispersive X-ray spectroscopy and transmission Kikuchi diffraction. X-ray diffraction provided insight into the phase composition and evolution of residual stress state and magnitude of the individual layers. In addition, to clarify whether B diffusion between the different layers takes place during deposition, atom probe tomography was applied to the multilayer coating with lower bilayer periodicity. The microstructural and chemical

investigations were accompanied by cross-sectional hardness mappings via nanoindentation with high lateral resolution and micromechanical bending tests. The study was complemented by experiments on reference single layers of both materials which allow a thorough conclusion about the effects and changes provoked by the implemented multilayer architecture at different length scales.

**2:40pm B2-MoA-4 Effect of the Substrate Treatment on the Microstructure of CVD Ti(C,N)/Al<sub>2</sub>O<sub>3</sub> Hard Coatings**, Christiane Wächtler, C. Wüstefeld, TU Bergakademie Freiberg, Germany; M. Šima, J. Píknar, Dormer Pramet, Czechia; D. Rafaja, TU Bergakademie Freiberg, Germany  
Although the use of protective Ti(C,N)/Al<sub>2</sub>O<sub>3</sub> coatings produced by chemical vapour deposition (CVD) on cemented carbide (WC-Co) substrates is the state of the art in the high-speed metal cutting, the effect of the substrate treatment on the microstructure and properties of such coatings is not fully understood yet. In this contribution, the role of the size of the tungsten carbide grains (1.9  $\mu\text{m}$  and 0.7  $\mu\text{m}$ , respectively) and the substrate treatment (as-sintered, wet blasted, ground or polished) was systematically investigated for a constant amount of the cobalt binder (10 wt.%) in the cemented carbide. The hard coatings with different architectures, i.e., the TiC<sub>0.6</sub>N<sub>0.4</sub> monolayers and complete TiC<sub>0.6</sub>N<sub>0.4</sub>/Al<sub>2</sub>O<sub>3</sub> stacks, were deposited using the same parameters of the CVD process.

The microstructure analyses carried out using scanning electron microscopy with electron backscatter diffraction, transmission electron microscopy, laboratory X-ray diffraction and nanobeam synchrotron diffraction revealed that the kind of the substrate treatment strongly influences the preferred orientation and the lateral size of the grains in the coatings, as well as the residual stress in both phases (fcc-Ti(C,N) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). Finally, the adhesion of the coatings to the substrate was quantified using scratch tests. The strongest preferred orientation of crystallites, which was {211} in fcc-Ti(C,N) and {001} in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, developed in coatings with consistently narrow grains. The texture was always weakened, when coarse Ti(C,N) and/or Al<sub>2</sub>O<sub>3</sub> grains grew in the coatings in addition to the narrow grains. The dependence of the texture degree and the grain size on the substrate treatment was also observed for the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer, although the bonding layer between fcc-Ti(C,N) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> consisted of very small crystallites having no pronounced preferred orientation. The comparison of the single-layer Ti(C,N) coatings with the Ti(C,N)/Al<sub>2</sub>O<sub>3</sub> stacks helped us to understand the effect of the additional thermal exposure of the samples during the Al<sub>2</sub>O<sub>3</sub> deposition on the microstructure of the Ti(C,N) layer.

The results of this study emphasize that the surface condition of cemented carbide substrates needs to be considered as it has a clear impact on the microstructure formation of the Ti(C,N)/Al<sub>2</sub>O<sub>3</sub> coatings produced in CVD processes.

**3:00pm B2-MoA-5 Novel ZrB<sub>2</sub> and HfB<sub>2</sub> Metaldiboride Coatings by LPCVD**, Mandy Höhn, M. Krug, B. Matthey, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

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

In this work the preparation of metal diboride coatings of ZrB<sub>2</sub> and HfB<sub>2</sub> by CVD is described. A LPCVD process using MeCl<sub>4</sub> (Me = Zr or Hf), BCl<sub>3</sub>, H<sub>2</sub> and Ar is applied. At deposition temperatures between 800°C and 1000°C diboride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour. The deposited diboride layers show well defined crystallites with a high hardness up to 32 GPa for ZrB<sub>2</sub> and 38 GPa for HfB<sub>2</sub>. In dependence of substrate temperature and precursor ratio layers with different textured crystalline structure were obtained with different deposition rates. Phase composition and structure were examined using SEM and EDX-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 350 MPa and 600 MPa.

A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In wear tests a high performance of the CVD diboride coatings was observed. HfB<sub>2</sub> coated inserts showed a higher lifetime in comparison with state-of-the-art CVD- and PVD-TiB<sub>2</sub> coatings in face-milling TiAl6V4.

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3:20pm **B2-MoA-6 Diamond Coatings on Cutting Tools Applied to Super-Hard Workpiece Materials**, *Michael Woda*, CemeCon AG, Germany; *J. Fuentes*, Hufschmied Zerspanungssysteme GmbH, Germany; *W. Puetz*, *M. Wegh*, *C. Schiffers*, *S. Bolz*, *O. Lemmer*, CemeCon AG, Germany

Thin film Diamond as pure sp<sup>3</sup> bonded crystalline carbon is able to significantly improve cutting tool wear performance. Diamond coatings are typically deposited by the means of hot filament CVD processes on an industrial scale nowadays. The basic principle of the corresponding deposition technology and its resulting diamond coating properties are introduced in this presentation.

When applying these diamond thin films to cutting tools containing a cemented carbide substrate and possessing complex geometries, the machining of a large set of highly abrasive work piece materials can be enabled. These materials include Carbon Fiber Reinforced Plastics (CFRP), Ceramic Matrix Composites (CMC), zirconium oxide ceramics, hypereutectic aluminum silicon alloys, graphite or even cemented carbide. This work presents some of the latest results of selected case studies revealing the benefits of CVD diamond coatings at cutting operations on these very challenging and super-hard work piece materials.

3:40pm **B2-MoA-7 Study on Small-Volume and Flow-Type Hard DLC Film Process Using Substrate-Surrounding Microwave Plasma**, *Hiroyuki Kousaka*, Gifu University, Japan

INVITED

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction, the application of DLC (Diamond-Like Carbon) is spreading gradually and steadily. Plasma CVD is one of the promising manufacturing methods of DLC due to its excellent capability for coating 3-dimensional shapes; however, its coating speed is typically not so high, ~1 μm/h due to the use of low-density ( $n_e \sim 10^8\text{-}10^{10} \text{ cm}^{-3}$ ) plasma with DC or RF discharge. At such a deposition rate, batch processing of a large number of parts (substrates) is essential for cost reduction. However, in the coating of machine parts, flow processing of a small number of parts may be desirable. To achieve this, it is necessary to coat one to several parts at a drastically increased coating speed.

For further increasing the coating speed of DLC, we have proposed an ultra-high-speed DLC coating at over 100 μm/h employing much higher-density plasma ( $n_e \sim 10^{11}\text{-}10^{13} \text{ cm}^{-3}$ ), which is sustained by microwave propagation along plasma-sheath interface. In this work, we investigated the effect of atomic composition of DLC film on the deposition rate and hardness in such ultra-high-speed DLC coating. Si-containing a-C:H films (one type of DLC) were deposited on steel substrates by different 2 methods: DC plasma and microwave-excited high-density near plasma, or our newly proposed method, where the gas composition of Ar, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and TMS, and the duty ratio of microwave and substrate bias were changed. Note that the substrate bias was fixed to be -500 V. For example, under the same condition except microwave injection, the deposition rate and hardness of the DLC deposited by DC plasma were 2.5 μm/h and 11.8 GPa, respectively; while the deposition rate and hardness of the DLC deposited by microwave-excited high-density near plasma were 156 μm/h and 20.8 GPa, respectively. The atomic composition of the films was evaluated by XPS for C, O, and Si, and RBS-ERDA for H/C ratio. Within the range of our results, the hardness films were almost linearly decreased from 6 to 22 GPa with decreasing hydrogen content from 45% to 22%, being independent from the composition of C and Si.

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country D - Session B4-2-MoA

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

**Moderators:** *Dr. Naureen Ghafoor*, Linköping University, Sweden, *Dr. Marcus Günther*, Robert Bosch GmbH, Germany, *Dr. Fan-Yi Ouyang*, National Tsing Hua University, Taiwan

1:40pm **B4-2-MoA-1 Amorphous Carbon Coatings for Tribological Applications in Hydrogen and Natural Gas Environments**, *Thomas Gradt*, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

INVITED

For long distance land and overseas transport of large quantities natural gas is usually liquefied. Methane (CH<sub>4</sub>), the main component of natural gas, has a boiling temperature of -161.5°C, which is much lower than the pour point of any liquid lubricant. Therefore, only dry running tribosystems can

be employed in this temperature range, which is a challenge for frictionally stressed mechanical components.

Also for long distance transport of hydrogen liquefaction is an option. With a temperature of -253°C for liquefied hydrogen (LH<sub>2</sub>) the conditions for tribosystems are even more severe. Furthermore, also for the utilization in gaseous form, in many cases purity requirements impede lubrication by oils or greases. Another requirement is that technical systems containing natural gas or hydrogen need to be inertized from time to time. Therefore, the function of the moving parts must be ensured not only in the reactive media, but also in inert environment.

It is well known that among the solid lubricants graphite and most amorphous carbon coatings show good lubricity in humid air and hydrogen environment, but the question arises if this is also true for methane and very low temperatures.

For identifying suitable carbon-based solid lubricant coatings, ball-on-disk model tests with several variants of a-C:H and ta-C were carried out in gaseous hydrogen, methane and nitrogen. Some coatings were also tested in liquid methane. The results show friction coefficients below 0.1, with lowest values of about 0.01 in CH<sub>4</sub> at room temperature. Also wear coefficients in the order of 10<sup>-8</sup> mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup> for most coatings indicate that amorphous carbon coatings are suitable for frictionally stressed components in hydrogen and natural gas environment.

2:20pm **B4-2-MoA-3 Effect of Bio-Lubricants on Wear and Friction of Borided Ti<sub>6</sub>Al<sub>4</sub>V Alloy**, *A. Nieto-Sosa*, *G. Rodríguez-Castro*, *J. Escobar-Hernández*, *A. Meneses-Amador*, *José Arciniega-Martínez*, *H. Martínez-Gutiérrez*, National Polytechnic Institute, Mexico

In this study, titanium borides were formed on the surface of Ti<sub>6</sub>Al<sub>4</sub>V alloy by powder pack boriding at 1100 °C during 5, 10 and 20 h. Under these treatment conditions, 3 thicknesses consisting of a Ti<sub>2</sub>B outer phase and a TiB inner phase (whisker) were formed. The morphology and layer thickness were determined by scanning electron microscopy (SEM), while the identification of phases was carried out by X-ray diffraction. The maximum thickness of the Ti<sub>2</sub>B phase was measured in 10 μm. The hardness of the layers was determined by Vickers instrumented indentation exceeding 20 GPa. In addition, the instrumented indentation tests were used to calculate the fracture toughness and residual stresses of titanium boride layers. Linear reciprocating wear tests were carried out under dry and lubricated conditions. To evaluate the effect of bio-lubricants, phosphate buffer saline, ringer's solution and sesame oil were used at different contact pressures. Wear mechanisms were identified by SEM. The behavior of the coefficient of friction and the wear rates were analyzed for each of the formed systems.

2:40pm **B4-2-MoA-4 Experimental and Numerical Evaluation of Multi-Pass Scratch on Borided Armco Iron**, *Jesús Vidal-Torres*, SEPI ESIME Instituto Politécnico Nacional, Mexico; *A. Ocampo-Ramírez*, Universidad Veracruzana, Mexico; *G. Rodríguez-Castro*, *I. Campos-Silva*, *A. Meneses-Amador*, SEPI ESIME Instituto Politécnico Nacional, Mexico

Thermochemical treatments are used for increasing the surface mechanical properties of iron and steels. The wear on mechanical components caused by sliding contact is an important parameter in the field of tribology. In this study, the wear resistance of ARMCO pure iron hardened by the powder-pack boriding process was evaluated, using unidirectional sliding. The boriding treatment was carried out at temperatures of 1123 K for 1, 2 and 3 h of exposure time. Surface properties such as hardness and Young's modulus were obtained by the nanoindentation technique. Fracture toughness of the three layer/substrate systems were obtained by Vickers indentation. The wear test was performed by multi-pass scratch using an Al<sub>2</sub>O<sub>3</sub> ball (6 mm diameter) as a counterpart under normal loads of 20 N. The sliding distances were 125, 250, 375 and 500 mm (25, 50, 75 and 100 passes). Archard's model was used to obtain the wear coefficient. Finite element method applying mesh nonlinear adaptivity was used to evaluate the surface wear on the borided samples. It was found that wear resistance was mainly influenced by both the fracture toughness value and thickness of the boride layers.

3:00pm **B4-2-MoA-5 Microstructure and Tribological Characteristics of Binary Refractory Metal Nitride Coatings**, *Yu-Hsien Liao*, *S. Hsu*, *F. Wu*, Dept. of Materials Science and Engineering, National United University, Taiwan

This study focused on microstructure evolution and mechanical behavior of binary refractory metal nitride systems films, including (MoHf)N, (WHf)N and (MoW)N. The phase, adhesion, and wear behavior variations were discussed in terms of material selection. With a radio frequency, RF,

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magnetron dual gun co-sputtering system, the binary refractory metal nitride thin films were fabricated at a fixed Ar/N<sub>2</sub> inlet gas ratio of 12/8 sccm/sccm. The structure of (MoHf)N thin film exhibited MoN, Mo<sub>2</sub>N, and MoN<sub>2</sub> phases, while the (WHf)N thin film possessed WN and Hf<sub>4</sub>N<sub>3</sub> phases. As for the (MoW)N thin film multiple phases including WN, MoN, and Mo<sub>2</sub>N were observed. The (MoW)N and (WHf)N possessed adhesion level of HF3 and HF4, respectively, indicating a poor adhesion due to the exist of tungsten element. On the other hand, (MoHf)N thin film showed an index of HF2. The wear results reflected a similar trend, For the (MoHf)N coating, the track maintained a smooth surface and the film kept intact after a wear length of 100m. On the contrary, the wear tracks of (MoW)N and (WHf)N coatings showed cracking and peeling after the wear test, indicated a weaker tribological behavior.

Keywords: Microstructure; Refractory metal nitride; Multiple phase; Adhesion; Wear.

## 3:20pm B4-2-MoA-6 Hyper-Doping of Boron Carbide Ablators for Laser Fusion, Gregory Taylor, Lawrence Livermore National Lab, USA

Boron carbide (B4C) is a material with outstanding mechanical properties, chemical inertness, and low density. It is currently the leading candidate for use as the next generation amorphous ablator for inertial confinement fusion (ICF). Several approaches to deposit B4C ablaters have been explored with promising recent results. However, the doping B4C for ICF applications has not been investigated. In this work, we investigate the feasibility of incorporating high concentrations of Si, Ge, and W dopants (i.e., hyper-doping) via combinatorial magnetron sputter deposition of ultrathick B4C films. We focus on the influence of the dopant type and concentration on film growth mode and major film properties of relevance to ICF, including residual stress, crystallinity, density and its uniformity, and chemical stability.

## 3:40pm B4-2-MoA-7 Influence of Si Content on the Mechanical Properties, Microstructure and Tribological Behaviors of (AlCrNbSiTi)N Coatings, Yun-Chen Chan, S. Hsu, P. Chen, J. Duh, National Tsing Hua University, Taiwan

High-entropy alloy nitride coatings (HEANs) characterize superior mechanical strength, high oxidation resistance, thermal stability, corrosion resistance and wear resistance. As a result, it is a potential candidate in the protective hard coating field in recent years.

In this study, the (AlCrNbSiTi)N coatings were co-sputtered by radio-frequency magnetron sputtering. The power for the silicon target was varied from 0 watts to 120 watts and the silicon concentration of coatings varied from 0 (at. %) to 10.6 (at. %). As the silicon content in coatings increased to 4.4 (at. %), the coatings exhibited the maximum hardness of 31 (GPa) due to the mechanism of dislocation pile-up. However, as the silicon content in coatings exceeded 4.4 (at. %), the hardness of coatings started to decrease, which was attributed to the appreciable amounts of softer amorphous segregation. Furthermore, the incorporation of silicon interrupted the growth of the column structure due to the spinodal decomposition of amorphous SiN, and (AlCrNbTi)N. Thus coating structure changes from a loose column structure to a dense featureless structure.

Last but not the least, the coating density was calculated from the data measured by XRR analysis. As the silicon content in the coating exceeded 4.4 (at. %), the lack of long-range ordering and free volume in amorphous structure lowered the packing density of the coatings, which led to the poor mechanical properties of the coatings. Nevertheless, the results exhibited that the coating characterized the highest packing density as the silicon content in coatings is 4.4 (at. %), exhibiting the optimal mechanical properties, which is strongly correlated to the crystallinity of the coatings.

## 4:00pm B4-2-MoA-8 Effect of CrMoN Addition on the Thermal Stability and Tribological Property of TiVN Coatings, Y. Chang, He-Qian Feng, National Formosa University, Taiwan

The ternary nitride TiVN coatings can be regarded as a solid solution of TiN and VN, where V atoms infiltrate into the TiN lattice and replacing some Ti atoms. The addition of V atoms to TiN improves the mechanical and frictional properties. A further improvement of thermal stabilities and tribological performance of TiVN coatings can be achieved by a possible approach involving the replacement of monolayered coatings by multilayers. In this study, gradient-and-multilayered TiVN/CrMoN coatings were synthesized by cathodic-arc evaporation. During the coating process of TiVN/CrMoN, CrMoN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates and improved thermal stabilities. An impact fatigue test using a cyclic loading device and ball-on-disc wear tests were conducted to evaluate the correlation between tribological properties and coating structures of the deposited

coatings. Vacuum annealing and high temperature oxidation higher than 600 °C were conducted to evaluate the thermal stabilities of the coatings. Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. The microstructure of the deposited coatings was investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy-dispersive X-ray analysis spectrometer (EDS). Hardness of the films were obtained using nanoindentation measurement. The oxidation states of the oxidized coatings were identified using an X-ray photoelectron spectroscope. The addition of CrMoN into TiVN to form a multilayer architecture provides an alternative for a hard-and-lubricious coating. The design of gradient-and-multilayered TiVN/CrMoN coatings is anticipated to be advantageous in applications to enhance the thermal stability and tribological property of mechanical parts.

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country B - Session B6-MoA

#### Computationally-aided Materials Design

Moderators: Dr. Davide G. Sangiovanni, Linköping University, Sweden, Prof. Wan-Yu Wu, National United University, Taiwan

#### 1:40pm B6-MoA-1 Selection of Photosensitive Materials on Metal Oxide Surface by Using Machine Learning, Yen-Hsun Su, National Cheng Kung University, Taiwan

INVITED

Sustainable energy strategies, particularly solar-to-hydrogen production, are anticipated to overcome the global reliance on fossil fuels. Thereby, materials enabling the production of green hydrogen from water and sunlight are continuously designed, e.g., ZnO nanostructures coated by gold sea-urchin-like nanoparticles, which employ the light-to-plasmon resonance to realize photoelectrochemical water splitting. Due to the complex growth of Gold sea-urchin-like nanoparticles (GSNPs) and the need for a precise prediction of their surface plasmon wavelength, genetic-algorithm-based artificial neural networks (GANNs) are used to determine the relationship between synthesis parameters and the surface plasmon wavelength of GSNPs grown via seed-mediated growth assisted by machine learning. Herein, a low-data test is trained by varying the ratio and concentration of gold seeds, sodium citrate, hydroquinone, and HAuCl<sub>4</sub>. Then, a big data confirmation is conducted through massive parameter collection from over 684 samples. The well-trained GANN can guide parameter selection for seed-mediated growth to obtain the desired surface plasmon wavelength. In additions, such light-to-plasmon resonance is strongly impacted by the size, the species, and the concentration of the metal nanoparticles coating on the ZnO nanoflower surfaces. Therefore, a precise prediction of the surface plasmon resonance is crucial to achieving an optimized nanoparticle fabrication of the desired light-to-plasmon resonance. To this end, we synthesized a substantial amount of metal (gold) nanoparticles of different sizes and species, which are further coated on ZnO nanoflowers. Subsequently, we utilized a genetic algorithm neural network (GANN) to obtain the synergistically trained model by considering the light-to-plasmon conversion efficiencies and fabrication parameters, such as multiple metal species, precursor concentrations, surfactant concentrations, linker concentrations, and coating times. In addition, we integrated into the model's training the data of nanoparticles due to their inherent complexity, which manifests the light-to-plasmon conversion efficiency far from the coupling state. Therefore, the trained model can guide us to obtain a rapid and automatic selection of fabrication parameters of the nanoparticles with the anticipated light-to-plasmon resonance, which is more efficient than an empirical selection. The capability of the method achieved in this work furthermore demonstrates a successful projection of the light-to-plasmon conversion efficiency and contributes to an efficient selection of the fabrication parameters leading to the anticipated properties.

#### 2:20pm B6-MoA-3 On the Modeling of Particle Growth in Film Deposition, Rahul Basu, JNTU, India

The understanding and simulation of the nucleation of particles in a thin substrate is of importance in many areas of deposition technology. The deposition or insitu growth of disperse particles requires tuning of parameters to avoid continuous growth and agglomeration. Thin film nucleation can be modeled with spherical or cylindrical particle morphology. Among the parameters involved are Heat transfer coefficients and the "under cooling" or thermal driving force dependent on the boundary and initial conditions. A stable moving interface can be expressed as a function of time and radius and hence, the radial growth can be

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expressed as a power of time, and other parameters. A simulation using WOLFRAM with the equations of heat and mass transfer is used. A quasi-steady state solution results where the growth is stabilized until a desired size and distribution is arrived at. The prediction of this state is important in formation of various structures like in-situ growth for thin film devices and protective coatings.

## 2:40pm B6-MoA-4 First-Principles Investigations of the Physical Properties of Experimentally Feasible Novel Aluminum Nitride Polytypes, *Mowafiq Mohammad Al-Sardia*, Jejun University, Republic of Korea

We present the results of a first-principles study on the structural stability and electronic and optical properties of new aluminum nitride (AlN) polytypes. The study includes the experimentally or theoretically known phases of AlN wurtzite (WZ), zincblende (ZB), and rock salt (RS) structures, which complement the pressure-dependent phase diagram of this industrially important compound. In addition to the structures of AlN considered in previous studies, we evaluated the dynamic stability of various novel phases: viz., SiC(4H), ZnS(15R), BeO, 5-5, TiAs, NiAs, MoC, Li<sub>2</sub>O<sub>2</sub>, and NiS. These were predicted recently in a high-pressure data-mining study of more than 140000 variations of the AlN structure, which claimed that they were either stable or nearly stable based on first-principles calculations. On the basis of the new AlN polytypes, the physical properties of all considered phases were compared, and the common trends and differences were determined. According to the phonon band structure calculations, nine phases of these new polytypes are free from imaginary frequencies. This indicates adequate dynamic stability and the experimental accessibility of the polytypes. Additionally, the calculated cohesive energies of the dynamically stable phases are comparable to those of WZ-AlN and those specified in the available literature. Furthermore, the observed electronic structures and optical properties indicate that the polytypism of AlN can be a practical tool for refining its physical and chemical properties. The new phases show significant potential for use in future AlN electronic and optoelectronic applications.

## 3:00pm B6-MoA-5 Computational Supports to Identify Structural and Elastic Relationship of Metastable Crystalline And Amorphous Thin Films Alloys: Mo<sub>1-x</sub>Ni<sub>x</sub> and Mo<sub>1-x</sub>Si<sub>x</sub> Case Studies, *C. Li*, 1State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, China; *G. Abadias*, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; *Philippe Djemia*, LSPM UPR 3407, France

**INVITED**  
Metastable Mo<sub>1-x</sub>Si<sub>x</sub><sup>1</sup> and Mo<sub>1-x</sub>Ni<sub>x</sub><sup>2</sup> alloy films with 0 ≤ x ≤ 1 were elaborated by magnetron co-sputtering. Amorphous or crystalline state were identified by x-ray diffraction while their mass density and atomic volume by x-ray reflectivity. Their elastic properties were investigated by combining the Brillouin light scattering (BLS) and the picoseconds ultrasonics (PU) techniques with additional conventional nanoindentation tests. A transition from bcc-crystalline to amorphous state is observed for a Si content, x<sub>Si</sub> ~ 0.19 and Ni content, x<sub>Ni</sub> ~ 0.26 while fcc-crystalline to amorphous state transition is observed for x<sub>Ni</sub> ~ 0.73. These structural transitions are accompanied by modifications of physical and mechanical properties s, namely, longitudinal out-of-plane modulus C<sub>33</sub>, and out-of-plane shear modulus C<sub>44</sub>. In the crystalline regions, a pronounced softening of the shear elastic C<sub>44</sub> constant from 110 GPa to 60 GPa for MoSi and from 65 GPa to 45 GPa for MoNi, is observed. The longitudinal modulus C<sub>33</sub> has experienced a softening from 420 GPa to 300 GPa for MoSi and from 390 GPa to 280 GPa from both pure Mo and Ni. This behavior is an intrinsic consequence of the high Si and Ni supersaturation, leading to lattice instability. In the MoSi amorphous state, the evolution of the elastic properties exhibits two distinct behaviors depending on the electronic properties and metallic or covalent character of the amorphous alloys. For 0.19 ≤ x<sub>Si</sub> ≤ 0.5, the metallic character of the solid solutions is maintained and the elastic properties are remarkably stable. For x<sub>Si</sub> > 0.5, a reduction in the atomic density is progressively observed and the amorphous alloys acquire a covalent character. We are again witnessing a progressive softening of the elastic stiffness constants while, surprisingly, both the longitudinal and transverse acoustic velocities increase continuously. In general, the analysis of the evolutions generally highlights the interdependence between the structural and elastic properties of the non-equilibrium phases formed between Mo and Si or Ni. Inter-relationships are discussed with help of ab initio molecular dynamics (AIMD) and density functional theory calculations (DFT). Glassy solid state of alloys made of 256 atoms, was obtained from cooling down the melt from 3500 K to 300 K using the NVT ensemble and the Nose thermostat, followed by a relaxation of the cell with NPT ensemble and Langevin thermostat for at least 15 ps by

steps of 1.5 fs. Special quasi-random structures were built to mimic the random crystalline alloys.

<sup>1</sup>A Fillon *et al.*, Phys.Rev.B 88, 174104(1-16) (2013)

<sup>2</sup>G. Abadias *et al.*, Phys.Rev.B 65, pp. 212105(1-4) (2002)

## 3:40pm B6-MoA-7 On the Quantification of Lattice Distortions and Their Correlation with Kinetics in High Entropy Sublattice Nitrides, *Ganesh Kumar Nayak*, Montanuniversität Leoben, Austria; *A. Kretschmer*, TU Wien, Austria; *J. Sälker*, RWTH Aachen University, Germany; *P. Mayrhofer*, TU Wien, Austria; *M. Hans*, *J. Schneider*, RWTH Aachen University, Germany; *D. Holec*, Montanuniversität Leoben, Austria

Nitride-based ceramic materials serve high hardness and good thermal stability and have been attractive for high-temperature applications for decades. To improve these properties of materials in ceramics, the concept of alloying was revolutionized in multi-component or high-entropy alloys (HEAs), where five or more elements are distributed randomly on a crystalline lattice in equiatomic or near-equiatomic composition. One crucial form of these ceramics is high-entropy sublattice nitride (HESN), which is built upon the concept of HEAs. Four core effects have been postulated for such materials to stem from the configuration entropy: high configurational entropy, severe lattice distortion, sluggish diffusion, and cocktail effects.

Despite the significant progress in recent years, proper quantification of the lattice distortions in HESNs and their effect on kinetics by altered local chemistry is still missing. The HESN systems considered for this ab initio study are structurally stable. Their models consist of metals distributed on the metal sublattice by the special quasi-random structure (SQS) method. Taking advantage of knowing the positions of all atoms in our structural models, we present a novel statistical approach for measuring the lattice distortions and discuss their correlation with the activation energies for vacancy-driven migration mechanisms in HESNs. Our analyses focus on comparing low and high entropy systems (as measured by the number of elements) for systems exhibiting small and large local distortions and similar and different nominal bond lengths of the forming binary nitrides. With the help of quantum-mechanical calculation, we evaluate the impact of the local composition and increasing high-entropy environment, which can significantly alter the activation energies consisting of vacancy formation energy and migration barrier contributions.

Our results undoubtedly demonstrate that the claimed sluggishness of the diffusion in HESNs is more composition and/or environment-specific than a general feature of all high entropy systems. Explicitly we will also present this statistical approach that can be used to support the argument of spinodal decomposition. Finally, we will show that the diffusion also significantly correlates to the electronic structure, namely the *d*-states, of the diffusing transition metal impurity.

## 4:00pm B6-MoA-8 Machine-Learning Guided Ab-Initio Exploration of Thermal/Mechanical Properties in Transition Metal Nitrides, *Andrea Kretschmer*, TU Wien, Institute of Materials Science and Technology, Austria; *M. Fedrigo*, Oerlikon Digital Hub, Germany; *L. Lezuo*, TU Wien, Institute of Materials Science and Technology, Austria; *K. Yalamançhili*, *H. Rudigier*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P. Mayrhofer*, TU Wien, Institute of Materials Science and Technology, Austria

Ab-initio calculations have proven an efficient tool for exploration of fundamental material properties. However, in the context of solid solutions, the required cell dimensions for accurate predictions still require significant computational expense, barring the progress in high-throughput exploration. We have remedied this weakness with machine-learning (ML) models that are trained on the results of density-functional theory calculations, thus guiding the computationally expensive ab-initio exploration by computationally cheap data science. We investigated the phase space of all equimolar fcc solid solution nitrides of the group IVb-VIb nitrides + Al, with 1 to 5 metals in the compounds.

Using the DFT calculated energies of the multinary nitrides (published in [1]), we obtained the driving force for decomposition of the equiatomic multinary solid solutions into more stable phases for more than 16000 individual reactions. We trained different ML modelson this data and we developed some feature encoding strategies for the models to work on. The outcome is that a simple linear regression on a particular feature encoding is able to predict the driving force for decomposition quantitatively with an R<sup>2</sup> score of about 90%. This model is also capable of applying the concepts of entropy or strain stabilization [1] to predict stable phases beyond the current dataset.

The elastic constants of 230 nitrides have been iteratively calculated, starting from a base of ~30 compositions. ML regression models were trained and optimized to extrapolate the properties of these compositions and suggest points of interest for further ab-initio calculations, including Elastic Net, Random Forest, Gradient Boosting and Support Vector Regression. In the end, an aggregated model built on top of these four showed the best performance as measured by the  $R^2$  score. This ML model was then fed more data in every iteration, increasing the prediction efficacy. After calculation of 230 alloys, the performance of the different models was cross-checked in a blind-test using the existing data. The best performing models reached correlation scores  $R^2$  between 0.79-0.92 for different elastic properties such as bulk, shear, and Young's modulus, and Cauchy pressure. Thus, the ab-initio trained ML model is able to make confident predictions on the mechanical properties within this chosen phase space of nitrides (~630 alloys), these properties were also validated on 12 magnetron sputtered nitride coatings.

[1] Kretschmer, A., et al. (2022). Strain-stabilized Al-containing high-entropy sublattice nitrides. *Acta Materialia*, 224, 117483. <https://doi.org/10.1016/j.actamat.2021.117483>

4:20pm **B6-MoA-9 Descriptors Development for Stability Prediction of N-Doped High Entropy Alloy Coatings: A DFT Study**, *Chih-Heng Lee*, National Tsing Hua University, Taiwan; *J. Lee*, Ming Chi University of Technology, Taiwan; *H. Chen*, National Tsing Hua University, Taiwan

To achieve the desired hardness, strength, or ductility in high entropy alloy (HEA) coatings, doping element into the interstitial sites of HEA is a good method. Density functional theory (DFT) is often used to analyze, predict and design the physiochemical properties of alloys in the wide range of composition space. However, although DFT modeling has great potential to predict and design of HEA coating, it is very difficult to consider all the inequivalent doping sites present due to the low symmetry characteristic of HEA. In this study, we use 1st nearest neighbor (1NN) environment, local potential, and electrostatic potential via DFT calculation to be descriptors to predict the N doping energy in VNbMoTaWTiAl<sub>0.5</sub> coating systems to construct more stable N-doped models. Our results show that the Pearson correlation coefficient between 1NN environment and the N doping energy reached ~ 0.80, implying that the (1NN) environment could be a good descriptor to predict the doping energy of N in each interstitial site. The Pearson correlation coefficient between local potential / electrostatic potential and N doping energy reached ~ -0.7 without outlier, revealing that the interstitial site with higher potential energy of electron behave lower doping energy. To explain this result, we proposed that the electrons at high-potential interstitial site are more energetically preferred to combine with the orbital of doped N atom due to the high electronegativity of N. To test the universality of these descriptors, we plan to use high-throughput screening method to find the capability of these descriptors in the wide range of different alloys. We hope our approaches could efficiently predict stable N-doped HEA coating models (in interstitial sites) and further apply to broaden systems.

4:40pm **B6-MoA-10 Structural Configuration of Simple Functional Groups on (100) Si Surfaces**, *Benjamin Whitfield*, *R. Fleming*, Arkansas State University, USA

Silicon is a widely utilized semiconductor material with applications ranging from computer chips to solar panels. A realistic description of the surface of Si can improve the understanding of Si surface chemistry, especially in the presence of functional groups. In this study, the structural configuration of the Si (100) surface is studied for several terminating groups, including methyl, hydroxyl, fluoromethyl, and double-bonded oxygen. Relaxed surface geometries are calculated using density functional theory (DFT) structural optimization, along with bond dissociation energies and bond lengths at 0 K. This study provides a deeper understanding of the structure of functionalized silicon surfaces, leading to pathways to produce new advanced silicon-based materials.

5:00pm **B6-MoA-11 Bayesian Optimization-Assisted Sputter Deposition of Molybdenum Thin Films with Desired Stress and Resistivity**, *Ankit Shrivastava*, *M. Kalaswad*, *D. Adams*, *H. Najm*, Sandia National Laboratories, USA

We introduce a Bayesian optimization (BayesOpt) based approach to guide the sputter deposition of molybdenum (Mo) thin films with desired residual stress and electrical resistivity. Thin films are of key importance in various technologies, including, e.g., semiconductor and optical devices. In thin film sputter deposition, process parameters, such as deposition power, vacuum chamber pressure, and working distance, can affect film physical properties, such as residual stress and resistivity. Excessive film residual

stress as well as high resistivity can negatively affect the performance of devices; hence, choosing the optimum combination of process parameters that produce thin films with residual stress and resistivity within a desired range is essential. However, considering that the experiment is the available black-box "function" to evaluate these physical properties from process parameters, it is clear that the associated expense of full exploration of the design space for process optimization purposes is prohibitively expensive. BayesOpt is ideal for optimizing black-box functions without reliance on gradient information, and can find optimal process parameters with minimal evaluations.

In this work, we seek a combination of two primary process parameters (deposition power and pressure) such that 1) residual stress and resistivity of Mo thin films are within a specified range, and 2) the variations in the stress are least susceptible to stochastic fluctuations in the deposition process parameters. To achieve this, we use BayesOpt to optimize an objective function, custom-built using observed stress and resistivity data, targeting both criteria. This involves incorporation of knowledge of stress dependence on pressure obtained from existing experimental observations into a stress-pressure surrogate, whose gradients are employed in the objective function. This surrogate, and thus the objective function, are updated based after each new measurement, ahead of the next BayesOpt step. We illustrate the performance of BayesOpt in the exploration of the Mo thin film deposition design space (power and pressure), arriving at optimal conditions that meet desired constraints on stress and resistivity.

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

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

**Moderators:** Dr. Naureen Ghafoor, Linköping University, Sweden, Dr. Marcus Günther, Robert Bosch GmbH, Germany, Dr. Fan-Yi Ouyang, National Tsing Hua University, Taiwan

**8:20am B4-3-TuM-2 Is It Meaningful to Quantify Vacancy Concentrations of (Ti,Al)N Thin Films Based on Laser-Assisted Atom Probe Tomography Data?**, *Marcus Hans*, Materials Chemistry, RWTH Aachen University, Germany; *M. Tkadletz*, Department of Materials Science, Montanuniversität Leoben, Austria; *D. Primetzhofer*, Department of Physics and Astronomy, Uppsala University, Sweden; *H. Waldl*, Christian Doppler Laboratory for Advanced Coated Cutting Tools, Montanuniversität Leoben, Austria; *M. Schiester*, Materials Center Leoben Forschung GmbH, Austria; *M. Bartosik*, Department of Materials Science, Montanuniversität Leoben, Austria; *C. Czettl*, CERATIZIT Austria GmbH, Austria; *N. Schalk*, Christian Doppler Laboratory for Advanced Coated Cutting Tools, Montanuniversität Leoben, Austria; *C. Mitterer*, Department of Materials Science, Montanuniversität Leoben, Austria; *J. Schneider*, Materials Chemistry, RWTH Aachen University, Germany

Recently, it was proposed to quantify vacancy concentrations based on laser-assisted atom probe tomography (APT) data for a (Ti,Al)N film with a nanolamellar architecture, grown by chemical vapor deposition (CVD). However, the measurement accuracy of APT depends on the evaporation conditions. To determine, whether vacancy concentrations can be reliably estimated based on APT data, we systematically compare measurements with an ultraviolet (UV) as well as a green laser to ion beam analysis data. First, monolithic TiN and AlN films, which are stoichiometric within the measurement uncertainties of ion beam analysis, are investigated. In case of TiN an electric field strength of  $39.4 \text{ V nm}^{-1}$  and a nitrogen content of 49.0 at.%, consistent with ion beam analysis data, is obtained with both lasers, when using pulse energies of 5 pJ (UV laser) and 0.1 nJ (green laser). However, significant differences can be observed for monolithic AlN as nitrogen contents from 41.9 to 35.8 at.% and 48.4 to 41.4 at.% are measured, depending on variations of the pulse energies of the UV and green laser, respectively. In order to mimic nanolamellar architectures for correlative compositional analysis by ion beam analysis and laser-assisted APT, a multilayered TiN/AlN/TiN film is synthesized and significant deviations with respect to the nitrogen content are evident for the AlN layer. While the average N concentration from ion beam analysis is 51 at.%, N contents from laser-assisted APT data are only 38 at.% (UV laser) or 41 at.% (green laser). Hence, the nitrogen content of the AlN layer is underestimated from laser-assisted APT data by at least 10 and up to 13 at.% and this significant discrepancy cannot be explained by the measurement uncertainties. Thus, the here presented data emphasize that it is not meaningful to quantify vacancy concentrations of (Ti,Al)N thin films solely based on atom probe data.

**8:40am B4-3-TuM-3 The Oxidation Behavior of VMoN Thin Films Deposited by High Power Pulsed Magnetron Sputtering**, *Nan-Cheng Lai, J. Huang*, National Tsing Hua University, Taiwan

The purpose of this study was to investigate the oxidation behavior of VMoN thin film deposited by High Power Pulsed Magnetron Sputtering (HPPMS) with different duty cycles. Vanadium nitride (VN) and molybdenum nitride ( $\text{MoN}_x$ ) are two promising materials for protective coatings on cutting tools because of the formation of Magnéli oxide phases at high temperature, thereby increasing the wear resistance and prolonging the service life of the industrial products. Due to the increasing demands of dry cutting, the oxidation during cutting and the accompanying severe degradation of the protective coatings becomes a crucial issue in the tool industry. Therefore, the oxidation behavior of VN and MoN coatings has been widely studied [1-2]. Previous research indicated that the tribological properties of Mo-N based coatings could be enhanced by adding vanadium [3]. The resultant ternary VMoN coatings possess better mechanical properties than the counterpart binary coatings, VN and MoN. However, there has been little research on the oxidation behavior of VMoN coatings. For the applications on tool industry, it is important to understand the oxidation behavior of VMoN coatings. In this study, the VMoN thin films with thickness of  $1 \mu\text{m}$  were deposited on both sides of Si substrate by high power pulsed magnetron sputtering (HPPMS). The duty

cycles were controlled to be 3%, 5%, 7%, and 9%. After deposition, the ratios of V/Mo and (V+Mo)/N were determined using electron probe of microanalysis (EPMA) and the microstructure of the coatings was observed by scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to characterize the crystal structure and the preferred orientation of the coatings. The residual stress of the specimens was measured by laser curvature method (LCM) and average X-ray strain (AXS) combined with nanoindentation methods [4,5]. The oxidation behavior of the coatings was investigated using thermo-gravimetric analysis (TGA) at temperature ranging from 300 to 800°C in Ar atmosphere. From the experimental results, the oxidation behavior of the VMoN coatings was discussed.

[1] G. Gassner et al., Tribol. Lett. 17 (2004) 751.

[2] T. Suszkoa et al., Surf. Coat. Technol. 194 (2005) 319.

[3] W. Wang et al., Surf. Coat. Technol. 387 (2020) 125532.

[4] C.-H. Ma et al., Thin Solid Films 418 (2002) 73.

[5] A.-N. Wang et al., Surf. Coat. Technol., 262 (2015) 40.

**9:00am B4-3-TuM-4 Correlation Between Microstructure and Mechanical Properties of B<sub>4</sub>C Thin Films Deposited by Pulsed Laser Deposition**, *Falko Jahn, S. Weißmantel*, Laserinstitut Hochschule Mittweida, Germany

Being the third hardest known material with in addition outstanding thermal and chemical resistance, boron carbide is a very promising coating material for applications in the field of abrasive wear protection. We already could prove that B<sub>4</sub>C thin films produced using pulsed laser deposition reliably show extraordinary mechanical properties like an indentation hardness up to 47 GPa. The substrate temperature during the deposition process turned out to be crucial for the extreme hardness [1]. However, the underlying mechanism to the found correlation remained unrevealed.

We now present the results of our investigations on the correlation between the mechanical properties and the microstructure of the produced boron carbide films. Furthermore, we propose and discuss a probable mechanism for the achieved super hardness. One important requirement to these studies was the improvement of the deposition process to significantly reduce the droplet incorporation. Thus, we were able to produce boron carbide films with film thicknesses > 3 μm that enable XRD and TEM analyses.

In addition, the influence of intrinsic film stresses on the mechanical film properties were investigated. These stresses result from the deposition technique of PLD. Furthermore, we present a laser-based relaxation method that can be fully integrated into the deposition process. That enables the deposition of completely stress-free, smooth and super hard boron carbide thin films.

[1]F. Jahn, S. Weißmantel, Properties of Boron Carbide Thin Films Deposited by Pulsed Laser Deposition, Surface and Coatings Technology (2021) 127480. <https://doi.org/10.1016/j.surfcoat.2021.127480>.

**9:20am B4-3-TuM-5 Evaluation of Fracture Toughness of Borided Materials by Cross-Sectional Scratch Testing**, *F. Alfonso-Reyes, André Ballesteros-Arguello, J. Martínez-Trinidad*, SEPI ESIME Instituto Politécnico Nacional, Mexico; *A. Ocampo-Ramírez*, Universidad Veracruzana, Mexico; *G. Rodríguez-Castro*, SEPI ESIME Zacatenco, Mexico; *A. Meneses-Amador*, SEPI ESIME Instituto Politécnico Nacional, Mexico

A numerical-experimental study of the fracture toughness of nickel and iron borides obtained by cross-sectional scratch test was carried out. The nickel borides were formed on an Inconel 718 superalloy and iron borides were formed on an AISI 316L steel. The powder-pack boriding process was developed at 1223 and 1273 K and 6 h of exposure time for the Inconel 718 superalloy and the AISI 316L steel, respectively. The scratch tests were carried out on the cross-sections of both borided materials using a CSM Revetest-Xpress commercial equipment with a Vickers indenter. The scratch distance was of 1.5 mm with a load range from 3 – 4.5 and 2.5 – 3.1 for the nickel and iron borides, respectively. The applied loads and damage observed at the samples surface (with half cone geometry) were used to estimate the fracture toughness of the system. The numerical model based on the finite element method of the cross-sectional scratch testing was developed considering the same test conditions. The numerical results were used to establish parameters employed in the methodology of fracture toughness by cross-sectional scratch testing.

# Tuesday Morning, May 23, 2023

9:40am **B4-3-TuM-6 Stress Evolution in Binary Metal Alloy Systems**, *Tong Su*, Brown University, USA; *J. Robinson*, *G. Thompson*, The University of Alabama, USA; *E. Chason*, Brown University, USA

While metal alloy films are used in many applications, there is limited stress evolution investigations during their growth as compared to elemental films. Here, we provide preliminary measurements of the stress evolution in the Mo-V and W-V systems, with each alloy forming a solid solution. Different alloy compositions were sputter deposited at different growth rates with the stress measured by an in-situ wafer curvature measurement technique. For both systems, the steady-state stress was measured as a function of growth rate at these different compositions. The results are discussed in terms of stress-generating mechanisms that have been proposed for elemental systems, where the alloy stress is a superposition of the effects from the two components.

10:00am **B4-3-TuM-7 Molecular Engineering of Inorganic Thin Film Interfaces for Accessing Multiple Novel Properties for Diverse Applications**, *Ganpati Ramanath*, Rensselaer Polytechnic Institute, USA

**INVITED**

Engineering the stability and properties of heterointerfaces in systems involving thin films and nanomaterials is essential for diverse applications, e.g., in electronics, energy conversion and storage. This talk will describe the use of molecular nanolayers to tailor chemical, mechanical, thermal and electronic properties of metal-ceramic and metal-thermoelectric interfaces. I will show that introducing molecular nanolayers (e.g., organosilanes, thiols, organophosphonates) at inorganic interfaces can produce remarkable multifold enhancements in interfacial fracture energy during static and dynamic loading, and thermal and electronic transport. These results are germane to engineering the chemical and mechanical stability of thin film composites, and accessing unusual mechanical responses, and tuning interfacial electrical and thermal transport for energy and electronics applications. Interfacial molecular nanolayers also open up new possibilities for studying interface fracture nanomechanics through macroexperiments. Electron and ion beam spectroscopy, and X-ray and electron diffraction, supported by theoretical calculations, show that the property enhancements are due to molecular nanolayer-induced alterations to the inorganic interface chemistry and structure. Key mechanisms include strong covalent bonding and chelation, interfacial oxide scavenging, diffusion curtailment, and altered phase formation pathways. Stacking molecularly-tailored inorganic interfaces can trigger unusual interfacial phenomena, such as, viscoelastic bandgaps, and the design of high-interface-fraction organic-inorganic nanocomposites wherein the molecularly-induced interface properties *become* materials properties.

**Select References:** [Sci. Rep.](#) 12, 10788 (2022); [Nature Comm](#) 9, 5249(2018); [ACS Appl. Mater. Interf.](#) (2017); [ACS Appl. Mater. Interf.](#) 8, 4275 (2016); [Nature Mater](#) 12, 118 (2013); [Scripta Mater.](#) 121, 42-44 (2016); [Phys. Rev. B](#) 83, 035412 (2011); [Nature](#) 447, 299 (2007); [ACS Appl. Mater. Interf.](#) 9, 2001 (2017); [ACS Appl. Mater. Interf.](#) 8, 4275 (2016); [Appl. Phys. Lett.](#) 109, 173904 (2016).

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

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

**Moderators:** Dr. Naureen Ghafoor, Linköping University, Sweden, Dr. Marcus Günther, Robert Bosch GmbH, Germany, Dr. Fan-Yi Ouyang, National Tsing Hua University, Taiwan

1:40pm **B4-4-TuA-1 Magnetron Sputter Deposition of Ultrathick Boron Carbide Coatings on Spherical Substrates for Inertial Confinement Fusion**, J. B. Merlo, G. Taylor, S. Shin, L. Bayu Aji, J. Bae, L. Sohngen, S. Kucheyev, Lawrence Livermore National Laboratory, USA

Boron carbide has attractive properties for use as ablator capsules for inertial confinement fusion (ICF). Creating an ultrathick, uniform, defect-free film on a rolling spherical substrate has many challenges, including delamination and fracture due to residual stress and nodular growth defects, which are believed to originate from particulates deposited onto the film surface during growth. We have systematically studied effects of direct-current (DC) versus radiofrequency (RF) driven magnetron sputter deposition, substrate temperature, chamber pressure, and the target to substrate distance for amorphous boron carbide films deposited on stationary planar substrates. Here, we describe how these deposition parameters are optimized when the process is transferred to coating rolling spherical substrates.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344 and by General Atomics under Contract 89233119CNA000063.

2:00pm **B4-4-TuA-2 Corrosion and Electrical Insulation Properties of SiO<sub>x</sub> Thin Films Deposited by Microwave PECVD**, Atreya Danturthi, R. Drummond Brydson, University of Leeds, UK; I. Kolev, Hauzer, Netherlands; L. Yang, A. Bell, G. Wu, University of Leeds, UK

Smart sensor technology is currently being developed and incorporated into several industries as part of the Industry 4.0 scheme to optimise energy input to industrial equipment thereby reducing carbon emissions.

These smart sensors applied on wheel bearings of EVs are prone to premature electrical failure due to current passage from dc/ac motors and also corrosion because of exposure to extreme environments. One of the solutions to this problem is developing electrically insulating and corrosion-resistant coatings that could be applied to the existing system. Current research is focussing on Al<sub>2</sub>O<sub>3</sub>-based coatings for these applications deposited using plasma spray/ electrolytic oxidation. However, Al<sub>2</sub>O<sub>3</sub> coatings produced using the above methods were porous requiring additional sealing to be useful in insulation and corrosion-resistant applications. Therefore, Si-based coatings using  $\mu$ -plasma enhanced chemical vapour deposition (PECVD) are being explored in this current study as the properties of silicon-based coatings can be varied through variations of nitrogen, oxygen, and silicon composition and the fact that PECVD is capable of producing denser coatings than PVD. In addition, higher deposition rates can be achieved using precursors such as hexamethyldisiloxane (HMDSO)/ hexamethyldisilazane (HMDSN) due to their high vapour pressures thereby reducing manufacturing cost.

In this study, HMDSO and O<sub>2</sub> gases were used to deposit SiO<sub>x</sub> coatings at varying gas flow ratios (1:12, 1:16, 1:20),  $\mu$ -powers (2 and 4kW) and coating thicknesses (3 - 10  $\mu$ m) to study their impact on corrosion & insulation properties. Characterisation techniques such as Calo test, scratch testing, Rockwell C adhesion test, Fourier Transform Infrared spectroscopy, Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy, X-ray diffraction were used for characterisation. In addition, cyclic polarisation and electrochemical impedance spectroscopy were used for corrosion behaviour characterisation, and finally I-V measurements to ascertain insulation behaviour. Preliminary corrosion results of all the coated samples showed significant improvement in corrosion resistance compared to bare high-speed steel substrate. In particular, coatings deposited at 4kW ( $\mu$ -power) and 1:12 (HMDSO:O<sub>2</sub>) gas flow ratio had very low corrosion currents (a few pA) indicating high corrosion resistance.

2:20pm **B4-4-TuA-3 High-Throughput Methodology for The Realization of High-Entropy High-Dielectric-Constant Ba(Ti,Zr,Ta,Hf,Mo)O<sub>3</sub> Film-Based Metal-Oxide-Semiconductor-Related Devices**, Kao-Shuo Chang, National Cheng Kung University (NCKU), Taiwan; V. Nguyen, No.1, University Road, Taiwan; T. NAGATA, National Institute for Materials Science, Japan **INVITED**  
The use of a high-throughput sputtering technique for the fabrication of high-entropy high-dielectric-constant (high-k) Ba(Ti,Zr,Ta,Hf,Mo)O<sub>3</sub> film libraries on Si substrates and sub-nm equivalent-oxide-thickness (EOT) metal-oxide-semiconductor (MOS) devices and metal-oxide-semiconductor field-effect transistors (MOSFETs) will be presented. The elemental variations and amorphous microstructures were characterized using high-throughput X-ray fluorescence (XRF) and X-ray diffraction, respectively. The film library was patterned into 100 MOS configurations, and their dielectric constants and losses were systemically mapped. The MOSFETs after rapid thermal annealing (RTA) exhibited excellent characteristics, including an on/off current ratio of  $\gg 10^6$  and a saturated field-effect mobility of 288 cm<sup>2</sup>×V<sup>-1</sup>×s<sup>-1</sup>. Small variations in the threshold voltage and negligible changes in the maximum drain current were also under various positive and negative gate-bias stress conditions before and after the RTA. Our results indicated the potential of the Ba(Ti,Zr,Ta,Hf,Mo)O<sub>3</sub> films for use in a gate-first process for advanced gate stack-related devices.

3:00pm **B4-4-TuA-5 Effects of Nitrogen Flow Ratio on the Mechanical and Anticorrosive Properties of Co-sputtered (TiZrHfTa)<sub>x</sub>N<sub>x</sub> Films**, Tzu-Yu Ou, National Taiwan Ocean University, Taiwan; L. Chang, Ming Chi University of Technology, Taiwan; Y. Chen, National Taiwan Ocean University, Taiwan

In this study, (TiZrHfTa)<sub>x</sub>N<sub>x</sub> films were prepared through co-sputtering with four sputter guns. The stoichiometric ratio x of (TiZrHfTa)<sub>x</sub>N<sub>x</sub> films was varied by adjusting the reactive gas ratio of f<sub>N2</sub> (N<sub>2</sub>/(N<sub>2</sub> + Ar)) at 0, 0.4, and 0.7. With an f<sub>N2</sub> of 0, the fabricated metallic Ti<sub>0.23</sub>Zr<sub>0.22</sub>Hf<sub>0.30</sub>Ta<sub>0.25</sub> film, namely N00, exhibited a valence electron concentration of 4.25, a bcc phase with lattice constants of 0.3395 nm, a hardness of 8.0 GPa, and a Young's modulus of 148 GPa. The introduction of N into the TiZrHfTa crystallites transformed the phase from bcc to fcc. N04 [(Ti<sub>0.22</sub>Zr<sub>0.30</sub>Hf<sub>0.17</sub>Ta<sub>0.31</sub>)N<sub>0.83</sub>] and N07 [(Ti<sub>0.33</sub>Zr<sub>0.34</sub>Hf<sub>0.13</sub>Ta<sub>0.20</sub>)N<sub>0.88</sub>] films were prepared when f<sub>N2</sub> was set at 0.4 and 0.7, respectively. The N04 and N07 films exhibited a common fcc phase with lattice constants of 0.4490 and 0.4464 nm, respectively. The N04 and N07 films exhibited hardness values of 33.2 and 32.2 GPa and Young's modulus values of 379 and 363 GPa, respectively. The corrosion resistance of (TiZrHfTa)<sub>x</sub>N<sub>x</sub> films was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy.

4:00pm **B4-4-TuA-8 Magnetron Sputter Deposition of Boron Carbide in Ne and Ar Plasmas**, Liam Sohngen, S. Shin, L. Bayu Aji, G. Taylor, J. Bae, A. Engwall, J. Hammons, S. Kucheyev, Lawrence Livermore National Laboratory, USA

Boron carbide ceramic films have many applications, including wear resistant coatings and fuel capsules for inertial confinement fusion (ICF). However, the deposition of boron carbide films by conventional magnetron sputtering with an Ar plasma suffers from relatively low deposition rates. Here, we explore the deposition of boron carbide with a Ne plasma, which is ballistically better matched to B and C and is expected to exhibit larger sputtering yields than Ar. We study plasma discharge characteristics, ion and atom energy distributions, and properties of films deposited with different substrate tilt angles in both direct-current (DC) or radio-frequency (RF) mode in Ar or Ne plasmas. Results show that film properties are dominated by the effect of the working gas on the plasma discharge and gas phase scattering of depositing species flux rather than by sputtering ballistics and energetics.

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country A - Session B3-WeM

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

**Moderators:** Konrad Fadenberger, Robert Bosch GmbH, Germany, Dr. Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands

11:00am **B3-WeM-10 ta-C by Magnetron Sputtering Using a Newly Designed Cylindrical Rotating Cathode with Significantly Enhanced Sputter Power Density**, *Andreas Lümkmann*, Platit AG, Switzerland; *J. Kluson, M. Učík*, Platit a.s., Czechia; *H. Bolvardi*, Platit AG, Switzerland

Platit presents its sputtered ta-C coatings (tetrahedrally-bonded hydrogen-free carbon) with high fraction of sp<sup>3</sup> hybridized carbon atoms. These coatings belong to the 3rd generation in the Platit DLC family and are designated as DLC3 coatings. Deposition of DLC3 coatings is performed by our Pi411 PLUS coating unit, an extremely flexible coater. In the DLC3 configuration, this device is equipped beside three arc cathodes situated in the doors also with one central cylindrical sputtering cathode. High strength magnetic field and very efficient target cooling are the key features of the cathode.

A newly designed Magnetron Sputtering cathode will be presented achieving significantly enhanced sputtering power densities on the target surface. Whereas in the case of our conventional cathode the magnetic field design corresponds to more or less cylindrical arrangement, the new co called "F-Type" cathode is equipped with a specific moveable magnetic core. The core is periodically moving in the longitudinal direction along the cathode axis. It results in the possibility to reach very high power densities, especially for industrial DC magnetron sputtering. For the delivered power of 25kW the maximal value of power density goes up to 800W/cm<sup>2</sup>.

Not only the hardware part of the technology but also the fine-tuned coating process is indispensable for the synthesis of novel high quality DLC coatings. Here the substrate heat management is of especial importance. On the other side high productivity and low machine maintenance needs are achieved.

Platit DLC3 coatings are characterized by very high microhardness around 50GPa and sp<sup>3</sup> to sp<sup>2</sup> ratio above 50%, by very low friction coefficient and low roughness. Examples of applications for which the technology was successfully used will also be shown.

11:20am **B3-WeM-11 High Performance ta-C Coatings with Enhanced Temperature Stability for Industrial Applications**, *Klaus Böbel*, Bosch Manufacturing Solutions, Germany; *S. Wetzel, J. Jiao*, Bosch Automotive Products, China

BOSCH is one of the pioneers of DLC coating and is operating coating centers worldwide since 1995. For our products we develop coatings with high performance and tailored for specific demands.

Ta-C layers are extremely hard hydrogen free diamond-like carbon layers with excellent mechanical and chemical properties developed for the most demanding applications in industry. BOSCH is successfully applying these coatings in large-scale mass production for over 10 years using its own high rate pulsed ta-C source. The technology allows high coating rates (>2.5µm/h with one source in 2-fold-rotation) and high coating thicknesses to guarantee efficient and economical operation. Results from the optimization of ta-C coatings for high temperature load will be presented. The influence of adhesion layer material, deposition technology and corresponding process parameters has been investigated using a DoE approach in combination with nano scratch analysis. The optimized layer system performed excellently during application withstanding temperature pulses well above 500°C.

11:40am **B3-WeM-12 DLC Coatings for Mechanical Seals Applications**, *S. Tervakangas*, Oerlikon Balzers Coating Finland Oy, Finland; *N. Manninen, Julien Keraudy*, Oerlikon Surface Solutions AG, Liechtenstein; *O. Jarry*, Oerlikon Balzers Coating Germany GmbH, Germany

Mechanical face seals are today of great importance in many applications e.g. in pumps, compressors, mixers, electric motors and transmissions.... Due to their high hardness, high resistance to wet corrosion and capability to resist high temperatures, various ceramics such as Silicon Carbide (SiC) are successfully being implemented in process pumps dealing with corrosive and abrasive fluids. However, ceramic components of devices such as mechanical seals of pumps face considerable tribological challenges

that can ultimately affect performance and reduce the life of the larger system; particularly dry running conditions may occur during starting and stopping or if occasional overloading occurs between the sliding faces leading to temperature increases and possible damages to the sliding faces as well as surrounding elastomer seals. Ultrananocrystalline diamond (UNCD) is a well-established solution to protect SiC seals from abrasive wear in extreme conditions. However, diamond coatings produced by conventional chemical vapor deposition (CVD) exhibit high surface roughness, which very often leads towards coating the counterface seal too in order to prevent wear. Diamond Like Carbon Coatings are cost-effective alternatives to UNCD especially for seals operating by intermittence in dry mode. They provide an extremely low friction in dry and lubricated modes and high wear resistance. The objective of the present study is to investigate the tribological performance of different DLC coated SiC when simulating mechanical face seal applications. Dry wear tests were carried out in air at room temperature by using a laboratory tribotest where two discs are rotated against each other face to face. The results show that all DLC coatings results in significantly lower friction and temperature than uncoated SiC and are therefore an interesting alternative to diamond coatings commercially available today. Amongst the DLC coatings, ta-C are particularly promising due to their unique combination of friction and wear reduction. The benefits from using ta-C coatings include lower running cost compared to diamond coatings and the possibility to use a more simple seal design.

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country D - Session B8-1-WeA

#### HiPIMS, Pulsed Plasmas and Energetic Deposition I

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

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

INVITED

Efficient metal-ion-irradiation during film growth with the concurrent reduction of gas-ion-irradiation, are realized for high-power impulse magnetron sputtering (HiPIMS) by the use of a synchronized, but delayed, pulsed substrate bias. In this way, the growth of stress-free, single phase  $\alpha$ -W thin films is demonstrated without additional substrate heating or post-annealing. By synchronizing the pulsed substrate bias to the metal-ion rich portion of the discharge, tungsten films with a  $\langle 110 \rangle$  oriented crystal texture are obtained as compared to  $\langle 111 \rangle$  orientation obtained using a continuous substrate bias. At the same time, a reduction of Ar incorporation in the films are observed, resulting in the decrease of compressive film stress from  $\sigma = 1.80$  to 1.43 GPa when switching from continuous to synchronized bias. This trend is further enhanced by the increase of the synchronized bias voltage, whereby a much lower compressive stress  $\sigma = 0.71$  GPa is obtained at  $U_s = 200$  V. In addition, switching the inert gas from Ar to Kr has led to fully relaxed, low tensile stress (0.03 GPa) tungsten films with no measurable concentration of trapped gas atoms. Room-temperature electrical resistivity is correlated to the microstructural properties, showing lower resistivities for higher  $U_s$  and having the lowest resistivity (14.2  $\mu\Omega\text{cm}$ ) for the Kr sputtered tungsten films. Moreover, we showed a very low resistivity of 13.9  $\mu\Omega\text{cm}$  at an ultrathin thickness of  $\sim 10$  nm grown on  $\text{SiO}_2$  without substrate heating or post annealing. The realization of self-ion-irradiation by accelerated  $W^+$  ions in HiPIMS discharge has an important role at the growth phase of nucleation and island growth, and consequently to the development of larger grains. These results illustrate the clear benefit of utilizing selective metal-ion-irradiation during film growth as an effective pathway to lead grain growth and to minimize the compressive stress induced by high-energetic gas ions/neutrals during low temperature growth of high melting temperature materials.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The concept of Bipolar HiPIMS was introduced some years ago by different groups and consist in applying a positive pulse with controlled pulse width and amplitude voltage after the conventional HiPIMS negative pulse [1]. This positive pulse allows the accurate acceleration of the positive metal ions towards the substrate, thus, promoting improved film properties such as reduced stress, higher film densification, improved mechanical properties - such as hardness or wear resistance- or better coverage of 3D complex parts.

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

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

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

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

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

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

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

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

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

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

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

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

# Wednesday Afternoon, May 24, 2023

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

Influence of different concentrations of Si into AlTiN and AlTiCrN coatings and multilayer architecture deposited by HIPIMS is discussed in two sections. The first one reports on the crystallographic phase stability investigations done by XRD, the microstructural TEM observations and the micromechanical studies to understand the role of the Si addition on these two nitride coatings. It was noticed that the Full Width at Half Maxima (FWHM) that can be correlated to the coating grain size, increases with Si addition for AlTiSiN coatings but not in the case of AlTiCrSiN coatings. The instrumented value for the wear resistance of these strain-hardened nitride coatings (Hardness/Young's Modulus ratio) was estimated to 0.09 for both coatings independently of the Si content and compared to the multilayer coating. The second discusses the investigations on the oxidation mechanisms and the kinetics of the oxide growth at 950 °C for various durations, mainly through a detailed description of the oxide layers by combining the investigations of X-ray Diffraction, Transmission Electron Microscopy, Dynamic Secondary Ion Mass Spectrometry and the Atom Probe Tomography of the different coatings. Thanks to isotopic oxidation tests with sequential time duration  $^{16}\text{O}/^{18}\text{O}$  and SIMS depth profile analyses, the rule of cationic diffusion process and the growth mechanism for each oxide scales have been proposed to explain the oxidation kinetics. Concerning the thermal resistance of the AlTiN coating at 950 °C, the introduction of Si below 5 at.% has largely increase the oxidation set point, from 800 °C to 950 °C (or even highest). The oxidation study for AlTiCrSiN coating has reported a different oxide scale morphology, a pure  $\text{TiO}_2$ -rutile nearer the surface, followed by the Al-rich oxide, then mixed oxide region of  $(\text{AlCr})_2\text{O}_3$  with small islands of  $\text{TiO}_2$  and an amorphous  $\text{SiN}_x$  surrounding the different oxide. A regular oxidation kinetic has been recorded for the AlTiCrSiN coating and no influence of the addition of Si has been recorded. For the moderate Si contents, thanks to an optimization of nanoscale thicknesses, a multilayer TiAlSiN/TiAlCrSiN coating architecture can inhibit the formation of  $\text{TiO}_2$  top-layer and also promotes the formation of Al-rich protective oxide layer.

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

### PVD Coatings and Technologies I

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

8:00am **B1-1-ThM-1 New Challenges and Opportunities for PVD Coatings in Metal Cutting Applications**, *Aharon Inspektor*, Carnegie Mellon University, USA **INVITED**

Many leading hard and superhard PVD coatings were developed as protective layers for cutting tools. Accordingly, the machining shop became a proving ground for testing new coatings and for the development of new concepts in materials science. In this talk, we will study how the ongoing 4<sup>th</sup> industrial revolution, with a multi-level connectivity of sensors, machines and systems and with computer controlled automated facility system, will affect the current machining routines. We will first examine the current criteria for choosing the right tool for the application, (and explain why many new coatings remain underutilized). Then we will review the basic features of Industrial Internet of Things (IIOT) revolution. And conclude by discussing how the expected changes in machining shop will affect the manufacturing landscape, change tooling criteria and likely open new opportunities for hard coated cutting tools.

8:40am **B1-1-ThM-3 Custom-Fit Hipims Coatings for Cutting Tools Used in a Wide Variety of Machining Applications**, *Stephan Bolz, B. Mesic, O. Lemmer, W. Kölker, C. Schiffers*, CemeCon AG, Germany

Coated cutting tools are used in many different machining applications. One of them is heavy duty machining. In this application, high wear resistance is primarily achieved by the highest possible thickness of the protective coating. To deposit such thick layers with good adhesion around the cutting edge, their residual stress must be kept as low as possible.

Completely different machining applications are, for example, hard machining or machining of austenitic stainless steel. Here, it is preferable to go for sharp edged cutting tools in combination with a thin and very hard wear protective layer.

As different as the applications may be, the HiPIMS technology offers the most possibilities in the PVD sector to specifically adjust coating properties.

The presentation will show how we can tailor properties of HiPIMS coatings for all different applications by adjusted selection of process parameters.

9:00am **B1-1-ThM-4 Film Growth Control at Cutting Edges to Overcome Edge Rounding**, *Otmar Zimmer, T. Litterst*, Fraunhofer Institute for Material and Beam Technology (IWS), Germany; *T. Kruelle*, Technical University Dresden, Germany

Cutting edges are often coated with hard and wear resistant films. These films are typically based on metal nitrides, - oxides or - carbides. They are deposited with thin film technologies such as PVD or CVD.

Unfortunately the geometries of the cutting edges are changed by the coating, in particular the edge radius is enlarged (edge rounding). Therefore the film thickness is limited and the initial radius of the uncoated tool must be smaller than the target radius of the coated edge.

A new coating process based on vacuum arc PVD was developed to overcome this situation. By means of selected coating materials and process conditions the film growth at edges can be controlled properly within certain limits. So it is possible to grow up edge sharper than the initial edge geometry.

The potential of this coating approach is great, because the film thickness limitation will be overcome. On the other hand the coating process is simplified because the edges to be coated can have a higher radius. So adhesion issues or local overheating are avoided.

Beside the new coating process also an evaluation method for the edges stability under different load conditions was developed and used. It is based on a well defined grinding process directly at the edge. Significant differences between various coating materials were found. Also a hypothesis concerning key parameters and the mechanism of the "sharpening effect" was established. Demonstrator tools were prepared this way. Edge analyses and application tests were performed. The paper gives an overview about the technological approach, testing procedures and results and also a couple of examples.

9:20am **B1-1-ThM-5 Computational Tool for Analyzing Stress in Thin Films**, *Eric Chason, T. Su, Z. Rao*, Brown University, USA

Stress in thin films can have a significant impact on performance and reliability of the devices they applied to, so there is a large motivation for understanding and controlling it. The stress is affected by many parameters (growth rate, temperature, microstructural evolution, composition, particle energy for sputter deposition, etc.) which offers numerous pathways to modify it. Over the past few years, we have developed a kinetic model that can predict the stress evolution under different conditions. This model has been incorporated into a computer program to analyze wafer curvature measurements of stress. Non-linear least squares fitting is used to determine a set of kinetic parameters that best explain the data. These parameters can then be used to predict and optimize the film stress. The program is implemented as a web-based application with associated instruction manuals to describe its use and physical basis. The program has a user-friendly interface that allows the user to customize the fitting range and which parameters are made to be common among the multiple data sets. This presentation will explain the physical basis of the model and give examples of its use.

9:40am **B1-1-ThM-6 Effect of CrAlN Coating Properties on Impact Fatigue of Tool Steel**, *K. Bobzin, C. Kalscheuer, M. Carlet, Muhammad Tayyab*, Surface Engineering Institute - RWTH Aachen University, Germany

The tools in forming processes like cold forging are subjected to cyclic impact loads. Physical vapor deposition (PVD) coatings can further improve the service life of such tools given the effect of coating properties on the fatigue behavior of coated substrate is well-understood. Previous investigations on the cyclic impact loading of PVD coated tool steels mainly correlate the plastic deformation of the substrate to the resulting coating cracks and delaminations. However, the influence of coating properties in such cases needs further clarification. Therefore, the current work aims to investigate the combined effect of thickness, morphology, elastic-plastic properties and residual stress state of the coating on the impact fatigue behavior of coated tool steel substrates. For this purpose, two CrAlN coatings with Al/Cr-ratio of  $x_{Al/Cr} = 0.12$  and  $x_{Al/Cr} = 0.52$ , each with a thickness of  $s = 1.7 \mu\text{m}$  and  $s = 3.5 \mu\text{m}$ , were deposited on HS6-5-2C substrates. The residual stresses were measured by focused ion beam-digital image correlation (FIB-DIC) ring-core method. The elastic-plastic properties of the coatings were determined by nanoindentation. The coated samples were subjected to cyclic impact testing with an initial Hertzian contact pressure  $p_H = \sim 9.7 \text{ GPa}$  and frequency  $f = 50 \text{ Hz}$ . The fatigue behavior was studied by analyzing the impact impressions for fatigue cracks with scanning electron microscopy after  $N = 0.1, 0.5$  and 1 million impacts. An increase in coating thickness led to higher compressive residual stresses of  $\sigma > -3 \text{ GPa}$  along with a decrease in indentation hardness  $H_{IT}$  of the coating. Such behavior could be attributed to a longer columnar morphology of thick coatings resulting in higher inclination and inter-columnar shearing under indentation load. This combined effect of the considered coating properties further influenced the impact fatigue as the thick coatings led to reduced resistance of coated substrates against initiation of fatigue cracks. The investigation contributes to adjusting coating thickness and resulting coating properties for higher tool service life in applications involving cyclic impact loading.

10:00am **B1-1-ThM-7 Toward Energy-efficient Physical Vapor Deposition: Routes Fordensification of  $(\text{Ti}_{1-x}\text{Al}_x)_{1-x}\text{W}_x\text{N}$  Thin Films Grown with no External Heating**, *Xiao Li, A. Pshyk, B. Bakht*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *M. Johansson Jöesaar, J. Andersson*, SECO Tools AB, Sweden; *I. Petrov*, University of Illinois at Urbana, USA; *L. Hultman, G. Greczynski*, Linköping Univ., IFM, Thin Film Physics Div., Sweden

In view of the sustainable development goals and to satisfy the demand for growing dense, hard coatings for protecting temperature-sensitive substrates, the quest for lowering energy consumption during thin film growth by magnetron sputtering becomes of pressing importance. Here, we introduce a method which replaces thermally-driven adatom mobility, necessary to obtain high-quality fully-dense films, with that supplied by effective low-energy recoil generation resulting from high-mass metal ion irradiation of the growing film surface. This approach enables the growth of dense and hard films with no external heating at substrate temperatures  $T_s \leq 130 \text{ }^\circ\text{C}$  in a hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS/DCMS) setup involving a high mass ( $m > 180 \text{ amu}$ ) HiPIMS target and metal-ion-synchronized bias pulses. Compared to conventional PVD methods, the energy savings are as much as 64%.

First, the effect of the metal ion mass on the densification, phase content, nanostructure, and mechanical properties of metastable cubic  $\text{Ti}_{0.50}\text{Al}_{0.50}\text{N}$

based thin films is reviewed. Three series of  $(\text{Ti}_{1-x}\text{Al}_x)_{1-x}\text{Me}_x\text{N}$  (Me = Cr, Mo, W) films are grown with  $x$  varied intentionally by adjusting the DCMS power. Results reveal a strong dependence of film properties on the mass of the HiPIMS-generated metal ions. All layers deposited with  $\text{Cr}^+$  irradiation exhibit porous nanostructure, high oxygen content, and poor mechanical properties. In contrast,  $(\text{Ti}_{1-x}\text{Al}_x)_{1-x}\text{W}_x\text{N}$  films are fully-dense even with the lowest  $W$  concentration tested,  $x = 0.09$ . We then discuss the effects of the high-mass  $W^+$  irradiation on film properties with  $W^+$  energy  $E_{W^+}$  (~90-630 eV, controlled by substrate bias voltage amplitude  $V_b$ ) and  $x$  (0.02-0.12, controlled by the HiPIMS pulse length). Results reveal that a strong coupling exists between the  $W^+$  incident energy and the minimum  $W$  concentration required to grow dense layers. We establish that dense, high-quality coatings can be obtained provided that the  $W^+$  momentum transfer per deposited metal atom is sufficiently high. Finally, the behavior of  $(\text{Ti}_{1-x}\text{Al}_x)_{1-x}\text{W}_x\text{N}$  films upon annealing in vacuum up to 1000 °C is demonstrated.

10:20am **B1-1-ThM-8 Effects of Nitrogen Contents on the Microstructure and Corrosion Resistant Evaluation of ZrTiNbSiFeNx High Entropy Alloy Coatings**, *Chen Wei-Yang, K. Yu-Lin*, National Taiwan University of Science and Technology, Taiwan; *L. Bih-Show*, Chang Gung University, Taiwan; *L. Jyh-Wei*, Ming Chi University of Technology, Taiwan

The high entropy alloy (HEA) coatings has been widely studied since 2004 because of their unique mechanical properties, good corrosion and high temperature oxidation resistance. In this study, the nitrogen contained ZrTiNbSiFe HEA coatings were grown using a high power impulse magnetron sputtering (HiPIMS) system. Six ZrTiNbSiFeNx thin films containing different nitrogen contents were grown under different Ar to nitrogen flow rate ratios. The chemical compositions of HEA films were analyzed by a field emission electron probe microanalyzer (FE-EPMA). The crystalline structures of HEA films were evaluated by an X-ray diffractometer. The cross-sectional morphologies of HEA films were analyzed by a field emission scanning electron microscope and a transmission electron microscope. The nanoindenter, scratch tester, and pin-on-disk wear tester were employed to study the hardness, adhesion and tribological properties of each HEA film, respectively. Effects of Ar to nitrogen flow rate ratios and nitrogen contents on the phase, microstructure, and mechanical properties of ZrTiNbSiFeNx thin films were explored in this work. The polarization curve and surface corrosion morphology of the film in 3.5 wt.% sodium chloride aqueous solution were tested by a potentiostat, and it was found that the corrosion resistance of the film was better than that of 304 SS.

10:40am **B1-1-ThM-9 Development of a Multilayer Ti/TiN/TiAlN/ReN Coating System and Evaluation of their Microstructural, Mechanical and Tribological Properties**, *Hernán Darío Mejía Vásquez, G. Bejarano Gaitán*, University of Antioquia, Colombia

The need to improve the wear resistance of hot work steels in applications such as injection and extrusion of aluminum alloys, and high-speed steels for machining different parts in manufacturing processes, have led to the development of new materials in the form of coatings. With the purpose of improving the wear resistance of the M2 high-speed steel, a multilayer coating system consisting of 1, 10, 20, 30 and 40 Ti / TiN bilayers was developed, followed by a TiAlN monolayer and an outer layer of ReN. The selection of the ReN is because this nitride is one of those considered super hard, with hardness around 40 GPa and also has a high chemical and thermal stability. The (Ti/TiN)<sub>n</sub>/TiAlN/ReN multilayer coatings were co-deposited onto AISI M2 steel by the DC and R.F. magnetron sputtering techniques with a total thickness of 2000 nm. For the deposition of the coatings, Ti, Al and Re targets were used, as well as argon for the deposition of titanium and a mixture of Ar / N<sub>2</sub> for the TiN, TiAlN and ReN layers. The SEM images of the cross section revealed a dense and homogeneous columnar growth structure, whose roughness and grain size decreases with the increase in Ti / TiN bilayers, as evidenced by the AFM measurements. The X-ray patterns showed peaks of the fcc cubic phases of ReN, TiAlN and TiN with preferential growth in directions (111) and (110), while only a single peak (110) was observed for Ti with bcc structure. The critical load, determined by the scratch test, increased from 25 N to 40 N with the increase in the number of bilayers of the coating. This behavior is associated with the growing compressive residual stresses of the multilayer system as the number of bilayers increases, which was determined by measuring the radius of curvature of selected samples before and after coating them. The hardness of the coatings increased from 22 GPa to 35 GPa and the wear volume decreased substantially with the increase in the period of the Ti / TiN bilayers. The greater resistance to wear is associated with the higher hardness, less roughness and greater adhesion of the

coatings as the number of bilayers increases. All deposited coatings showed greater performance in wear tests than uncoated steel.

11:00am **B1-1-ThM-10 High-Power-Density Sputtering of Industrial-Scale Targets: Micromechanical Case Study of Al-Cr-N**, *Fedor F. Klimashin*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *A. Lümkemann*, PLATIT AG, Switzerland; *J. Kluson, M. Ucik, M. Jilek*, PLATIT a.s., Czechia; *J. Michler, T. Edwards*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The coatings of cubic (Al,Cr)N are known for their exceptional protective properties, particularly high wear and oxidation resistance. Industrially, these coatings are mainly produced by means of cathodic arc evaporation (CAE). To further improve their performance, elimination of microscopic growth defects (e.g. droplets) is required. One way to achieve this goal could be to utilise a sputtering process. The large dimensions of the targets, however, pose an enormous technological challenge as rather small power (and plasma) densities can be achieved resulting ultimately in underperformance of sputter-deposited coatings.

Here, we introduce a novel sputtering technology allowing to reach high power densities for industrial tube targets. This is realised on the principle of a longitudinal movement of the magnetron inside the target. In doing so, peak power densities of 840 W/cm<sup>2</sup> for the overall power of 25 kW have been achieved. We then produced a series of the novel (Al,Cr)N coatings by sputtering Al<sub>60</sub>Cr<sub>40</sub> and Al<sub>70</sub>Cr<sub>30</sub> targets (Ø110x510 mm) and compared them to the benchmark CAE (Al,Cr)N coatings. Most of the sputtered coatings have stoichiometric composition, smooth surface and a moderate amount of growth defects. Significant improvements through recipe optimisation could be achieved resulting in hardness (about 35 GPa) and wear rates equal to those of current state-of-the-art CAE coatings. Interestingly, however, micropillar splitting tests revealed a significantly lower fracture toughness (2.5–3 MPa√m) as compared to their CAE counterparts (4–5 MPa√m). Finally, we also compare the results with a series of other industrial ceramic-like coatings, e.g. CrN, (Al,Ti)N, (Al,Ti,Si)N, TiB<sub>2</sub>.

11:20am **B1-1-ThM-11 Triboactive CrAlN+XS Coatings Deposited by Pulsed Arc PVD**, *K. Bobzin, C. Kalscheuer, Max Philip Möbius*, Surface Engineering Institute - RWTH Aachen University, Germany

Arc physical vapour deposition (PVD) is a widely used technology for coating deposition. Besides its advantages regarding deposition rate and the degree of ionization it shows open potential for reduced droplet emission and surface roughness respectively without a decreased deposition rate as with filtered arc PVD. A reduced surface roughness is highly relevant in tribological applications where friction reduction is targeted, especially under dry-running conditions. CrAlN+XS coatings with X = Mo, W show potential for friction and wear reduction under dry-running conditions due to their ability to form the solid lubricants MoS<sub>2</sub> and WS<sub>2</sub>. However, the deposition of electrically low conductive materials like MoS or WS is challenging for arc PVD at the current state of the art. Pulsed arc PVD is a promising technology to reduce droplet emission and surface roughness and additionally vaporize low conductive materials. In this work, CrAlN+XS coatings were developed using pulsed arc PVD. Basic coating and compound properties were analyzed regarding the influence of the incorporation of triboactive elements S, Mo, W. Additionally, a variation of pulse parameters was investigated on CrAlN+MoS coatings. Subsequently, tribological investigations of the CrAlN+XS coatings were performed under dry-running conditions using a pin on disk (PoD) tribometer. Besides wear and friction analysis the tribofilms on the coated basic parts and the uncoated 100Cr6 counter parts were investigated by Raman spectroscopy. Using pulsed arc PVD can decrease the droplet emission and therefore the surface roughness of the coatings. Under dry-running conditions the triboactive coatings show significantly lower wear. Additionally, the coefficient of friction (CoF) can be decreased compared to uncoated steel references. Nevertheless, further coating development is required to decrease the CoF to industrial relevant levels. For the first time CrAlN+XS coatings X = Mo, W were deposited using pulsed arc PVD. The CrAlN+MoS coating shows the highest sulfur content of xS = 9 at.-% verified by electron probe micro analysis (EPMA). Tribofilm analysis provided the proof of concept that CrAlN+MoS coatings deposited by pulsed arc PVD can form the solid lubricant MoS<sub>2</sub> under tribological load. This could be consistent with a reduced CoF. The results showed that pulsed arc PVD is a promising technology for applications where the evaporation of electrically low conductive target materials is required for coating deposition and a low surface roughness is targeted.

# Thursday Morning, May 25, 2023

11:40am **B1-1-ThM-12 Mechanical and Electrochemical Properties of AlCrN/Fe<sub>x</sub>N Coating Deposited onto AISI 4140 Steel**, *Omar Ramirez-Reyna*, National Polytechnic Institute, Mexico; *J. Pérez-Álvarez*, University of Guadalajara, Mexico; *G. Rodríguez-Castro*, National Polytechnic Institute, Mexico; *C. Rivera-Tello*, University of Guadalajara, Mexico; *A. Meneses-Amador*, National Polytechnic Institute, Mexico

In this study, aluminium chromium nitride (AlCrN) and iron nitrides (Fe<sub>x</sub>N) layers were formed on the surface of AISI 4140 steel through the cathodic arc PVD and gas nitriding processes, respectively. Three systems were evaluated by mechanical, adhesion and corrosion tests: AlCrN monolayer coating [AlCrN], duplex coating formed by AlCrN onto an iron nitrides interlayer [AlCrN/Fe<sub>x</sub>N] and only nitrided substrate [Fe<sub>x</sub>N]. The physicochemical characterization was performed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The AlCrN coatings thicknesses were 2.2 and 3 μm for AlCrN and AlCrN/Fe<sub>x</sub>N, respectively; whereas for Fe<sub>x</sub>N it was 10 μm. The mechanical properties were obtained by cross-sectional Berkovich indentation tests, where the Fe<sub>x</sub>N interlayer in the duplex coating AlCrN/Fe<sub>x</sub>N increase the hardness respect the single processes. Moreover, the adhesion of the coatings was evaluated in accordance with the VDI 3198 norm. The AlCrN/Fe<sub>x</sub>N coating presented the best adhesion. Finally, the coatings were evaluated by Potentiodynamic Polarization (PD) and Electrochemical Impedance Spectroscopy (EIS), using a conventional three electrode cell. All experiments were performed in a NaCl 3.5% wt. solution at 25 °C. In conclusion, the AlCrN/Fe<sub>x</sub>N duplex coating exhibited better behaviour under same testing conditions as compared with the AlCrN and Fe<sub>x</sub>N coatings, due to the presence of the iron nitrides interlayer.

12:00pm **B1-1-ThM-13 Mechanical and Electrochemical Properties for SiC<sub>x</sub>N<sub>y</sub> Coating as a Function of Nitrogen Content**, *L. Chang, Pin-Feng Huang, B. Chen, S. Tsai*, Ming Chi University of Technology, Taiwan

Amorphous silicon carbon nitride (a-SiC<sub>x</sub>N<sub>y</sub>) coatings were prepared on boron-doped silicon and 304 stainless steel substrates by high-power pulsed magnetron sputtering system. Employing the structural and chemical analysis by XRD, XPS(X-ray photoelectron spectroscopy), FE-EPMA(Field Emission-Electron Probe Micro-Analyser) and Raman spectroscopy, it was possible to determine that this coating presents a structure formed by an amorphous zone (a-SiC<sub>x</sub>N<sub>y</sub>). The a-SiC<sub>x</sub>N<sub>y</sub> coating with 23.3 at.% N demonstrates a hardness value of 21.7 Gpa. The friction coefficient of the coating with a high C-C bond content against a WC ball is as low as 0.07. The electrochemical behaviors of the deposited coatings in 3.5 wt.% NaCl solution were studied by using potentiodynamic polarization, electrochemical impedance spectroscopy, OM and SEM. The results show that the coated 304 stainless steel displays a better resistance to uniform and pitting corrosion than the bare material.

**Keywords:** SiC<sub>x</sub>N<sub>y</sub>, HiPIMS, Electrochemical properties, Amorphous

## Hard Coatings and Vapor Deposition Technologies Room Pacific F-G - Session B5-ThM

### Hard and Multifunctional Nanostructured Coatings

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

9:00am **B5-ThM-4 High-Temperature Properties of Multicomponent Nitride Coatings Deposited by PVD**, *Yuxiang Xu*, Guangdong University of Technology, China

**INVITED**

Al-containing transition metal nitrides possess high hardness and excellent wear resistance and, therefore, have been widely applied as protective coatings on tools and components. Whereas the development of advanced machining techniques and the application of difficult-to-cut materials require high-performance surface coatings, especially at elevated temperatures. This work used the alloying method to construct multicomponent nitrides to tailor their thermal stability, oxidation resistance, and tribological properties.

The TiAlCrZrTaWN coating with a mixing entropy of 14.8 J/mol·K was deposited using DC magnetron sputtering. Upon annealing, a retarded spinodal decomposition to AlN-rich and AlN-depleted nanosize domains can be recognized in the TiAlCrZrTaWN coating, accompanied by age-hardening. The occurrence temperature of peak hardness shifts from 800 °C of TiAlN to 900 °C of TiAlCrZrTaWN. Moreover, a high hardness of ~31 GPa can be obtained for TiAlCrZrTaWN after annealing at 1100 °C. The coherent

precipitation of wurtzite AlN was detected at the grain boundaries at 1000 °C.

For oxidation behavior, arc-evaporated TiAlCrTaWN coating was investigated in detail. The synergistic effect of Cr, Ta, and W significantly improves the oxidation resistance of TiAlN coatings. During the oxidation process, Cr promotes the formation of a dense Al<sub>2</sub>O<sub>3</sub> layer in the early stage, Ta slows down the rate of inward diffusion of O through the TiO<sub>2</sub> layer in the middle stage, and W forms nano-oxides at the interface to improve the combination of oxide scale and underneath nitride. Thermal stability and oxidation resistance are jointly improved in the TiAlCrTaWN system.

To decrease the high-temperature friction of nitride coatings, Mo and Cu were introduced to the TiAlN coating. Alloying with Mo can reduce the friction coefficient at room temperature with water vapor aid and distinctly increase the wear resistance. While the tribological behavior of TiAlMoN is similar to TiAlN at 600 °C. The co-addition of Mo and Cu promotes the formation of Mo–O/Cu–O oxide tribolayer with the novel nanocore-shell structure during friction at 600 °C. The array of Mo–O/Cu–O nanopillars inside the wear track provides low shear resistance and decreases the friction pair's contact area, thus decreasing friction from high temperatures.

In a word, alloying is versatile in changing the high-temperature properties of hard nitride coatings. And alloying elements need to be explicitly selected for specific goals.

9:40am **B5-ThM-6 Effect of Ion Density Flux Ratio on Properties of Protective Hard (Ti,V)B<sub>2</sub> Coatings Sputtered by Cylindrical Magnetron**, *Daniel Karpinski, P. Karvankova, C. Krieg*, Platit AG, Switzerland; *J. Kluson*, Platit a.s., Czechia; *B. Torp*, Platit Inc., USA; *A. Lümkmann*, Platit AG, Switzerland

Titanium diboride doped by vanadium (Ti,V)B<sub>2</sub> coating as well as pure TiB<sub>2</sub> due to their densely packed hexagonal structure with strongly covalently bonded boron atoms separated by metallicity bonded metal layers exhibits very high hardness  $H \geq 40$  GPa, high elastic modulus  $E \geq 500$  GPa, very high melting point about 3000 °C, high chemical inertness, and therefore low sticking to soft metals. Thanks to these outstanding properties, the TiB<sub>2</sub> has nowadays become very attractive as a protective coating in industrial applications e.g., non-ferrous metal machining such as aluminum-based, and titanium-based metals, etc. and coin stamping. The hard TiB<sub>2</sub> is becoming a good alternative to hard tetrahedrally amorphous carbon (ta-C) with high amounts of diamond bounds (sp<sup>3</sup>), due to its high deposition rate, low roughness, and cleaner process. Moreover, both TiB<sub>2</sub> as well as ta-C coatings often exhibit high compressive macro-stress above -5 GPa which can lead to adhesion failure. High compressive stress can be relaxed already by small additions of VB<sub>2</sub> [1], and/or can be tuned by controlling the ion density flux to deposition flux ratio ( $J_i/J_d$ ) [2]. On top of that, the addition of V to TiB<sub>2</sub> has no significant effect on the mechanical properties unlike the  $J_i/J_d$ . Except varying the bias voltage and/or magnetron power, the  $J_i/J_d$  controlling is not possible in most conventional sputtering systems. In this study the industrially developed SCIL® (sputter coatings induced by lateral glow discharge) technology was used to independently control the  $J_i$ . In the SCIL® technology [2], the coating is deposited by sputtering of the central cylindrical cathode, and in the meantime, a secondary discharge (LGD) is also ignited between two cylindrical lateral electrodes. One of these lateral electrodes is acting as an anode – powered by a positive potential (LGD®), while the other is a typical arc cathode. During the sputtering process, the arc cathode has been shielded to avoid the deposition of the evaporated materials on the substrates. Where the  $J_i$  is then controlled by tuning the electron current to the anode (LGD®).

[1] Ch. Mitterer, V. L. Terziyska, M. Tkadletz, L. Hatzenbichler, D. Holec, V. Moraes, A. Lümkmann, M. Morstein, P. Polcik, *Synthesis and characterization of sputtered (Ti,V)B<sub>2</sub> hard coatings*, ICMCTF (2019) oral contribution.

[2] R. Zemlicka et al., *Enhancing mechanical properties and cutting performance of industrially sputtered AlCrN coatings by inducing cathodic arc glow discharge*, Surface & Coatings Technology 422 (2021) 127563.

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10:00am **B5-ThM-7 Development of TiB<sub>2</sub> Coatings in a New Generation Industrial Reactor Based on Hybrid DC-Pulsed and HIPIMS Magnetron Sputtering on HSS Steels – A Tribological Study, Gonzalo Garcia Fuentes, J. Fernández, J. Fernández-Palacio, AIN, Spain; H. Gabriel, PVT Vakuum Technik, Germany**

Titanium di-boride (TiB<sub>2</sub>) 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<sub>2</sub> is well known to exhibit low moderate toughness, which limits its 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 HIPIMS/DC\_pulsed industrial scale system equipped with 4 sputtering evaporators and a 500/300 mm H/W effective working volume is chosen to implement the TiB<sub>2</sub> coating formulations.

TiB<sub>2</sub> coatings were prepared on M2 HSS tool steel using HIPIMS conditions as a function of the BIAS potential, and tuning those pulse length and frequencies providing the maximum sputtering yield of the diboride target. In addition, the hybrid HIPIMS/DC\_pulsed mode was implemented using two targets in opposition around the sample holder volume. Alternative deposition configurations such as gradient (increasing) DC\_pulse power mode on constant power HIPIMS have been designed and characterized.

The coating microstructures have been characterized using x-ray diffraction and scanning electron microscopy in top and cross-sectional view. Nano-indentation hardness and standard wear rate were carried out to frame the overall mechanical properties at room temperature. It has been found that the HIPIMS coatings (without DC\_pulse co-sputtering) exhibit good adhesion on M2-steel, and less tendency to crack under indentation loading as the BIAS potential decreases. On the other hand, the indentation hardness of the hybrid deposited coatings (HIPIMS and DC\_sputtered) decrease as the DC\_pulsed/HIPIMS power ratio of the opposing targets increases.

The frictional properties of the TiB<sub>2</sub> coatings are tested against aluminium. A test matrix of variables such as temperature (RT-300°C) and sliding-speed (10-50 cm/s) has been set in order to identify the mild-to-severe galling threshold conditions at the TiB<sub>2</sub> - Aluminium interfaces. The comparison of the frictional properties of the deposited TiB<sub>2</sub> coatings with benchmark TiN and CrN HIPIMS sputtering coatings sliding against aluminium clearly indicated that the TiB<sub>2</sub> can be considered an effective antigalling coating.

10:20am **B5-ThM-8 Nanoporous/Nanocomposite Thin Films by Magnetron Sputtering Deposition in Helium and Other Light Gases: New Materials and Applications, Asunción Fernández, Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Spain**

**INVITED**

He ions (100 eV-500 keV) and He plasma-surface interactions have been widely investigated due to their technological interest related to damage in nuclear reactor materials. The formation of He filled high pressure nanobubbles and porous fuzz structures have been widely reported as undesired damage effects. The work to be presented aims to transform the formation of defects (i.e. gas bubbles, porosity) in a solid matrix into an opportunity for the controlled fabrication of nano-structured thin films and coatings by using "magnetron sputtering (MS)" deposition with He and N<sub>2</sub> as process gas. Results on this bottom-up fabrication methodology and the characterization of microstructure and composition will be shown for the case of nanoporous He-charged silicon [1] and N<sub>2</sub>-charged silicon oxinitride [2] films. A revision of up to now proposed applications will be presented with special details for the use of the new "solid-gas" nanocomposite materials as <sup>4</sup>He and <sup>3</sup>He solid targets for nuclear reaction studies [3]. Among others the reduction of the refractive index or the fabrication of nanostructured catalytic coatings are proposed. The use of flexible supports and electron tomography for the 3D reconstruction at the nano-scale will be respectively illustrated for newly investigated matrix elements as Co and Cu with Helium as process gas.

In summary the presented results will show a perspective interdisciplinary and collaborative international research covering the synthesis, advanced characterization and applications of functional thin films and coatings prepared by plasma assisted magnetron sputtering deposition in He and other light gases.

[1] R. Schierholz, B. Lacroix, V. Godinho, J. Caballero-Hernández, M. Duchamp, A. Fernández. *Nanotechnology* 26 (2015) art.nr. 075703

[2] V. Godinho, T. C. Rojas, A. Fernández. *Microporous and Mesoporous Materials* 149 (2012) 142-146

[3] A. Fernández, D. Hufschmidt, J.L. Colaux, J.J. Valiente-Dobón, V. Godinho, M.C. Jiménez de Haro, D. Fera, A. Gadea, S. Lucas. *Materials & Design* 186 (2020) art.nr. 108337.

11:00am **B5-ThM-10 Mechanical Properties of Epitaxial TiN(001)-TiC(001) Superlattices, Moïshe Azoff-Slifstein, Rensselaer Polytechnic Institute, USA; S. Lee, University of Connecticut, USA; D. Gall, Rensselaer Polytechnic Institute, USA**

Superlattices of 1- $\mu$ m-thick epitaxial TiN(001)-TiC(001) layers are deposited on MgO(001) at 1100 °C in order to explore superlattice hardening in a cubic nitride-carbide materials system. The processing gas during reactive magnetron sputtering is alternately switched between Ar/N<sub>2</sub> and Ar/CH<sub>4</sub> mixtures to obtain TiN-TiC superlattice films with equal nitride and carbide fractions and a variable superlattice bilayer period  $\Lambda = 1.5$ -30 nm, as measured using X-Ray diffraction (XRD)  $\vartheta$ - $2\vartheta$  superlattice peaks. XRD  $\omega$ -rocking curves indicate strong crystalline alignment with a peak width increasing from 0.1 - 0.6° with decreasing  $\Lambda$ . Reciprocal space maps confirm a cube-on-cube epitaxy of alternating rock-salt structure TiN(001) and TiC<sub>x</sub>(001) layers and indicate fully-strained TiN(001)-TiC(001) superlattices which are coherent with the MgO(001) substrate for  $\Lambda = 3$  and 30 nm but are partially relaxed for  $\Lambda = 6$  and 13 nm. Scanning electron microscopy analyses show surface protrusions due to misoriented grains which increase in density from  $\rho = 0.4$  to 1.0  $\mu\text{m}^{-2}$  for  $\Lambda = 1.5$  to 3 nm but then decrease back to  $\rho = 0.06 \mu\text{m}^{-2}$  for  $\Lambda = 30$  nm. The misoriented grains cause large variations in nanoindentation measurements, resulting in an artificial depth-dependent hardness  $H$  for 20, 80, and 10% of indentations for multilayers with  $\Lambda = 1.5, 6,$  and 30 nm, respectively. Accounting for these deviations allows to determine  $H$  and the elastic modulus  $E$  as a function of  $\Lambda$ : The TiN-TiC superlattice system demonstrates an increase in  $H$  from 23 to 34 GPa with increasing  $\Lambda = 1.5$  to 6 nm, followed by a decrease to  $H = 30$  GPa for  $\Lambda = 30$  nm. Similarly,  $E$  increases from 450 GPa for  $\Lambda = 1.5$  nm to a maximum of 750 GPa for  $\Lambda = 6$  nm and a subsequent drop to  $E = 450$  GPa for  $\Lambda = 30$  nm. The observed superlattice hardening is attributed to local strain variations and dislocation pinning at the TiN-TiC interfaces.

11:20am **B5-ThM-11 Tensile and Compressive Stress in Sputtered Cu/W Nanomultilayers: Correlation with Microstructure, Thermal Stability, and Thermal Conductivity, Giacomo Lorenzin, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; M. bin Hoque, University of Virginia, USA; D. Ariosa, Universidad de la Republica, Montevideo, Uruguay; L. Jeurgens, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; E. Hoglund, J. Tomko, P. Hopkins, University of Virginia, USA; C. Cancellieri, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland**

Physical vapor deposition (PVD), in particular magnetron sputtering, is a commonly adopted technique to produce nanomultilayer (NML) materials because it allows a full control of thickness, period, and interface roughness by tuning deposition parameters. During the growing procedure, however, internal residual stress is generated in the forming multilayer. Stress represents one of the main factors determining failure and reliability issues, hence affecting the durability and the performance of functional coatings. Nevertheless, for some specific applications, a controlled level of stress is desirable to enhance target properties like mechanical strength, thermal stability, and thermal conductivity. For this reason, it is of paramount importance to study the relation between deposition parameters and stress states in NMLs. Copper-tungsten (Cu/W) multilayers are one of the most widely used nanomaterials in electronic, optical, and sensing devices because of the combination between the electrical and thermal properties of Cu and the mechanical strength of W.

In this work, Cu/W multilayers were deposited by magnetron sputtering, achieving configurations with opposite stress values (i.e., tensile and compressive) by tuning deposition parameters. Stress was monitored both in-situ by measuring the substrate curvature and ex-situ by XRD. Stress values derived with these two techniques were compared and the difference was ascribed to interface stress, whose values have opposite signs in tensile and in compressive multilayers. Samples with opposite stresses exhibit also different microstructures, which were characterized by SEM, STEM, XRD, and sputter depth profiles acquired with XPS. In particular, tensile NMLs have a more disordered structure than the compressive ones. When annealed at temperatures >700°C, Cu/W NMLs degrade and transform into nanocomposites (NCs) with W nanoparticles embedded in a Cu matrix. Stress states and microstructure affect the transition temperature, with compressive NMLs exhibiting a better thermal stability and resistance to degradation. In addition, out-of-plane thermal conductivity was extensively characterized in NMLs and in NCs and, once

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again, compressive samples outperform the tensile counterpart. Within this work, we were able to show how a fine tuning of deposition parameters can lead to Cu/W NMLs with different stress states and microstructures, and we highlighted the effects on the thermal stability and the thermal conductivity. This paves the way to stress tailoring in multilayers for specific properties and applications.

**11:40am B5-ThM-12 Investigation of Thermal Properties of PECVD Ti-Si-C-N Nanocomposite Coatings, Alexander Thewes, L. Broecker, IOT TU Braunschweig, Germany; H. Paschke, T. Brueckner, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany; C. Sternemann, M. Paulus, DELTA TU Dortmund, Germany**

Ti-based nanocomposite coatings are known for high hardness values, drawing attention to tribological applications, where the wear reduction on tool surfaces can be achieved by protective thin films. In this case, nanocomposite structures are made of nanocrystalline (nc-) grains embedded in an amorphous (-a) matrix, increasing the hardness due to the Hall-Petch effect. In addition to high hardness, this is due to outstanding properties concerning the coefficient of friction (e.g. Ti-C-N) and the oxidation resistance (e.g. Ti-Si-N). In this study, Ti-Si-C-N nanocomposite coatings were investigated and possibly combining advantageous properties of Ti-C-N and Ti-Si-N coatings. The coating deposition was tailored to form a graded system, beginning with TiN and gradually increasing the amount of Si and C to form Ti-Si-C-N. The a-matrix partially consists of Si<sub>3</sub>N<sub>4</sub> phases, which are highly resistant against oxidation, act as diffusion barrier for O<sub>2</sub>, and enclose the nc-Ti(C,N) grains, that are vulnerable towards oxidation. To understand the fundamental principles behind Ti-Si-C-N nanocomposite coatings and their thermal properties, the phase composition and micro- and nanostructure were investigated by means of X-ray diffraction, Raman spectroscopy, SEM, and tempering behavior of samples. EPMA analysis was used to correlate the chemical composition with the coatings build-up and thermal properties. Ti(C,N) phases were identified under use of X-ray diffraction, with a strong pronunciation of the (200) reflex. The 2D detector enabled an analysis of preferential orientations of crystalline lattices. By these means, a texture was identified. Via Raman spectroscopy, a-C was detected as a mixture of D-band and G-band phases. *In-situ* X-ray diffraction experiments at 900 °C showed only minor signs of oxidation compared to room temperature. A sample tempered at 900 °C for 1 h in air composed of 2.5 µm oxide layer with 0.8 µm of as-deposited Ti-Si-C-N coating underneath. These results are promising to use Ti-Si-C-N as a protective coating in high temperature applications, e.g. on extrusion dies in hot extrusion of copper.

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country D - Session B8-2-ThM

#### HiPIMS, Pulsed Plasmas and Energetic Deposition II

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

**9:00am B8-2-ThM-4 Hipims Deposition of Ultrathick Au-Ta Coatings: Effects of Deposition Rate and Substrate Tilt, Leonardus Bimo Bayu Aji, E. Kim, J. Merlo, S. Shin, G. Taylor, L. Sohngen, A. Engwall, A. Baker, D. Strozzi, B. Bocklund, E. Moore, A. Perron, S. Kucheyev, Lawrence Livermore National Laboratory, USA**

Targets for indirect-drive inertial confinement fusion require hohlraums. These are centimeter-scale sphero-cylindrical heavy-metal cans with wall thicknesses of ~10 microns or larger. The fabrication of hohlraums by physical vapor deposition is challenging as it involves ultrathick coatings on non-planar substrates in the oblique angle deposition regime. Here, we study Au-Ta alloy films deposited on rotating non-planar substrates by high power impulse magnetron sputtering (HiPIMS) at different deposition rates and substrate tilt geometries. We use mass-resolved ion energy spectrometry and optical emission spectroscopy to monitor plasma discharge characteristics. Results show that the deposition rate can be effectively used to control the major film properties relevant to ICF applications, including residual stress and electrical resistivity.

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

**9:20am B8-2-ThM-5 Self-Sputtering Identification in Helium HiPIMS Discharge with Molybdenum Target, Abderzak el-Farsy, E. Mmorel, Laboratoire de Physique des Gaz et des Plasmas, France; Y. Yoann Rozier, SuperGrid Institute, Villeurbanne, France; T. Minea, Laboratoire de Physique des Gaz et des Plasmas, France**

Magnetron sputtering is a worldwide used process for thin film deposition covering a large panel of applications. In the last two decades, High Power Impulse Magnetron Sputtering (HiPIMS) has been developed and intensively studied. It is an ionized vapor deposition technique exploiting the high plasma density generated during a short time when a huge power ( $> 10^7$  W/m<sup>2</sup>) boosts the plasma.

In this contribution, we analyzed the current-voltage waveforms during HiPIMS discharge period working with helium as background gas and a 1-inch molybdenum target. The gas pressure was fixed at 5 Pa, and the pulse duration was 90 ms with a repetition frequency of 50 Hz. From the current waveform of the discharge, two phases were identified: (i) a current peak (up to 90 A) reached at the pulse start ( $t < 30$  µs) followed by (ii) a decay transition between 30 to 90 µs towards a steady-like state ( $I \sim 35$  A).

To highlight the physical process behind this behavior, a study was carried out by increasing the applied voltage of the target until 1000 V. Optical emission spectroscopy (OES) qualitatively tracks the neutral and ionized species of He and Mo present in the ionization region. In addition, the plasma electron density can be evaluated from the line profiles of H<sub>α</sub> and H<sub>β</sub> emissions *via* the Stark effect by high-resolution OES. Combining all this information, it comes out that the self-sputtering process sustains the discharge in the second part of the pulse (30-90 µs) when the high voltage is applied, while the gas itself (He) plays the dominant role in the beginning, being responsible for the peak current.

**9:40am B8-2-ThM-6 On Working Gas Rarefaction in High Power Impulse Magnetron Sputtering, Kateryna Barynova, S. Suresh Babu, University of Iceland; M. Rudolph, Leibniz Institute of Surface Engineering (IOM), Germany; J. Gudmundsson, University of Iceland**

The ionization region model (IRM) is applied to explore the working gas rarefaction in high power impulse magnetron sputtering discharges operated with graphite, aluminum, copper, titanium and tungsten targets. The various contributions to working gas rarefaction including electron impact ionization, kick-out by the sputtered species, and diffusion, are evaluated and compared for the different target materials, over a range of discharge current densities. For all cases the working gas rarefaction is found to be significant, and to be caused by several processes, and that their relative importance varies between different target materials. In the case of a graphite target, electron impact ionization is the dominating contributor to the working gas rarefaction, with 55 - 64 % contribution, while kick-out, or sputter wind, has negligible influence, whereas in the case of tungsten target, kick-out dominates, with 39 - 48 % contribution. The relative role of kick-out by the sputtered species increases and the relative role of electron impact ionization decreases with increased mass of the target atoms. The main factor influencing how much each process contributes to working gas rarefaction is the mass of the target species, while it is not clear how the ionization potential and the cohesive energy, that determines the most probable velocity with which the sputtered particles leave the target, influence the relative contribution of the various terms.

**10:00am B8-2-ThM-7 Spokes in HiPIMS: Help or Hindrance?, Julian Held, University of Minnesota, USA; P. Maaß, M. George, W. Breilmann, S. Thiemann-Monjé, V. Schulz-von der Gathen, A. von Keudell, Ruhr University Bochum, Germany**

**INVITED**

Spokes are long wavelength oscillations observed in the magnetized region of high power impulse magnetron sputtering (HiPIMS), as well as other ExB discharges. Initially, spokes in HiPIMS were observed as regions of intense light emission, moving along the E x B direction of the discharge, just above the cathode surface. By now, it has become clear that these bright structures are accompanied by intense fluctuations in electron density, temperature, and plasma potential. These variations in plasma potential might lead to electron and ion heating, as well as increased transport of charged species across the magnetic field lines. As such, spokes have long been considered a possible pathway in increasing the deposition rate of HiPIMS discharges.

In this contribution, we will review our current understanding of the physical mechanisms creating and sustaining the spokes. Based on this, we will try to answer whether spokes have a positive influence on either the deposition rate or the energy of ions and whether or not they can be

manipulated to improve these advantages.

10:40am **B8-2-ThM-9 Effect of Plasma Nitriding Pretreatment on the Mechanical and Wear Properties of Tungsten Carbide Substrate, and AlCrN Coating Deposited by High-Power Impulse Magnetron Sputtering**, *F. Yang*, Department of Mechanical Engineering, National Taiwan University of Science and Technology, and Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan; *T. Liu, Guan-Lun Shen, I. Chen*, Department of Materials Engineering, Ming Chi University of Technology, Taiwan; *Y. Kuo*, Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taiwan; *C. Chang*, Department of Materials Engineering, Ming Chi University of Technology, and Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

This paper examines the mechanical and wear properties of Tungsten Carbide substrates subjected to plasma-nitriding (PN) before, and after being coated with AlCrN by high-power impulse magnetron sputtering (HiPIMS). Low-temperature (~300 °C) plasma nitriding treatment was applied for various durations (0 hr, 0.5 hr, 1 hr, and 1.5 hr) with the aim of maximizing the adhesion strength and wear resistance by improved the mechanical properties of the tungsten carbide substrate for after AlCrN coating. XPS and TEM revealed the effect of plasma nitriding on the tungsten carbide substrate, the diffusion of nitrogen into the tungsten carbide substrates to form new nitrides as such W-N and C-N bonding. Result in the hardness is enhanced from 1534 to 2034 Hv. After that, the AlCrN deposited on nitride tungsten carbide substrate by HiPIMS process. The measurement results indicate that the adhesion strength was improved from 70 to above 150 N, and the hardness was enhanced from 2257 to 2568 Hv with increasing plasma nitriding durations. Due to substrate hardening effect led to the wear rate can be decreased from 14.5 to 3.4 (10<sup>-8</sup> mm<sup>3</sup>/Nm). Therefore, the AlCrN coating deposited on tungsten carbide substrate with plasma nitriding pretreatment is proved can enhance the mechanical and wear properties of the AlCrN thin film.

Keywords: plasma nitriding, high-power impulse magnetron sputtering, AlCrN coating

11:00am **B8-2-ThM-10 Highly Ionized Pulse Sputtering of Seed Layers for Through Silicon Vias**, *Juergen Weichart*, Evatec AG, Switzerland

Directional deposition based on HiPIMS has been developed for barrier and copper seed layers in Through Silicon Vias (TSV) with very high aspect ratios up to 20:1. Due to demanding particle and uniformity requirements stationary sputtering with a large target diameter up to 450mm is needed. To avoid redeposition rotating magnets must be designed carefully, which is even more important due to the return effect of metal ions to the target in HiPIMS discharges. A concept of adjustable magnets has been developed to enable a stable peak current with progressive target erosion. High frequency synchronized bias is applied on the pedestal for insulating substrates with an appropriate matching for the highly dynamic impedance conditions at low duty cycles. The challenges to achieve good uniformities on 200mm or on 300mm substrates for the deposition rate, the deposition profile in the vias, and the specific resistivity are demonstrated. With increasing ion impact the average grain size increases from 30 to 70nm, accompanied by an increase of the (002) over the (111) orientation, as measured by  $\Theta$ -2 $\Theta$  measurements. Typically, in deep Silicon etched vertical vias of 5 $\mu$ m diameter and 25 $\mu$ m depth, hence with an aspect ratio (AR) of 5:1, the minimal side wall coverage is 4% for Ti or Ta and 2% for Cu, while in vias of 10 $\mu$ m diameter and 100 $\mu$ m depth (AR 10:1) the minimal side wall coverage is 2% for Ti or Ta and 1% for Cu. The difference between Cu and Ti or Ta is explained by the high sputter yield of Cu, which reduces the effective ionization degree for Cu in the plasma. For the subsequent enforcement by well-developed electroplating processes of Cu (ECP) for heterogeneous integration it has been found that 20nm of the seed layer is sufficient.

11:20am **B8-2-ThM-11 Deposition Environment and Microstructure of Transition Metal Nitride Thin Films Deposited at CMOS-Compatible Temperatures for Tunable Optoelectronic and Plasmonic Devices**, *Arutian P. Ehasarian*, Sheffield Hallam University, UK; *R. Bower*, Imperial College London, UK; *D. Loch*, Sheffield Hallam University, UK; *A. Berenov*, *B. Zou*, Imperial College London, UK; *P. Hovsepian*, Sheffield Hallam University, UK; *P. Petrov*, Imperial College London, UK

Plasmonic metamaterials based on transition metal nitrides have received significant interest to enable environmentally stable and tunable optoelectronic devices. However, the deposition conditions for achieving low optical losses and synthesis temperatures which are compatible with

semiconductor processing are unclear. We have deposited binary, ternary and layered transition metal nitride thin films based on titanium and niobium nitride using constant-current High Power Impulse Magnetron Sputtering (HiPIMS) without substrate biasing. Enhanced plasma density, dissociation of nitrogen molecules and metal-to-nitrogen ratio are investigated using optical emission spectroscopy and energy-resolved mass spectroscopy as factors influencing the microstructure and optical properties of the materials.  $N^+$ :  $N_2^+$  ratios exceeding 1 were achieved at high peak power density in a stable deposition process due to constant current control mode of operation. The temporal evolution of the discharge operating in a constant current regime is discussed. Epitaxial films on MgO substrates and polycrystalline films on glass and steel both showed low optical losses at a deposition temperature of less than 300°C. A random texture was observed at film thicknesses of 50 nm with Nb-containing films exhibiting an enhanced (200) texture attributed to bombardment by a heavier ion. Continuous well-defined layers with thickness of 5 nm were obtained as observed by TEM. Tunability of the plasma frequency in the ultraviolet to visible spectral ranges was achieved through the Ti:Nb ratio. The dense grain boundaries obtained in the HiPIMS deposition environment may contribute to efficient plasmon dispersion in the material. The thin film quality combined with the scalability of the deposition process indicates that HiPIMS can pave the way towards the industrial fabrication of next generation plasmonic devices.

11:40am **B8-2-ThM-12 On the Connection between the Self-Sputter Yield and Deposition Rate in High Power Impulse Magnetron Sputtering Operation**, *Jon Tomas Gudmundsson*, University of Iceland; *M. Rudolph*, Leibniz Institute of Surface Engineering (IOM), Germany; *K. Barynova*, University of Iceland; *J. Fischer*, Linköping University, Sweden; *S. Suresh Babu*, University of Iceland; *N. Brenning*, *M. Raadu*, KTH Royal Institute of Technology, Sweden; *D. Lundin*, Linköping University, Sweden; *H. Hajihoseini*, University of Twente, Netherlands

The magnetron sputtering discharge is a plasma discharge-driven physical vapor deposition technique, that is utilized in a range of industries. When the magnetron sputtering discharge is driven by high power unipolar pulses of low repetition frequency, and low duty cycle, it is referred to as high power impulse magnetron sputtering (HiPIMS). HiPIMS operation results in increased ionization of the sputtered species and lower deposition rate than the dc magnetron sputtering discharge, when operated at the same average power. The HiPIMS discharge can contain a large fraction of ionized sputtered material. This means that, at least some fraction, often a significant fraction, of the ions involved in the sputter process are ions of the target material. This also implies that a large fraction of the ions of the sputtered species can be attracted back to the target and is not deposited on the substrate to form a film or coating. Self-sputtering and the self-sputter yield are therefore expected to play a significant role in HiPIMS operation, and have a decisive impact on the film deposition rate, at least for metal targets. We have applied the ionization region model (IRM) [1] to model HiPIMS discharges in argon with a number of different targets [2,3], to study various processes, such as working gas rarefaction and refill processes, the electron heating mechanisms, ionization probability and back-attraction of the sputtered species, and recycling mechanisms. It will be discussed how these processes depend on the mass and ionization potential of the target atom, the discharge current density, and self-sputter yield of the target.

[1] Huo *et al.*, Journal of Physics D: Applied Physics **50**, 354003 (2017)

[2] Gudmundsson *et al.*, Surface and Coatings Technology **442**, 128189 (2022).

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## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country C - Session B1-2-ThA

#### PVD Coatings and Technologies II

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

1:20pm **B1-2-ThA-1 Contemporary Trends in the Decorative Coatings**, *Ivan Kolev, A. Fuchs, P. Immich, H. Vercoulen, D. Barnholt*, IHI Hauzer Techno Coating B.V., Netherlands

Decorative coatings have been increasingly used since 1990's in various applications and end products. Originally applied to door handles and sanitary hardware from the premier segment, their use has expanded towards mobile appliances and automotive interior and exterior parts. Nowadays, decorative PVD and PECVD finishes are widely spread in a broad range of consumer products covering almost the whole price range. This spread comes with continuously growing demand for wider range of colors from one side and improved or new functional properties from other side. Originally limited to variations of golden and metal colors, today's market demands deep black, rose gold, purple, brown, blue and other colors. Next to the appearance, properties like scratch, corrosion and fingerprint resistance become a must. For many applications, which are in direct contact with the human body, antimicrobial properties are highly desired. In the automotive industry, aesthetics often needs to be combined to the possibility of back lighting or radar transparency. To meet all this, the individual benefits of different PVD and PECVD technologies need to be combined in a single process.

In this talk, we are presenting the current state of the contemporary decorative industrial coatings combining technologies such as UBM sputtering, HIPIMS, arc evaporation and (microwave) PECVD. The paper discusses color development, radar transparency, antibacterial properties and hydrophobic performance.

1:40pm **B1-2-ThA-2 Metallic Chromium Coatings with Different Thicknesses on Polycarbonate Surface**, *Filipa Ponte, P. Sharma, N. Figueiredo, S. Carvalho*, CEMMPRE, Department of Mechanical Engineering, University of Coimbra, Coimbra, Portugal

Over the years, polymer engineering comes out as a benefit for the automobile industry. Polymers are known for their good properties such as flexibility, durability, and lightweight material with low-cost production make them perfect for their various uses in automobiles, including for decorative purposes, and that is why they can be found almost everywhere from the dashboard, logos, and door panels to the exterior body and much more. To provide a decorative look on the polymer surface, in the present study, a metallic coating of Chromium (Cr) is deposited via magnetron sputtering on Polycarbonate (PC) polymer surface. Deposition of metallic coating directly onto the polymer surface is a challenge as the coatings are subjected to external thermal shocks or impact stresses and as a result, can easily crack. To overcome this challenge, the coating has been done after pre-treatment of the polymer surface i.e., plasma etching. The selection of plasma etching parameters has been carried out by changing bias voltage (400 V to 300 V, or without bias), etching time (450 sec to 150 sec), and pressure (0,4 Pa and 1 Pa). After analyzing the impact of these different etching parameters, the PC polymer surfaces were plasma treated at 300 voltage bias, 1 Pa pressure for 150 seconds, and then, coated with a Cr layer at ~0.74 nm/sec deposition rate. This plasma etching treatment, not only helps in saving from cracking of Cr coating, but it also provides good adhesion on the polymer surface. This study includes the optimization of the thickness of the Cr layer with lower defects (pinholes, cracking, reflectivity, hardness, and surface energy). The pretreated and untreated polymer surfaces were characterized for a wide range of thicknesses from ~400 nm to ~1600 nm. It has been observed that up to 1400 nm, we can achieve a shiny, noncracking, and adhesive Cr coating on this polymer surface.

**Keywords:** Plasma etching, Metallic coating, Magnetron sputtering, Polycarbonate

2:00pm **B1-2-ThA-3 Effect of O<sub>2</sub> Addition During Magnetron Sputtering Deposition on the Growth and Chemistry of Ag Thin Films**, *Ramiro Zapata*, Laboratoire Surface du Verre et Interfaces UMR 125 / Institut de Nanosciences de Paris UMR 7588, France; *R. Lazzari*, Institut des Nanosciences de Paris UMR 7588, France; *H. Montigaud, M. Balestrieri, I. Gozhyk*, Laboratoire Surface du Verre et Interfaces UMR 125, France

In the context of Ag-based low-emissive glazing developed by glass manufacturers, magnetron sputtering deposition is the industrially relevant technique to grow thin films of a wide range of materials, ranging from metals to dielectrics and semiconductors. Microstructural control of the active Ag layer used for infra-red reflection is a crucial issue, since its electrical conductivity ultimately drives the glazing thermal insulation efficiency. It is thus of great importance to better understand the link between deposition process parameters and the Ag film growth mechanism.

In this work, the effect of O<sub>2</sub> addition on the microstructure and the electrical and chemical properties of Ag nanometre-thick films grown on SiO<sub>2</sub> was explored using a custom sputtering deposition setup, by means of *in situ* X-ray photoelectron spectroscopy (XPS) and real-time measurements of electrical film resistance and Surface Differential Reflectance Spectroscopy (SDRS).

The impact of O<sub>2</sub> addition turned out to be divided into three regimes, depending on its relative amount in the incoming gas flux into the deposition chamber. *In situ* XPS analysis showed that mixtures of metallic Ag and Ag oxides (both surface oxides and bulk-like Ag<sub>2</sub>O) were obtained in varying proportions depending on the O<sub>2</sub> flux used during deposition. In parallel, real-time electrical resistance measurements allowed for the detection of the percolation threshold thickness, in which a conductive Ag network is formed on the surface of the substrate. Such a threshold was lowered by increasing O<sub>2</sub> flux (Fig-A), but at the expense of final film resistivity. Finally, SDRS measurements were used to characterize the Ag nanoparticles formed during the initial stages of the 3D "Völmer-Weber" growth mechanism, namely nucleation, growth and coalescence. Information on the film morphology evolution were inferred from the plasmonic response using simulations from the *Granfilm* software, with the conclusion that O<sub>2</sub> addition leads to changes in nanoparticle aspect ratio, surface oxidation state and density (Fig-B). The latter was also confirmed by a statistical analysis of Transmission Electron Microscopy images for each condition.

2:20pm **B1-2-ThA-4 Effect of Molybdenum Interlayer on Mechanical and Elevated Temperature Tribological Properties of Molybdenum Nitride-Coated D2 Steel**, *Te-Hsin Liu, J. Huang*, National Tsing Hua University, Taiwan

Hard coatings are commonly used in industrial applications to prolong the service lifetime of cutting tools. Tribological property is one of the important properties that could be enhanced by hard and protective coatings, by which wear rate can be decreased and better protection to the tools is provided. For environmental protection, dry cutting is becoming a requirement in the manufacturing processes, in which high-speed cutting at elevated temperature will increase the wear rate of hard coating and the underlying tool. Molybdenum nitride (Mo<sub>2</sub>N) is regarded as one of the promising coating materials for the tools applied at elevated temperature, because Mo<sub>2</sub>N will form a Magnéli phase with self-lubricating property at high temperature such that the coating can maintain good wear resistance. However, our previous study found that the Mo<sub>2</sub>N coatings deposited on D2 steel by the high-power pulsed magnetron sputtering (HPPMS) was with insufficient adhesion strength that induced delamination during wear test. In this study, Mo interlayer with various thicknesses was introduced to enhance the adhesion of the Mo<sub>2</sub>N coating. The objective of this study was to investigate the influence of Mo interlayer on the adhesion and tribological properties of Mo<sub>2</sub>N coatings on D2 steel substrate. Mo<sub>2</sub>N coatings with different thicknesses of Mo interlayer were respectively deposited by HPPMS and DC magnetron sputtering on D2 steel substrate. Compared with the traditional DC magnetron sputtering, HPPMS can achieve higher ionization rate and plasma density due to the high instantaneous peak power, where the adatoms can obtain higher energy and thereby producing coatings with better crystallinity. After deposition, X-ray diffraction was used to identify the crystal structure. The cross-sectional and surface morphology were determined using field emission scanning electron microscope microscopy. The compositions of the specimens were measured by an electron probe microanalyzer. The residual stress of both coating and interlayer was separately measured using the average X-ray strain method. The hardness of specimens was

determined by nanoindentation. The adhesion strength of the coatings was evaluated by scratch test, and the wear rate was measured by pin-on-disk test at temperature ranging from room temperature to 600 °C. From the experimental results, the effects of Mo interlayer on the adhesion strength and the tribological properties of Mo<sub>2</sub>N coatings on D2 steel will be discussed.

**2:40pm B1-2-ThA-5 Enhanced Adhesion and Thermal Stability of Thick (Al,Cr)<sub>2</sub>O<sub>3</sub> Coatings on Hot Work Steel**, *K. Bobzin, C. Kalscheuer, Parisa Hassanzadegan Aghdam*, RWTH Aachen University, Germany

Crystalline aluminium oxide coatings deposited by chemical vapor deposition (CVD) at temperatures  $T > 1,000$  °C are state of the art for wear and oxidation protection in manufacturing processes such as cutting and die casting applications. In recent years physical vapor deposition (PVD) gained great interest to synthesize crystalline aluminium oxide phases at lower process temperatures  $T \leq 700$  °C by modification of the binary Al-O system using Cr. Thereby, High Speed PVD showed a high potential to synthesize crystalline (Al,Cr)<sub>2</sub>O<sub>3</sub> with high thickness  $s > 15$  µm. However, previous studies showed that increasing adhesion between substrate and coating is required concerning the targeted applications. Therefore, various interlayer systems were taken into account in this study to enhance the compound adhesion between (Al,Cr)<sub>2</sub>O<sub>3</sub> and hot-work steel 1.2344. Hereby, AlCrN interlayers with different thicknesses, architectures and bias voltage were deposited on steel 1.2344. Three AlCrN interlayers were produced with varying thicknesses  $5 \mu\text{m} < d < 11 \mu\text{m}$  at constant bias voltage. Moreover, two graded AlCrN<sub>g</sub> interlayers were deposited at different bias voltages. Deposition of the functional (Al,Cr)<sub>2</sub>O<sub>3</sub> layer is initially omitted to analyze the adhesion strength between substrate and interlayer. In a next step, compounds of 1.2344 and AlCrN/(Al,Cr)<sub>2</sub>O<sub>3</sub> with total thickness of  $21 \mu\text{m} < s < 30 \mu\text{m}$  were produced. Hereby, the thickness of functional layer  $s_f$  is varied between  $16 \mu\text{m} < s_f < 25 \mu\text{m}$  in order to analyze the effect of functional layer thickness. Moreover, the thermal stability of the AlCrN/(Al,Cr)<sub>2</sub>O<sub>3</sub> coatings was investigated by annealing tests in vacuum at  $T = 1,000$  °C and  $T = 1,200$  °C, with regard to the application on cutting and casting tools. Thereby, the diffusion behavior of the interlayer was the focus of investigations. In comparison to (Al,Cr)<sub>2</sub>O<sub>3</sub> coated substrate, the AlCrN<sub>g</sub>/(Al,Cr)<sub>2</sub>O<sub>3</sub> coated steel compounds show no spallation at the edge of the Rockwell imprints and scratches at higher normal forces. The results thus show that the application of graded AlCrN<sub>g</sub> interlayer increases the adhesion of thick (Al,Cr)<sub>2</sub>O<sub>3</sub> coating on 1.2344. Moreover, no diffusion processes leading to chemical and structural changes was obtained after annealing processes. This confirmed the thermal stability of the AlCrN<sub>g</sub>/(Al,Cr)<sub>2</sub>O<sub>3</sub> coatings during annealing up to a temperature of  $T = 1,200$  °C. Therefore, thick (Al,Cr)<sub>2</sub>O<sub>3</sub> coatings,  $s \approx 30$  µm, deposited by HS-PVD in combination with a graded AlCrN<sub>g</sub> interlayer provide a high potential for the protection of hot-work steel against thermal loading up to  $T = 1,200$  °C.

**3:00pm B1-2-ThA-6 Combinatorial Synthesis of Novel Compositionally, Mechanically, and Structurally Heterogenous CuWCrTi Alloys with Unique Properties**, *Michal Zitek*, Montanuniversität Leoben, Austria; *E. Rossi*, Università degli Studi Roma Tre, Italy; *G. Konstantopoulos*, National Technical University of Athens, Greece; *M. Sebastiani*, Università degli Studi Roma Tre, Italy; *J. Keckes*, *R. Daniel*, Montanuniversität Leoben, Austria

Complex coatings with compositional, mechanical, and structural gradients over a wide area are powerful in seeking perspective materials with specific combination of properties. Multielement CuWCrTi alloy is an auspicious candidate for such aim as it contains elements, which well differ in their mechanical properties and tend to form various phases with unique microstructure and properties, depending on the total amount of each element.

We have selected 13 different CuWCrTi alloy compositions in total as they formed on a static 3" Si wafer during magnetron co-sputtering deposition from Cu, W, Cr and Ti targets operated at an optimized discharge power ensuring homogenous thickness of the alloy over the entire wafer area and nearly equiatomic composition of the alloy at its center. Due to large compositional variations and limited miscibility of the elements, solid solutions, nanocomposites, and metallic glasses have been found to form, having unexpected combinations of hardness and elastic modulus. Even alloys composed primarily of elements exhibiting low hardness and elastic modulus such as Ti and Cu (e.g., Cu<sub>51</sub>W<sub>25</sub>Cr<sub>8</sub>Ti<sub>16</sub>) achieved high values of hardness ranging between 7 and 8.5 GPa.

This work demonstrated a potential of combinatorial synthesis approaches for rapid development of multielement alloys with a wide range of elemental and phase compositions, microstructures, and unique

mechanical properties, proving, at the same time, the importance of multi-technique characterization tools with 2D (XRD, EDX) and 3D (nano-XRD, nanoindentation) mapping capabilities for a fast determination of processing-structure-property relations in new nanostructured materials.

**3:20pm B1-2-ThA-7 Deposition Aspects of High Entropy Alloy Nitride Coatings with Arc-PVD**, *Tim Krülle, M. Kuczyk*, TU Dresden, Germany; *M. Leonhardt, O. Zimmer, J. Kaspar*, Fraunhofer Institute for Material and Beam Technology (IWS), Germany; *C. Leyens*, TU Dresden, Germany

High Entropy Alloy (HEA) Nitrides are an interesting material system intended for sophisticated wear and high temperature applications, due to its core effects, such as entropic stabilization of solid solutions, severe lattice distortion, sluggish diffusion kinetics and the cocktail effect. Such materials could be easily synthesized by means of Cathodic Arc Evaporation (CAE) in various gas atmospheres, leading to metallic or ceramic HEAs. In previous works high hardnesses up to 37 GPa could be obtained [1-3]. In this contribution new results on different HEA nitride coatings (HfNbTaTiVZr-N and AlCrTaTiZr-N) will be presented, deposited by means of DC Cathodic Arc Evaporation from compound metal targets. The presentation will give an overview on the dependency of the deposition parameters, such as the nitrogen partial pressures, nitrogen flow and bias potential on the evaporation behaviour of the targets and the (spatial) chemical composition, mechanical properties and the coating structure as well. Analysis were carried out by different methods, for instance SEM, EDS, nanoindentation, XRD or TEM. Furthermore, peculiarities of the evaporation process, such as the evaporation behaviour of the metal compound targets will be discussed.

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- [3] Kuczyk, Krülle, Zawischa, Kaspar, Zimmer, Leonhardt, Leyens, Zimmermann: Microstructure and mechanical properties of high entropy alloy nitride coatings deposited via direct current cathodic vacuum arc deposition; doi.org/10.1016/j.surfcoat.2022.128916.

**3:40pm B1-2-ThA-8 Compositional Modulations in Coatings Synthesized by Cathodic Arc Deposition from a Multi-Element Target with Substrate Rotation**, *Nicholas Bandiera, S. Veldhuis*, McMaster University, Canada

Compositional modulations through the thickness are reported in a near-equimolar AlCrTaTiZr high-entropy nitride (HEN) and a Al<sub>57</sub>Ti<sub>35</sub>Ta<sub>8</sub> nitride coating. The coatings were synthesized by reactive cathodic arc deposition with two-fold substrate rotation from single powder metallurgical targets. High Angle Angular Dark Field (HAADF) Transmission Electron Microscopy (TEM) images of a Focused Ion Beam (FIB) lamella show a repeating, layer-like pattern with nanometer-scale periodicity. While evident as Z-contrast, Energy-dispersive X-ray spectroscopy (EDX) was used to quantify the pronounced, off-nominal fluctuations of the metallic element concentrations through the thickness. The periodicity and pattern of the modulations are governed by the combination of two known effects: the substrate's hypotrochoidal motion, and the non-homogeneous distribution of the film-forming species in the plasma. Using a widely accepted model for the cathodic arc plasma plume, the radial and angular flux distributions for the light and heavy elements from the target were determined experimentally by depositing on stationary substrates, followed by EDX and ball-cratering. A general line-of-sight, flux-tracking program was developed to model a substrate undergoing two-fold or three-fold rotation from one or more multi-element sources. The experimental average deposition rate was used to scale the simulated flux to coating thickness and secondary effects such as occlusion, re-sputtering and sticking probabilities were considered. The simulated line intensity profiles of the coatings are compared to those extracted from the HAADF lamella with excellent agreement and the relative concentrations match the EDX data. In the HEN, changing the table rotational speed decreased coating hardness and toughness, implying these modulations may enhance properties not unlike the engineered nano-multilayer coatings synthesized with multiple targets. A coating designer should consider the phenomena described herein when employing substrate rotation when the target contains elements with a large disparity in atomic masses.

# Thursday Afternoon, May 25, 2023

4:00pm **B1-2-ThA-9 Modifications of Structure Tuning and Mechanical Properties on CoCrNi Medium-Entropy Alloys Films by Multiple Strengthening Mechanism**, *Chia-lin Li*, National Taiwan University, Taiwan

To modify the microstructures and enhance the mechanical properties of CoCrNi medium-entropy alloys films (MEAFs), multiple strengthening will be multiple strengthening methods will be introduced in this study. We will add rare-earth, neodymium, and metalloid, boron, elements into the MEAFs system to introduce precipitation and solid solution strengthening. CoCrNiNd<sub>x</sub>B<sub>y</sub>MEAFs will be deposited onto silicon wafers using DC/RF magnetron three-target co-sputtering of CoCrNi, B and Nd targets. Nd and B concentrations in CoCrNi-based films were controlled by various DC/RF sputtering powers. The effects of multiple dopants on the phases, microstructures, and mechanical properties on these MEAFs will be investigated systematically. The influences of Nd and B contents on the microstructure of MEAFs were studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Meanwhile, mechanical properties were examined by a nanoindentation. Based on present results, when Nd and B concentrations was increased to approximately 0.5 and 1.0 at.%, respectively, hardness increased to 10.8 GPa from 9.0 GPa of CoCrNi MEAFs. A discussion on the phase structure and strengthening mechanisms will be given further in this study based on the experimental results.

## Hard Coatings and Vapor Deposition Technologies Room Pacific D - Session B7-ThA

### Plasma Surface Interactions, Diagnostics and Growth Processes

**Moderators:** Dr. Yin-Yu Chang, National Formosa University, Taiwan, Prof. Arutiun P. Ehasarian, Sheffield Hallam University, UK, Dr. Yolanda Aranda Gonzalez, University of Minnesota, USA

1:20pm **B7-ThA-1 On (simple) Measurement of Energy and Momentum Transport Between Process Plasmas and Substrates**, *Holger Kersten, T. Trottenberg, M. Klette, L. Hansen*, IEAP, U Kiel, Germany; *F. Schlichting*, IAEP, U Kiel, Germany

**INVITED**

For optimization of plasma-based processes as thin film deposition or surface modification, respectively, suitable diagnostics are required. In addition to well-established plasma diagnostic methods (e.g. optical emission spectroscopy, mass spectrometry, Langmuir probes, etc.) we perform examples of "non-conventional" low-cost and simple diagnostics, which are applicable in technological plasma processes. Examples are the determination of energy fluxes by calorimetric probes and the measurement of momentum transfer in sputtering by force probes [1].

In particular, energy and momentum transport through the plasma sheath by charge carriers as well as by energetic neutrals are of interest and can be detected by these diagnostics. Total energy fluxes from plasma to substrate are measured by special calorimetric sensors. A typical method is the passive thermal probe (PTP) based on the determination of the temporal slope of the substrate surface temperature (heating, cooling) in the course of the plasma process. By knowing the calibrated heat capacity of the sensor, the difference of the time derivatives yields the integral energy influx (deposited power) to the surface. Simultaneously, the electrical current to the substrate can be obtained and by variation of bias voltage the contributions of charge carriers can be determined. Moreover, the use of a PTP as collector of a retarding potential analyzer (RPA) allows for energy-selective measurements and studying even the energy influx due to neutrals.

Furthermore, for thin film deposition by sputtering it is essential to determine the sputtering yield as well as the angular distribution of sputtered atoms. In addition to simulations (TRIM, TRIDYN etc.) an experimental determination of the related quantities is highly demanded. For this purpose, we developed a suitable interferometric force probe. The sensitive probe bends a few  $\mu\text{m}$  due to momentum transfer by the bombarding and released particles, i.e. sputtered target atoms and recoiled ions. By knowing the material properties of the cantilever and by measuring its deflection, the transferred momentum, e.g. the force in  $\mu\text{N}$  range, can be determined experimentally.

[1] Benedikt, J., Kersten, H., Piel, A., *Plasma Sources Sci. Technol.* **30**(2021), 033001.

2:00pm **B7-ThA-3 Chemical Stability of Sputter Deposited Silver Thin Films**, *Diederik Depla*, Ghent University, Belgium

Thin silver films are used in a wide range of applications including antibacterial coatings and different optical devices. Silver thin films are deposited on a large scale as part of spectral selective thin films to improve the insulating properties of glazings. These multilayers consist of a stack of a metal layer sandwiched between two dielectric layers such as aluminum doped zinc oxide, TiO<sub>2</sub>. The multilayer acts as an optical filter to control the heat flux through architectural glazings. The filter must combine a high visual with a low infrared transmittance. The optical properties of silver makes it the preferred metal in this application. The fabrication of a thin silver film is challenging due its inherent three-dimensional growth on substrates such as most oxide films in the multilayers. Due to the tendency for 3D growth, continuous films can only be obtained at relative high mean film thicknesses. Therefore, strategies have been developed to overcome this problem. The most common approach is the deposition of metal seed layers prior to the silver deposition. The seed layer is typically a non-continuous thin film which affects the silver film growth.

Silver films are vulnerable to humid air. Therefore, the multilayer is deposited on the interior of the double glazing. Double glazings will normally fail due to internal fogging, when moisture appears between the panes. With an anticipated 20 year lifetime of double glazing, the long term chemical stability of silver thin film is an important feature.

To get a better understanding of the degradation of silver thin films, silver films with a thickness below 50 nm were deposited on glass using DC magnetron sputtering. The chemical stability of the films was investigated by exposure of the film to a droplet of a HCl solution in a humid atmosphere. The affected area was continuously monitored with a digital microscope. The affected area increases approximately linearly with time which points to a diffusive mechanism. The slope of the area versus time plot, or the diffusivity, was measured as function of the HCl concentration and film thickness. The diffusivity scales linearly with the HCl concentration. The role of a aluminum seed layer was also investigated. It is shown that the diffusivity for Al seeded Ag films is much lower. The film growth process is studied based on AFM, resistivity measurements, SEM and transmission measurements. The behavior as function of the film thickness is more complex as it shows a maximum, and seems to challenge the understanding of this straightforward stability test as no strong correlation was found with the aforementioned film diagnostics.

2:20pm **B7-ThA-4 Electron Drift and Electron Property Studies in HiPIMS by Incoherent Thomson Scattering**, *T. Dubois, S. Tsikata*, CNRS-ICARE, France; *Tiberiu Minea*, Université Paris-Saclay, France

Magnetized laboratory sources such as planar magnetrons exhibit rich physics beyond their broad interest for various applications. There is increasing evidence for the complex role played by the electrons during the high-power impulse operation of the planar magnetron discharge.

This work discusses recent findings from a high-performance non-invasive incoherent Thomson scattering implementation on a planar magnetron in HiPIMS (High Power Impulse Magnetron Sputtering). The technique probes the electron properties (electron temperature, density) and dynamics (drift velocity) in the ionization region with an unprecedented time and space resolution.

The electron temperature is observed to be isotropic during pulsing (identical radial and azimuthal temperatures, measured, respectively, along the magnetic field and parallel to the  $E \times B$  drift). However, the electron drift shows clear anisotropy and the azimuthal electron drift evolves according to a changing balance of  $E \times B$  and diamagnetic electron drifts. In contrast, the radial movement of electrons (measured parallel to the magnetic field) can be attributed to plasma expansion/contraction and centrifugal forces. Additional information on particle dynamics during pulsing and relaxation in the afterglow are presented. Two time scales characterize the variation of plasma properties in the afterglow. The differences in the discharge behavior in argon and helium will be discussed.

2:40pm **B7-ThA-5 Engineered Phase Differences between HiPIMS Power and Substrate Bias for Improved Mechanical Properties of TiN and CrN**, *Ying-Xiang Lin, P. Liu*, National Chung Hsing University, Taiwan; *D. Wu*, National Chinan International University, Taiwan; *W. Wu*, National United University, Taiwan

In order to enhance the hardness, density, and adhesion of the deposited film, a substrate bias was normally applied during the deposition to attract ions to the substrate to increase the bombardment of the Ar<sup>+</sup> on the film. However, an excessive ion bombardment also causes an extremely high compressive residual stress of the film and leads to peeling off. Therefore, adjusting the substrate bias voltage to obtain a proper ion impact on the film is an important factor in the process. High-power pulsed magnetron sputtering (HiPIMS) is an advanced technology of conventional magnetron sputtering. The plasma density of HiPIMS is three levels higher than conventional magnetron sputtering due to its high ionization rate. Therefore, a high amount of charged particles are generated in the HiPIMS process. Applying a DC bias voltage in HiPIMS process helps these charged particles reach the substrate, but a high amount of charged particles also causes the bias fail instantaneously. Meanwhile, two groups of high-energy ions of gas and target were observed when the pulse is turned on and off, respectively. Therefore, adjusting the phase differences between HiPIMS power and substrate bias becomes critical in a HiPIMS deposition process. However, the effect of applying synchronized and phase difference bias on the film deposition between CrN and TiN has not been detailed discussed.

In this study, different phase difference bias of HiPIMS deposited TiN and CrN layer was individually investigated. A DC substrate bias was also used for comparison. The plasma composition in front of the target and substrate was individually analyzed by optical emission spectroscopy (OES), and it was found that Ti<sup>+</sup>, Cr<sup>+</sup>, N<sub>2</sub><sup>+</sup>, and Ar<sup>+</sup> increased significantly at the substrate after applying DC bias and pulsed bias. According to the XRD, SEM, and AFM results, the grain size and surface roughness of TiN and CrN decreased when a DC bias was applied. The N/Ti and N/Cr ratio of TiN and CrN samples with a phase difference of 100 μs pulsed bias and synchronized pulsed bias was 0.99 and 0.96 respectively. The residual stress of the film can be reduced by applying a phase difference bias during the process. It has been found that the ion signal strength in the plasma can affect the nano-hardness and corrosion resistance. In the TiN process, the Ti<sup>+</sup> and Ar<sup>+</sup> intensity increases at a phase difference of 100 μs, and the hardness and polarization resistance increase. CrN plasma is dominated by Cr<sup>0</sup>, and the strength of both Ar<sup>+</sup> and Cr<sup>+</sup> plasma decreases with phase difference bias.

3:00pm **B7-ThA-6 Influence of Microwave Power and Substrate Biasing on the Structure and Properties of Zinc Tin Nitride Films Deposited via Microwave Plasma-Assisted R-HiPIMS**, *Caroline Hain*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Swiss Cluster AG, Bern University of Applied Sciences, Switzerland; *K. Wiecezrak, D. Casari, A. Sharma, A. Xomalis*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *P. Sturm*, Tofwerk AG, Switzerland; *J. Michler*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland; *A. Hessler-Wyser*, EPFL, Switzerland; *T. Nelis*, Bern University of Applied Sciences, Switzerland

Zinc tin nitride (ZTN) is a semiconductor, which has been gaining in interest in the field of optoelectronics (including photovoltaics) due to the possibility to vary the bandgap within the ultraviolet to infrared range. It is considered as a possible replacement for InGaN, as it includes Earth-abundant and cost-efficient Zn and Sn, is non-toxic and has a band gap up to approx. 2.0 eV, which has been reported to be relatively insensitive to disorder<sup>1-3</sup>. Different fabrication approaches have been used, including molecular beam epitaxy (MBE), direct-current (DC) and radiofrequency (RF) magnetron sputtering and reactive sputtering<sup>1,4-8</sup>, where the structure and optoelectronic properties of the obtained films were investigated. However, there remain questions regarding the influence of deposition conditions on these aspects of ZTN films. To this end, series of ZTN films of the same chemical composition but different structuring were deposited via microwave plasma-assisted high power impulse magnetron sputtering (MAR-HiPIMS), which has previously been used by us to produce high quality nitrides. The structure was modified by varying the applied microwave power and substrate bias. The obtained films were analysed using X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM) and UV/Vis spectrometry. The obtained differences in film structure and properties were linked to the changes in the deposition environment, which was characterised through *in situ*

diagnostics, including studying HiPIMS I(V,t) curves, time-resolved optical emission spectroscopy (OES), time-of-flight mass spectrometry (ToF-MS), time-resolved Langmuir probe and retarding field energy analyser (RFEA).

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3:20pm **B7-ThA-7 Influence of Duty Cycle on Microstructure of TaN Coatings Prepared by High-Power Pulse Magnetron Sputtering Technique**, *Yung-Chi Chang*, National United University, Taiwan; *F. Wu*, National United University,, Taiwan

Nowadays quality requirements, such as higher hardness, wear resistance, sufficient toughness and adhesion strength are gathering much more attention for transition metal nitride, TMN, hard coating field. The selection of materials among various possible coating systems and related manufacturing processes is quite a challenge and requires careful consideration on the properties in the developing choices. 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, TaN thin films are sputtered through high-power pulse magnetron sputtering, HPPMS, at different duty cycle. At a fixed power of 200 watt and a Ar/N<sub>2</sub> ratio of 18/2 sccm/sccm, the frequency and pulse off time, the related duty cycle and the shape of the current and voltage are manipulated. With the decrease of the duty cycle, the peak power increases when the high energy is applied in a short period of time, leading to an increase in ionization rate and plasma density. For such increase in plasma density, the grain size of TaN film is reduced within a well-defined columnar structure. This leads to the improvement in mechanical behavior, elastic modulus, and wear resistance of the films.

3:40pm **B7-ThA-8 Synthesis of Vanadium Dioxide and Vanadium Pentoxide Nanoparticle Films Using Magnetron-Based Gas Aggregation Source**, *A. Kuzminova, N. Khomiakova, J. Prokes, T. Kosutova, M. Prochazka, Ondrej Kylian*, Charles University, Prague, Czech Republic  
Nanoparticles and nanoparticle-based films have nowadays become one the most studied classes of materials. The popularity of this family of materials is foremost due to their unique physicochemical properties and high surface-to-volume ratio that makes them highly attractive for use in various technological fields such as (bio)detection, catalysis and photocatalysis or gas sensing. This is especially true in the case of metal-oxide nanoparticles. Naturally, the critical step is the controlled, cost- and time-effective and reliable synthesis of nanoparticles with the required structure/functionality. One of the possible strategies that receive increasing importance is the use of magnetron-based gas aggregation sources, i.e., the technique in which the nanoparticles are formed as a result of spontaneous nucleation of supersaturated vapors generated by the sputtering of a solid target. While the majority of so far reported results dealt with metallic NPs, we investigate in this study the applicability of such nanoparticle sources for the synthesis of metal-oxide nanoparticles, namely vanadium oxide ones. A two-step process for the production of vanadium oxide nanoparticles was followed. In the first step, the metallic nanoparticles are produced by a conventional GAS system. Such produced nanoparticles are subsequently annealed in the air. It is shown that the proper selection of the deposition and annealing conditions allows the production of highly porous vanadium dioxide or vanadium pentoxide nanoparticle films, as witnessed by detailed characterization of the resulting materials by electron microscopy and X-ray spectroscopic techniques (XPS and XRD). Furthermore, it was found that while the coatings with a high fraction of VO<sub>2</sub> phase exhibit thermally induced switching of electrical conductivity, V<sub>2</sub>O<sub>5</sub> nanoparticle films are suitable for use as substrates for non-plasmonic surface-enhanced Raman spectroscopy (SERS) that offer not only a high detection limit but also excellent spectral reproducibility and stability, i.e., features problematic for conventionally used metallic SERS substrates.

# Thursday Afternoon, May 25, 2023

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4:00pm **B7-ThA-9 Diagnostics with an Optically Trapped Microparticle in the Sheath of an Asymmetric CCP**, *Viktor Schneider, J. Schleitner, H. Kersten*, Institute of Experimental and Applied Physics, Kiel University, Germany

Applications of low-temperature plasmas range from etching processes and coatings of solids to plasma medicine and basic research. Important plasma parameters such as density, temperature or composition of the species are diagnosed using many established methods [1]. However, it is difficult to probe the extremely important sheath region, which is only a few millimeters thick and, thus, not accessible with macroscopic probe methods, as they themselves change the plasma. In recent years, therefore, microparticles have been qualified as probes for so-called non-conventional plasma diagnostic purposes. Due to their size and their behavior in the plasma, they, in particular, are well suited for increasing the spatial resolution and, thus, providing information in addition to common diagnostics [2].

In this study SiO<sub>2</sub> microparticles are in an optical trap to manipulate them in the environment of a capacitively coupled asymmetric radio frequency discharge. In contrast to common plasma diagnostic tools (e.g. Langmuir probes, calorimetric probes, mass spectrometers etc.), in the  $\mu$ PLASMA (microparticles in a discharge with laser assisted manipulation) experiment particles can be regarded as noninvasive single probes [3]. The displacement of the particle in the laser trap is observed to measure a force while it is moving relatively to the plasma, either deeper into the sheath or into the plasma bulk.

Force profiles at different pressures and rf-powers have been performed in the sheath of an asymmetric capacitively coupled plasma. The force is mainly determined by the particle charge and the electric field in the sheath region. Thus, the measured force while moving a single particle from the bulk plasma towards the electrode surface show a characteristic profile with a maximum and a decrease close to the electrode.

Furthermore, the benefit of the presented technique is the possibility to retain the particle even after the plasma is turned off providing the possibility to perform additional studies, e.g. on the residual particle charge.

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4:20pm **B7-ThA-10 Investigating the Plasma Physics of Plasma-Enhanced Pulsed Laser Deposition of Photocatalytic Thin Films**, *Matthew Hill*, University of York, UK

Photoelectrochemical water splitting is one of the many applications of thin films in modern technology, producing hydrogen fuel from water using sunlight. Photoelectrodes are a key part of this technology, which use solar energy to dissociate water molecules into hydrogen and oxygen. Metal oxides such as titanium dioxide have been established as the most prevalent materials for thin films applied to photocatalysis due to their active and efficient photocatalytic properties. Pulsed laser deposition (PLD) is a widely accepted method of producing high-quality metal oxide thin films. However, PLD has limitations which make it suboptimal for depositing thin films as the process limits the control of the stoichiometry of the deposited film, usually requiring additional background oxygen gas to improve thin film growth. Plasma-enhanced pulsed laser deposition (PE-PLD) is a novel method which uses a metal target instead of a metal oxide target, and oxygen plasma instead of oxygen gas, which reacts more readily with the ablated material, allowing for greater control of the stoichiometry. Despite its promising potential, PE-PLD remains an active area of research. The overarching goal of this particular research is to develop a deeper understanding of the underlying plasma physics and chemistry of thin films such that they can be created according to specific criteria rather than empirical observations. This contribution presents results from modelling the laser ablation of different photocatalytic materials using the 2D hydrodynamic laser ablation code POLLUX as well as measurements of the densities of O and N in the background plasma using Two-photon Absorption Laser-Induced Fluorescence (TALIF). For the laser ablation, we investigate the evolution of key parameters such as plasma density and temperature when the target material is changed from titanium to e.g., tantalum, zinc, copper, aluminium and gold. The results showed that the atomic number of the material significantly affected the electron temperature and mass density of the subsequent plasma plume, with both

parameters increasing with atomic number, whilst the mass density of the material appeared to have no effect on the electron temperature or particle density of the plumes. The TALIF measurements gave absolute measurements of the reactive N and O species in the background plasma for a range of N<sub>2</sub>/O<sub>2</sub> mixtures, allowing control of the ratio of reactive O and N species in the plasma interacting with the plume ablation. These results provide an understanding of the underpinning processes of PE-PLD as well as the design of specific metal-oxide and oxynitride thin films.

4:40pm **B7-ThA-11 Thin Film Modification in a DC Microplasma – Understanding the Importance of Ions under Atmospheric Pressure Conditions for the Plasma Surface Interaction**, *Luka Hansen*, Institute of Experimental and Applied Physics, Kiel University, Germany; *N. Kohlmann, L. Kienle*, Institute of Materials Science, Kiel University, Germany; *H. Kersten*, Institute of Experimental and Applied Physics, Kiel University, Germany

The plasma surface interaction is one of the most discussed topics in plasma technology. The large number of interacting (plasma) species and simultaneously running processes aggravates the understanding of the plasma surface interaction. For low-pressure thin film deposition, structure zone diagrams visualize the most important parameters and their influence on the growing thin film [1]. Substrate temperature and the energy flux from the plasma to the surface strongly influence the grain structure and the texture of the film. The energy flux is composed from multiple components such as kinetic and recombination energy of ions, fast neutrals and radiation [2]. The expression of the different components should also influence the film structure, as large kinetic contributions also transfer momentum to the surface and densify the film.

For atmospheric pressure plasmas a highly collisional environment is present. Therefore, no large kinetic energies and momentums of individual ions or fast neutrals are expected. The difference in the energy flux composition may change the thin film properties and the transferability of the universal structure zone diagrams has to be questioned.

A normal glow atmospheric pressure DC microplasma was developed and characterized [3]. Its design enables the utilization of thin film coated TEM grids as electrodes to study the plasma-induced surface modifications of the electrode surfaces. Significant differences between the thin films used as either anode or cathode have been found, stressing the importance of ions despite the atmospheric pressure conditions. Further, these differences depend on the working gas (Ar or He) and correlate with the measured energy fluxes to the surfaces. Combination of different plasma diagnostics resulted in a postulated energy balance at the cathode, showing the important ion power transfer mechanisms. The different power transfer mechanisms explain the differences in the thin film modification [4].

In the near future *in situ* experiments with the microplasma being integrated into the TEM similar to previous proof of principle experiments [5] are planned. The *ex situ* observed surface modifications should be visible in real time. The current state of these experiments as well as the design of the *in situ* microplasma cell will be presented in addition to the obtained *ex situ* results.

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## 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 Superhard Tungsten-tantalum Diboride (W,Ta)<sub>B<sub>2</sub></sub> Coatings Prepared by High Power Impulse Magnetron Sputtering HiPIMS, Rafal Psiuk, P. Denis, Institute of Fundamental Technological Research, Polish Academy of Sciences, Poland; Ł. Kurpaska, National Centre for Nuclear Research, Poland; T. Mościcki, Institute of Fundamental Technological Research, Polish Academy of Sciences, Poland**

Modern industry requires highly wear-resistant materials in many applications. Some demands can only be met by superhard materials. While diamond and cubic boron nitride are very popular in many areas of industry they possess also major drawbacks – high pressure during synthesis or affinity to iron. Superhard tungsten borides may be alternative to traditional superhard materials in many applications. They are superhard, have good thermal and chemical stability. They are also thermally and electrically conductive. Additionally they do not require high pressures during synthesis and their properties can be enhanced by alloying with transition metals, like titanium[1], zirconium[2], and others.

High power impulse magnetron sputtering was successfully recognised by industry. Because of high ionization during the process this technique can produce high quality, dense materials with comparatively low substrate temperatures. Studies on tungsten borides prepared by HiPIMS have not been sufficiently researched yet.

In this work we present deposition and characterization of tungsten-tantalum diboride (W,Ta)<sub>B<sub>2</sub></sub> coatings prepared by HiPIMS. We evaluated the influence of pulse duration, substrate temperature and substrate bias on properties of (W,Ta)<sub>B<sub>2</sub></sub> films. Crystalline structure was obtained at 250°C. High hardness above 40 GPa measured by nanoindentation was obtained simultaneously with good adhesion to steel substrates evaluated by scratch-test. Changing the pulse duration highly affected the B/(W+Ta) ratio which had influence on properties of coatings. Deposited films was thermally stable up to 1000°C in vacuum, and was able to withstand oxidation in 500°C

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**BP-ThP-2 First Principles Calculation of Thermal Properties for an Aeronautic Ni Alloy, Luis Dacal, M. Lima, Instituto de Estudos Avançados (IEAv - DCTA), Brazil**

“Density Functional Theory” (DFT) is a well established and powerful method for modeling and calculating materials properties from the atomic scale point of view. The also called “First Principles Calculations” uses the Quantum Mechanics to give us unprecedented access to the origin of macroscopic behavior of materials. It is the ultimate tool to explore, understand and design materials performance in a wide range of operational demands.

Despite of its power, DFT has a significant disadvantage, namely its high computational cost when modeling complex materials or structures that request a large number of atoms (hundreds) to describe the correspondent unit cell. At the same time, nowadays, High Performance Computing (HPC) Centers and, obviously, ingenuity have been used to expand our possibilities.

In this work, we present the initial step of a long term study devoted to model aeronautic materials to be submitted to extreme operational conditions, mainly temperature. We chose inconel 718 as the base material that will be protected by a Thermal Barrier Coating (TBC) as, for example, yttria-stabilized zirconia. Due to the high computational cost described above, the very first step was to calculate the thermal conductivity of pure Ni, that corresponds to more than 50% of the alloy composition and whose results are presented here.

In the next steps, we plan to improve the inconel 718 description and devote special care to the modeling of the inconel and TBC interface, always taking into account the compromise between computational cost and results quality.

We employed the ABINIT code [1] for the ground state and forces over atoms calculations. The pseudopotential was taken from the PSEUDO DOJO site [2] and thermal conductivity was obtained using the PHONO3PY code [3]. The main calculations were performed at CENAPAD-SP (National Center for High Performance Computing in São Paulo – Brazil).

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**BP-ThP-3 Direct Deposition of Nano-crystalline Diamond Coating on Steel (SS 301), Nikhil C, Indian Institute of Technology, Madras, India; R. Kannan, Indian Institute of Technology Madras, India; R. Kannan, P. Bagaria, Kapindra Precision Engineering Pvt. Ltd., India; N. Arunachalam, M. Ramachandra Rao, Indian Institute of Technology, Madras, India**

Direct CVD diamond coating deposition on ferrous alloy substrates, such as stainless steel and high-speed steel, has been hardly achieved, owing to the catalytic effect of iron and the rapid diffusion coefficient of carbon in iron. These problems originally come from the high substrate temperatures in CVD diamond coating processes, typically >750°C. Also, this high process temperature leads to substrate deterioration like thermal softening of steel substrates. To overcome these problems, several counter measures have been developed in terms of the surface stabilization of the substrate. Having an interlayer between the ferrous substrate and the diamond film has been most frequently used to prevent carbon diffusion and catalytic reaction. In this present study, nano-crystalline diamond (NCD) films have been directly deposited on stainless steel (Grade 301) substrate without any interlayer via Hot-filament CVD process. Grit blasting (for better coating-substrate interface) followed by proper nano-diamond seeding surface pre-treatment procedure is adopted prior to diamond deposition for better quality NCD film. To prevent substrate deterioration from high temperature, the filament to substrate distance was carefully chosen so that the substrate temperature was ≈600°C. Physical characterization of deposited film was analyzed through Raman spectroscopy, Scanning electron microscopy and X-ray diffraction method. The cross-section study of the substrate-coating interface confirms the formation of a carbide layer and non-diamond carbon phases before the NCD film formation. Hence, direct deposition of NCD film on SS 301 substrate has been accomplished successfully with visibly strong coating adherence. Further studies such as tribological analysis and adhesion study of coated samples and change in substrate material properties after diamond deposition are underway. All these results will be presented and discussed.

**BP-ThP-4 Synergistic Effect of He for the Incorporation of Ne and Ar During Magnetron Sputtering Fabrication of Gas-Charged Silicon Films: A Microstructural and Chemical Characterization Study, Asunción Fernández, V. Godinho, Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Sevilla, Spain; J. Colaux, Synthesis, Irradiation & Analysis of Materials (SIAM) Platform, Namur Institute of Structured Matter (NISM), University of Namur, Belgium; J. Ávila, Synchrotron SOLEIL and Université Paris-Saclay, France; J. López-Viejobuena, J. Caballero-Hernández, D. Hufschmidt, M. Jiménez de Haro, Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Sevilla, Spain; S. Lucas, Laboratoire d'Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Belgium; M. Asensio, Madrid Institute of Materials Science (ICMM), CSIC, Cantoblanco, Spain**

Solid films containing gas-filled nanopores (nanobubbles) have several unique characteristics: they allow a large amount of gas to be trapped in a condensed state with high stability, and provide a route to tailor the overall mechanical, optical and electromagnetic properties of the films [1-3]. In addition to ion implantation procedures, the bottom-up magnetron sputtering (MS) using He as process gas has been proven to be an innovative and versatile methodology to produce He-charged silicon films [1,2,4,5]. Of particular interest is the use of these “solid-gas” nano-composite materials containing <sup>4</sup>He and <sup>3</sup>He as solid targets for nuclear reaction studies [4,5]. The incorporation of heavier noble gases such as Ne and Ar is also of interest in this field. In this work, we demonstrate a synergistic effect when using He-Ne and He-Ar mixtures during the MS

deposition of Si films. Together with the He incorporation, higher amounts of Ne and Ar can be trapped as compared to pure Ne and Ar plasmas. Microstructural and chemical characterizations are reported in this work by Ion Beam Analysis (IBA) and Scanning and Transmission Electron Microscopy (TEM and SEM, including EDS). In addition to gas incorporation, He promotes the formation of larger nanobubbles. Most interestingly, for the case of Ne, a combination of high resolution X-ray photoelectron and absorption spectroscopies (XPS and XAS) reveal that the binding energy of the Ne 1s photoemission peak and the inflection point in the Ne K-edge absorption spectra show a strong dependence on the nanobubbles size. The proposed methodology provides a new way to optimize the fabrication of Ne and Ar solid targets by achieving the required amounts of trapped gas. New perspectives appear to characterize the spectroscopic properties of the noble gases in a condensed state without the need for cryogenics or high-pressure anvil cells.

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## BP-ThP-5 Custom Coating Solution for Coin Minting Dies, *Guillaume Wahli, J. Wehrs, S. Kaminski, A. Lümekmann*, PLATIT AG, Switzerland

When coating stamps, punches and coin minting dies, ensuring surface quality is essential. These surfaces require smooth, dustless coatings with excellent adhesion to accurately replicate highly detailed relief structures. The requirements increase when minting dies are used to produce proof coins, where temperature-sensitive materials are often used. They have narrow tolerances and can only be coated within a certain temperature range.

For coin minting dies, PLATIT has developed a Custom Coating Solution for high-quality coatings. With this contribution we present Ceramicoin, a dedicated PVD coating for coin minting dies and its dedicated PVD unit named S-MPuls. Specific holders were developed for various stamp sizes and geometries or customized upon request. Guaranteed smooth dust-free coatings were realized, since the surface to be coated faces downwards; the target is placed on the bottom of the coating chamber.

The SPUTTER technology from PLATIT is supported by LGD® (Lateral Glow Discharge) to ensure very good coating adhesion to the base material; thus, there are no droplets and no layer defects on the substrates. Ceramicoin is a TiB<sub>2</sub>-based hard coating replicates every detail of the surface and is thus a significant advantage for coin appearance and design features.

## BP-ThP-6 Influence of the Period of a Multilayer TiN / TiAlN Coating System on its Microstructure and Electrochemical Behavior for Potential Applications in Hot Work Steel, *Hernán Darío Mejía Vásquez, G. Bejarano Gaitán*, University of Antioquia, Colombia

In order to improve the wear resistance of hot-working AISI H13 steel, different surface modifications such as plasma nitriding and hard coatings of TiN, TiCN and TiAlN, among others, have been used. TiAlN is perhaps one of the most commonly used coatings due to its high resistance to wear and oxidation at high temperatures. However, the evaluation of its corrosion resistance has been poorly studied. This research work focused on the design of a TiN / TiAlN multilayer coating system deposited by the DC magnetron sputtering technique deposited on AISI H13 steel to evaluate the influence of the bilayer period on the microstructure and corrosion resistance of the multilayer system. For this purpose, coatings with periods of 20, 30, 40 and 50 nm were deposited for a total thickness of 1500 nm. The coatings presented a columnar growth structure whose density and column width decreases with the bilayer period as determined by SEM. The XRD patterns show a crystalline structure with well-defined peaks of TiN and TiAlN grown in the preferential orientations (111) and (220), whose crystallite size decreases with the number of bilayers, which was confirmed by TEM analysis. The roughness and grain size went from 15 to 5 nm and from 30 to 10 nm for periods of 50 nm to 20 nm, respectively, as evaluated by AFM. Polarization curves and electrochemical impedance spectroscopy exhibited lower corrosion currents and much greater polarization resistance as the bilayer period decreases. The greater resistance to corrosion of the multilayer system, as the number of bilayers increases, is associated with the smaller grain size, greater density of the coatings and greater number of interfaces with the decrease of the period, which progressively hinders the penetration of the electrolyte from the surface of the coating until the interface with the substrate. On the other hand,

oxygen diffusion is also inhibited. All deposited coatings exhibited greater corrosion resistance than uncoated H13 steel.

## BP-ThP-7 Diamond Synthesis on 2-Inch Si Substrates by Mode Conversion Type Microwave Plasma CVD, *Akira Inaba*, Chiba Institute of Technology, Japan

Diamond is the material with the highest hardness in nature, the highest thermal conductivity, chemically stable, and excellent wear resistance, so it has been applied industrial. Microwave plasma CVD method is one of diamond synthesis methods. In this study, we investigated the effects of differences of the gas introduction point on the surface morphologies and quality of diamond films prepared on 2-inch Si substrates using of mode-conversion microwave plasma CVD.

A Si substrate ( $\phi$ 2 inch, t: 3 mm) scratched with diamond powder and ultrasonically cleaned with acetone was used as the substrate. CH<sub>4</sub>-H<sub>2</sub> mixture gas was used as the reaction gas, CH<sub>4</sub> flow rate: 2, 20 sccm, H<sub>2</sub> flow rate: 200, 300 sccm, microwave power: 1250, 1750 W, pressure: 10, 13.4 kPa, synthesis time was fixed to 3 h, respectively. Reaction gas was supplied to the substrate from the upper and the side. For the evaluation of the deposit, surface observation by a scanning electron microscope (SEM), surface profile measurement using a microscope, and qualitative evaluation by a Raman spectrometer were performed.

As a result of SEM observation, a deposit with a clear shape was observed. The results of surface profile measurement using a microscope showed a concave profile when CH<sub>4</sub> gas was introduced from the upper direction and a convex profile when CH<sub>4</sub> gas was introduced from the lateral direction. From the Raman spectra of the products measured coaxially from the center of the substrate. A peak at 1333 cm<sup>-1</sup> attributed to diamond and a peak at 520 cm<sup>-1</sup> attributed to Si are observed at all measurement points. In addition, there is a tendency that the peak height attributed to diamond decreases from the center to the edge of the substrate. Evaluation of the IDia/IDLC ratio in the Raman spectra from the various distances on the same axis, film quality was decreased comparison with from the center and the edge of the substrate.

As a conclusion, investigation of the effects of the difference of the gas introduction point on the surface morphologies and film quality of the deposits, the film quality decreased from the center to the edge of the substrate regardless of the difference of the gas introduction point.

## BP-ThP-8 The Phase Transformation and Mechanical Properties of Magnetron Co-Sputtering (MoHf)N Coatings through Heat Treatment, *S. Hsu, Yu-Hsien Liao, F. Wu, Y. Chang*, Dept. of Materials Science and Engineering, National United University, Taiwan

In this study, the influence of heat treatment temperatures on microstructure and mechanical properties of the magnetron co-sputtering (MoHf)N coatings were investigated. The relationships between phase, hardness, modulus, and tribological behavior were analyzed. The (MoHf)N films were fabricated at a fixed Ar/N<sub>2</sub> inlet ratio of 12/8 sccm/sccm and 350°C with tuning of the Hf target input power. Three (MoHf)N thin films of Hf variation co-deposition at 2.3, 7.4 and 10.2at% were produced and compared. The vacuum annealing was conducted at 500, 650, and 750°C for 1 hr. The as-deposited (MoHf)N binary nitride coatings exhibited polycrystalline microstructure with B1-MoN,  $\gamma$ -Mo<sub>2</sub>N, and  $\beta$ -Mo<sub>2</sub>N multiple phases. After 750°C vacuum annealing, increase in hardness from 20.1 to 28.4 GPa was obtained. Similarly, the H<sup>3</sup>/E<sup>2</sup> increased from 0.163 to 0.298, and the H/E ratio also increased from 0.1 to 0.102. The wear rate was reduced from 201.0 to 112.6  $\mu\text{m}^3/\text{Nm}$ . The microstructure of (MoHf)N binary nitride coatings did not evolve significantly, however the mechanical behavior become stronger after vacuum annealing, meaning (MoHf)N coatings exhibited a great resistance to elevated temperature environment.

Keywords: Heat treatment; Microstructure; (MoHf)N; Multiple phase; wear resistance

## BP-ThP-9 Realistic Structural Properties of Amorphous SiN<sub>x</sub> from Machine-Learning-Assisted Molecular Dynamics, *Ganesh Kumar Nayak*, Montanuniversität Leoben, Austria; *P. Srinivasan*, Universität Stuttgart, Germany, Austria; *J. Todt, R. Daniel, D. Holec*, Montanuniversität Leoben, Austria

Machine-learning (ML)-based interatomic potentials can enable simulations of extended systems with an accuracy that is largely comparable to DFT but with a computational cost that is orders of magnitude lower. Molecular dynamics simulations further exhibit favorable linear (order N) scaling behavior.

Amorphous silicon nitride (a-SiN<sub>x</sub>) is a widely studied noncrystalline material, yet the subtle details of its atomistic structure and mechanical properties are still unclear. Due to the small sizes of representative models, DFT cannot reliably predict its structural properties and hence leaves an anisotropic order parameter. Here, we show that accurate structural models of a-SiN<sub>x</sub> can be obtained using an ML-based inter-atomic potential. Our predictions of structural properties are validated by experimental values of mass density by X-ray reflectivity measurements and by radial distribution function measured by synchrotron X-ray diffraction. Our study demonstrates the broader impact of ML potentials for elucidating structures and properties of technologically important amorphous materials.

**BP-ThP-10 Reactive Remote Plasma Sputtering of Titania Thin Films Using r.f. Substrate Biasing, Joseph Lawton, University of Surrey, UK; S. Thornley, Plasma Quest Limited, UK; M. Baker, University of Surrey, UK**

Remote plasma sputtering (RPS) is an industrial deposition technology with an increased processing space that overcomes challenges associated with improving coating characteristics through expanded control of deposition conditions. A high-density low-energy plasma is generated in a side chamber that is directed onto the sputter target using two electromagnets. Sputtering only occurs when a target bias is applied. This setup enables separate control over the target current and voltage. The high-density plasma at the target makes the technology an inherently energetic ionised PVD technique. Full target erosion and independent control of the plasma conditions allows high deposition rates of reactive processes to be achieved at large target-to-substrate distances. The addition of radio frequency (r.f.) substrate biasing further enables a range of energetic growth conditions achievable and allows deposition onto glass, silicon, and plastics. The large processing space and many processing parameters of RPS has previously been used to control the stress [1], grain size [2], and texture [3] of thin films deposited for a wide range of technologically important materials.

Titania thin films have been deposited by reactive RPS from a metallic target using simple constant mass flow control of oxygen with no feedback control. The deposition conditions and r.f. substrate bias have been varied. Different conditions allow selectivity of rutile or amorphous phases and the rutile texture. The correlations between processing parameters, thin film microstructure, and optical properties are discussed.

[1] – L. García-Gancedo, J. Pedrós, Z. Zhu, A.J. Flewitt, W.I. Milne, J.K. Luo, C.J.B. Ford, Room-temperature remote-plasma sputtering of c-axis oriented zinc oxide thin films, *J. Appl. Phys.* 112 (2012). <https://doi.org/10.1063/1.4736541>.

[2] – K. O'Grady, L.E. Fernandez-Outon, G. Vallejo-Fernandez, A new paradigm for exchange bias in polycrystalline thin films, *J. Magn. Magn. Mater.* 322 (2010) 883–899. <https://doi.org/10.1016/j.jmmm.2009.12.011>.

[3] – S. Han, A.J. Flewitt, Control of grain orientation and its impact on carrier mobility in reactively sputtered Cu<sub>2</sub>O thin films, *Thin Solid Films.* 704 (2020) 138000. <https://doi.org/10.1016/j.tsf.2020.138000>.

**BP-ThP-11 Influence of Process Gas on Properties and Residual Stress State of TiAlCrSiN PVD Coatings, K. Bobzin, C. Kalscheuer, M. Carlet, Muhammad Tayyab, Surface Engineering Institute - RWTH Aachen University, Germany**

The hard machining of high strength materials such as powder metallurgical high-speed steel requires cutting tools with higher wear and crack resistance. TiAlCrSiN hard coatings deposited by physical vapor deposition (PVD) can potentially improve the tool life in such cases. However, the process gas used during PVD can influence the application behavior of the coated tools. Therefore, the present study aims to investigate the effect of argon and krypton atmospheres on coating morphology, residual stress state, elastic-plastic properties and cutting performance of coated tools. For this purpose, TiAlCrSiN coatings with comparable process parameters were deposited on cemented carbide substrates under Kr, Ar+Kr and Ar atmospheres. The resulting difference in the residual stress state of the coatings was analyzed using focused ion beam-digital image correlation (FIB-DIC) ring-core method. Moreover, the indentation hardness  $H_{IT}$  and indentation modulus  $E_{IT}$  were determined by nanoindentation. The cutting performance of the coated tools was investigated during milling of high-speed steel HS6-5-3C. The Rockwell indentation tests showed a good adhesion between the substrate and investigated coating variants. However, the morphology of the coatings

changed from columnar under Kr to fine crystalline under Ar. The increased involvement of Ar in the deposition process led to higher residual stresses and indentation modulus  $E_{IT}$  of TiAlCrSiN coatings. Moreover, the Kr atmosphere resulted in a reduced indentation hardness  $H_{IT}$  of the deposited coating as compared to Ar+Kr and Ar atmospheres. Finally, the coated tools showed a comparable flank wear width  $V_B$  after the cutting tests. The findings from the present study contribute to a viable process gas selection for improved cutting performance of PVD coated tools.

**BP-ThP-12 Control of TiN Thin Film Properties by the Energy of Sputtered Atoms in DC Magnetron, Abderzak el-Farsy, LPGP - Université Paris Saclay, France; J. Pierson, T. Gries, L. de Pouques, IJL - Université de Lorraine, France; J. Bougdira, IJL - Université de Lorraine, France**

In this study, the energy flux of sputtered atoms on a substrate was correlated to the properties of titanium nitride (TiN) films deposited using direct current magnetron sputtering (dcMS) under mixed Ar and N<sub>2</sub> atmospheres. The neutral titanium sputtered atoms velocity distribution functions (AVDFs) were measured by tunable diode-laser induced fluorescence (TD-LIF), and the flux of particles and their energy were derived. Mass spectrometry was used to characterize the energy-resolved flux of the ions. It was found that the neutral sputtered atoms flux and deposition rate were in good agreement, indicating that the flux of the neutral titanium ground state represents the number of deposited atoms. Moreover, TiN films were deposited at different gas pressures and at various Ar/N<sub>2</sub> gas mixtures close to the conditions where stoichiometric TiN was formed, without bias voltage and heating of the substrates. The energy flux of the sputtered neutral Ti into the substrate was calculated from TD-LIF measurements. At a relatively low magnetron discharge pressure of 0.4 Pa, we demonstrated that the energy of sputtered neutral Ti impinging on the substrate is higher than the energy flux of ionized particles corresponding mainly to Ar<sup>+</sup>. Thus, the influence of the energy flux of the sputtered atoms on the texture and microstructure of the films is revealed. The (200) texture was obtained at 0.4 Pa when the energy flux of the sputtered atoms was higher than the ion energy flux. At 1.3 Pa where the sputtered atoms energy flux is one order lower compared to 0.4 Pa the (111) texture was obtained. The high-energy flux of the ground state of Ti sputtered atoms seems to allow stress removal in the films.

**BP-ThP-13 Fabrication of TiN Coatings Using Superimposed HiPIMS and MF: Effect of Target Poisoning Ratios and MF Power, Bih-Show Lou, Chang Gung University, Taiwan; W. Yang, J. Lee, Ming Chi University of Technology, Taiwan, Republic of China**

The high power impulse magnetron sputtering (HiPIMS) technique has been widely studied due to its ability to generate high density plasma and high ionization rate for deposition of thin films with denser microstructure and good mechanical properties. However, the lower deposition rate of HiPIMS limits its application in industry. In the first part of this study, a superimposed HiPIMS and medium frequency (MF) power supply coating system was used to deposit TiN coatings under 5 different target poisoning ratios, 30%, 40%, 50%, 60%, and 70%, controlled by a plasma emission monitoring (PEM) system. In the second part, the on-time ratios between superimposed MF and HiPIMS power per cycle was adjusted from 1.5, 3.0, 6.0, 12.0, 18.0, 24.0 to deposit TiN films under 50% target poisoning status. Effects of target poisoning ratios and the on-time ratios between MF and HiPIMS per cycle on the deposition rate, microstructure, mechanical properties and electrical resistivities of TiN coatings were investigated. We found that the power averaged deposition rate of TiN film decreased with increasing target poisoning ratio, whereas the hardness showed an increasing tendency. On the other hand, the power averaged deposition rate of TiN film increased with increasing on-time ratios between MF and HiPIMS per cycle and the hardness showed a decreasing tendency.

**BP-ThP-14 Adhesion of Hydrogenated DLC Coatings on Polymer Substrates, Akira Chikamoto, P. Abbraha, Meijo University, Japan**

Demand for lightweight polymer mechanical parts is on the rise, but thermal softening of the polymer and reduced wear resistance in sliding contact with other surfaces significantly limit its application. Many research papers have reported the formation of DLC films with different sp<sup>3</sup>/sp<sup>2</sup> ratios on metallic and polymeric substrates. However, the bonding state of the DLC thin film coatings with the bulk substrate surface lacks detailed analysis and understanding. We put forward a proposal that takes care of the thermal softening and high wear volume by coating the polymer with hydrogenated diamond-like carbon (DLC), a high-strength thin film layer with a very low coefficient of friction. This inherent property of DLC film controls the frictional heat and wear volume under sliding conditions with other materials. Therefore, we can potentially realize applications of

polymeric sliding mechanical parts of the same material or against a different material.

This research deals with the relationship between the structures, threshold bonding energy, and thermal expansion of a hydrogenated DLC film and polymer substrate to give insight into the adhesion of the two surfaces. We used radiofrequency plasma-enhanced chemical vapor deposition (RF-PECVD) with methane and argon gas as the precursors. Varied ion energy is irradiated to change the bonding state of the polymer and the hydrogenated DLC thin film. Our presentation details the evaluation of adhesion strength using X-ray photoelectron spectroscopy and Time-of-Flight secondary ion mass spectrometry compared to the adhesion strength measurements by scratch tests.

**BP-ThP-15 e-Poster Presentation: Fabrication of Pt-Nanocluster Decorated Porous Ni/MoS<sub>2</sub> for Hydrogen Evolution Reaction Application, Po-Chun Chen, National Taipei University of Technology, Taiwan**

A facile and state-of-the-art approach to synthesize porous Ni/MoS<sub>2</sub> decorated with the Pt-nanoclusters for a synergistic effect on hydrogen evolution reaction (HER). The breakthrough of the research is to conduct a promising chemical vapor deposition approach to generate the 3D porous structure MoS<sub>2</sub> by completeness reactions between the sublimation and the deposition. Additionally, the Pt-nanoclusters and Ni are straightforwardly introduced by a hierarchical chemical reduction process to enhance the catalytic activity. Therefore, the porous MoS<sub>2</sub> and Pt-decorated porous Ni/MoS<sub>2</sub> were employed as the electrochemical catalyst for HER. The results showed that the CVD process and the decorated Pt-nanoclusters play important roles in determining the HER catalytic activity. The porous MoS<sub>2</sub> largely increased the surface area and active reaction site for the HER performance. In addition, the decoration of Pt-nanoclusters on porous Ni/MoS<sub>2</sub> can demonstrate the synergistic effect of the Pt-decorated porous Ni/MoS<sub>2</sub>. So, the overpotential ( $\eta_{10}$ ) and the Tafel slope of the Pt-decorated porous Ni/MoS<sub>2</sub> are determined in 43 mV and 56 mV/dec, respectively. The promising approach to synthesizing Pt-decorated porous Ni/MoS<sub>2</sub> for adjustment of different compositions is discussed in this study.

**BP-ThP-16 Optimization of Doping Content for Sputtered a-C:H:Si:O Coatings, Abqaat Naseer, M. Evaristo, T. Bin Yaqub, S. Carvalho, University of Coimbra, Portugal; M. Kalin, University of Ljubljana, Slovenia; A. Cavaleiro, University of Coimbra, Portugal**

Initially developed in the late 90s, a-C:H:Si:O, conveniently also known as diamond-like nanocomposite, is one of the most industrially acclaimed carbon-based coating material. Owing to a combination of low-friction, anti-sticking, and oxidation resistance, its applications cover a wide range of sectors; from aerospace to the food industry. While, it is widely accepted that interpenetrating a-C:H and Si:O networks are responsible for the improved protective nature of these coatings, the individual and synergistic role of dopants (Si, O, H) on structure and properties is not very well understood. With the aim to develop an understanding of the relationship between coating composition, structure, and properties; this study explores the role of increasing Si, O, and H doping in the amorphous carbon matrix. The individual and admixed effect of dopants on hardness, reduced modulus, surface energy, and thermal stability of coatings will be discussed. To summarize our findings, Si doping results in increased hardness, thermal stability, and surface energy. The role of O is mainly influenced by the Si content, and therefore with an increasing O/Si ratio a decrement in mechanical and thermal performance is observed. On the other hand, H doping leads to improved mechanical properties but restricts the maximum operating temperature of the coatings. This evolution in coating properties with respect to the possible formation of a-C:H/Si:O networks and Si-C linkages will be discussed. Thereby, while exploring the effect of doping on properties of a-C:H:Si:O coatings, suitable coating stoichiometry for achieving desired application performance will be presented.

**BP-ThP-17 Surface Quality Improvement for Ge Device with Ozone ALD Formed Interfacial Layer and In-situ Hydrogen Plasma Treatment, Pei-Hsiu Hsu, National Tsing Hua University, Taiwan; D. Ruan, Fuzhou University, China; K. Chang-Liao, National Tsing Hua University, Taiwan, China**

In this research, ozone (O<sub>3</sub>) plasma with high oxidation ability has been applied for high quality interfacial layer (IL) formation. However, an undesirable equivalent oxide thickness (EOT) growth seems to be unavoidable, which may degrade the electrical performance for germanium (Ge) n-type metal oxide semiconductor field effect transistor (nMOSFET). Notably, the EOT can be thinned and quality of IL of Ge nMOSFET can be kept with an additional post hydrogen plasma treatment. As a result, Ge

nMOSFET with O<sub>3</sub>+H<sub>2</sub> plasma treatment exhibits lower subthreshold swing and higher on-off current ratio.

**BP-ThP-18 On the High Temperature Oxidation Behavior of AlCrBN/TiAlNbSiN Multilayer Coatings with Addition of Boron and Silicon, Y. Chang, He-Qian Feng, K. Huang, National Formosa University, Taiwan**

A multicomponent nitride with multilayer structure design is one of the most promising methods for improving the comprehensive performance of TiAlN-based hard coatings applied to high temperature applications. In this study, nanostructured AlCrN/TiAlNbN and AlCrBN/TiAlNbSiN multilayer coatings were deposited using multi-target cathodic arc evaporation. This work investigates the structure evolution of the different coatings with oxide scale growth and diffusion processes occurring during oxidation at high temperature of 900 °C, and the roles of B and Si addition in their oxidation resistance were examined. Different oxidation mechanisms of the coatings are discussed. The deposited AlCrN/TiAlNbN coating showed a typical columnar structure with nanolayer stacking (average bilayer periodic thickness ~14.8 nm). A titanium-rich oxide layer was formed on the surface, and the inner oxide layer of the oxidized AlCrN/TiAlNbN coating was mixed metal oxides with major Al<sub>2</sub>O<sub>3</sub> that retarded further oxidation. The addition of AlCrN into the TiAlNbN acted as an oxidation barrier to inhibit the oxidation of TiAlNbN. The AlCrBN/TiAlNbSiN coatings, which had average bilayer periodic thickness 11.4 nm ~12.2 nm, showed fine-fibrous growth morphologies and refining effects of B and Si in the AlCrBN/TiAlNbSiN coatings, and they possessed better high temperature oxidation resistance than that of AlCrN/TiAlNbN. Oxidation behaviors of the AlCrBN/TiAlNbSiN with different AlCrBN layer thicknesses were studied. The AlCrBN/TiAlNbSiN with larger layer thickness of AlCrBN possessed the best oxidation resistance among the investigated coatings due to the formation of a protective oxidized layer with a mixture of metal oxides, which reduced inward diffusion of oxygen during oxidation.

**BP-ThP-19 Annealing Modulated Microstructural and Electrical Properties of PEALD-derived HfO<sub>2</sub>/SiO<sub>2</sub> Nanolaminates on AlGaIn/GaN, B. Wang, Y. Li, M. Chen, Duo Cao, F. Liu, W. Shi, Shanghai Normal University, China**

In the current work, HfO<sub>2</sub>/SiO<sub>2</sub> nanolaminates and HfO<sub>2</sub> films were grown on AlGaIn/GaN substrates via plasma-enhanced atomic layer deposition. A comparative study of how rapid thermal annealing modulates the microstructural and electrical properties of both films has been presented. It is found that the HfO<sub>2</sub>/SiO<sub>2</sub> nanolaminate keeps an amorphous structure when thermally treated below 600 °C, whereas crystal grains appear within the 800 °C annealed sample. High-temperature annealing facilitates the transformation from Hf-O and Si-O to Hf-O-Si in the HfO<sub>2</sub>/SiO<sub>2</sub> nanolaminates, forming an HfSiO<sub>x</sub> composite structure simultaneously. The 800 °C annealed HfO<sub>2</sub>/SiO<sub>2</sub> shows a low k value and large leakage current density. While the 600 °C annealed HfO<sub>2</sub>/SiO<sub>2</sub> possesses an effective dielectric constant of 18.3, a turn-on potential of 9.0 V, as well as a leakage density of 10<sup>-2</sup> μA/cm<sup>2</sup> at gate biases of both -10 and 2 V, revealing good potential in fabricating high electron mobility transistors.

**BP-ThP-20 Self-Formation of Dual-Phase Nanocomposite nc-ZrN/a-ZrCu Coatings by Reactive Magnetron Co-Sputtering, Stanislav Haviar, M. Červená, University of West Bohemia, Czechia; A. Bondarev, Czech Technical University in Prague, Czechia; R. Čerstvý, P. Zeman, University of West Bohemia, Czechia**

Recently, magnetron sputter deposition has been demonstrated to be a suitable deposition technique for the preparation of metallic glasses as thin films (TFMGs). TFMGs can be prepared in a wide composition range by exploiting the sputter deposition advantages. Moreover, TFMGs have shown properties and characteristics that are superior to BMGs, and metallic and ceramic coatings, e.g., a better balance of ductility and strength. The amorphous structure of TFMGs, along with their unique properties, also provides a possibility to combine TFMGs with nanocrystalline materials in a heterogeneous dual-phase structure. This might allow us to overcome the shortcomings of both types of materials and further improve the properties or even discover novel properties based on the synergetic effect of the two phases.

The study focuses on the preparation of dual-phase thin-film materials in the ternary Zr-Cu-N system by reactive magnetron co-sputtering and systematic investigation of their structure and properties. The coatings were deposited in argon-nitrogen gas mixtures using three unbalanced magnetrons equipped with two Zr targets and one Cu target, operated in HiPIMS and DC regime, respectively. All the coatings were deposited onto rotating substrates with rf biasing without external heating. The elemental composition of the coatings was controlled in a very wide composition range.

# Thursday Afternoon, May 25, 2023

We have demonstrated that reactive magnetron co-sputtering allows the preparation of a new type of the Zr–Cu–N coatings with a nanocomposite structure consisting of two phases, crystalline ZrN and glassy ZrCu. So far, only the nanocomposite Zr–Cu–N coatings based on ZrN and Cu phases have been reported in the literature [1,2]. We show that by varying the process parameters, such as the target power densities, repetition frequency and nitrogen fraction in the gas mixture, we are able to control the elemental composition of the coatings so that the stoichiometry of the two phases remains as much the same as possible and only the volume fraction of the phases is varied. The structure of the as-deposited coatings exhibits a gradual transition from amorphous-like to very fine-grained to nanocrystalline. This transition is reflected in changes in the microstructure and surface morphology and affects the mechanical properties, deformation behavior and corrosion resistance.

[1] J. Musil, J. Vlcek, P. Zeman et al.: Jpn. J. Appl. Phys. 41 (2002) 6529.

[2] J. Musil, M. Zítek, K. Fajfrlík, R. Čerstvý: J. Vac. Sci. Technol. A 34 (2016) 021508.

## **BP-ThP-21 Structural Configuration of Functionalized Amorphous Silica Surfaces using Classical and *ab initio* Molecular Dynamics, Azharul Islam, R. Fleming, Arkansas State University, USA**

Silica has numerous applications across various sectors of technology, including concrete production, glass production, and semiconductor technology. The surface chemistry of amorphous silica is critical for enabling these technologies, yet many aspects of the detailed surface chemistry of amorphous silica are still not fully understood when surface functional groups are present. In this study, we use computational simulations to understand the bonding mechanisms and atomistic structure of the amorphous silica surfaces passivated with different functional groups. Amorphous silica surfaces are first generated by melt-quench dynamics using classical molecular dynamics (MD). Then, subdomains of these surfaces containing an undercoordinated surface atom are selected for *ab initio* density functional theory (DFT) calculations. Relaxed surface geometries including hydroxyl, methyl, and fluoromethyl passivating groups are determined from DFT-based structural relaxation calculations, along with Born-Oppenheimer MD at 300 K to determine the bond dissociation energy, bond length, and angle. This study provides a deeper understanding of the structure of functionalized silica surfaces, leading to pathways to produce new advanced silica-based materials.

## **BP-ThP-22 The Mechanical and Corrosion Resistance Properties Study of Ultra-thick DLC Film by Filtered Arc Ion Plating (FAIP), Hao-Wen Cheng, Industrial Technology Research Institute, Taiwan**

In this study, a PVD thick film was developed with Filtered Arc Ion Plating (FAIP). The features of the hard coating film made through FAIP was investigated, including mechanical properties, surface characteristics and corrosion resistance on different thickness films. The result shows the DLC film developed has advanced mechanical properties and compactness from the high ionized rate of FAIP process.

For the mechanical properties, the adhesiveness of the multi-layer DLC film by FAIP reached 14~15N and the hardness reached 15~16 GPa. The film also passed 30 hours of Salt Spray Test. The Ultra-thick DLC Film has been successfully adopted by various industries like car/truck components.

# Friday Morning, May 26, 2023

## Hard Coatings and Vapor Deposition Technologies

### Room Town & Country C - Session B1-3-FrM

#### PVD Coatings and Technologies III

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

**8:00am B1-3-FrM-1 Effect of Wettability Modification of Ti-Al-Based Thin Films on Heat Transfer Exchange During Water Drop Cooling, Alexis Carlos Garcia Wong, G. Marcos, Institut Jean Lamour - Université de Lorraine, France; G. Castanet, O. Caballina, F. Lemoine, Laboratoire d'Energétique et de Mécanique Théorique et Appliquée, France; J. Pierson, T. Czerwicz, Institut Jean Lamour - Université de Lorraine, France**

Heat production constitutes about 70% of the world's primary energy consumption. Better thermal management of industrial processes would be a step toward the energy transition process. The development of sufficiently compact and affordable extractors and heat exchangers is an urgent industrial challenge. Spray cooling on a hot surface is one of the most effective heat extraction techniques. When a droplet is in contact with a wall, the liquid heats up and boils, extracting a high energy amount during this process. However, no dedicated exchange surfaces have yet been designed to exploit the full potential of this cooling technique. The study of heat transfers associated with the impact of a water drop on hot surfaces with controlled properties (wettability, roughness) is essential to achieve this goal. We used time-resolved infrared thermography (TR-IRT) to measure the contact temperature and determine the heat extracted by water drops. For this purpose, the upper surface of a sapphire substrate (transparent in the IR) must be covered with a highly IR-emissive layer. The method requires an opaque surface, with a micrometer thickness to neglect the thermal resistance of the deposit, and it must also withstand the impact of the drops while being thermally stable. The temperature reduction produced by the drop impact is observed through the sapphire without being disturbed by the drop presence [1].

We revealed that opaque TiAlN and TiAl thin films are an attractive choice for this application. All the studied films were deposited by magnetron sputtering. Scanning electron microscopy, optical profilometry, and X-ray diffraction were performed for morphological and structural characterizations of the films. In addition, the wettability of the films was investigated by contact angle measurements and the emissivity by Fourier transform infrared spectroscopy. The effect of different wettability of the Ti-Al-based films on the heat transfer during droplet impact at different temperatures from 80 to 300°C was analyzed by TR-IRT. The heat flux and energy extracted by the drop projection onto hot walls of different wettability were determined. Superhydrophilic TiAlN displays better results than hydrophobic TiAl alloys due to the larger contact area between the drop and the surface. Biphilic surfaces with spatially variable wetting properties are supposed to improve the heat transfer of the boiling system [2]. We are currently exploring the effect of different sizes of hydrophobic patches in a hydrophilic matrix to assess the impacts on the cooling efficiency.

[1] G. Castanet *et al.*, *Phys. Fluids*, 30, 12, (2018).

[2] H. Cho *et al.*, *Nat. Rev. Mater.*, 2, 2, (2016).

**8:20am B1-3-FrM-2 Rf-Bias Assisted, Combinatorial Sputtering of Conductive (TiZr)N Hard Coatings on Insulating Substrates, Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; M. Watroba, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; J. Sommerhaeuser, S. Zhuk, J. Patidar, A. Wiecek, S. Siol, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland**

Ternary transition metal nitrides are promising materials for many applications as they offer advantages in microhardness and higher oxidation resistance compared to binary counterparts. A common challenge in the deposition of these materials is oxygen contamination during the sputtering process. This oxygen contamination adversely affects the functional properties of the coatings, especially their hardness and electrical properties. Here we present a practical approach to grow virtually oxygen-free (Ti, Zr)N coatings, even on insulating substrates.

To cover the completely compositional range of (Ti, Zr)N we employ combinatorial reactive co-sputtering from Ti and Zr targets in Ar/N<sub>2</sub> atmosphere. The depositions are carried out with or without applying a low-power RF substrate bias to the substrate holder with the goal to reduce the oxygen contamination the growing film. The compositional gradients are complemented by orthogonal deposition temperature

gradients to cover entire regions of the synthesis diagram in individual depositions. Automated mapping characterization (XPS, XRF, XRD, 4 point probe) is used to evaluate the structure and composition as well as electrical properties of the libraries. Nano-indentation mapping for evaluation of the mechanical properties is performed on selected combinatorial libraries. For selected parameter sets, UHV-transfer XPS is performed. Comparison of oxygen contamination in UHV and ambient conditions linked to changes in the films' microstructure depending on the synthesis conditions.

The structural analyses indicate solid solution formation over the entire compositional range as described by Vegard's Law. The oxygen contamination of the films is evaluated using combinatorial sputter-depth profiles. Irrespective of the composition of the films, the RF-bias leads to a dramatic reduction of the oxygen-contamination, which is reflected in a significant improvement in the films' conductivity as well as hardness. In addition, the RF-bias leads to a denser microstructure and improved oxidation resistance in ambient conditions as evidenced by XPS oxidation studies. The approach presented here provides a practical route to synthesize nitrides with improved phase purity that can be applied to many different material systems.

**8:40am B1-3-FrM-3 The Microstructure and Properties of Highly (111)-Oriented Nano-Twinned Cu-Ag Thin Film Prepared by DC Sputtering System, Ko-Chieh Hsueh, National Tsing Hua University, Taiwan; J. Lee, F. Ouyang, National Tsing Hua University, Taiwan**

The Moore's Law pushes the size of electronic devices continue to shrink. Thus, the traditional solder joint technology cannot be used as interconnect any more. To solve this problem, metal-to-metal direct bonding is regarded as the promising replacement technique. In this study, we used the Direct Current sputtering technology to deposit highly (111)-oriented nano-twinned Cu-Ag thin films with doped Cu concentration from 2.3 at% to 6.6 at %. The results show that higher Cu concentration in Ag facilitates the reduction of fine nanocrystalline region and enhancement of nanotwinned region. The X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) analysis revealed that the (111) texture is up to 99% that offered the fastest diffusivity among different crystalline planes of Cu and Ag, effectively shortening bonding time. Due to increased nucleation sites, the grain sizes of films decreased with higher Cu concentration. The surfaces roughness of films is below 8 nm, providing an excellent property for three dimensions-Integrated Circuit (3D-IC) metal to metal direct bonding. The highest hardness of nanotwinned Cu-Ag thin films can reach 2.87 GPa, but the resistivity is still low. The correspond mechanisms will be discussed in this talk. The finding in this study demonstrate nanotwinned Ag-Cu thin film is a promising new material as a substitute for traditional solder in 3D-IC packaging.

**9:00am B1-3-FrM-4 High Gain CMOS inverter with Vertically-Stacked Hybrid PVD-Formed IWZO TFT and Monolithic FinFET, Yu-Hsin Chen, National Tsing Hua University, Taiwan; D. Ruan, Fuzhou University, China; K. Chang-Liao, National Tsing Hua University, Taiwan**

The monolithic three dimension integrated circuit (3D-IC) is promising technology in overcoming the area limitation in realizing the more than Moore's law. However, it is hard to fabricate the second layer high performance device without single crystal Si material. Recently, thin film transistor (TFT) is applicable to the back-end-of-line due to its low thermal budget fabrication process. In this work, a vertically stacked complementary p-type Si FinFET and n-type amorphous indium tungsten zinc oxide TFT, which have symmetric electrical characteristics, have been demonstrated. The vertically-stacked hybrid inverter could be operated at the low voltage and exhibit the high voltage gain. The excellent performance exhibited in the proposed hybrid complementary FinFET/TFT based inverter has the great potential for monolithic 3D-IC circuits in the future.

**9:20am B1-3-FrM-5 Development of New Magnetron Sputter Deposition Processes for Inertial Confinement Fusion Targets, S. O. Kucheyev, S. Shin, L. Bayu Aji, G. Taylor, A. Engwall, J. Merlo, L. Sohngen, Lawrence Livermore National Laboratory, USA; J. Bae, General Atomics, USA**

The demonstration of fusion ignition at Lawrence Livermore National Laboratory in December 2022 has opened up new opportunities for fundamental and applied research. All inertial confinement fusion (ICF) experiments require laser targets. Magnetron sputter deposition is an enabling technology for laser target fabrication. Solutions are readily available for the deposition of most sub-micron-thick elemental films on planar substrates. However, major challenges still remain for the development of robust deposition processes in regimes of ultrathick (over about 10 microns) coatings and non-planar substrates. These challenging

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deposition regimes are directly relevant to laser target applications, including both spherocylindrical hohlraums and spherical ablators for ICF targets. Understanding underlying physical mechanisms for a specific material system is crucial for process development, given the overall complexity of the deposition process, its nonlinear dependence on deposition parameters, and a very large process space, often precluding conventional process optimization approaches. Here, we describe our approach to developing new deposition processes with examples from our ongoing studies of glassy boron carbide ceramics for next generation ICF ablators and non-equilibrium gold-tantalum alloys for hohlraums for magnetized ICF schemes. Emphasis is given to two major challenges of ultrathick coatings related to achieving process stability and reducing residual stress.

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**Bold page numbers indicate presenter**

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