Plenary Lecture
Room Town & Country A - Session PL-MoM

Plenary Lecture
Moderator: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

8:00am **PL-MoM-1 Plenary Lecture: Recent Trends in Artificial Photosynthesis: Atomistic/Surface Design and Probing of Nano-Photocatalysts***, Li-Chyong Chen,* National Taiwan University, Taiwan **INVITED**

Photocatalytic CO_2 conversion to hydrocarbon fuels, which makes possible simultaneous solar energy harvesting and CO_2 reduction reaction (CO_2RR), is considered a killing-two-birds-with-one-stone approach to solving the energy and environmental problems. However, the development of solar fuels, or the so-called artificial photosynthesis, has been hampered by the low photon-to-fuel conversion efficiency of the photocatalysts and lack of the product selectivity. Recent advances in development of integrated nanostructured materials have offered unprecedented opportunity for photocatalytic CO_2RR, as depicted in my recent invited review article [1]. Here, selective cases in nanomaterials, especially, atomistic design and synthesis of highly functioning nano-photocatalysts, will be illustrated [2-4]. Ascertaining the function of in-plane intrinsic defects and edge atoms is necessary for developing efficient photocatalysts. A perfect planar layer is usually inactive to catalysis. Vacancy clusters, as well as the reconstructed and imperfect edge configurations enable CO_2 binding to form linear and bent molecules. To make the energy conversion techniques towards practical solutions, some key questions need to be addressed. For instance: **What are the determining steps for CO_2RR?** Advancements in the *in situ* and *operando* synchrotron radiation-based spectroscopies, including X-ray absorption [5] and X-ray photoelectron spectroscopy (XPS), *etc.*, along with various vibrational spectroscopies, such as Raman and Fourier transform infrared spectroscopy (FTIR), and scanning electrochemical microscopy [6], have enabled scientists to probe the geometric, bonding and electronic information of the catalyst and obtain atomistic insights into the catalytic surfaces and reaction mechanisms. Selective cases utilizing these probing techniques will be illustrated.

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Coatings for Use at High Temperatures
Room Pacific E - Session A1-1-MoM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Dr. Sebastien Dryepondt, Oak Ridge National Laboratory, USA, **Gustavo García-Martín**, REP-Energy Solutions, Spain

10:00am **A1-1-MoM-1 Bill Sproul Award and Honorary ICMCTF Lecture: Strategies for the Development of Robust and Stable, but also Functional Ceramic Coatings***, **Paul Mayrhofer**[1],* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

For mechanically dominated load profiles, nitrides are preferred, while oxide materials offer better protection against high-temperature corrosion. Thus, when mechanical and thermal loads are combined, the nitrides used should also have excellent temperature and oxidation resistance. How to develop such nitride materials that can withstand both high mechanical and thermal loads will be the focus of this presentation. In addition, we will also discuss the excellent supercapacitor properties of transition metal nitrides.

Using transition metal nitride coatings, we will discuss important guidelines for material development to improve strength, fracture toughness, and stability. In particular, the stability (emphasis on phase stability to composition and temperature, but also to oxidation) of nitrides is a highly interesting task. For example, while the face-centered cubic (fcc) structure of TiN_x has a relatively large homogeneity range, the fcc structure of other transition metal nitrides (such as MoN_x and TaN_x) is extremely sensitive to small chemical variations, even if only the vacancy concentration changes. We will use these model systems to explore the possibilities of alloy and structural developments.

Among the many alloying elements that have been studied for (Ti,Al)N-based coatings, tantalum is one of the most versatile, capable of simultaneously increasing strength, fracture toughness, thermal stability, and oxidation resistance. This can be further improved when alloyed with Si and reactive elements.

The concept of high entropy is also very beneficial for hard ceramic thin films. We will see that, for example, (Hf,Ta,Ti,V,Zr)N and (Al,Cr,Nb,Ta,Ti)N easily outperform their commonly used binary or ternary constituents in terms of thermal stability and thermomechanical properties. In addition, all of the highly entropic ceramic sublattice thin films studied were relatively insensitive to variations in deposition parameters-which is good because their properties are at a high level.

With superlattice coatings, we will discuss how such nanolamellar microstructures can also simultaneously improve strength and fracture toughness.

However, we will also investigate the performance of electrochemical supercapacitors, which strongly depends on chemical stability, accessible surface area, and electrical conductivity. Transition metal nitrides are also excellent candidates for this purpose, but must have a very open-pore microstructure. Glancing angle deposition enables the fabrication of such zigzag-structured electrodes based on γ-Mo_2N, combining excellent electrochemical energy storage capabilities with excellent mechanical flexibility.

The individual concepts allow the materials to be designed to meet the ever-growing demand for further coatings tailored to specific applications.

10:40am **A1-1-MoM-3 Ti_5Si_3/$TiAl_3$ Multilayer Coatings as Oxidation Protection for γ–TiAl***, **Peter-Philipp Bauer**,* German Aerospace Center and Brandenburg University of Technology Cottbus, Germany*; R. Swadźba,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland*; L. Klamann,* German Aerospace Center, Germany

Titanium aluminides exhibit a high specific strength and a decent oxidation resistance up to 800 °C. This renders TiAl an excellent structural material for turbine blades. With the intention to increase the oxidation resistance at temperature above 800 °C, a large variety of different oxidation protection coatings were developed. It turned out that a combination of a diffusion inhibiting interlayer consisting of the Ti_5Si_3 phase and an oxidation resistant top layer of the $TiAl_3$ phase provided an excellent oxidation resistance. As a further development, a novel multilayer coating system of alternating Ti_5Si_3 and $TiAl_3$ layers were introduced. This design is expected to have exhibit a good oxidation resistance but also the high crack tolerance.

The coating system was produces by a continuous process using magnetron sputtering with elemental Ti, Al and Si targets. The performance of the coating was evaluated by cyclic oxidation tests in air at 900 °C for 1000 cycles (1h each) combined with thermogravimetric analysis. Scanning and transmission microscopy as well es x-ray diffraction was used to trace the oxidation and phase transformation processes.

Contrary to the expectations, the multilayer coating system showed only an insufficient oxidation protection. Although a good oxidation resistance was given during the first 100 cycles, at longer oxidation times the coating suffered under sever oxidation. In this talk, the failing mechanism as well as the lessons learned will be presented.

11:00am **A1-1-MoM-4 Max-Phase Based PVD Coatings as Protection for Lightweight Materials in High Temperature Environments***, **Nadine Laska**, R. Anton,* German Aerospace Center, Germany*; R. Swadzba,* Lukasiewicz Research Network - Institute for Ferrous Metalurgy, Poland*; P. Nellessen,* German Aerospace Center, Germany

MAX-phases are of increasing interest as coating material for high temperature applications due to their unique combination of metallic and ceramic properties. Especially the alumina forming MAX phases of Cr_2AlC, Ti_2AlC or Ti_2AlN are promising as oxidation resistant coatings. Unfortunately, degradation of MAX phases is observed when applied on various Ti- or Ni-based alloys by interdiffusion processes between coating and alloy and the associated Al-depletion. This degradation is not present when MAX-phases are applied on the Al-rich γ-TiAl based alloys, which leads to an inward diffusion of Al from the substrate alloy into the coating and finally to a stabilization of the thermally grown alumina layer.

In the present work, the coating deposition process to get the MAX phases was DC magnetron sputtering using pure elemental targets of Ti or Cr, Al and C and in case of the Ti_2AlN MAX-phase based coating, nitrogen as reactive gas. No additional heating was applied during the sputtering process, the obtained substrate temperature was self-adjusted due to the target power. Prior to coating deposition, an Ar-plasma etching process for surface cleaning using a bias voltage of 500V and a frequency of 100 kHz was carried out for 15min. Using a threefold rotation, homogenous all-around coatings of about 10 µm were achieved with the desired stochiometric composition of the MAX-phases. The formation of the MAX-phase in the sputtered coatings was characterized during a post-annealing process at 800°C by in situ HT-XRD measurements as well as by SEM equipped with EDS and WDS, as well as by TEM with electron diffraction.

The MAX-phase coatings were tested under cyclic oxidation conditions. They provide a good oxidation protection of the γ-TiAl alloys due to the development of a protective alumina layer up to 850°C for up to 300 hrs in laboratory air. The performance of the MAX-phases is strongly depended on the substrate material and the accompanying interdiffusion processes between coating and substrate. Therefore, the Ti-Al-C based coating is more favored on TiAl alloys due to the thermodynamic stability of the Ti_2AlC MAX phase in particular in the presence of the γ-TiAl phase. In comparison, the Cr_2AlC MAX phase degrades after just 100 hrs at 850°C due to the formation of chromiumcarbides next to alumina.

11:20am **A1-1-MoM-5 Oxidation behaviors of (AlCrSiTi)N coatings on AISI 304 steel: A Combinatorial Study***, **Sheng-Yu Hsu**, S. Chang, J. Duh,* National Tsing Hua University, Taiwan

Hard protective coatings have been widely applied in manufacturing industries to improve the performance and durability of workpiece. Scientists and engineers have dedicated to develop advanced coating materials which can be operated in harsh environments, e.g., electrochemical corrosion, high temperature oxidation. However, developing new materials has always been a crucial yet time-consuming task in materials science and engineering.

In this study, an experimental combinatorial approach via co-sputtering technique to efficiently investigate the effect of coating composition on the high temperature oxidation behaviors of (AlCrSiTi)N-coated AISI 304 steel under 700°C is demonstrated. From the elemental quantification results of 1-hour oxidized (AlCrSiTi)N, the oxygen content strongly correlates to the as-deposited coating composition, showing highest oxygen content (lowest oxidation resistance) of Ti rich composition and lowest oxygen content of Cr rich composition. TEM characterization exhibits that three oxide layers are formed after oxidation: spinel-Cr_2MnO_4 (originated from substrate diffusion), corundum-Cr_2O_3, and a thin layer of nano-crystalline mixed oxide. Except for Ti rich composition, an additional TiO_2 layer forms at the outermost layer. This study successfully demonstrates the efficiency and efficacy of developing advanced coating materials of superior high

[1] **Bill Sproul Awardee**

temperature oxidation resistance via experimental combinatorial approach.

11:40am **A1-1-MoM-6 Enhanced Pitting Resistance of Cathodic Arc Evaporated AlCrXN Coatings***, O. Hudak, F. Bohrn, P. Kutrowatz, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; E. Ntemou,* Ion Physics Group, Department of Physics and Astronomy, Uppsala University, Sweden*; D. Primetzhofer,* Ion Physics Group, Department of Physics and Astronomy, Uppsala University, Austria*; L. Shang, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; **Helmut Riedl,*** Institute of Materials Science and Technology, TU Wien, Austria

With current state-of-the-art corrosion resistant coatings being far from optimized, it is of great interest to further investigate the fundamental mechanisms and underlying driving forces that dominate the degradative process.Particularly saline environments represent a technological frontier, where high-performance components suffer accelerated breakdown through a localized corrosion mechanism called-- pitting. Porosities, macroparticles, and the overall columnar growth morphology of physical vapor deposited coatings makes them particularly susceptible to inward-diffusion of corrosive media. Here, especially chloride ions play a key-role allowing for an accelerated attack at the coating substrate interface.

In a first step, this study provides a systematic approach on highlighting preferred diffusion pathways of corrosive NaCl-rich media of $Al_{0.7}Cr_{0.3}N$-based PVD thin films deposited on low alloy steel. Through an array of high-resolution techniques, such as TEM, ToF-SIMS, APT and t-EBSD, we intend to break down the possible diffusion paths from a micrometer to a nanometer scale, providing newest insights on the corrosion process. In a second step, this study showcases a doping strategy, as well as thermal treatment as viable approaches for improving the corrosion behavior of the previously discussed AlCrN system. In order to investigate the beneficial effects of the dopant, a series of $Al_{0.7}Cr_{0.3-y}X_yN$ coatings were deposited with varying alloying contents. Electrochemical tests of the as-deposited, as well as thermally treaded coatings were conducted using a three-electrode cell set up, whereupon extrapolations of Tafel-plots were used to evaluate the corrosion resistance.

Keywords: Corrosion Resistance; Pitting; Cathodic Arc Evaporation; PVD coatings; Diffusion Pathways;

12:00pm **A1-1-MoM-7 Novel Approaches for the PVD Synthesis of Advanced Aluminide Thin Films: The Example of Ruthenium-Aluminide***, **Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal aluminides are known for their use as high temperature materials in aerospace and gas turbine engine applications. Their best-known representatives of these intermetallics are NiAl, TiAl and FeAl. All these materials suffer from brittle behavior at room temperature and limited operating temperature of approx. 800°C. A relatively new and unknown candidate with improved properties regarding ductility, toughness and high temperature resistance is the RuAl. Thin film synthesis can enable the exploitation of their full potential for example as protective coatings at high temperature conditions. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering.Different approaches were conducted, including a multilayer thin film approach combined with a post-annealing as well as direct magnetron sputtering from a compound target to study the formation of the cubic B2 RuAl phase. Depending on the synthesis route, different microstructures and corresponding properties of the thin films were obtained, analyzed by electron microscopy and XRD techniques.

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, $(CoCrNi)_{92.7-x}Al_{7.3}Nd_x$ (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 ~1.86 µm for the Nd-free film, and it decreased initially to ~1.65 nm with the increasing P_{Nd} and then increased to ~1.91 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 $(CoCrNi)_{100-x-y}Si_xNd_y$ Medium Entropy Alloy Films***, **Hui-Wen Peng**, C. Hsueh,* National Taiwan University, Taiwan

A series of $(CoCrNi)_{100-x-y}Si_xNd_y$ 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, $(CoCrNi)_{90}Nd_{10}$ 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 $(CoCrNi)_{90}Nd_{10}$ 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 $(CoCrNi)_{90}Nd_{10}$ 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 $NdNi_5$ 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 µm 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 $Si_{0.58}Nd_{5.59}$ film due to the grain refinement and precipitation strengthening. However, the hardness decreased at $Si_{0.58}Nd_{6.06}$ 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 **INVITED**

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^+ 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^+ 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^2, linearly increased with increasing nitrogen 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 multi-layered 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.Ghaoor***, *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).

Coatings for Biomedical and Healthcare Applications
Room Pacific F-G - Session D1-1-MoM

Surface Coatings and Surface Modifications in Biological Environments I

Moderators: Dr. Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Dr. Kerstin Thorwarth**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

10:00am **D1-1-MoM-1 Ion Release Study of Ag-Cu and Ag-Cu-Mg Coatings Deposited by Magnetron Sputtering***, **Serdar Sonay Ozbay,*** Deakin University, Coventry University, Australia*; G. Taghavi Pourian Azar,* Coventry University, UK*; J. Sharp, G. Rajmohan,* Deakin University, Australia*; A. Cobley,* Coventry University, UK

Ag and Cu thin film coatings are widely studied as antibacterial coatings to functionalise surfaces to fight antibiotic-resistant bacteria and healthcare-acquired infections (HAI) in hospitals. Although the precise antibacterial mechanisms of these metals are still being investigated, metal ion release has been proposed as one of the main mechanisms for their antibacterial action. In this study, we have deposited Ag-Cu ($Ag_{75}Cu_{25}$-$Ag_{50}Cu_{50}$-$Ag_{25}Cu_{75}$) alloy coatings using magnetron sputtering technique on various substrates including non-woven PET fabrics, silicon wafers and glass microscope slides. Obtained coatings were characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV-visible spectroscopy techniques. As a tool to predict antibacterial activity, the coated non-woven PET fabrics were immersed in saline solution for up to 48 hours and the released metal ion concentrations were measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES). Additionally, the ion release test results of the Ag-Cu alloys were compared to the pure Ag and Cu coatings, and the effect of galvanic cell formation on the metal ion release was discussed. Furthermore, Ag-Cu-Mg ternary alloy coatings were deposited to investigate the effect of Mg on the Ag and Cu ion release characteristics. According to the results, the $Ag_{75}Cu_{25}$ coating solved two critical problems which were present in the pure coatings. First, compared to the pure Ag coating, the Ag ion release was improved, and its plateauing behaviour was not observed. Second, the rapid Cu ion release, which was seen in the pure Cu coating, was changed to a steady release. Ternary Ag-Cu-Mg alloy coatings showed further reduction in both the Cu and Ag ion release. However, the effect of Mg on the Cu ion release was more significant compared to the Ag ion release. Overall, the present study suggests that Ag-Cu-Mg ternary alloys are promising coating candidates for hospital settings where long-term and steady antibacterial activity is needed.

10:20am **D1-1-MoM-2 Effect of Pulsed DC Mode on the Surface Properties of Pure Magnesium Substrates Treated with PEO***, **Cristian Esneider Peñuela Cruz**, E. Hernández Rodríguez,* Universidad de Guanajuato, Mexico*; A. Herrera,* Univiversidad de Guanajuato, Campus DICIVA, Mexico

Magnesium is a promising metallic material for the manufacture of bioabsorbable orthopedic implants since in addition to being biodegradable and biocompatible, it has mechanical properties like to those of human bone. However, despite these properties, its poor resistance corrosion resistance has prevented its technological application. A solution to improve its corrosion resistance is to use a surface treatment, such as that provided by plasma electrolytic oxidation (PEO). This technique is used to apply ceramic-type coatings on metals and is widely used in biomedical applications. Therefore, in this work, we carried out a study on the effects generated by the square wave frequency of the pulsed DC mode on the surface properties of pure magnesium sheet by applying TiO_2-based coatings using the PEO technique.Anatase-TiO_2 powders were incorporated into the electrolytic solution due to their good biocompatibility and high corrosion resistance. Coatings were developed using 0.210 g of TiO_2, a current density of 200mA/cm^2, two frequencies of 2 Hz and 10 Hz were evaluated. Data acquisition of voltage transients in the PEO processes was carried out, showing that, in the first stage of the PEO process, as the frequency increases, there is a rapid growth of the voltage, indicating rapid passivation of the magnesium surface. A transversal section of the coatings was observed by optical microscope at 400x, and images showed three regions: the substrate, the substrate-coating interface, and the bulk of the coating. Through X-ray diffraction analysis (XRD), the presence of TiO_2 and MgO into the coatings was identified as a result of the PEO technique. The potentiodynamic polarization curves (Tafel) were employed to investigate the corrosion resistance of a pure Mg substrate and the coated ones, in Hanks' balanced salts. Preliminary results show that Icorr is reduced from 1.471 µA to 454.127 nA, indicating an improvement on the corrosion resistance.

Keywords: Magnesium, corrosion, PEO, surface treatment.

10:40am **D1-1-MoM-3 Non-Stick Thin-Film Metallic Glasse (Tfmg) Coating for Reducing Trauma***, **Helmi Son Haji**, J. P. Chu,* National Taiwan University of Science and Technology, Taiwan*; P. Yiu,* Ming Chi University of Technology, Taiwan

Thin Film Metallic Glasse (TFMG) that refers to a specific group of amorphous multi-component metallic alloys, has special characteristic such as smooth surface, high hydrophobicity, high strength, low friction, good ductility, low surface free energy and good thermal stability exceeding those of other ceramics and alloys coatings. The non-stick characteristic of hydrophobic materials makes them ideal for medical devices such as cutting blade, tattoo needle and syringe needle. This presentation reports on the coating of the medical devices with Zr-based (ZrCuAlTa) TFMG to reduce trauma to the skin. Preclinical study proved that TFMG-coated needle has 33% less endothelial damage than bare needle, showed some clinical benefits such as anti-adhesion, and reduced invasion. Confirm the good biocompatibility and hemocompatibility. Furthermore, clinical study showed TFMG coating could preventing the adhesion of platelet by up to 77% and cancer cells by up to ~87%. Analysis on porcine tissue and polyurethane rubber shows TFMG-coated needles has lower cutting force by up to ~24%, frictional forces by up to ~24%, and resistance to insertion by up to ~44%. TFMG also proved to enhance the sharpness of cutting blades, when tested repeatedly on hairless skin, the surface roughness increases only 8.6% far below the bare that reach 70%, preserving the cutting quality of surgical instruments. Experimentation on live pig and pig skins demonstrated that TFMG could reduce the spread of the pigment to the surface of surrounding skin by up to 57%, resulted narrower tattoo lines of higher density indicating that could be useful in high-resolution tattooing, reducing trauma in skin indicating with no secretion of fluids immediately after tattooing, has faster wound closing and faster healing compared with bare needle.

11:00am **D1-1-MoM-4 Synthesis of Antimicrobial Surfaces by Glancing Angle Deposition with Natural Seeds***, **Chuang Qu**, J. Rozsa, M. Running, S. McNamara, K. Walsh,* University of Louisville, USA

This research focuses on the synthesis and characterization of bio-inspired artificial antimicrobial surfaces. The antimicrobial surfaces studied in this research are surfaces that are covered with nanoscale protrusions, which are observed in nature such as cicada wings and dragonfly wings [1]. These nanoscale protrusions, mostly nanopillars and nanocones, achieve antimicrobial by mechano-bactericidal: the bacteria are deformed by being punctured into the protrusions and eventually killed [2]. Even though research groups have published papers on mechano-bactericidal surfaces [1, 3, 4], there are still some challenges in this research: 1) the synthesis, scaling-up and fine control of the artificial nanoscale protrusions are still challenging; 2) the mechano-bactericidal mechanism is not universal. The challenge of the synthesis comes from the fact that the three dimensional protrusion features for puncturing the bacteria have to be much smaller than bacteria, as small as only a couple nanometers. The proper spacing of the protrusion features is also required to allow the deformation of the bacteria. However, the sub-100 nm, high aspect-ratio, three-dimensional (3D) features are challenging to obtain through traditional nanofabrication methods, especially by top-down nanofabrication techniques.

Our research group proposed to use glancing angle deposition (GLAD) to recreate cicada-wing-mimicry antimicrobial surfaces [5]. GLAD is a bottom-up process for achieving complex 3D nanofeatures. The use of seeds alters the distribution of the features, and hexagonally packed nanofeature arrays are recreated. However, the requirement of the nanosphere seeds adds complexity to the process: the preparation of a monolayer of nanospheres is challenging, and the area of the seeds can be limited if seeding is not properly conducted. In the current research, we discuss the possibility of synthesizing the mechano-bactericidal antimicrobial surfaces by GLAD without predetermined seeds. The design and control of the process for synthesizing the antimicrobial surfaces are addressed in the study. Multiple materials are used for creating nanoscale protrusions for uncovering the mechano-bactericidal mechanism. The characterization of the surfaces, including the morphology, the superhydrophobicity, and the effectiveness of the antimicrobial property are presented. Finally, potential integration methods of the surfaces with nanoscale protrusions and biomedical implants are discussed in the study.

11:20am **D1-1-MoM-5 FDA Regulatory Considerations for Performance Evaluation of Coatings in Medical Devices***, **Nandini Duraiswamy**,* U.S. Food and Drug Administration , USA **INVITED**

Coated medical devices are used in millions of interventional and diagnostic procedures, and as permanent implants for treatment of intended patient populations throughout the world. The surgical implants can vary from those used for acute treatments such as interventional catheters to the more complex chronic implants such as drug-eluting coronary stents. The intended uses for the coatings on such implants can also vary such as additively manufactured porous metal surfaces for biological fixation (or osteointegration), non-degradable or degradable polymer with drug mixture for reducing cell proliferation and maintain vessel patency, or metallic coating on endosseous dental implants for biological fixation. These coated medical devices are regulated by Food and Drug Administration (FDA), Center for Devices and Radiological Health (CDRH) (Center for Devices and Radiological Health | FDA). The FDA-recognized international device-specific standards (Recognized Consensus Standards (fda.gov)) are used to assess performance, however the presence of thin coatings on medical devices often lack appropriate test methods for performance assessments of coatings. For example, coating are commonly used on guidewires and catheters, which are used for percutaneous cardiovascular interventions. Seven out of eleven Class I recalls and majority of MDRs in 2013-2014 were related to the "Wire, Guide, Catheter" device category (ProCode DQX). Some of those recalls resulted due to manufacturing changes to the coatings because the Environmental Protection Agency (EPA) wanted manufacturers to eliminate a surfactant, a carcinogen used in Teflon coatings, by 2015 [U.S. Environmental Protection Agency | US EPA]. There is a growing public health need to be able to identify any bad formulations of coatings early on through in vitro testing for the safety of the patients. In addition, the use of varied (or new) formulations of coatings further adds to the complexity of assessing risk of delamination in the patients and testing requirements, and expectations for minimum performance criteria for FDA regulatory clearance or approval. Results from prior research at the Office of Science and Engineering Labs (OSEL) (Office of Science and Engineering Laboratories | FDA) will also be shared as examples.

12:00pm **D1-1-MoM-7 Post-Anodization and Additives Role Towards the Effective Control of Bio-Degradation of Mg Alloys***, **Zeeshan Ur Rehman**, B. Koo,* Changwon National University, Republic of Korea

Mg and its alloys are widely seen as potential candidates for orthopedic implants and devices, due to their excellent biocompatibility and optimum mechanical properties. However, the major issue with Mg is its high corrosion rate in human body fluid/Chloride containing environment. This would make the implant failure possibility very high, before the bone tissues recovery, thus a sustainable surface treatment is mandatory before promoting the widespread use of Mg in biomedical implants. In this study, the Pre-coated Mg samples using plasma electrolytic oxidation techniques were further processed through sol-gel and dip coating technique. Various additives such as chitosan, Melamine, EDTA and PVA, with varying concentration were used in the sol-gel matrix. The finally obtained samples were characterized using SEM, XRD, EDS, FTIR, XPS for surface molecular and microstructural observations. Furthermore, biodegradation properties were analyzed using EIS, Potentiodynamic polarization and weight loss method to study the degradation rate of the coated samples. The result showed that post-anodization treatment under optimized concentration of the stated additives has slowed down the degradation significantly.

Keywords: AZ31, Orthopedic implant, Post PEO, biodegradation, SEM

New Horizons in Coatings and Thin Films
Room Town & Country B - Session F5-MoM

Machine Learning and Process Modeling for Coating Design and Production

Moderators: Adam Obrusnik, PlasmaSolve s.r.o., Czechia, **Ferenc Tasnadi**, Linköping University, Sweden, **Petr Zikán**, PlasmaSolve s.r.o., Czechia

10:00am **F5-MoM-1 Thin Film Process Modeling at Different Scales - from Kinetic Simulation to Digital Twin***, **Andreas Pflug**,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany **INVITED**

Modern products require coating stacks with increased complexity and precision as well as improved throughput, reproducibility and environmental footprint. Simulation is a valuable asset to reach these goals by modelling deposition reactor dynamics as well as thin film growth on atomistic level.

The various physical scales of thin film deposition can be addressed by either model-driven or data-driven codes. The first category is based on physically accurate models, that need only few unknown internal parameters but require high computational power. Examples are the Direct Simulation Monte Carlo (DSMC) and Particle-in-Cell Monte-Carlo (PIC-MC) methods for description of gas flow and plasma processes at low pressure and Molecular Dynamics (MD) or kinetic Monte Carlo (kMC) methods for modeling atomistic processes in thin film growth. Despite of their high computational demand, these methods are useful for getting insights into the functionality of novel deposition setups and plasma sources.

A complementary approach uses data-driven simulation codes, which are based on simplified, semi-empirical models or machine learning methods. On the one hand, they need a significant amount of internal data in order to be adjusted to represent specific process conditions, on the other hand they usually require only low computational power, which enables to do parameter optimization or use them as real-time capable digital twins for model-based in-situ process control.

This talk shows various examples for model-based simulation of PVD processes. Furthermore, it demonstrates how to use data obtained by physical modeling in order to create a digital twin for prediction of the coating uniformity on 3D substrates in a sputter reactor for optical coatings.

10:40am **F5-MoM-3 Coater-Scale Model of DC Magnetron Sputtering***, **Andrej Roštek**,* Masaryk University / PlasmaSolve s.r.o., Czechia*; P. Zikán,* PlasmaSolve s.r.o., Czechia*; J. Tungli,* Masaryk University, Czechia*; A. Obrusník,* PlasmaSolve s.r.o., Czechia

Magnetron sputtering is a widely used technique for the deposition of metal and compound layers for numerous technical applications. However, optimizing a sputtering process is a challenging task, especially since each industrial customer has specific requirements and expectations.

In order to improve properties of deposited coatings it is essential to understand the physics influencing them. Since the physical processes in magnetron sputtering are complex, it is often necessary to employ computer simulations. There has been a lot of work done in this regard [1-3], however, the simulations typically focused only on one part of a sputtering process, such as target erosion, sputtered atom transport, or the discharge properties.

This contribution attempts to provide a bigger picture by creating a coater-scale model which is a combination of two sub-models: (1) The bulk plasma model, which is a fluid model describing the plasma between the target and the substrate. It mostly affects ion bombardment. (2) The cathode plasma model, which is a particle-based model where ions and electrons are traced in the electric and magnetic field in the close vicinity of the target where the plasma sheath resides. This model affects mostly the target erosion. Its implementation is similar to our previous model from [4].

Together, these two models provide insight into various phenomena such as ion flux distribution, which determines target erosion, and the magnitude of ion bombardment at the substrates, which is a key determiner of the coating performance properties (residual stress, hardness, composition). Moreover, parametric studies can be performed so that the influence of pressure, substrate bias voltage, position of the electrodes, and others can be studied.

This model will be validated against experimental data.

References:

[1] C. Feist, A. Plankensteiner, J. Winkler *Studying Target Erosion in Planar Sputtering Magnetrons Using a Discrete Model for Energetic Electrons*Proceedings of the Conference: COMSOL, 2013

[2] S. Mahieu et al. *Monte Carlo simulation of the transport of atoms in DC magnetron sputtering* Nucl. Instrum. Methods Phys. Res. B, 243 (2), 2006, 313-319

[3] E. Shidoji, N. Nakano, T. Makabe *Numerical simulation of the discharge in d.c. magnetron sputtering* Thin Solid Films, 351 (1–2), 1999, 37-41

[4] A. Rostek *Simulating ion flux to 3D parts in vacuum arc coating: Investigating effect of part size using novel particle-based model* Surf. Coat. Technol., 449, 2022, 128954

11:00am **F5-MoM-4 High-Throughput Simulations to Predict History Dependence of Feedback Control During Reactive Magnetron Sputtering***, **Josja Van Bever**, K. Strijckmans, D. Depla,* Ghent University, Belgium

Feedback process control [1] of reactive sputtering is often required to achieve specific thin film properties. Although conceptually simple, it is far from trivial to make it reliable and reproducible. Two major problems can be identified.

First, depending on the initial state of the process two S-shaped process curves can be obtained under certain conditions [1]. Many suggestions have been made for the observation of this "*double hysteresis phenomenon*" such as target erosion, chamber heating, or anode effects. But even when these effects are excluded, the phenomenon can still be observed (figure 1) [2]. Hence it seems to be of a fundamental nature. Independently of the experimental observations, the simulation of the processes at the cathode facing the gas discharge led to the prediction of a double hysteresis [3].

Secondly, the *convergence of the feedback process* strongly depends on the history of the target process. Simulation of the transient target states may therefore also assists to improve this convergence.

In the first part of the presentation we present *high-throughput simulations* for double hysteresis behavior as a function of different process and material parameters [4, 5]. *New measures* are introduced that characterize the hysteresis with a single number and that vary in a continuous way as a function of these parameters. This allows us to *elucidate the nature of the double valued state during feedback control* and to explain for which materials and under which conditions this behavior is expected to occur (figures 2 and 3) [4].

In the second part we discuss the *application of this analysis* to feedback measurements of aluminum. A correct preparation of the target subsurface can speed up the feedback process and a *first direct proof of double hysteresis during feedback control* is delivered. Next, the measures from the high-throughput simulations are applied to investigate the role of diffusion [6] on the double valued nature of the process conditions achieved during feedback control.

Additional figures and references are found in the supplementary material.

11:20am **F5-MoM-5 Evatec Fabric – a Thin-Film Process and -Metrology Data Tracking System for Large-Scale, Automated Data Analysis in R&D Labs**, ***Clemens Nyffeler****, O. Rattunde, D. Jaeger, H. Zangerle, R. Gmuender,* Evatec AG, Switzerland

Managing data in an R&D lab is often tedious manual work and leads to heterogenous, incomplete data. To ensure reproducibility, information about experimental setups, process hardware, and -conditions, and sample pre-treatment, must be kept in addition to the primary results. Consolidating and harmonizing datasets for large-scale, overarching data science projects constitutes a substantial additional effort.

At Evatec we developed a system, designed to automate these things in the specific context of thin film process development and verification. Substrate information, hardware configuration, process log-data, and measurement results are linked together based on wafer-ID.

In contrast to traditional manufacturing execution systems (MES), the *Evatec Fabric* can dynamically reconstruct the chronology of events for each wafer without need to define a process flow in advance. This allows our scientists and engineers a wide degree of flexibility in carrying out their work.

A data-processing component, programmed in python, uses various algorithms, models, and data-fitting techniques to process the raw data, produced by process systems and metrology instruments. It extracts useful parameters and statistics that are stored in a highly structured and contextualized way, enabling data science and machine learning projects based on clean, homogenous data.

11:40am **F5-MoM-6 Predicting Reactive PVD Processes Using Global Process Modeling – a Physics-Based Alternative to Machine Learning**, ***Petr Zikán****, A. Obrusnik,* PlasmaSolve s.r.o., Czechia

Developing, transferring, or troubleshooting reactive PVD processes has always been a challenge. This can be partly attributed to the non-linear behavior of these processes. Additionally, the fundamental variables that drive the physics (e.g., plasma density and potential, the energy of sputtered and ionic species, …) are hard to measure, thus, often unknown in practice.

Another typical challenge is the number of consistent experiments available about the process. Experiments and their analysis are expensive and time-consuming. It is not uncommon that there are only a few (< 10) experiments available. This is the main limitation of machine-learning methods as these require large data sets (> 100).

In this contribution, we describe an alternative, physics-based approach that works well even with a low number of experiments. We illustrate that it is possible to formulate such a model for a whole coater that is either free of fitting parameters or contains only a few of them and they have a clear physical meaning. These models additionally contain coefficients, such as pumping speed, sputtering yields, or effective coating areas. These parameters are either known (pumping speed), can be obtained from the literature (sputtering yields), or can be pre-computed using 2D or 3D simulations (effective coating areas) for the coater and loading at hand.

Once created, such a model can reproduce the material composition across coaters and coater conditions with the accuracy of a few atomic percent. By correlating the process model outputs with literature data, the tool can also make predictions about the performance parameters of the coating (e.g., hardness). The approach will be illustrated in the case of nitride- or carbide-based ceramic coatings.

The specific global process model being discussed is not a simulation tool only but also an analytical tool in the sense that it works with a coater log at the input and combines machine log analytics with simulation data. As of submitting this abstract, the tool was already leveraged in five projects aimed either at process transfer between coaters (R&D scale) or achieving better process reproducibility (at MP-scale).

12:00pm **F5-MoM-7 Structure and Crystallographic Properties of Multi-Material Coatings Deposited in a Combinatorial Sputter Plant Compared to Simulations from the Machine Level to Microstructure**, ***David Böhm,*** TU Wien, Austria; *T. Schrefl,* Danube University Krems, Austria; *A. Eder,* MIBA High Tech Coatings GmbH, Austria; *C. Eisenmenger-Sittner,* TU Wien, Austria

Structure and crystallographic properties of multi-material thin films can be described with an interactive ray tracing software that simulates film deposition in arbitrary sputtering geometries, the so-called Virtual Machine (VM). Although based on a line-of-sight model, the VM also takes into account the decay of the flux density of the particles due to gas phase scattering. To further enhance the prediction capabilities of the VM a microstructure simulation package, based on rate equations and on the Potts Modell, was built.

At the machine level the VM recreates a real combinatorial DC-sputter plant from 3D models including the static arrangement of multiple targets, the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. For the deposition process, individual sample points can be defined on the substrate to which the line-of-sight model is applied, taking kinematics into account. The resulting thickness and sequence of the layers is used to visualize the thickness-resolved composition. Post-processing the time dependent thickness and temperature data the crystallographic phases with their associated XRD patterns are calculated from a library of binary phase diagrams for the simulated film.

Applying the rate-equation model to a generated layer architecture the microstructure can be calculated. First it is decided whether Frank-van-der-Merwe (continuous layer) or Volmer-Weber growth (island layer) occurs. The distribution of islands follows a thermodynamic equilibrium approach, which considers the process of island formation while minimizing the free energy of the island surface. The crystallite structure of the matrix material surrounding the islands is calculated by a spatially scaled Potts Modell. The Monte Carlo simulator is initialized with a crystallite structure generated using the Voronoi construction of the crystallite density determined from empirical data using rate equations.

Since volume diffusion is not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples, the above-mentioned comparisons are presented.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-1-MoM

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces I

Moderators: Dr. Damien Faurie, Université Sorbonne Paris Nord, France, **Dr. Michael Tkadletz**, Montanuniversität Leoben, Austria

10:00am **H1-1-MoM-1 In-situ Imaging of Au Bicrystals and Hydrogen Charged Iron**, ***Wendy Gu,*** Stanford University, USA; *M. Kiani,* Cornell University, USA; *A. Lee, A. Parakh,* Stanford University, USA **INVITED**

High resolution in-situ imaging is useful for understanding deformation, plasticity and fracture at internal microstructural features and under complex environmental conditions. Here, I will describe in-situ transmission electron microscopy (TEM) tension testing of Au bicrystal thin films that each contain a single grain boundary. This allows us to correlate the stress-strain curve and failure mode (e.g. twinning mediated fracture) to the grain boundary misorientation angle and grain boundary energy. Then, I will describe synchrotron transmission X-ray microscopy (TXM) of hydrogen charged iron thin films. This investigation is meaningful for understanding hydrogen degradation of metals, which is highly relevant to the green hydrogen economy. Home-built in-situ tension stages are used to test single edge notched samples. TXM is used to detect the formation of voids of ~100 nm to microns in size at the crack tip while simultaneously performing electrochemical hydrogen charging. We find that voids are elongated perpendicular to the loading direction, and highly localized at the crack tip during hydrogen charging in intergranular failure. Dynamic (time-dependent) TXM imaging enables the observation of void-mediated crack growth, as well as the coalescence of the primary crack with secondary cracks. Cracks and additional plasticity occur at grain boundaries during transgranular failure. These observations are discussed in the context of the predominant hydrogen embrittlement mechanisms.

10:40am **H1-1-MoM-3 High-Throughput Surface Analysis for Accelerated Thin Film Materials Development***, S. Zhuk, A. Wieczorek, K. Thorwarth, J. Patidar,* ***Sebastian Siol****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

New functional coatings are instrumental for the advancement of many sustainable technologies. As demands for functional properties are increasing, the materials and associated parameter spaces are becoming more complex. Combinatorial physical vapor deposition coupled with automated characterization and data analysis is routinely used to accelerate the development of new multi-functional thin films. Surface analysis using X-ray photoelectron spectroscopy (XPS) plays an important role in conventional thin film materials development. However, in combinatorial materials science methodology XPS analysis is much less common. In this presentation, we will show how spatially-resolved, automated XPS mapping can complement other high-throughput characterization techniques and provide unique insights in complex phase-spaces. Different use cases for high-throughput surface analysis will be presented, from the development of corrosion-resistant thin films [1] over phase-analysis in nano-crystalline materials [2] to combinatorial interface studies.[3] We will present results on the development of different inorganic thin films, including conductive ceramics, as well as semiconducting oxides and nitrides. In particular, we will introduce and discuss how measurements of the Auger parameter can augment standard XPS analysis for a robust and meaningful high-throughput analysis of air-sensitive and semiconducting samples.[2,4] Such studies can give insight not only into the chemical state of the constituent elements, but also their coordination and consequently the structure of the investigated materials. Finally, we will highlight how combinatorial XPS, coupled with clean inert-gas or UHV transfers can help to not only characterize light element contamination, but also oxidation resistance in air-sensitive coatings.

The concepts presented here are easily transferable to other material systems and can be adapted in standard measurement equipment.

[1] Siol et al., Acta Materialia, 2020, **186**, 95-104

[2] S. Zhuk et al. Appl. Surf. Sci., 2022, **601**, 154172

[3]S. Siol et al. Advanced Materials Interfaces, 2016, **3**, 24, 1600755

[4] A. Wieczorek et al. 2022, arXiv:2207.14123

11:00am **H1-1-MoM-4 Advanced Experimental Techniques Quantifying Thin Film Delamination at the Nano-Scale***,* ***Alice Lassnig****, C. Gammer, S. Zak, M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Interface stability between thin films and substrates is a prerequisite to ensure overall reliability of multi-component structures since such interfaces are known to be mechanically weak. Thus, a deep understanding of the mechanisms involved in the delamination process throughout their length scales is crucial and allowing to improve their reliability. Previously [1] we could demonstrate by means of a FIB-based characterization technique that intrinsic film properties can significantly influence interface adhesion and that plastic deformation occurring during delamination of the films can be understood as a toughening mechanism preventing delamination, as confirmed by finite element modelling [2].

To understand the mechanisms involved during thin film delamination, dedicated fracture experiments were designed to study the fracture behavior of ductile thin films using bending beam and push to pull geometries in situ under the transmission electron microscope. Particular focus is set on the thin film- interface delamination interaction to study the influence of thin film deformation behavior. On selected thin film systems strain mappings are conducted to quantify the thin film deformation during delamination within the transmission electron microscope.

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[2]S. Žák, A. Lassnig, M.J. Cordill, R. Pippan, Finite element-based analysis of buckling-induced plastic deformation, J. Mech. Phys. Solids. 157 (2021). https://doi.org/10.1016/j.jmps.2021.104631.

11:20am **H1-1-MoM-5 New Generation In Situ Process Control of Chemical Composition of Compound Materials and Superalloys During PVD Process***,* ***George Atanasoff****,* AccuStrata, Inc., USA

Multiple challenges associated with thin film deposition accuracy, and especially the challenge of real-time control of chemical composition for compound films and superalloys, spread over the entire contemporary thin film vacuum coating industry. These challenges predominantly affect the new-generation thin films such as high entropy superalloys (HESA), wide band semiconductors (WBS), Extreme UV and X-Ray coatings and others. Traditional in situ process control technologies are not adequate to the challenge: they monitor either the attained optical thickness of the film on the substrate, or the mass of the deposited material. In rare cases plasma optical emission or X-Ray fluorescence are used, but they both do not offer sufficient accuracy to meet the requirements for real time in situ monitoring.

A novel *in situ* PVD process control system for the manufacturing of high-precision thin films, based on simultaneous atomic absorption and optical emission spectrometry in the vicinity of the substrate (AtOMS), is presented. By simultaneous monitoring the atomic concentration of up to 6 metals in the deposition plum under the substrate together with the optical emission of a variety of particles and radicals, the method provides accurate deposition rate and film composition control during deposition, as well as control of extremely thin films and pre-engineered interface layers. The presented technology is viewed as an enabling technology for real time composition control of HESA and WBS for thermal barrier and bond coatings, anticorrosion, stimuli-response and other advanced coatings. Being agnostic to the type or the motion of the substrate, AtOMS technology is suitable for control of alloys and WBS deposited on complex substrates and composite materials. AtOMS provides real time deposition rate and film composition measurements utilized for dynamic feedback process control. The fiber optics design of the system allows flexibility and reconfigurability for fast and seamless installation in almost all legacy PVD equipment.

We present our most recent experimental results from *in situ* monitoring of variety of thin films such as Si, Mo, Al, In, Ti, Co, Cu, Au, B and compound thin films (MoSix, AlSix, WSix, ITO, NiCr) deposited by a magnetron sputtering, MBE and E-Beam evaporation. Results for the achieved accuracy, stability and repeatability under various equipment configurations and monitored materials in manufacturing environment are also presented. The results validate the applicability and practicality of combined atomic absorption/ optical emission spectroscopy in the deposition of WBS and superalloys as well as for combinatorial discovery of new HESA and WBS.

11:40am **H1-1-MoM-6 Influence of Al Incorporation and N Stoichiometry on the Thermal Stability of (Ti,V,Zr,Nb,Hf,Ta)N Thin Films***,* ***Deborah Neuß****, M. Hans, G. Fidanboy, H. Lasfargues, C. Azina, S. Mráz,* RWTH Aachen University, Germany*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; J. Schneider,* RWTH Aachen University, Germany

Recently, the concept of high entropy alloys has been transferred to ceramic thin films such as transition metal aluminum nitrides. In the present work $(Ti,V,Zr,Nb,Hf,Ta)_{1-y}N_y$ (TMN) and $((Ti,V,Zr,Nb,Hf,Ta)_{1-x}Al_x)_{1-y}N_y$ (TM,AlN) films were grown by reactive sputtering using a hybrid co-deposition geometry. The thermal stability was studied through vacuum annealing in a temperature range from 700 to 1300 °C and subsequently the films were analyzed regarding chemical composition, phase formation as well as mechanical properties.Configurational entropy contributions on the metal sublattice exceed 1.5R for all configurations, increasing in TMN as well as (TM,Al)N from overstoichiometric to understoichiometric compositions: from 1.57R up to 1.79R in case of TMN films as well as from 1.69R to 1.86R for (TM,Al)N films. Spatially-resolved compositional analysis at the nanometer scale has been carried out using atom probe tomography (APT). In case of (TM,Al)N films a dual-phase structure is readily observed in the as deposited state as aluminum decorates the grain boundaries and the formation of Al-rich regions is enhanced after vacuum annealing at 700 °C. Thus, surface diffusion, as driving force for Al segregation dominates the phase formation regardless of the higher configurational entropy compared to TMN. Contrary, in the as deposited state of TMN, all metals are equally distributed and no segregation is observed. The onset of thermal decomposition for TMN films occurs after annealing at 1100 °C independent of the N content and the formation of V-rich clusters is observed. Thus, it is noteworthy that despite the similar values computed for the metal sublattice configurational entropy for TMN and TMAlN films significant differences in decomposition behavior and hence thermal stability are observed. Nanoindentation of as deposited TMN revealed the elastic modulus increasing with N-content from 329 ± 10 GPa (41 at.% N) to 420 ± 9 GPa (56 at.% N). Despite the presence of a secondary Al-rich phase at the grain boundaries, the elastic modulus of (TM,Al)N films increases from 354 ± 21 GPa (45at.% N) to 395 ± 8 GPa (56 at.% N).

Topical Symposia
Room Town & Country A - Session TS1-1-MoM

Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications I

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Klaus Böbel**, Bosch Manufacturing Solutions, Germany

10:00am **TS1-1-MoM-1 The Effect of Microstructure on the Hydrogen Storage Capacity of Ti_xZr_{1-x} Thin Films***, **Ido Zukerman**, M. Buzaglo,* Divison of Chemistry, NRCN, Israel*; S. Hayun,* Department of Materials Engineering, Ben Gurion University of the Negev, Israel

Metal hydrides (MH_x) provide a promising solution for a future hydrogen-based energy system due to their high hydrogen storage density and safety advantages compared to compressed or liquefied hydrogen. Thin films were proposed to ease the absorption/desorption cycles by maximizing the surface-to-volume ratio. In this study, we suggest controlling the macro- and micro- structure of Ti_xZr_{1-x} thin films, in order to reduce the absorption/desorption temperature and to increase the rate and absorbed hydrogen volume. To achieve this goal, a series of Ti_xZr_{1-x} thin films were deposited using pulsed-DC magnetron co-sputtering technique. Low sputtering power, high working pressure, or floating bias conditions resulted in an open columnar structure (i.e., zone 1 microstructure). High negative bias (< -150 V), however, promoted a dense columnar structure (i.e., zone T microstructure). The thin film's hydrogenation was conducted as follows: The samples were held at 623 K under vacuum (< $5x10^{-3}$ Pa) for 1 hr for surface activation, then the chamber was filled with pure hydrogen to $2.0±0.1x10^4$ Pa and cooled to room temperature. The samples were held under H_2 for additional 24 hours at room temperature. Temperature-Programmed Desorption (TPD), Glow Discharge Spectroscopy (GDS), and electron microscopy were used to study the microstructure of the films, hydrogen storage capacity, desorption temperature, and the durability for multiple absorption/desorption cycles.

10:20am **TS1-1-MoM-2 Transition Metal – Doped Ni/YSZ Anode Functional Layers for Solid Oxide Fuel Cells Produced via Magnetron Sputtering***, K. Steier,* Manchester Metropolitan University, UK*; I. Jang, A. Hankin,* Imperial College London, UK*; P. Kelly, **Justyna Kulczyk-Malecka**,* Manchester Metropolitan University, UK

Solid oxide fuel cells (SOFCs) convert the chemical energy stored in fuels, such as hydrogen and gaseous hydrocarbons, directly into electrical power and thermal energy through electrochemical reactions. State-of-the-art SOFC anodes consist of a cermet of nickel and yttria-stabilised zirconia (YSZ) to increase the reactive sites at the anode/electrolyte interface, generating so-called triple-phase boundaries. The quantity of triple-phase boundaries in nanostructured materials increases through finer particle sizes, resulting in enhanced performance. For that reason, the magnetron sputtering technique, which offers elemental distribution at the nanoscale, high deposition rates, reproducibility, scalability and excellent uniformity over large-area substrates has been chosen as the deposition method to fabricate anode functional layers (AFLs) for SOFCs.

Nanostructured NiO-YSZ thin films have been previously produced by reactive pulsed DC magnetron co-sputtering of metallic targets of zirconium-yttrium and nickel, defining the optimal deposition parameters to create state-of-the-art AFLs. Based on recent studies, the future of oxide-based anode materials for SOFCs will greatly focus on reducing Ni catalyst content through alternative non-precious metal doping and increasing the cell performance by tailoring the microstructure of the AFL. This would allow Ni coarsening to be mitigated and maintain the nanostructure over the lifetime of the cell. Therefore, in this study complex transition metal oxides, such as vanadium, tantalum or manganese oxides, were doped into SOFC anodes to study their influence on the structural and morphological properties of magnetron sputtered AFLs. The effect of the dopant's concentration on the properties of Ni-YSZ films in as-deposited, pre-annealed and reduced state was analysed using SEM, EDS, XRD and XPS. To characterise the electrochemical performance of the deposited films, polarisation curves were obtained from SOFC single stack assemblies under hydrogen and air flows for anode and cathode, respectively, at operating temperatures of 750, 800 and 850 ℃.

10:40am **TS1-1-MoM-3 Surface Modification of Graphite Felt Electrode for Vanadium Redox Flow Batteries by High Entropy Alloy Oxide Thin Films: Effect of Oxygen Gas Flow Ratios***, **Krishnakant Tiwari**, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University of Technology, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Vanadium redox flow battery (VRFB) is one of the most promising renewable large scale energy storage devices. Electrode is one of the key components of VRFB which has significant effect on the energy efficiency and cost of the system. Carbon-based materials are widely used as electrodes in VRFB due to their lower electrical resistance and better corrosion resistance. However, untreated carbon-based electrode shows poor catalytic activity for redox reaction towards vanadium ions and cannot meet the development needs of VRFB. Among several surface modification methods, deposition of nanoparticles on the graphite felt (GF) electrode has been widely used. However, the poor uniformity of deposited nanoparticles results in a low charge transfer rate and poor adhesion. In this work, we investigated a surface modification approach for the graphite felt electrode by depositing refractory VNbMoTaW high entropy alloy oxide (HEAO) films grown under different oxygen flow rates using a high power impulse magnetron sputtering (HiPIMS) system for improving the performance and economic competitiveness of VRFB. Surface morphology of HEAO modified GF electrodes were examine using FESEM, contact angle test, Raman analysis, XRD and XPS. The electrochemical performances of GF electrodes modified with HEAO films grown under different oxygen gas flow ratios were compared. The flow cell test of HEAO modified GF electrodes was performed to demonstrate the charge-discharge capacity, voltage efficiency and energy efficiency at different current densities. The cycling test illustrated the stability of the VNbMoTaWOx film layer on graphite felt, where no significant decay in efficiencies was observed. The effect of oxygen gas flow ratios on the phase, chemical compositions, and electrochemical performance of the HEAO films were also discussed.

11:00am **TS1-1-MoM-4 Temperature Dependency of Specific Electrical Conductivity of DLC Coatings***, S. Danninger,* University of Applied Sciences Upper Austria*; **Francisco Delfin**,* University of Applied Sciences Upper Austria, Argentina*; C. Forsich, D. Heim, M. Schachinger,* University of Applied Sciences Upper Austria*; B. Rübig, C. Dipolt, T. Müller,* Rubig GmbH & Co KG, Austria

DLC coatings show a favourable combination of both low friction coefficient and high wear resistance and are therefore widely used for technical applications. To increase the film's electrical conductivity for special applications (e.g., coatings for electrodes) common methodes are film doping with nitrogen or metals. This study, however, investigates the decrease of electrical resistivity of un-doped DLC coatings through an increase in deposition temperatures above 450 °C.

DLC coatings were produced by means of PA-CVD using pulsed DC discharge. Temperatures of 450 °C, 500 °C and 550 °C were used to deposit a-C:H and a-C:H:Si films on various steel substrates. Process gas consisted of a mixture of argon, acetylene, and HMDSO as silicon precursor. Additionally, coatings with process gas consisting of 20 % hydrogen were produced respectively. Afterwards, for coatings deposited at 450 °C a tempering was conducted at 550 °C to exclude only heat treatment related effects. An amorphous silicon interlayer was used as an electric insulator between substrate and coating. To measure the specific electrical resistivity of all coatings the van der Pauw method employing four contact points was performed. Further coating characterizations included GDOES and EDX analysis and the measurement of layer hardness through nanoindentation. Raman spectroscopy was performed, and the spectra were compared to estimate the hydrogen content and hybridization of the DLC coatings.

Silicon free DLC films showed a clear decrease of specific electrical resistivity with an increase of deposition temperature. Values dropped from 10^7 µΩ cm at 450 °C to under 10^4 µΩ cm at 550 °C, reaching levels comparable to graphite. While the specific electrical resistivity of these a-C:H films decreased with higher deposition temperatures, a hardness increase of more than 70 % was measured over the temperature range. The average hardness of 350 HV at 450 °C rises to 600 HV for 550 °C. Process gas consisting of 20 % hydrogen decreased specific electrical resistivity even more by at least 60 %, while also slightly raising surface hardness. For a-C:H:Si coatings the specific electrical resistivity exceeded the measurement setup's detection limit of about $1.9{\cdot}10^7$ µΩ cm, as they seem to be highly electrically insulating. Hydrogen containing process gas did not show any effects on silicon doped coatings. With this new process approach electrically conductive and hard a-C:H coatings could be produced without metal- or nitrogen-doping with thicknesses up to 120 µm only through an increase of deposition temperature.

11:20am **TS1-1-MoM-5 High Efficiency of Metal Oxide Catalysts for Vanadium Redox Flow Battery***, **Chen-Hao Wang**,* National Taiwan University of Science and Technology, Taiwan **INVITED**

The development of sustainable energy resources such as wind and solar is urgently needed to diminish the environmental impact of fossil fuels. Nevertheless, energy storage systems (ESS) are required to store and stabilize such intermittent and random clean energy sources. Among various energy storage devices**,** the vanadium redox flow battery (VRFB), first invented by Skylla-Kazacos and co-workers in the 1980s, is one of the most promising large-scale energy storage devices owing to its design flexibility, extended cycle life, and safe operation. Furthermore, VRFB avoids cross-contamination due to employing the same electroactive element (vanadium) for both half-cells. VRFB comprises three essential components: membrane, electrolyte, and electrode. To store energy, it uses the redox couples of the electrolyte, $V^{3+}/V^{2+,}$ and VO^{2+}/VO_2^+, on the negative and positive sides, respectively. The membrane behaves as a separator for the two half-cells and maintains electroneutrality by passing hydrogen ions through it. The electrode does not participate in the redox reaction but provides a reaction site for active species. Therefore, some active electrodes with metal oxide-based catalysts are used in the VRFB to enhance performance. In this talk, we will introduce metal oxides, e.g., $W_{18}O_{49}$, CeO_2, and $BiVO_4$, which have excellent electrochemical activities, making VRFB more powerful.

Keywords: Energy storage system, vanadium redox flow battery (VRFB), electrode modification, energy efficiency

12:00pm **TS1-1-MoM-7 Effect of Mg Doping on Characterization and Cycling Performance of $LiCoO_2$ Thin Film Cathode for Lithium-Ion Batteries***, **Tai-Yan Liu**, J. Huang, C. Liu,* National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIBs) are the most popular energy storage devices for portable electronics and electric vehicles due to their high energy density, long cycling lifetime and no memory effect. Lithium cobalt oxide ($LiCoO_2$, LCO) is the first commercialized cathode materials for LIBs. It has many advantages such as favorable rate capability, excellent capacity retention, and high theoretical specific capacity compared with other cathode materials. However, LCO has severe structural destruction due to irreversible phase transition under high cut-off voltage above 4.2V, which causes rapid capacity fading and structural instability during repeated cycling. Therefore, electrochemically inactive element doping is studied to improve structural stability. Among many dopants, Mg is regarded as a promising element to achieve better cycling performance for LCO. Hence, we deposited Mg-doped lithium cobalt oxide (Mg-LCO) thin films for cathode materials. Co-sputtering method and post annealing were utilized to grow Mg-LCO thin films. Firstly, Al foils were sequentially cleaned in 95% ethanol and DI water for 10 min, respectively. Secondly, $LiCoO_2$ (99.99%) and MgO (99.99%) targets were co-sputtered via RF magnetron sputtering system to deposit Mg-LCO thin films on Al foils at 250 °C for 60 min in Ar/O_2 mixed gas atmosphere. The RF power of the $LiCoO_2$ target was fixed to 100W and the RF power of the MgO target was varied from 0 to 60W. Afterwards, the Mg-LCO thin films were annealed at 600°C in air for 4h via a tube furnace. From XPS and sheet resistance measurement, Mg successfully doped into LCO thin films and replaced Li sites thereby increasing the sheet resistance. SEM images showed granular size and thickness in the Mg-LCO films decreased with the MgO working power from 0 to 60W. TEM and XRD investigations revealed that the Mg-LCO thin films were layered structure and polycrystalline with (003) preferred orientation. Finally, in half-battery test, the 60W Mg-LCO thin film cathode exhibited better voltage plateaus and capacity retention than 0W, 30W Mg-LCO in the voltage range of 3.0-4.2 V at 0.2 C rate after 30 cycles. According to the above results, the structure of LCO thin film after Mg doping was more stable during charge/discharge process. In future, we will study the electrochemical performance of LCO thin films with higher Mg doping amount. Further, we will do the high voltage cycling tests (above 4.5V) and combine electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to investigate redox kinetics of high voltage Mg-doped $LiCoO_2$ thin film cathode.

Special Interest Talks
Room Town & Country A - Session SIT1-MoSIT

Special Interest Session I

Moderator: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

1:00pm **SIT1-MoSIT-1 Residual Stress Measurement on Hard Coatings and the Evaluation of Energy Relief Efficiency of Architectured Coatings*, Jia-Hong Huang,*** National Tsing Hua University, Taiwan **INVITED**

Hard coatings deposited by physical vapor deposition are usually sustained high residual stress that could lead to many problems in the applications, such as delamination and spallation of coating, thereby reducing the service duration of the products. To solve residual stress problem in hard coatings, the stress should be correctly measured. In the first part of this talk, the method of stress measurement will be reviewed, mainly focusing on the $\cos^2\alpha\sin^2\psi$ X-ray diffraction method [1] and a recent developed technique, the average X-ray strain (AXS) method, which was a more accurate technique based on the previous $\cos^2\alpha\sin^2\psi$ method [2]. Examples of the applications will be briefly mentioned. In the second part of the talk, the estimation of stress relief efficiency by metal interlayer using an energy balance model will be introduced. One of the most common approaches in dealing with residual stress issue is by introducing a metal interlayer in between the hard coating and substrate, by which residual stress is expected to be partly relieved and adhesion strength of the coating may be enhanced. However, the selection of metal and the thickness of interlayer is usually based on empirical rules without theoretical basis. Therefore, the efficiency of stress relief by using a specific metal with a certain thickness cannot be properly estimated. Recently, we proposed an energy balance model to evaluate the energy relief efficiency by the interlayer and further understand the relation between stress relief and plastic deformation [3]. The model hypothesized that stored elastic energy in the hard coating and the bending energy in the Si substrate could be partially relieved by the plastic deformation of the metal interlayer. The model has been applied on TiN/Ti, ZrN/Ti and ZrN/Zr bilayered coatings on Si substrate, where the energy relief efficiency can be estimated; furthermore, the contributions of energy relief by hard coating and substrate are separately assessed. The model was also applied on TiZrN/TiN/Ti tri-layered coatings on Si substrate, and the energy relief efficiency was successfully evaluated.

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Coatings for Use at High Temperatures
Room Pacific E - Session A1-2-MoA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Gustavo García-Martín, REP-Energy Solutions, Spain, **Dr. Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

1:40pm **A1-2-MoA-1 Microstructural Changes of Yttria-Containing MMC-Coatings and Their Influence on Hot Corrosion, Wear and Mechanical Behavior***, **Christoph Grimme**, C. Oskay, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

While very high inlet temperatures increase the efficiency of turbines, they lead to the requirement of oxidation resistant bond coats for TBC systems. MCrAlY (M: Ni and/or Co) coatings are used for turbine blades in a broad field of applications. However, their deposition processes by HVOF or EB-PVD are cost-intensive and limited by line-of-sight. Galvanic co-deposition methods can be utilized to apply these types of coatings at lower cost and without line-of-sight limitations. This technique also opens the possibility to incorporate different metallic and ceramic particles alongside with galvanically deposited Ni, Co, and Ni/Co. Coatings for turbine components should not only improve the oxidation resistance of the system, but also increase the hot corrosion resistance to ensure an extended lifetime. One of the most aggressive attack in turbines originates from vanadium present in the fuel to be burned in gas turbines. It forms eutectic ashes with Na_2SO_4 from fuel or air ingestion of NaCl to form low melting V_2O_5/Na_2SO_4 compounds [1].

In this study, a novel galvanic co-deposition method was used to incorporate yttria particles in the Ni-coatings. Thereafter, the pristine Ni/Y_2O_3 coatings were enriched with Al and/or Cr by pack cementation. By the co-depositon of yttria alongside with nickel not only the oxide formation, but also the oxide adherence could be strongly improved due to the reactive element effect [2]. It was proven, that Y_2O_3 is also able to react with V_2O_5 to form high melting YVO_4 and thereby avoiding the formation of highly corrosive, low melting V_2O_5/Na_2SO_4 compounds. The influence of Y_2O_3 on oxidation and hot corrosion, as well as wear and mechanical properties compared to unmodified NiAl coatings was studied.

It was found that additions of nanosized Yttria in the Ni-coating cause a significant grain refinement after the aluminum diffusion process, with the grains being much larger for yttria-free coatings. Hardness measurements revealed an increase of approx. 100 HV1 for MMC NiAlY coatings compared to coatings without dispersed nano–Y_2O_3 particles. Furthermore, significant improvements of the thermocyclic oxidation behavior and hot corrosion resistance were achieved by the incorporation of Y_2O_3 to the metallic coatings.

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[2]J. Stringer,*Mater. Sci. Eng. A***1989**, *120*, 129–137.

2:00pm **A1-2-MoA-2 Surface Refinement by Aluminide Diffusion Coatings and Its Effect on the Oxidation Behavior and Creep Strength of Additively Manufactured Fe- and Ni-Based Alloys***, **Ceyhun Oskay**, L. Mengis,* DECHEMA-Forschungsinstitut, Germany*; A. Kulig, H. Daoud,* Neue Materialien Bayreuth GmbH, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany*; U. Glatzel,* University of Bayreuth, Germany and Neue Materialien Bayreuth GmbH, Germany

Additive manufacturing (AM) has created new possibilities for the rapid production of metallic components and has received considerable interest by a variety of industries such as chemical, energy and transportation, since this form of production of parts and/or spare parts can lead to the independence from supply chains. Furthermore, AM can offer the tailoring the component design, microstructure, and mechanical properties according to the requirements [1]. One of the major drawbacks of the AM is the requirement of a post-processing, since the components in the as-printed condition always possess a significantly high surface roughness and high internal stresses. This leads to a deterioration of their service-relevant properties such as oxidation resistance and fatigue strength. The industrial surface post-processing is usually conducted by grit blasting and heat treatment and is therefore usually difficult to apply for large parts with complex geometries. Even after these post-processing, AM components may still require improvement in their oxidation resistance, as process temperatures steadily increase for higher efficiencies. At higher service temperatures, the enrichment of Al at the surface by diffusion coatings has been shown to be very effective to protect Fe- and Ni-based alloys from oxidation. Such coatings form and maintain a slow-growing and dense alumina scale [2,3].

In this study, pack cementation was utilized to deposit aluminide diffusion coatings on additively manufactured (via Laser Powder Bed Fusion, LPBF) Fe- and Ni-based alloys to chemically modify and refine their surface simultaneously. A significant reduction of the surface roughness as well as sealing of the pores in the vicinity of the surface was observed after the coating deposition. Quasi-isothermal oxidation tests up to 1000 h were conducted at 800°C and 1000°C in laboratory air for aluminized and uncoated LPBF specimens. A significant improvement of the oxidation behavior was observed for the aluminized LPBF alloys compared to uncoated alloys. Creep tests were conducted at 800°C and 1000°C to characterize the performance of LPBF alloys with and without aluminide coatings. These results were compared with aluminized and uncoated wrought samples under the same conditions. Furthermore, load effects on scale formation and re-healing, depletion of the oxide former and crack formation were discussed for the AM alloys.

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[2] D.K. Das, Prog. Mater. Sci 58 (2013) 151-182

[3] B.L. Bates et al., Surf. Coat. Technol. 204 (2009) 766-770.

2:20pm **A1-2-MoA-3 Influence of High Temperatures on the Friction and Wear of Highly Stressed Exhaust Systems***, **Martin Dienwiebel**,* Institute for Applied Materials IAM - Karlsruhe Institute of Technology, Germany*; T. König,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; T. Kimpel,* Institute for Applied Materials IAM, Karlsruhe Institute of Technology, Germany*; D. Kuerten, A. Kailer,* Fraunhofer Institute for Mechanics of Materials IWM, Germany **INVITED**

We investigated the atmospheric effect of exhaust components on the wear of cast iron against chromium plated steel at temperatures up to 800 °C. Reciprocating wear tests of a cylinder plate configuration were performed in air and a low-oxygen CO_2-N_2-O_2 atmosphere and analyzed afterwards.

At temperatures above 400 °C a tribological induced oxide layer is formed at the interface, a so-called “glaze layer”, which replaces an adhesive regime and leads to a strong decrease of wear. The investigation proves a layered structure out of a porous lower and a highly compacted upper part with different chemical compositions. A change of atmospheres shows low impact on this tribological mechanism above a threshold temperature of 400 °C, assuming sufficient oxidation times of the generated wear particles, which agglomerate, were compacted and sintered due to the tribological stresses and temperatures. Based on this finding, a temperature related sinter or phase transition process is postulated to determine the glaze layer formation independently of comparable small atmospheric differences. At the adhesion dominated regime of lower temperatures a Carbon enriched layer of 400 nm thickness was observed in the CO_2-N_2-O_2 atmosphere and is made responsible for a decrease of wear.

3:00pm **A1-2-MoA-5 Surface Refinement of Additively Manufactured Components: Microstructure and Mechanical Properties***, **Agata Kulig**,* Neue Materialien Bayreuth GmbH, Germany*; C. Oskay, L. Mengis,* DECHEMA-Forschungsinstitut, Germany*; H. Daoud,* Neue Materialien Bayreuth GmbH, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany*; U. Glatzel,* University of Bayreuth, Neue Materialien Bayreuth GmbH, Germany

Laser Powder Bed Fusion (L-PBF) is already used for manufacturing complex parts with high precision. However, the high cost of surface finishing is still a limiting factor for the spread of L-PBF components in various industries. The high surface roughness and their resulting residual porosity influence the mechanical properties, especially dynamic ones. In this presentation, the pack cementation process will be introduced as a novel method to refine the surface roughness and the microstructure in the surface zone as well as to improve the mechanical behavior of L-PBF parts.

The effect of the pack cementation process on the resulting microstructure in the surface zone of L-PBF specimens was investigated. For this purpose, different Fe- and Ni-Basis alloys were investigated. The surface roughness of as-built and as-modified L-PBF specimens was measured. Finally, the tensile strength as well as the fatigue behavior of both as-built and as-modified specimens will be presented.

3:20pm **A1-2-MoA-6 Oxidation Behavior of Novel Cr-Si Diffusion Coatings Applied by the Slurry Technique***, **Michael Kerbstadt**,* DECHEMA, Germany*; E. White,* DECHEMA, USA*; M. Galetz,* DECHEMA, Germany

Diffusion coatings are widely used in high temperature applications to enhance the oxidation and corrosion resistance of metals and alloys. Commonly Al, Cr, or Si are enriched at the surface in order to form protective oxide scales during exposures at high temperatures. Al, Cr and Si-based diffusion coatings are mostly achieved by pack cementation, where the deposition occurs via a gas diffusion process. For pack cementation the substrates are usually fully embedded into a powder mixture, which is labor-intensive and requires extensive furnace fixturing to be heated-up during each run. For an Al diffusion coating, an alternative slurry process is well established, where the slurry is sprayed onto the metallic surfaces by an air brush. The coating is then established during a subsequent heat treatment by interdiffusion between the metallic particles from the slurry and the substrate. For sufficient diffusion rates during the heat treatment, the existence of a liquid phase at the interface of the substrate surface and the slurry particles is necessary. Because of the high melting point of Cr, the deposition of Cr-based diffusion coatings by the slurry technique has been challenging. Cr-Si slurry coatings have recently been successfully developed at the Dechema-Forschungsinstitut. These newly developed slurry coatings are applied using an aqueous suspension where distilled water is used as the solvent. Higher Cr-activities, due to the partial liquid state, enable higher coating thicknesses when compared to similar coatings applied by pack cementation. This creates a larger reservoir of the protective oxide-forming elements Cr and Si, resulting in longer-lasting protection from the coating.

In this work the oxidation behavior of novel Cr-Si slurry coatings applied on the austenitic steel Sanicro 25 and the Ni-base alloy Inconel 617 are investigated. A Cr and Si enriched diffusion zone of more than 100 µm could be achieved on both materials. Isothermal and cyclic (1h/cycle) oxidation exposures at 900°C for 1000 h in lab air were carried out. To classify the results, samples with coatings applied by pack cementation and also bare substrate materials were exposed under the same conditions. To determine the weight gain samples were removed after 300 h, 700 h and 1000 h. Analysis by XRD, SEM and EPMA was performed to determine the structure and composition of the oxide layers and the degree of oxidative attack. Due to the increased amount of protective elements, the slurry coated samples showed a lower overall mass gain and decreased oxidation attack during the exposures.

3:40pm **A1-2-MoA-7 Use of Machine Learning Algorithms to Optimize and Customize Aluminide Diffusion Coatings***, **Vladislav Kolarik**, M. Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany*; P. Praks,* IT4Innovations National Computing Center, VSB - Technical University of Ostrava, Czechia

Aluminide diffusion coatings are a highly efficient and economic technique to protect steels against corrosion at high temperatures in aggressive media such as molten salts or steam. They are easy to apply using different methods of deposition such as spraying or brushing with a subsequent heat treatment to form the diffusion coating. Machine learning algorithms offer a huge potential for optimization as well as for customization of the coatings to a particular application with different substrate steels and media. The experimental effort can be minimized reducing the costs significantly and accelerating the development. In this context the present work investigates the use of machine learning to determine the coating process parameters that lead to the targeted coating characteristics and properties.

First, the entire coating system and its manufacturing process was fully parametrized considering every single parameter having influence on the coating. Variable input parameters have been defined: green slurry thickness, slurry viscosity, aluminum particle size, curing temperature and time, heat treatment temperature and time. Other input parameters such as the substrate steel, surface roughness, slurry composition, purity of the aluminum particles, slurry deposition method and air as atmosphere were kept constant. Output parameters characterizing the diffusion coating were defined: coating thickness, number of layers and their thicknesses, pores concentrations and FeAl precipitations in the Fe2Al5 layer. Assessment criteria for the targeted properties were defined, such as an overall thickness of 100 to 120µm, three allowed layers (Fe2Al5, FeAl, Fe+FeAl), and a porosity less than 5%. Algorithms from Machine learning such as CatBoost were chosen to undertake the first approaches. Experimental values from former projects were used to train the software for calculating the impact of process parameter variation on the coating properties and to validate the outcome.

4:00pm **A1-2-MoA-8 Self-Healing Aluminide Coatings***, **Fernando Pedraza**, R. Troncy, L. Boccaccini, G. Bonnet,* La Rochelle University, France*; X. Montero,* MTU, Germany*; M. Galetz,* DECHEMA-Forschungsinstitut, Germany

Upon high temperature exposure, the Al reservoir of the aluminium diffusion coatings is lost by oxidation (2-8%) and by interdiffusion (20-35%) [**1**]. This lowers oxidation and mechanical resistance in nickel-based superalloys. Thermodynamically stable γ/γ' $(NiPt)_3Al$-based coatings were thus considered [**2**] but they require appropriate contents of Pt and of Hf to provide adequate oxidation resistance [e.g. **3**]. Since the cost of Pt (and of Hf) is quite high, such stable coatings cannot be applied to the low pressure turbine components that operate at lower temperatures (T<1050°C) where simple aluminide coatings suffice [**4**]. The use of diffusion barriers has been proposed to arrest interdiffusion [e.g. **5**] but such layers can embrittle the whole coating system. In contrast, composite $NiAl$-Al_2O_3 coatings [**7**] display adequate mechanical properties [**6**] and the high exothermicity between preoxidized Ni powders or coatings and Al [**8,9**] is buffered, hence avoiding projection of molten metal [**10**].

Based on this, this paper investigates the synthesis of self-healing aluminide coatings made of a conventional nickel aluminide matrix where preoxidized Al-rich Ni_xAl_y microreservoirs are embedded [**11**]. The idea is that the oxide shell covering the microreservoirs governs the outward diffusion of the Al-rich intermetallic core whenever the matrix is depleted in Al upon oxidation. For such purpose, Ni_2Al_3 powders were first fabricated by pack aluminizing a Ni plate that was subsequently crushed and milled, preoxidized and then added a nickel-electroplating bath. A final slurry aluminizing process was conducted. The study was conducted on pure Ni as a model of the Ni-based superalloys. Subsequent isothermal oxidation at 1000°C was conducted for 48h in air. The main results show that the Al depletion in conventional simple aluminide coatings ranged between 32 and 45 at% while the ones containing the microreservoirs only lost 11 at% thereby showing the promising character of these coatings. The mechanisms of formation and of degradation of the coatings will be highlighted.

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4:20pm **A1-2-MoA-9 Continuous Al-supply to Cr_2AlC MAX Phase Coatings During Oxidation at High Temperature***, **Clio Azina**, M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; J. Gonzalez-Julian,* Chair of Ceramics, RWTH Aachen University, Germany*; P. Eklund,* Linköping University, IFM, Sweden*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Phase stability is likely to be one of the most important specifications which determine the lifetime of materials operating in extreme environments. In the case of MAX phases, the weakly bonded A-elements diffuse along the basal planes when a thermal load is applied or when in presence of oxidizing environments. The A element then reacts with the oxidizing environment and forms a protective oxide scale. That is the case of the Cr_2AlC MAX phase in which Al diffuses to the surface and forms an Al_2O_3 scale. However, the Al depletion below the surface causes the local decomposition of the MAX phase into the binary carbide, Cr_7C_3.

In this work, the possibility of continuously supplying Al to Cr2AlC coatings is investigated in order to avoid the formation of the carbide layer. To this end, Cr2AlC substrates with different microstructures were used as substrates. These substrates were then coated with Cr2AlC by magnetron sputtering. The MAXonMAX assemblies were then oxidized in air, at high temperatures and the integrity of the assembly was assessed. Imaging allowed determining whether the different substrates allowed for Al transport across the substrate/coating interface and whether the concept of Al-supply from a MAX phase substrate to a MAX phase coating was viable. It appeared that the substrates played a major role in the oxidation behavior of the coatings as the oxide scale growth was impacted. This was attributed to the microstructure of the substrates which allowed for more or fewer diffusion channels depending on the grain size. Overall, the concept of Al-supply was shown to be successful when using fine-grained substrates but did not yield significant improvement when considering coatings grown on coarse-grained MAX phase substrate compared to those grown on conventional MgO substrates where Al supply does not occur.

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 $CH_3SiHCl_2/C_3H_6/H_2$ 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 $SiHCl_3/H_2$ 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$_2$ Multilayer Coatings***, **Michael Tkadletz,*** Montanuniversität Leoben, Austria*; A. Lechner, B. Sartory,* Materials Center Leoben Forschung GmbH, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

Chemical vapor deposited (CVD) TiN and TiB_2 are quite different materials, but both are frequently utilized as wear resistant hard coatings. CVD TiN exhibits a comparatively large grain size in the µm range, tensile residual stress and a moderate hardness. CVD TiB_2 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_2 were combined in two multilayer coatings with different bilayer periodicities of ~100 and ~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$_2$O$_3$ Hard Coatings***, **Christiane Wächtler,** C. Wüstefeld,* TU Bergakademie Freiberg, Germany*; M. Šíma, J. Pikner,* Dormer Pramet, Czechia*; D. Rafaja,* TU Bergakademie Freiberg, Germany

Although the use of protective Ti(C,N)/Al_2O_3 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 µm and 0.7 µm, 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 $TiC_{0.6}N_{0.4}$ monolayers and complete $TiC_{0.6}N_{0.4}/Al_2O_3$ 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 α-Al_2O_3). 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 α-Al_2O_3, developed in coatings with consistently narrow grains. The texture was always weakened, when coarse Ti(C,N) and/or Al_2O_3 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 α-Al_2O_3 layer, although the bonding layer between fcc-Ti(C,N) and α-Al_2O_3 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_2O_3 stacks helped us to understand the effect of the additional thermal exposure of the samples during the Al_2O_3 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_2O_3 coatings produced in CVD processes.

3:00pm **B2-MoA-5 Novel ZrB$_2$ and HfB$_2$ 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_2 and HfB_2 by CVD is described. A LPCVD process using $MeCl_4$ (Me = Zr or Hf), BCl_3, H_2 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_2 and 38 GPa for HfB_2. 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_2 coated inserts showed a higher lifetime in comparison with state-of-the-art CVD- and PVD-TiB_2 coatings in face-milling TiAl6V4.

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 sp3 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~10^8-10^{10} 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~10^{11}-10^{13} 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_4, C_2H_2, 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 -pruefung (BAM), Germany **INVITED**

For long distance land and overseas transport of large quantities natural gas is usually liquefied. Methane (CH_4), 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_2) 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_4 at room temperature. Also wear coefficients in the order of 10^{-8} $mm^3N^{-1}m^{-1}$ 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_6Al_4V Alloy***, A. Nieto-Sosa, G. Rodríguez-Castro, J. Escobar-Hernández, A. Meneses-Amador, **José Arciniega-Martínez**, H. Martínez-Gutierrez,* National Polytechnic Institute, Mexico

In this study, titanium borides were formed on the surface of Ti_6Al_4V alloy by powder pack boriding at 1100 °C during 5, 10 and 20 h. Under these treatment conditions, 3 thicknesses consisting of a Ti_2B 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 Ti2B 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_2O_3 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, magnetron dual gun co-sputtering system, the binary refractory metal nitride thin films were fabricated at a fixed Ar/N_2 inlet gas ratio of 12/8 sccm/sccm. The structure of (MoHf)N thin film exhibited MoN, Mo_2N, and MoN_2 phases, while the (WHf)N thin film possessed WN and Hf_4N_3 phases. As for the (MoW)N thin film multiple phases including WN, MoN, and Mo_2N 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 pealing 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 ablators 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_x 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 ^{o}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 nanoindention 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 $HAuCl_4$. 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 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***, Mowafaq 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_2O_2 , 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: $Mo_{1-x}Ni_x$ and $Mo_{1-x}Si_x$ 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 $Mo_{1-x}Si_x$[1]and $Mo_{1-x}Ni_x$[2] alloy films with $0 \le x \le 1$ 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_{Si} ~ 0.19 and Ni content, x_{Ni} ~ 0.26 while fcc-crystalline to amorphous state transition is observed for x_{Ni} ~ 0.73. These structural transitions are accompanied by modifications of physical and mechanical properties s, namely, longitudinal out-of-plane modulus C_{33}, and out-of-plane shear modulus C_{44}. In the crystalline regions, a pronounced softening of the shear elastic C_{44} constant from 110 GPa to 60 GPa for MoSi and from 65 GPa to 45 GPa for MoNi, is observed. The longitudinal modulus C_{33} 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 $0.19 \le x_{Si} \le 0.5$, the metallic character of the solid solutions is maintained and the elastic properties are remarkably stable. For $x_{Si} > 0.5$, 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.

[1]A Fillon *et al.*, Phys.Rev.B 88, 174104(1-16) (2013)

[2]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***, **Andreas 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. Yalamanchili, 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^2 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 desire 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 $VNbMoTaWTiAl_{0.5}$ 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-dopped 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.

Coatings for Biomedical and Healthcare Applications
Room Pacific F-G - Session D1-2-MoA

Surface Coatings and Surface Modifications in Biological Environments II

Moderators: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Dr. Kerstin Thorwarth**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

1:40pm **D1-2-MoA-1 Antibacterial Performance of DLC and Ag-doped DLC coatings with a Long Term Perspective***, **Maneesha Rupakula**,* Platit AG, Switzerland*; K. Sharma,* EPFL, Switzerland*; H. Bolvardi, B. Paul, G. Wahli,* Platit AG, Switzerland

DLC display properties such as high mechanical hardness, low coefficient of friction, high chemical inertness, and good biocompatibility. Due to their amorphous structure, doping with certain elements enhances functionality still preserving structural integrity. Ag doped DLC films form an interesting class of biomaterials being bactericidal along with other favourable physical properties. Where sterile or ultra-clean conditions need to be ensured, surfaces of components, instruments, parts of tactile and environmental surfaces can benefit from such hard biomaterials. For industrial relevance, 1) anti-bacterial response to both clinically relevant gram-positive and gram-negative bacterial strains and 2) antibacterial performance over longer-term needs to be explicitly studied and not inferred.

In this work, we addressed both antibacterial behaviour and its long-term effect over months. DLC films were prepared in a hybrid vapordeposition process to obtain Ag concentrations in DLC ranging 0 to 8.5%. DLC (No Ag) films display antifouling behaviour over bare substrate with antibacterial efficiency up to 30% for both gram-positive (S. aureus) and gram-negative (E. coli) bacterial strains. Hence, DLC (No Ag) films are considered intrinsically favourable as antibacterial surfaces. This passive antibacterial effect can vary widely when tuning mechanical film strength with change in carbon content. To obtain a constant efficiency with time, an active bactericidal effect with Ag doped DLC is necessary. At an optimal Ag-concentration of 6.9 % in DLC over DLC (No Ag), very high efficiencies of up to 99.6% were obtained for both types of bacterial strains. To motivate commercial implications of Ag-DLC the long-term antibacterial performance was also investigated. In aged samples (post de-oxidising treatment), the antibacterial efficiency was recovered up to 95% of its value pre-aging, encouraging an in-depth long-term study.

2:00pm **D1-2-MoA-2 TiN/NbN Superlattice Coatings Deposited by High Power Impulse Magnetron Sputtering Potential Candidate to Protect Medical Grade CoCrMo Alloys***, **Papken Hovsepian,*** Sheffield Hallam University, UK*; A. Ehiasarian, A. Sugumaran,* Sheffield Hallam University, United Kingdom*; I. Khan,* Zimmer- Biomet UK

In recent years significant progress has been made in the application of various ceramic, namely MeN functional coatings to engineer the surfaces of medical implants utilising metal-on-metal (MoM) articulation. TiN/NbN coatings were deposited on medical grade CoCrMo alloy by High Power Impulse Magnetron Sputtering, (HIPIMS). X-ray analysis revealed that the coatings exhibit single phase fcc crystal structure and (200) texture. LA diffraction analyses revealed the superlattice coating structure with bilayer thickness of 3.0 nm further confirmed by TEM imaging.

In dry sliding pin on disc tests TiN/NbN coatings exhibited friction coefficient of μ= 0.7 and wear coefficient of $K_c = 1.4 \times 10^{-14}\ m^3\ N^{-1}\ m^{-1}$ which were significantly lower as compared to the bare alloy.

Coating impact load fatigue resistance was studied by applying 500 N load for 1 million impacts using CemeCon impact tester which revealed coating high durability.

In the case of TiN/NbN coating deposited on CoCrMo substrate where $E_{coating} / E_{substrate}$ is as high as 1.81 indicating that the substrate does not provide the necessary load bearing support for the brittle thin film, the utilisation of the Berkovich indentation technique proved to be a potent approach to study coating material as well as structural response to applied concentrated load.

FIB/SEM analyses of the indented coatings revealed that in the hard-on-soft material systems cracks will initiate due to sub- coating substrate deformation and then propagate towards the coating surface. The FIB/SEM and low magnification XTEM analysis showed that an exceptionally strong TiN/NbN coating substrate adhesion bonding was achieved due to the utilisation of the HIPIMS pre-treatment.

High resolution XTEM analyses revealed first time that during the indentation a collective rotation and alignment of the individual layers of the superlattice stuck takes place without compromising coatings integrity which is clear evidence for the exceptionally high coating toughness.

In potentiodynamic polarization tests in 3% NaCl and Hank's solution TiN/NbN showed several orders of magnitude lower corrosion current and higher pitting potential compared to CoCrMo which guarantees excellent protection.

Inductively Coupled Plasma Mass Spectrometry analyses of TiN/NbN coated samples corroded in Hank's solution revealed that the leaching of harmful metal ions from CoCrMo was reduced to bellow the detection limit.

The high toughness of the superlattice structured TiN/NbNcoatings combined with their exceptionally high adhesion on medical grade CoCrMo and reliable barrier properties ranks them as a strong candidate for medical implant applications.

2:20pm **D1-2-MoA-3 3D Printed Ceramics Reinforced Ti6Al4V: Structural and Nano-Mechanical Characterization***, **Peter Apata Olubambi,** T. Tshephe,* University of Johannesburg, South Africa **INVITED**

Compositional formulations and improved materials processing methodologies are innovative approaches for confronting the challenges being faced by materials and biomedical engineers in designing and producing biocompatible components and implants with longer lifetimes having enhanced wear and corrosion resistances. In this study, the structural properties of 3D additively manufactured Ti6Al4V containing ZrO_2 printed through direct metal laser sintering technique at varying process parameters were investigated and reported. Results on the relationships between the micro-scale and nano-scale mechanical properties as well as the biocorrosion behaviours of the biocompatible composites in some selected simulated human systems are presented.

3:00pm **D1-2-MoA-5 A Remote Atmospheric Pressure Plasma-Assisted Textile Functionalization Process on Polymeric Scaffolds for Bone Tissue Engineering***, **Wei-Yu Chen**, J. Lee, T. An,* Taiwan Textile Research Institute, Taiwan*; A. Matthews,* University of Manchester, UK

The porous textile structure of nonwoven polylactic acid (PLA) possesses the potential of being applied to tissue engineering scaffolds. However, when adopting biodegradable polymers, including PLA, for bone tissue engineering scaffolds, the inert and hydrophobic surface properties of these materials not only lead to poor biocompatibility and osteoconductivity but also limit the efficiency of surface modification treatments, which include hydroxyapatite (HAp) deposition via alternate soaking processes. To develop a rapid, environmentally friendly and polymeric textile-suitable process to tackle these issues, a remote atmospheric pressure plasma (APP) system using a bespoke Pyrex chamber and acrylic acid monomer was utilised to deposit carboxylic acid functional groups onto the PLA surface, which are beneficial for performing the following alternate soaking process for HAp deposition. Being compared with the neat PLA, the plasma functionalized PLA exhibited a 16% improvement in hydrophilicity and showed better biocompatibility after HAp deposition. The stability of hydrophilicity and surface elemental composition of the APP-functionalized surface are also reported and the HAp-deposited PLA was examined by a scanning electron microscopy and energy dispersive X-ray analysis.

3:20pm **D1-2-MoA-6 Development of Modified Hydroxyapatite Composite Coating Prepared by the Thermal Spray***, **Jo-Han Yu,*** National Taipei University of Technology, Taipei Tech, Taiwan*; K. Feng,* Ming Chi University of Technology, Taiwan*; Y. Yang,* National Taipei University of Technology, Taipei Tech, Taiwan

This study shows the modified hydroxyapatite composite coating formed under different spray conditions by Flame Spray (FS). Pure crystalline HA has a low dissolution rate, which slows down the bone integration. However, bioactive glasses are a family of special glasses which are able to bond to bones and, if the glass composition is properly designed, even to soft tissues. In this experiment, the hydroxyapatite and bioactive glass will used Flame Spray (FS) to coating on 304 stainless steel surface. This experiment will be divide into two different parts for discussion. In the first part will analysis the microstructure, phase composition, mechanical properties and bonding test of the modified hydroxyapatite composite coating. Based on the results, the acetylene flow rate of 1.60 Nm^3/hr and the speed of spray gun is 250 mm/s, the spray times of Flame Spray (FS) using 2 times to conducting the experiments;The second part is the biocompatibility test of the modified hydroxyapatite composite coating, cell attachment morphology observation and human simulated body fluid immersion test.

3:40pm **D1-2-MoA-7 New Generation of Thin Films for Protection of Stainless Steel Against Corrosion and Bacterial Contamination***, **Akram ALHUSSEIN**, A. BELGROUNE, E. KAADY,* University of Technology of Troyes, France*; L. AISSANI,* University of Khenchela, Algeria*; R. HABCHI,* Lebanese University, Lebanon*; S. Rtimi,* Federal Polytechnic School of Lausanne, Switzerland

Coatings present a great solution to protect a material and give it multifunctional properties. The objective of our research is the development of new generation of protective and multifunctional coatings. In our studies, the deposition rate is controlled to obtain a uniform film of 1-3 µm thickness. The influence of process parameters on the coating physicochemical properties (morphology, microstructure …) and functional performance (corrosion resistance, biomedical properties…) is evaluated.

In this work, thin films were developed to protect stainless steel widely used in different severe environments in particular for maritime and biomedical applications. We present many strategies used for enhancing the coating efficiency based on the substrate used, the doped elements and coating architecture.

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4:00pm **D1-2-MoA-8 Effects of Silver Acetate Additives on Antimicrobial and Corrosion Behaviors of Plasma Electrolytic Oxidation Coatings on AZ31B Magnesium Alloy***, Yu-Tse Sung,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan*; C. Tseng,* Department of Materials Engineering & Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

In this study, the bioceramic composite coatings on AZ31B magnesium alloy were prepared by using plasma electrolytic oxidation (PEO) in alkaline solutions with sodium phosphate, sodium silicate, potassium fluotitanate and silver acetate additions. The effect of silver acetate content on antimicrobial and corrosion behaviors of PEO coatings on AZ31B magnesium alloy was investigated. The antimicrobial properties of PEO coatings were carried out by measuring the numbers of *Escherichia coli* bacterial colony after various incubation durations. The potentiodynamic polarization measurements were conducted to evaluate the corrosion behaviors of PEO coatings in simulated body fluid (SBF) solutions. The experimental results show that the antimicrobial effect of the PEO coatings is significantly improved with increasing silver acetate additive. More interestingly, the PEO coating with 0.2 g/L silver acetate addition exhibits a 100% antibacterial efficiency to *Escherichia coli* after incubation in 60 minutes. However, the potentiodynamic polarization curves display that the PEO coatings, as compared to AZ31 magnesium alloy, exhibit higher corrosion resistances in SBF solutions. Furthermore, the PEO coating with 0.15 g/L silver acetate addition shows the optimal corrosion resistance due to its lowest corrosion current density (Icorr), highest passivation breakdown potential (E_b) and largest polarization resistance value (Rp). In summary, the antimicrobial and corrosion behaviors of PEO coatings on AZ31B magnesium alloy can be pronouncedly improved by silver acetate additions.

4:20pm **D1-2-MoA-9 Tribocorrosion and Biological Analysis of Surface Coated by Polypyrrole Film and Zinc on Titanium Surfaces Treated by Plasma Electrolytic Oxidation***, **Maria Helena Borges**,* University of Campinas, Brazil, University of Illinois College of Medicine Rockford, USA*; H. Kanniyappan,* University of Illinois College of Medicine Rockford, USA*; V. Barão,* University of Campinas, Brazil*; M. Mathew,* University of Chicago College of Medicine Rockford, USA

Although titanium materials are the primary choice for biomedical implant applications due to their properties, the degradation generated by the tribocorrosion process has been reported to influence the success of implants. To overcome these issues, thin film coatings, inorganic agents, and surface treatments have been widely applied. In this context, conductive polymers, such as Polypyrrole (PPy), have demonstrated a promising application for implants due to their electrochemical properties. In addition, surface treatments such as plasma electrolytic oxidation (PEO) enhance mechanical and biological performance, mainly when associated with PPy film. However, considering implant failures can also be related to deficiencies in the osseointegration process, the electrodeposition of zinc (Zn) on the surface may promote an osteogenic substrate. Therefore, we aim to (1) investigate the tribocorrosion behavior of the surfaces treated by PEO and coated with PPy+Zn; (2) evaluate the osseointegration potential of the surface by the Zn incorporation *in vitro*. For this, commercially pure titanium discs were allocated into 4 groups: (1) machined; (2) PEO-treated; (3) PEO-treated followed by electrodeposition of PPy (PEO+PPy); (4) PEO-treated followed by electrodeposition of PPy and Zn (PEO+PPy/Zn). For tribocorrosion, tests were performed in three different modes: (1) free potential, (2) potentiodynamic, and (3) potentiostatic. A pin-on-disk tribosystem was used, and the number of cycles (2,000), frequency (1 Hz), and temperature (37ºC) parameters were selected to simulate the oral environments. For *in vitro* cell culture assays, the osseointegration potential was evaluated using MG-63 cells, which can classify the cells by their viability (alamarBlue assay), the number of live cells to dead cells (live-dead stain), how well the nucleus remained intact (DAPI), and cell adhesion efficiency (SEM). In addition, the mineralization property of the surface was determined using the Alizarin Red Staining (7 and 14 days), and the osteogenic differentiation potential was determined using the alkaline phosphatase activity for the period of 7 and 14 days. Our findings demonstrate that the PPy and PPy+Zn coating plays an important role in enhancing the tribocorrosion resistance. Furthermore, the PEO+PPy/Zn surface is cytocompatible and promising to improve the osseointegration process of implants.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Dr. Damien Faurie, Université Sorbonne Paris Nord, France, **Dr. Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Multimodal and *in Situ* Electron Microscopy to Understand Local Deformation Mechanics***, **Josh Kacher**,* Georgia Institute of Technology, USA **INVITED**

Understanding dislocation generation mechanisms and interactions with obstacles such as grain boundaries and other dislocations is central to understanding the mechanical behavior of metals and alloys, including thin films. This has motivated decades of research into the unit processes governing dislocation interactions by *in situ* transmission electron microscopy (TEM) mechanical testing, resulting in the establishment of basic rules that govern how these interactions occur. However, much of this research has been largely observation based with direct quantification of the interactions in terms of the local and global stress state limited. With the advent of high speed electron detectors and the continued improvement of quantitative *in situ* mechanical testing platforms, it is now possible to extract accurate information on the material stress state associated with dislocation generation and their interactions with surrounding microstructural features, spurring renewed interest into these fundamental dislocation interactions. These advances have necessitated the increased integration of data analytics based analysis of results as data acquisition rates now exceed what can be manually processed and understood. They also open new spaces for integration with computational simulations, beyond simple visual comparisons that are prone to human bias.

In this talk, I will discuss the development of advanced *in situ* TEM testing techniques, including local stress mapping and multimodal imaging via scanning nanobeam diffraction as well as quantification of the global sample stress state using MEMS-based nanomechanical testing platforms. I will discuss these advances in terms of two materials systems: understanding transgranular and intergranular dislocation mechanisms in ultrafine grained thin films and understanding the influence of the deformation-induced grain boundary state on dislocation/grain boundary interactions in coarse-grained thin films. For both of these systems, I will also discuss how irradiation induced defects affect local strain accommodation and active deformation mechanisms.

2:20pm **H1-2-MoA-3 Nanomechanical Characterization and Residual Stress Analysis in Thin ALD Coatings on 3D Printed Nano-Ceramics***, **Marco Sebastiani**,* Università degli studi Roma Tre, Rome, Italy

Recently, Nano-Architected Mechanical Metamaterials (NAMM) have been proposed as a novel class of lightweight and sustainable materials, where a unique combination between high strength and low density is achieved. Such materials are usually produced by Two-Photon Lithography (TPL) Direct Laser Writing (DLW) method, which allows for fast 3D printing with nanoscale spatial resolution.

Unfortunately, the improvement of strength is usually not accompanied by a similar improvement of toughness and ductility, because of the effects of imperfections and flaws on structural reliability.

In this work, we explore the effects of this ALD coatings, by different materials, on the strength and toughness of NAMM.

In particular, we present a detailed study on the effect of the coatings' residual stress on the apparent fracture toughness, showing that a significant change in the crack propagation mechanisms for different residual stress states in the thin film.

The residual stress in the films with thickness below 50 nm is measured by an improved FIB-DIC method, which was specifically optimized to achieve sub-micrometer lateral and depth resolution.

This study demonstrated that fracture toughness in additively manufactured nano-ceramics is, in contrast to macroscopic ceramics, is a surface dominated characteristic, where surface residual stress states can have a paramount effect on reliability and durability

2:40pm **H1-2-MoA-4 *In-Situ* Monitoring of Stress Evolution in Hipims-Deposited Ti-Al-N Films: Effect of Substrate Bias and Temperature*, Pedro Renato Tavares Avila*,** *O. Zabeida, L. Varela Jiménez, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

The origin of stress during film deposition is a topic of interest in the surface engineering community and requires appropriate investigation tools to explain the different mechanisms acting on the evolution of stress, and how they relate to process conditions and materials characteristics. The use of a single stress analysis methodology relying on *ex-situ* results cannot provide a complete insight into stress formation and makes the distinction among the different stress contributors difficult.

In the present work, we used *in-situ* curvature stress probing combined with *ex-situ* techniques such as $Sin^2\psi$ in depositions of TiAlN films, to understand the mechanisms underlying stress evolution. Films were prepared at room temperature (RT) and 300 °C, and four bias strategies, namely two conditions with constant values of 0 V and -75 V, and two conditions with a superposition of layers with alternating high and no bias have been applied.

At RT, the bias increase changed the stress from slightly tensile to compressive, with a small rise in hardness (H), while at 300°C, the use of higher bias increased the compressive intrinsic stress by 3 GPa along with H from 14 to 30 GPa. The combined stress analysis revealed three mechanisms acting in the evolution of intrinsic stress: 1) grain boundary (GB) closing (tensile), dominating at conditions of low adatom mobility and low ion energy bombardment; 2) atom insertion in GB (compressive), dominating at high mobility and low energy of bombardment, and 3) defect generation (compressive), dominating at highly energetic bombardment and low temperature.

In-situ stress probing allowed direct calculation of thermal stress (TS) and determination of the Coefficient of Thermal Expansion (CTE) and Poisson's ratio (ν) of TiAlN. CTE increased from 6.6 to 12.4 x 10^{-6} K^{-1} for higher bias, while ν was found to be 0.22.

The use of alternating bias showed a dependence of the structure and stress on the conditions of previous layers. When growing dense on porous films, the porous surface is initially filled, stopping the propagation of the less dense structure, resulting in an intermediate morphology between the conditions of 0 V and -75 V. In contrast, when growing porous on dense film, less structural change is observed, and the film resembles a dense layer deposited at a single high bias condition. Films with alternating -75/0/-75 V bias sequence presented the same H as films deposited at a single -75 V condition, but with stress 20% lower. Based on the above-described results, we will discuss the overall strategies to tailor the film stress level with respect to the specific applications and coating durability.

3:00pm **H1-2-MoA-5 High Strength and Deformability in 3D Interface Cu/Nb Nanolaminates Under Multiple Loading Orientations*, Justin Y. Cheng*,** University of Minnesota, USA*; S. Xu,* University of Oklahoma, USA*; J. Baldwin,* Los Alamos National Laboratory, USA*; M. De Leo,* University of Minnesota, USA*; I. Beyerlein,* University of California Santa Barbara, USA*; N. Mara,* University of Minnesota, USA

Bimetallic nanolamellar composites have been studied extensively to probe the influence of interface structure on mechanical properties in nanocrystalline alloys. Previously, we have shown that Cu/Nb nanolaminates incorporating 3D interfaces (3D Cu/Nb) containing chemical, crystallographic, and structural nanoscale heterogeneities in all spatial dimensions have remarkable strength and deformability compared to 2D interface counterparts (2D Cu/Nb) under *in situ* micropillar compression normal to interface planes. This work also demonstrated the role of 3D interface thickness relative to layer thickness in optimizing mechanical behavior. However, a detailed investigation of post-deformation microstructures was not completed. In this work, present *in situ* micropillar compression results on 3D Cu/Nb at normal and 45° inclination to interfaces to show that 3D Cu/Nb behaves more isotropically than 2D Cu/Nb and that 3D interfacial shear strength exceeds that of 2D interfaces. *Post mortem* TEM characterization of deformed 3D Cu/Nb microstructures provides insight on the effect that 3D interfaces have on energetically favored slip pathways in different loading conditions. Experimental results reveal key microstructural features indicating delayed shear instability, providing insight on possible methods for increasing strength and deformability in nanostructured alloys by controlling interface structure.

3:20pm **H1-2-MoA-6 Multiaxial Stress-Strain Transfer Across Indenter-Sample Interface During *in Situ* Indentation of Nanocrystalline Thin Films*, Michael Meindlhumer*,** *J. Todt,* Montanuniversität Leoben, Leoben, Austria*; A. Medjahed,* ESRF, The European Synchrotron, Grenoble, France*; M. Burghammer,* ESRF, The European Synchrotron, France*; M. Zitek, R. Daniel,* Montanuniversität Leoben, Leoben, Austria*; D. Steinmüller-Nethl,* CarbonCompetence GmbH, Wattens, Austria*; J. Keckes,* Montanuniversität Leoben, Leoben, Austria

Nanoindentation is routinely used to determine local mechanical properties of materials such as hardness and Young's modulus. Especially for the testing of thin films, the versatile nanoindentation method is used also on materials approaching a stiffness and hardness regime close to diamond, typically the indenter tip's material. Yet, up to now, the stress-strain response in the indenter tip remained unknown during testing of materials of extremely high hardness.

Contrary, in recent years, *in situ* cross-sectional X-ray nanodiffraction coupled with an indenter system has given new insights into the elasto-plastic deformation of thin films during indentation with a resolution down of 500 nm. In this work, the *in situ* indentation setup developed for the ID13 beamline at the ESRF was used for the first time to determine experimentally the multi-axial stress distributions across both the indenter and the tested material with a resolution below ~100 nm.

For this purpose, a 75 µm wide diamond wedge indenter tip with an opening angle of 60 deg and a tip radius of 2 µm, was coated using chemical vapour deposition with a nanocrystalline diamond thin film of 4 µm thickness. In order to test the mechanical response of the indenter-sample system, wedge samples with a thickness of ~70 µm were prepared by means of consecutive mechanical polishing, femtosecond laser ablation and focused ion beam milling steps from nanocomposite AlCrSiN, a biomimetic CuZr-ZrN multilayer and a nanocrystalline diamond thin films.

Prior to the *in situ* cross-sectional X-ray nanodiffraction experiment, the coated indenter tip is aligned parallel to the incident beam and perpendicular to the smaple using small-angle X-ray scattering microscopy. The samples of highly different elasto-plastic behaviour are loaded to the same indentation depths, which depending on the stiffness yields highly different loads. Therefore, unique multiaxial stress-strain transfer across the indenter tip-sample interface was evaluated for each sample system depending on the Young's modulus, hardness and the ability for plastic deformation of the indented material.

This new kind of indentation experiment allows for tor the first time to directly assess the multi-axial stress distributions in the contact area for both tip and tested volume. The thereby gathered results give unprecedented insights into the deformation of both indenter and tested (thin film) material.

3:40pm **H1-2-MoA-7 Film Thickness Effect on Stress Sign Transition in ITO Thin Films*, Jianhui Liang*,** *J. Zhang, K. Rubin, W. Johnson,* KLA Corporation, USA*; R. Schelwald,* KLA Corporation, Germany*; O. Amster,* KLA Corporation, USA*; B. Cuénod, R. Juttin,* EPFL, Switzerland

Indium tin oxide (ITO) is widely used as a transparent conductive thin film in the production of semiconductor devices including solar cells, liquid crystal displays (LCDs), light emitting diodes (LEDs), and sensors. However, various stress configurations are usually generated during ITO film growth, which can impact device performance. Stress-induced wafer bow changes the device planarity, impacting subsequent production processes. Stress can dramatically change the physical properties of the ITO film, potentially causing a failure of the ITO device. Quantitatively determining the stress generated during the ITO film formation and investigating the origin of the stress from a micro perspective provide tools to improve the quality of the ITO films and devices.

In this work, we report on the results of a quantitative study on the stress of ITO films with various thicknesses. ITO films were deposited on glass wafers by standard radio frequency sputtering at room temperature. The film thickness was characterized using optical reflectometry and the stress was characterized by high-precision stylus profilometry. A stress-type transition from tensile to compressive was observed with increased ITO film thickness. The highest tensile stress was 1.9GPa for the 13.7nm thick ITO film, and the highest compressive stress of -0.4GPa was found in ITO films thicker than 300nm.

A separate investigation of the surface morphology of the ITO suggests that the film follows Volmer-Weber growth, and the tensile stress originates from the impingement and coalescence of the newly-deposited film islands [1]. With the continuous deposition of the film, the grain size becomes larger and the structure transitions to a nanorod shape - fewer new islands emerge, thus decreasing the tensile stress. Compressive stress dominates and stabilizes at -0.4GPa for thicker ITO films. The origin of the post-coalescence compressive stress is consistent with the incorporation of excess material in the grain boundaries. This study reveals the thickness effect on the ITO film stress evolution, which can be a reference for the ITO film stress monitor and modulation during production process control.

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4:00pm **H1-2-MoA-8 Reactions of Metal-Tmhd Compounds in the Gas-Phase: Insights from Microreactor Studies Using Synchrotron Radiation***,* ***Sebastian Grimm****,* Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Germany*; P. Hemberger,* Paul Scherrer Institute, Switzerland*; B. Atakan,* Institute for Combustion and Gas Dynamics and CENIDE, University of Duisburg-Essen, Germany

In CVD deposition processes gas-phase reactions are often the inital steps, but gaseous intermediates can lead to unwanted film morphology, unsatisfactory purity or a depletion of the precursor, and consequently a reduction in growth rate. Understanding the decomposition mechanisms, especially the sequence of bond dissociation steps, is important for improving and modelling such processes.

Consequently, the analysis of the inital stages of growth is important and requires analytical techniques with sufficiently low detection limits for elusive gas-phase species. Because of limitations in various experimental techniques, it was until recently not possible to detect most of the postulated intermediate species and their temperatue-depdenent kinetics often remained unknown.1

We have overcome some of these challenges and demonstrated for various metal-organic precursors that by using a microreactor coupled to a very mild ionization source, we can detect and characterize elusive species, especially metal-containing intermediates, with short liftetimes below 50 µs.2,3

Here, the vacuum pyrolysis of aluminium and zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Al(tmhd)3 and Zr(tmhd)4, is investigated. In brief, the precursor is sublimed, subsequently transported by helium carrier gas and expanded through a pinhole into a resistively heated 1 mm inner diameter SiC-microreactor of 10 mm length. Species leaving the reactor are ionized by tuneable vacuum ultraviolet (VUV) synchrotron radiation, and characterized by imaging photoelectron photoion coincidence spectroscopy (i2PEPICO) and mass spectrometry at the Swiss Light Source.

In the experiments, hydrocarbons, oxygenated and metal-containing species were detected and characterized unambigously in the gas-phase at temperature from 450-950 K, which provides insights in the underlying decomposition mechanisms. Most importantly, we detected and characterized metal-bis(diketo)acetylacetonate-H, M(C11H19O2)(C11H18O2) as major inital decomposition product in the gas-phase at temperatures above 650 K, which subsequently forms M(C11H19O2)(C10H15O2) by a methyl loss. The temperature-dependent formation mechanisms of the assigned species will be discussed and compared to previous results on M(acac)x precursors.

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4:20pm **H1-2-MoA-9 How to Simultaneously Determine Absolute Thickness, Chemistry, and Other Properties of Crystalline Layers Using XRD***,* ***Thomas Degen****, M. Sadki, N. Norberg,* Malvern Panalytical, Netherlands*; N. Shin,* Deep Solution Inc., Korea (Democratic People's Republic of)

For the in-line absolute thickness analysis of FeZn layers on galvanized steel, we developed a Rietveld [1] based, full-pattern fitting method that fits a general layered structural model to a measured XRD Scan. The fitted model then delivers both the absolute layer thicknesses as well as the chemical composition of the layers and other key information like unit cell sizes, size/strain, and texture-related information for all phases of the model. The method is implemented in the Malvern Panalytical software package HighScore Plus [2] V5.1.

The layer thickness modeling is based on the variable and increasing absorption of X-rays in the layers with different chemistry and thickness. Basically, by integrating over all beam paths, we accumulate the reduction in the intensity of the total beam. Each layer adds a new absorption term with its own linear absorption coefficient. The method is theoretically correct, still, in practice, we need to know the packing factor and density of each layer. To solve that, we introduced an instrument-dependent (alignment, tube aging, etc) calibration factor for each layer. These calibration factors are determined from a dedicated data set, where many samples are characterized using multiple methods like SEM, wet analysis, etc.

The initial fit model comprises:

- Initial/expected thickness values, for all the phases
- Calibration factors for all phases determined based on analyzed knowns
- Intensity calibration factor to counteract tube aging
- Atomic phase models, typically taken from structural databases

Output after fit:

- Absolute thickness for all as layer-marked phases
- All other fit model parameters, like unit cells, size/strain information, texture index, and more, including estimated standard deviations
- Quality of fit indicators, Chi-Square, R_{wp} etc.

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Topical Symposia
Room Town & Country A - Session TS1-2-MoA
Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications II

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Klaus Böbel**, Bosch Manufacturing Solutions, Germany

2:20pm **TS1-2-MoA-3 Influence of Oxygen Content During the Deposition of Scandium Stabilized Zirconia Thin Films by Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS)***,* ***Isabel Fernandez Romero****,* Corporate Sector Research and Advance Engineering- Robert Bosch, Germany*; S. Klein, C. Engel,* Corporate Sector Research and Advance Engineering - Robert Bosch, Germany*; J. Fleig,* Technical University of Vienna, Austria

Hydrogen is one of the key energy carriers in the fight against current climate problems as H_2 can be produced using electrical energy from renewable sources and directly used in production processes, eg steel production or in chemical industry. Solid Oxide Electrolysis Cells (SOEC) transform electricity and water vapor into hydrogen (and oxygen) with the highest energetic efficiency among electrolyzer technologies

The cells of the SOEC require a dense, gas-tight, and thin electrolyte layer which is at the same time ionic conducting and electron blocking. Doped zirconia materials have been broadly used as a suitable material. Over the last years extensive research has been done to investigate the suitability of reactive vacuum techniques for their mass production.

In this work dense Scandium Stabilized Zirconia (ScSZ) layers have been successfully deposited on Gadolinium Doped Ceria (GDC) pellets using reactive High Power Impulse Magnetron Sputtering (r-HiPIMS) technique. The ceria ceramic was as substrate to mimic the microstructural conditions of the SOEC fuel and air electrode surfaces: polycrystalline, rough, and porous

By varying the oxygen content in the chamber (from 1 % to 4 %) the deposition mode can be changed from a non-poisoned (metallic) mode to a poisoned mode, decreasing the discharge voltage as well as the deposition rate but improving the stoichiometry of the ScSZ layers. This process variation modifies the microstructure and crystallinity of the film, which are related to the ionic conductivity and electron blocking ability of the film, thus offering a means to investigate the feasibility of the film as electrolyte material

2:40pm **TS1-2-MoA-4 Comparison of the Impacts of High Entropy Oxide/Alloy Coatings for Lithium-Sulfur Battery Separators***, **Ming-Roe Wann,** Y. Lin, S. Chung, J. Ting,* National Cheng Kung University (NCKU), Taiwan

The repeating formation and irreversible diffusion of liquid-state lithium polysulfides (LiPSs) during the discharge and charge of lithium-sulfur batteries (LSBs) represent the major challenge for the development of the high-performance LSB. Therefore, it is essential to alleviate the shuttling of LiPSs that dissolve in the electrolyte and cause the loss of active material. Herein, high entropy oxide (HEO) as an additive in the separator for LiPS trapping is reported. The HEO exhibits single phase spinel structure having a unique core-shell morphology. The HEO is also de-alloyed for enhancing the electrical conductivity. Both the HEO and de-alloyed HEO are subjected to material characterizations, including X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Then, lithium polysulfide adsorption test is done by ultraviolet–visible (UV-vis) test. For electrochemical analysis, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) measurements as well as cycle and rate performance are analyzed. The effect of the alloy percentage in HEO on battery performance is also addressed and discussed.

Keywords：High entropy materials, lithium-sulfur battery, lithium polysulfides

3:00pm **TS1-2-MoA-5 BaCeZrYO$_{3-\delta}$ Coatings Deposited by Solution Precursor Plasma Spray (SPPS) for Sustainable Energy Application***, **Yen-Yu Chen,** W. Zeng, C. Liu, G. Yao,* Chinese Culture University, Taiwan

Pervoskite-type proton-conductive ceramic materials have high potentials for the application of sustainable energy fields, such as protonic ceramic fuel cell (PCFC), ammonia fuel synthesis, carbon dioxide conversion, etc. In this study, perovskite-type proton-conductive coatings, BaCeZrYO$_{3-\delta}$ (BCZY), were deposited on NiO/BaZrYO$_{3-\delta}$ (BZY) composite substrates by a solution precursor plasma spray (SPPS) method. The precursors were consisted the BCZY species of the nitrate salts, and dissolved into de-ionic water. The NiO/BZY substrates were prepared by a die-pressing method. Several properties of the coatings were analyzed, including crystal phases by X-ray diffraction (XRD), microstructures by scanning electron microscope (SEM), electrical properties by electrochemical impedance spectroscopy (EIS), etc. The results of XRD show the coatings after post-coating annealing over 600^{o}C are mainly consisted of perovskite phases. The microstructure analysis of the BCZY coatings characterized by SEM show that the coatings are either consisted of overlapped splats of BCZY with a few of surface pores on the surface, or with porous structure by BCZY particle necking. The average thickness of the coating layers are about several microns. The formation mechanism of the BCZY coatings can be purposed as the BCZY precursor droplet breakup, liquid-phase evaporation, thermal pyrolysis of precursors, solid particles melting, and then the melting particles splatted and overlapped on the substrate to form the BCZY coatings. The details electrical property analysis of the BCZY coating samples are as mentioned in the following report.

3:20pm **TS1-2-MoA-6 Aluminum-Doped Non-Stoichiometric Titanium Oxide (Al-TiO$_X$) for Anode in Lithium-Ion Batteries***, **Guan-Bo Liao,*** National Cheng Kung University (NCKU), Taiwan*; Y. Shen,* Hierarchical Green-Energy Materials (Hi-GEM) Research Center, Taiwan*; J. Huang,* National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIBs) are regarded as the most promising recyclable energy storage system nowadays. Among those anodes, TiO_2 is a candidate due to its excellent safety and cycling performance. Moreover, a recent report suggested that non-stoichiometric titanium oxide (TiOx) has the high-rate capability as the non-stoichiometry creates more oxygen vacancies creating voids for ion transportation thereby facilitating lithium-ion diffusion. The report exhibits the fast-charging potential of TiOx. Nevertheless, the low capacity is still a problem. In this study, an aluminum-doped non-stoichiometric titanium oxide (Al-TiOx) was used as an anode in LIBs. Here, we used the sol-gel method followed by annealing to synthesize Al-TiOx. First, the Aluminum precursor was incorporated into titanium-based sol to form Al-TiO_2 gel. After evaporation and grinding, the Al-TiO_2 powder was formed. Second, the Al-TiO_2 powder was annealed in a reduced atmosphere to synthesize Al-TiO_x to increase the capacity and the rate capability further. The TEM and XRD results (shown as supplementary file) showed that aluminum was successfully doped in TiO_2 lattice. The best electrochemical results showed that the first cycle capacities were 480 and 350 mAh/g for Al-TiOx and TiOx respectively, which both exceeded the theoretical capacity of pristine TiO_2 (335 mAh/g). The cycling test also shows a good performance. Both Al-TiO_x and pure TiO_x remain stable for more than 200 cycles. Al-TiO_x also showedbetter rate capability than pure-TiOx. The Al-TiOx specific capacities are 131, 125, 115, 86, 70,40,25 mAhg^{-1} while TiOx showed 137,120,80,62,27,7,3 mAhg^{-1} for 0.1,0.2,0.5,1,2,5,10C respectively. EIS and GITT will be used to measure the diffusivity of Lithium-ion later.

After this study, we had a preliminary understanding of the anode performance of Al-TiOx. Recently, we are preparing in-operando measurements (**e.g., in-situ XRD, in-situ Raman…etc.**). We will observe the crystal structure change during charging-discharging using in-situ XRD and the defect analysis by in-situ Raman, especially focusing on the normal speed and fast-charging behavior.

3:40pm **TS1-2-MoA-7 Unveiling Capacitive and Diffusion-Limited Li-Ion Storage in Semiconducting 2d-Mos$_2$ Composited with Aluminium Nitride Nanoflowers for Flexible Electrodes of Supercapacitors***, D. Kaur,* ***Gagan Kumar Sharma,*** Indian Institute of Technology Roorkee, India

A flexible supercapacitor electrode can be realised by combining the exclusive characteristics of two-dimensional MoS2 layered material with a conventional key material, aluminium nitride (AlN). We present a bendable electrode that is straightforwardly grown on stainless-steel foil via a binder-free sputtering route. The inherent merits of good conductive pathways among MoS_2 nanolayers and enriched pseudocapacitive and dielectric activity from AlN nanoflowers enable synergism of intermixed porous structure. This unique surface morphology facilitates sulfur and nitrogen edges to make insertion/de-insertion of Li-ions more feasible to store electrochemical energy. The MoS_2-AlN@SS hybrid working electrode achieves a gravimetric capacitance of 372.35 F/g at a 5 mV/s scan rate with a wide potential window of 2 V in 1 M Li_2SO4 electrolytic aqueous solution. The composite thin film of better adhesion with the current collector exhibits a remarkably high specific power of 28.05 W h/kg at a specific power of 0.26 kW/kg, simultaneously an advanced cycling lifespan of 91% over 5,000 charge-discharge cycles. The capacity of the hybrid electrode is almost unperturbed under bending from 0º to 175º, while only ~5% degradation in capacitance was noticed at a flexing angle of 175º. These distinctive features of this electrode material elucidate the practical applicability and recommend it as a promising candidate in wearable bendable supercapacitors.

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4:00pm **TS1-2-MoA-8 Lithium Passive Diffusion and Surface Oxidation on Battery Materials at Room Temperature***, **Jozef Ociepa,*** OCI Vacuum Microengineering Inc., Canada

Passive Li diffusion is defined as the process of Li atom/ions migration under a concentration gradient and activated by thermal energy from atomic vibrations of the host structure at room temperature. This process of passive Li diffusion is important for a better understanding of the active diffusion processes that are happening in lithium-ion batteries (LIBs), where external energy component such as electrical potential is applied. It is expected that materials that exhibit good "natural" Li diffusion properties will perform much better under the external electrical potential. This approach offers a unique opportunity to observe the free movement of lithium atoms/ions into the solid structure and simplify the understanding of diffusion processes especially if single-crystal structures are used. The single-crystal structures are free from grain boundaries and the lithium diffusion process is limited to lattice diffusions such as interstitial, vacancies, and dislocations. This approach allows for categorizing materials that are attractive to lithium diffusion based on the pure lattice component. The characterizing techniques are Auger electron spectroscopy (AES) for tracing Lithium concentration on the surface (Li-KVV peak at 52eV) and Low Energy Electron Diffraction (LEED) for surface crystallography changes. The lithium concentration gradient is created on the surface of the host material by the evaporation of a thin film of lithium with an effective thickness from 5 Angstroms to 250 Angstroms under ultra-high vacuum conditions. The data obtained from these experiments are showing different lithium diffusion behavior on the selected materials and there is an indication of three categories of the characterized materials. 1-Rapid lattice diffusion of Li into HOPG and no change in the surface crystalline structure. 2-Moderate lattice diffusion of Li into CVD Diamond, SiC-6H, SiO2/Si(001, LiNbO3, and TiO2 and some changes in the surface crystalline structure. 3-No lattice diffusion of Li into Si single crystals, Ga2O3 and SrTiO3, and no long-range order in the surface crystalline structure. Comparison of the Li diffusion on SiC single crystals and polycrystalline structure shows faster Li diffusion on single-crystal. The exposure of lithiated SiC to an oxygen gas environment at 5x 10-6 Torr at room temperature indicates a Li diffusion toward the surface. This method simplifies the understanding of diffusion processes and limitations such as oxidation, plating, and the role of grain boundaries.

4:20pm **TS1-2-MoA-9 Development of Carbon-based PVD Coatings for Stainless Steel PEMFC's Bipolar Plates***, **Michaël Ougier**, M. Leroy,* IREIS/HEF group, France*; A. Chavanne,* HEF group, France*; H. Christophe,* IREIS/HEF Group, France

Proton Exchange Membrane Fuel Cells (PEMFC), employing dihydrogen as fuel, are promising energy sources (for their high energy conversion and near-zero emission), particularly for the automotive sector. In these electrochemical systems, bipolar plates (BPP) enable to electrically connect the cells and represent 20-30% of the total cost of the system, for about 70% of its mass and volume.

Stainless steel bipolar plates are widely used in fuel cell because of its combination of a good corrosion resistance and manufacturability. However, due to a native oxide layer they exhibit a high interfacial contact resistance. Additionally, in certain conditions, the harsh environment in a fuel cell is able to corrode stainless steel. By the deposition of coating onto the BPP surface, the electrical conductivity and the corrosion resistance can be greatly enhanced. Finally, the main objectives of coating are:

- to ensure an efficient protection against corrosion, avoiding electrolytic membrane contamination with metallic corrosion products.
- to minimize the electrical contact between the plate and the gas diffusion layer, guarantying low electrical losses.

A high-performance coating is therefore key to the durability and efficiency of the bipolar plates and of the fuel cell stack itself.

Among all deposition techniques, Physical Vapor Deposition (PVD) methods like magnetron sputtering and cathodic arc evaporation are able to deposit highly adherent, conductive and corrosion resistant coatings. PVD gold coatings have long been the reference solution to fulfill the above-mentioned requirements, and nowadays in heavy duty vehicles. However, treatment price is a sticking point for large volume commercialization and cost-effective alternative materials are now developed.

In this present work, we review the deposition methods and present experimental results on the performance of various PVD coatings such as gold, ceramic, and carbon-based coatings, with and without interlayer. Coupons of coated stainless steel are investigated both in simulated aggressive PEMFC environment (80°C, H_2SO_4 pH 3). Beyond these basic tests, accelerated corrosion stress tests are also be developed to simulate in a few hours the more detrimental conditions that can be encountered in the 7000 hours lifetime of the electrochemical system. Coating degradations mechanisms are evidenced by post-mortem coupons and plates analysis. Complementary to these corrosion tests, electrical contact resistance of the coated surface is also evaluated before and after corrosion tests.

Coatings for Use at High Temperatures
Room Pacific E - Session A1-3-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling III

Moderators: Gustavo García-Martín, REP-Energy Solutions, Spain, **Dr. Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

8:00am **A1-3-TuM-1 Excellent Tribological, Mechanical, and Anti-Corrosion Performance of Agro-Waste as Corrosion Inhibitor for Carbon Steelin an Acidic Environment***, **Omotayo Sanni**, J. Ren, T. Jen,* Department of Mechanical Engineering Science, University of Johannesburg, South Africa

Presently, in the field of corrosion, the main goal is to develop environment-friendly and effective corrosion inhibitors that can be utilized to substitute conventional corrosion inhibitors, which are toxic. Therefore, the present work aims to investigate the microstructures, mechanical, corrosion, and tribological performances of agro-waste as a potential inhibitor for mild steel in 2 M HCl solutions by electrochemical impedance spectroscopy, weight loss, and polarization methods. Results obtained showed that the highest inhibition efficacy of 97.8% was obtained with a 500 ppm concentration of the waste. The potentiodynamic polarization test shows that the waste behaves as a mixed inhibitor. The electrochemical result shows that the charge-transfer resistance was increased, while, current density decreased with inhibitor in the 2 M HCl solutions. The inhibition performance of the waste increased with increasing concentration at the studied inhibitor dosages, the inhibitor molecules' adsorption on the metal fits the Langmuir adsorption isotherms. The experimental results showed that the waste products significantly improved resistance to wear. In addition, excellent toughness, high hardness, preferable adhesion, and good corrosion resistance also contributed to improve the tribological properties. The scanning electron microscope equipped with energy dispersive X-ray spectroscopy test confirms the protection of the mild steel in the HCl solutions. The results derived in this paper could prove highly beneficial and provide fundamental insights about the efficient use of agro-waste as an effective inhibitor, as well as stimulate the industrial application of agro-waste on a large scale.

8:20am **A1-3-TuM-2 Study of Materials and Coatings for Use in High Temperature CO_2 Environments***, **Jianliang Lin**,* Southwest Research Institute, USA

Oxy-fuel sCO2 power cycles are a transformational technology for the energy industry, providing higher efficiency heat source energy conversion for conventional and alternative energy sources. However, the technology requires advanced thermal management/protection systems to accommodate high temperatures for turbine critical components, e.g. nozzles and blades. The paper presents a study of NiCr based alloys and protective coatings for use in CO_2 environments using a high temperature thermal cyclic test rig. The thermal cyclic test was performed on uncoated and coated coupon samples in ambient atmosphere and CO_2 environment at 800 ^oC and 1150 ^oC, respectively. One testing cycle includes 50 min annealing at peak temperature and 10 min cooling in air. The tested NiCr based alloys include Haynes 230, 625 alloy, HR-120 alloy, Inconel 718, and C22 alloy. The coatings include a nanocrystlline MCrAlY coating with a TiN diffusion barrier which was deposited using plasma enhanced magnetron sputtering (PEMS) technique, and a thermal barrier coating (TBC) system (MCrAlY bond coat and YSZ top coat) deposited by air plasma spray (APS).The nanocrystlline MCrAlY coating and TBC aimed at providing thermal and oxidation protection for different turbine critical components that see low temperature (e.g. 800 ^oC) and high temperature (e.g. 1150 ^oC), respectively. During the thermal cyclic tests, accumulative mass changes of the test coupons were recorded. The microstructure, chemistry, and phase changes of alloys and coatings after thermal cyclic tests were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The results showed that all uncoated alloys exhibited severe oxidation and degradation at 800 ^oC. The nanocrystlline MCrAlY coating alone provided sufficient thermal/oxidation protection for all alloys from 800 ^oC to 1050 ^oC in ambient atmosphere and CO_2 environment. However, additional TBC is needed for protecting the alloys for higher temperatures (>1150 ^oC).

8:40am **A1-3-TuM-3 Liquid Aluminum-Induced Wear of Ni-Based Superalloy at Elevated Temperatures***, **Hongfei Liu**,* Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), Singapore*; N. Gong,* Institute of Materials Research and Engineering (IMRE), Singapore*; R. Karyappa, T. Meng,* Institute of Materials Science and Engineering (IMRE), Singapore

Ni-based superalloys have long been developed for structural components towards high-temperature applications, e.g., turbine blades, incineration plants, nuclear reaction plants, etc., due to their high mechanical strength and stable chemistry. On the other hand, along with the rapid development in additive manufacturing (AM) and remanufacturing of metal alloys in the past decades, electrochemical corrosion and hot corrosion have been extensively applied for testing and evaluating the chemical stabilities of AM-superalloys, in comparison with their competitors fabricated by traditional methods, at room and elevated temperatures.

Liquid metal has been employed in heat exchanger at high temperatures due to its higher thermal compacity than other media, e.g., water. In comparison to high-temperature oxidation and hot corrosion studies, liquid metal-induced wear of Ni-based superalloy is relatively less in the literature.

We have recently studied liquid aluminum-induced wear of Ni-based single crystal superalloys, addressed atomic diffusions and surficial cracks after cooling down from high temperatures. In this presentation, we will be discussing the experimental results and their related mechanisms.

9:00am **A1-3-TuM-4 Characteristics and Resistance of CVD Hafnium Carbide Coating in Extreme Environments***, **Hyeon-Geun Lee**, J. Lee, D. Kim, B. Jun, W. Kim, J. Park,* Korea Atomic Energy Research Institute, Republic of Korea

Hafnium carbide (HfC) has a high melting point and excellent resistance to ablation, corrosion, and mechanical/thermal stress. HfC coating is mainly considered to ultra-high temperature protective coating for aerospace application. HfC coating has strong anti-ablation ability due to high melting point, outstanding mechanical properties, superior oxidation resistance, absence of phase change at high temperature. Also, its favorable performance makes it possible to expect resistance in other extreme environments. Recently, in the field of nuclear power research, research on accident tolerant fuel (ATF) system and new generation power plant system including molten salt reactor (MSR) is in the spotlight. Structure materials are exposed to harsh environments such as hydrothermal corrosion and high temperature steam oxidation in ATF system and high temperature molten salt corrosion in MSR system. Various corrosion and oxidation resistance coatings including metal, ceramics, and hybrid coating that can protect structural materials in these extreme environments have been studied. In this study, characteristics and resistance of CVD hafnium carbide coating in various corrosion and oxidation environments were studied. Chemical vapor deposition (CVD) can provide the high purity dense coating with excellent crystallinity and uniformity. A highly crystalline dense HfC which contains a small amount excess carbon is uniformly deposited on graphite substrate using low pressure CVD from $HfCl_4$-C_3H_6-H_2 system. High temperature oxidation and ablation properties of CVD HfC coating were investigated. Hydrothermal corrosion evaluation is carried out using autoclave at 360 ^oC, 19 MPa condition. The steam oxidation resistance was investigated at up to 1600 ^oC temperature with maximum 200 cm/s flow steam condition. Corrosion and oxidation resistance of HfC were analyzed compared to SiC, which is known to be excellent. High temperature molten chloride salt corrosion experiment was conducted at 650 ^oC in the controlled oxygen and moisture environments. The possibility of CVD HfC coating as a corrosion resistant coating of metal structural material were researched.

9:20am **A1-3-TuM-5 High Temperature Corrosion Protection of Zirconium Fuel Rods in Nuclear Reactors by Nanocrystalline Diamond (Ncd) Layers***, **Frantisek Fendrych**,* Institute of Physics Academy of Sciences of the Czech Republic

Motivation

Nanocrystaline diamond (NCD) film can be utilized as a protective coating for zirconium alloy (Zircaloy2) nuclear fuel cladding (NFC) of nuclear reactors. One big disadvantage of Zircaloy2 is that it reacts with water steam and during this (oxidative) reaction releases hydrogen gas, which partly diffuses into the alloy forming zirconium hydrides. Moreover, the large production of hydrogen gas can result into catastrophic hydrogen-air explosions (as occurred in the recent Fukushima accident, March 11, 2011).

Plasma CVD reactor

Diffuse plasma in the linear antennas microwave plasma enhanced CVD reactor was used for coating of cylindrical Zircaloy2 rods with NCD films. The combination of the linear antennas arrangement and the use of low pressures, > 1 mbar, a diffuse large area plasma is formed enabling large area 3D NCD deposition.

Testing of the protective NCD films

We have successfully demonstrated the possibility to cover a cylindrical rod-shaped Zircaloy2 nuclear fuel cladding by a 300 nm thick protective NCD layer using the linear antennas microwave plasma enhanced CVD. NCD coated Zircaloy2 rods underwent a set of corrosion tests, namely a reactor irradiation test and hot steam oxidation. SEM, Raman, XRD, XPS were employed. Oxidation of NCD coated and uncoated ZIRLO at 1000 °C is presented in supplemental document on **Figs.1,2**. It confirms that a thin NCD layer can serve as a anticorrosion protective coating on NFCs in the harsh environment of a nuclear reactor at substantially elevated temperatures.

Conclusions

Zirconium alloy ZIRLO of nuclear fuel cladding was covered by 300 nm thick protective nanocrystalline diamond NCD layer using special Linear Antennas pulsed MicroWave Plasma Enhanced CVD deposition technique. The NCD layer protects ZIRLO rods surface against hydrogen penetration and against oxidation during standard reactor run at about300 °C hot water steam and significantly decreases both in accidental case of overheating up to 800 – 1100 °C. NCD anticorrosion protection can up to 40% prolong lifetime of ZIRLO fuel rods and consequently enhances the uranium dioxide UO2 nuclear fuel burnup what leads to more efficient use of nuclear fuel in reactors. Final NCD/ZIRLO samples are longtime (for 2 years) tested by Westinghouse for real permanent run in Halden Norway experimental nuclear reactor. Application of presented research results for anticorrosion protection of power stations nuclear reactorsis proposed in EU and USA patents **[1,2]**.

References

[1] EU Patent No. 3047046 / 2020, WO 2015039636, A1, 2015, PCT/2014/000101.

[2] USA Patent No. 10916352 / 2021, WRB-IP, Ref. 000036-016; U.S. App. 15/022,536, 2021.

9:40am **A1-3-TuM-6 Effect of Vacuum Annealing on the Residual Stress of ZrN Thin Film deposited on Ni-based Superalloy Haynes 282**, ***Kuan-Che Lan**, C. Li,* National Tsing Hua University, Taiwan; *H. Tung,* Institute of Nuclear Energy Research, Taiwan

Transition metal nitride thin films deposited using physical vapor deposition (PVD) methods tend to experience a significant amount of residual stress. The existence of residual stresses in thin films can do influence on their mechanical properties greatly. It is believed that the processing of heat treatment can help relief the residual stress in a crystalline material. To study the effect of heat treatment after a PVD method, ZrN thin films deposited using the DC magnetron sputtering system on both Si and nickel-based superalloy Haynes 282 substrates was annealed in vacuum (4×10^{-6} Torr) at 950˚C. After vacuum annealing, the film thickness, the crystallographic structure and depth compositional distribution of the annealed ZrN thin film will be characterized by scanning electron microscope, the X-ray diffraction and Auger electron spectroscopy, respectively. Averaged X-ray strain method will be also applied to analyze the residual stress of the ZrN thin film on Haynes 282.

10:00am **A1-3-TuM-7 Study at Pilot Plant Scale on Biomass Corrosion Resistance of FeCr and CoCrMo Coatings Applied by HVOF**, *M. de Miguel Gamo, G. García Martín, M. Lasanta Carrasco, M. Lambrecht,* Universidad Complutense de Madrid, Spain; *F. Gonçalves,* Teandm - tecnologia engenharia e materiais s.a, Portugal; *M. Sousa,* teandm - tecnologia engenharia e materiais s.a, Portugal; *A. Bahillo, M. Benito,* Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Spain; ***Francisco Javier Pérez Trujillo**,* Universidad Complutense de Madrid, Spain

The replacement of coal by biomass combustion is considered as a promising option to reduce the emissions associated to this fossil energy source. At the same time, the energetic use of the biomass contributes to solve the problem of waste disposal. On the other hand, this renewable technology presents two main disadvantages: (1) the cost of biomass is higher than coal, what leads to a higher cost of the electricity production, (2) biomass combustion environment is extremely corrosive induced by the high amount of chlorine present in the fuel (gas) and/or the present of alkali and heavy metals in condensed deposits. The aggressive conditions commonly imply the use of austenitic or nickel-based alloys that increases the investment required. An alternative to mitigate corrosion and allow operation at more aggressive conditions, is the use of highly-corrosion resistant coatings over lower cost alloys, such as ferritic steels.

The present study compares the biomass corrosion behavior of two different coatings, FeCr and CoCrMo, applied by High Velocity Oxy-fuel (HVOF) on a 12%Cr steel to improve its oxidation resistance. The coated specimens were tested in a pilot plant installation and exposed to the flue gases from the combustion of two different agricultural biomasses (eucalyptus and wheat straw) for 2000 h at 600°C. The samples were weight monitoring at different times during the testsand characterized before and after oxidation tests by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). At the end of the exposures, both coatings, FeCr and CoCrMo, have shown a significant corrosion layer. Although, when the results were compared with the 12%Cr steel uncoated, it was confirmed that the application of both coatings reduces the weight gain of the steel, increasing its corrosion resistance. The obtained results make these coatings a promising alternative, that should be further investigated from the mechanical perspective, for enhancing the lifetime of in-service power plant components.

10:20am **A1-3-TuM-8 Sol-Gel Coating to Protect Materials Exposed Under Carbonates Used as a Thermal Energy Storage System in Central Tower Power Plants**, ***Gustavo García Martín**, M. de Miguel Gamo, M. Lasanta Carrasco, M. Lambrecht, F. Pérez Trujillo,* Universidad Complutense de Madrid, Spain

Zirconia-based sol-gel protective coatings have emerged as one of the most viable solutions to protect steels against molten salt corrosion in Concentrated Solar Power plants with nitrates as thermal energy storage. Thermal energy is used in the production of steam and electricity production subsequently, by means of the movement of a conventional turbine (Rankine cycle)

Central Tower design is a suitable technology to use new molten salts with higher thermal stability than nitrates, such as carbonates, which would allow plants to generate a higher amount of water vapour per unit of time, thus a higher conversion to electricity. Central receivers made of nickel-based material will increase the temperature from 565ºC with nitrates up to 800ºC with carbonates. Particularly, the outstanding eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 is presented as a real alternative nowadays. The drawback is its corrosion potential, hence protective coatings are being studied to enhance the endurance toward a levelized cost electricity (LCoE) reduction.

In support of these objectives, this work aimed at developing zirconia-based sol-gel protective coatings on the nickel-based alloy INCONEL 617 (Ni 53.28 wt.%, Cr 21.5 wt.%, Mo 8.80 wt.%) and the low chromo content alloy P91 (Cr 9.3· wt.%). Inconel would be used in high-temperature equipment such as receivers, exchangers, and high-thermal storage tanks. On the other hand, the ferritic-martensitic alloy might be used inlower-temperature parts, for instance, cold-temperature storage tanks, which could operate at 480ºC. Corrosion tests were performed at 480°C and 700°C up to 1000 h results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels. The results showed the promising behaviour of the coated substrates.

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 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 (MoN_x) are two promising materials for protective coatings on cutting tools because of the formation of Magnèli 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 1μm 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_4C 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_4C 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.

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).

Coatings for Biomedical and Healthcare Applications
Room Pacific F-G - Session D2-TuM

Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

Moderators: Dr. Hamdy Ibrahim, University of Tennessee at Chattanooga, USA, **Margaret Stack**, University of Strathclyde, UK

8:00am **D2-TuM-1 Empowering PVD-Coatings to Control the Time Dependent Chemical and Microstructural Coating Properties in Aqueous Electrolytes***, **Holger Hoche**,* Center for Structural Materials, TU-Darmstadt, Germany*; T. Ulrich,* Center for Structural Materials, TU Darmstadt, Germany*; P. Polcik,* Plansee Composite Materials, Germany*; M. Oechsner,* Center for Structural Materials, TU-Darmstadt, Germany **INVITED**

Intelligent PVD coatings, which can change their chemical composition and their surface structure in aqueous electrolytes have a great potential for various medical applications. Therefore the coating material must be able to maintain the corrosion resistance and simultanously release specific chemical species.

To achieve this, the authors developed a novel alloying concept for PVD coatings, where TiN-based coatings were alloyed with Mg and MgGd, respectively. Thereby, the corrosion protection capability of corrosive substrate materials, e.g. magnesium or mild steel, can be improved significantly [1]. Depending on the chemical composition of the coating, an adjustment of the corrosion resistance in NaCl electrolytes between 24h and 1000h is possible. Moreover, the developed alloying concept enables to get control of the time dependent chemical and structural properties in aqueous electrolytes: The chemical stability of the coating is determined the proportion of Mg and Gd in the entire TiN matrix: Under a corrosive load, the coating depletes of Mg and consequently, the chemical composition and the surface microstructure changes.

For the present study, TiN+Mg and TiN+MgGd coatings, respectively, are deposited using standard PVD magnetron sputtering technology. Therefore, TiMg and TiMgGd targets were produced using spark plasma sintering. The effect of the mentioned alloying concept on the time dependent chemical and structural changes during exposure of the specimens in NaCl electrolytes is comprehensively investigated. The underlying mechanisms and the resulting properties will be discussed.

[1] T. Ulrich, C. Pusch, H. Hoche, P. Polcik, M. Oechsner, Surface and Coatings Technology 422 (2021) 127496.

8:40am **D2-TuM-3 Early Detection of Fretting-Corrosion at the Hip Modular Junction Interface by Acoustic Emission Non-Invasive Technique***, **Bill Keaty**, Y. Sun,* University of Illinois at Chicago, USA*; M. Mathew,* University of Illinois - Chicago, USA*; D. Ozevin, J. Eapen, T. Zhang,* University of Illinois at Chicago, USA

Total hip replacement (THR) is becoming an increasingly common surgical procedure globally, as it is an end-stage treatment for patients suffering from osteoarthritis or trauma[1]. Early failure is a common occurrence in THRs due to tribocorrosion processes. As a result, a diagnostic method is necessary to catch early failure of THR before irreversible damage occurs. It was reported that the possible feasibility of acoustic emission (AE) technique can detect material degradation at the THR head-cup interfaces[2]. However, no investigation has been done at the modular junction interface, where fretting-corrosion occurs. It was hypothesized that the acoustic emission data could be correlated to the varying level of THR damage at the modular junctions.

A series of fretting-corrosion experiments were conducted with a custom-made fretting rig capable of collecting simultaneous mechanical, electrochemical, and AE data. ZrO2-Ti6Al4V couples were chosen to represent THR femoral head-neck interfaces for the fretting test. To investigate the efficacy of acoustic emission of detecting fretting-corrosion damages, the samples were subject to three different potentials to simulate (i) new implant: no corrosion at Ecathodic (ii) well function implant: normal corrosion at Eoc (iii) and damaged implant: accelerated corrosion at Eanodic. Bovine calf serum was selected as the electrolyte to simulate the synovial fluids. The standard electrochemical protocol was followed in the fretting under potentiostatic conditions.

The results showed that anodic potential conditions had the most significant increase in current during fretting of ±0.03 mA compared to Eoc conditions with a current increase of ±0.005 mA. This data agrees with the expected trend that the samples exposed to accelerated Eanodic corrosion will have a significant current increase while fretting. Mechanical data was obtained, expressed in the form of force vs. displacement as a friction loop, with an energy ratio of <0.2 for the entire testing (3600 cycles), indicating the partial slip fretting region[3]. The trend in-situ AE data displayed a pulse-like acoustic emission fluctuation, indicating a strong correlation between the fretting-corrosion processes and acoustic emission results. This is an ongoing investigation; the study will focus on linking the AE data and THR fretting-corrosion damages associated with the mechanistic transitions. This could be extremely helpful in the early prediction of THR failure in orthopedic implant patients and clinical practices.

[1]J. Geringer et al., *Metals and Surface Engineering*, 2011 [2]C. Lee et al., *J of the Mech Beh of Bio Mat*, 2019 [3]Fouvry et al, *Wear*, 1997

9:00am **D2-TuM-4 Corrosion Evaluation of Plasma Electrolytic Oxidation Coatings on Titanium Alloys For Biomedical Implant Application***, E. Sondgeroth, K. Cheng, Y. Sun,* UIC School of Medicine at Rockford, USA*; C. Takoudies,* UIC School of Medicine, USA*; E. Vries,* Faculty of Engineering Technology , University of Twente, The Netherlands, USA*; D. Matthews, N. Bolink,* Faculty of Engineering Technology , University of Twente, The Netherlands*; A. Yerokhin,* Department of Materials, University of Manchester, United Kingdom*; **Mathew Mathew**,* UIC school of medicine at Rockford, USA

Titanium is a widely used biomaterial in biomedical implants partly due to its good corrosion resistance which is chiefly attributed to the nano-scale passive layer on its surface(1). While the rates of corrosion for titanium implants currently seem to be low, the incorporation of mechanical wear in a corrosion environment such as the fretting-corrosion seen in a human femoroacetabular joint can result in devastating damage to titanium implants(2). Thus, coating technology may enhance the resistance to tribocorrosion damage. The objective of this study was to test the efficacy of Plasma Electrolytic Oxidation (PEO) coatings on titanium implants compared to bare titanium.

PEO was conducted under different conditions to produce six sample coating groups of varying electrolyte concentrations and thicknesses: $NaAlO_2$ + Na_3PO_4, $NaAlO_2$ + Na_3PO_4 (18 um thickness), $NaAlO_2$ + Na_3PO_4 + Al_2O_3, $NaAlO_2$ + Na_3PO_4 + PTFE NP_5, $NaAlO_2$ + Na_3PO_4 + PTFE NP_5 (thick), and $NaAlO_2$ + Na_3PO_4 + Al. The samples were washed for 10 mins each in isopropanol and DI water. Corrosion testing was conducted in Bovine calf serum 30 g/L (pH 7.4) to simulate synovial fluid and CP and EIS were collected. CP data was graphed as Potential versus Current Density and interpolated to find I_{corr} and E_{corr} for each test group. EIS data was plotted as Nyquist and Bode plots and fitted via a Rapid Electrochemical Assessment of Paint electrical circuit model to estimate each sample's corrosion resistance and coating capacitance.

The I_{corr} was 1.002 ±0.55μA/cm², 2.38±0.005 μA/cm², 0.88 ±0.48 μA/cm², 0.91±0.1 μA/cm², 0.41 ±0.31 μA/cm², and 0.069±0.0007 μA/cm² and E_{corr} was -0.39±0.17 V, -0.40±0.03 V, -0.36±0.15 V, -0.4±0.08 V, -0.47±0.03 V, -0.51±0.04 V, -0.53±0.02 V for each group, respectively. The data shows mild partial improvement in corrosion, especially corrosion potential, in the coated samples as compared to bare Ti. Overall, the results indicate that the coating assists in improving corrosion resistance. EIS data analysis also partially agrees with the improved corrosion resistance. It is worth noting that, the chemistry of the surface and structure of the coating will be influencing the parameters of the corrosion resistance. Particularly in the current study, the coatings displayed a severe porous nature, which may adversely affect the corrosion and wear properties. The hypothesis is partially validated, as the coating enhanced the corrosion resistance of the implant surface. The studies will continue to evaluate the surface properties and underlying mechanisms.

9:20am **D2-TuM-5 Large-Scale Metallic Nanotubes Array (MeNTA) with Plasmonic Nanoparticles for SERS Application***, **Alfreda Krisna Altama**, J. Chu,* National Taiwan University of Science and Technology, Taiwan*; P. Yiu,* Ming Chi University of Technology, Taiwan*; W. Chiang,* National Taiwan University of Science and Technology, Taiwan

The limitations in reproducing large-scale and highly-sensitive surface-enhanced Raman scattering (SERS) substrates are a major problem for practical applications. In this work, we report on our works about a periodic three-dimensional (3D) metallic nanostructure array, referred to as MeNTA fabricated using PVD processes developed for large-scale semiconductor engineering. Specifically, the MeNTAs were fabricated using metallic glass alloy, providing high strength, ductility, and good biocompatibility. For further development, over the MeNTAs deposited a uniform coating of gold nanoparticles (NPs) to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Using crystal violet (CV) as a probe molecule, the performance of an AuNP@MeNTA 3D-SERS substrate can be provided. Here we found a very low detection limit with a comparable enhancement factor. The SERS performance did not degrade for more than a week after installation, thereby demonstrating high stability and repeatability. This research provides useful guidelines for the low-cost fabrication of SERS substrates of high sensitivity.

9:40am **D2-TuM-6 Carbide-derived Carbon (CDC) for Implant Application: Tribocorrosion Kinetics and Mechanisms***, **Kyle Kinnerk**,* Department of Biomedical Engineering, University of Illinois at Chicago, USA*; Y. Sun, M. Daly,* Department of Civil, materials, and Environmental Engineering, University of Illinois at Chicago, USA*; M. Wimmer,* Department of Orthopedic Surgery, Rush University Medical Center, USA*; M. McNallan,* Department of Civil, materials, and Environmental Engineering, University of Illinois at Chicago, USA*; M. Mathew,* Department of Biomedical Sciences, UIC College of Medicine at Rockford, USA

Between 2000 and 2014, the estimated annual incidence of primary total hip replacement per 100,000 in the U.S. in the 55-70 year age range increased by 194.3% [1]. Previously, we fabricated carbide-derived carbon (CDC) on Ti6Al4V, and our finding indicated that CDC can provide superior protection to the substrate in a tribocorrosive environment. The objective of this work is to test CDC under three different electrochemical conditions, cyclic polarization (CP), OCP, and potentiostatic (PS), with the surface characterized by SEM-EDS and 3D profiler.

CDC was prepared on a Ti6Al4V substrate via the electrolysis approach[2]. Ti6Al4V was polished until the surface had a mirror-like finish (Ra<25 nm). Alumina was used as the pin to simulate a ceramic counter body, and bovine calf serum (BCS) was selected to emulate biological fluids. Two groups of samples were tested, alumina (Al_2O_3)-Ti6Al4V (control group) and alumina-CDC, using a custom tribometer with reciprocal sliding for 3600 cycles. A standard electrochemical protocol was followed, and CP, OCP, PS were usedfor the sliding stages. Electrochemical impedance spectroscopy (EIS) was conducted before and after the testing stage to analyze the local corrosion kinetics. SEM/EDS was used to observe the wear scar and obtain the surface composition, 3D profiler will be used to measure the wear volume, and ICPMS will be used to measure the metal ions concentration released into the BCS solution.

Based on the potentiodynamic results under sliding conditions, the CDC coated sample showed approximately 126-fold smaller carbon density variation (6.301×10^{-6} A/cm²) than the bare titanium alloy (7.577×10^{-4}A/cm²), implying that CDC has a smaller corrosion weight loss (K_c). The OCP results agree with the potentiodynamic results, where the potential drop of CDC (0.194V) is smaller than Ti6Al4V (0.7V), meaning that CDC can provide protection to the substrate material under tribocorrosive environment. Furthermore, SEM-EDS results indicate that CDC still remained on the surface after tribocorrosion testing for both electrochemical conditions. Therefore, it is possible that CDC can be smeared over the surface by mechanical motion and act as a solid lubricant at the interface. Potentiostatic condition will be included to fully evaluate CDC's tribocorrosion performance, and more characterization techniques will be employed to reveal the protection mechanism of CDC. In this work, we found that CDC can significantly improve the substrate's tribocorrosive resistance, showing that CDC is promising in further implant applications.

[1] M. Sloan et al., *J. Bone Jt. Surg.,* 2018 [2]Y. Sun et al., *Surf. Coat. Technol.,* 2021

10:00am **D2-TuM-7 PEKK as Biomaterials Under Fretting Corrosion Solicitations: May This Biopolymer Be Considered as New Hip Implant Component?***, **Jean Geringer**, J. Monnatte,* Mines Saint-Etienne, France*; G. Planche,* EPIC sarl, France*; J. Porteus,* Oxford Polymers, USA

Some materials dedicated to orthopaedic implants are well used from more than 40 years. About hip implants some PAEK, poly Aryl Ether Ketone, materials may have a right impact on the lifetime. PEEK, poly Ether Ether Ketone actually is under investigations. However PEKK, poly Ether Ketone Ketone, needs some improvements concerning Friction/Fretting corrosion resistance. From the fundamental point of view, PEKK was under investigations through this study about fretting corrosion investigations. Some fundamental investigations under these tribological conditions are not quite well described. This work aims at providing some fundamental results on tribology/tribocorrosion.

A typical fretting corrosion machine, Fig 1, allowed to manage 16 hours of experiments. Titanium alloy, Ti-6Al-4V, was the counter part in bovine serum. The displacement amplitude was sinusoidal with the amplitude of +-40µm.

This study aimed at establishing the fretting map and at drawing thanks to OCP, Open Circuit Potential, evolution the A ratio (Dissipated energy over the total energy) vs. OCP drop. This approach is well improved and the suggested ranking of contact was well achieved in accordance with previous results [1].

Under hip implants mechanical constraints PEKK material showed good performance under fretting corrosion solicitations compared to UHMWPE for example. Further investigations need to be performed in order to assess the capability of using as implants.

Figure 1

10:20am **D2-TuM-8 Fretting-corrosion (<5µm) Performance of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants***, **Yani Sun**, M. Daly, M. McNallan,* Department of Civil, Materials and Environmental Engineering, University of Illinois at Chicago, USA*; M. Mathew,* Department of Biomedical Sciences, UIC College of Medicine at Rockford, USA

Fretting-corrosion at the taper junction is one of the main causes of early failure of total hip replacement (THR)[1]. Previously, we have proved that carbide-derived carbon (CDC) can protect Ti6Al4V from tribocorrosive damages[2]. However, the fretting-corrosion behavior of CDC still remains unknown. Also, experimental fretting setups used in the literature simulate motions of 50 µm or higher[3], which might not simulate micromotions at the taper junction that leads to partial-slip fretting. Therefore, we aim to develop a device simulating a motion <5 µm while simultaneously collecting electrochemical data, and test CDC's fretting-corrosion behavior.

The fretting-corrosion apparatus mainly consists of a stepper motor, a force sensor, and a corrosion cell connected to a potentiostat. Two groups were designed as (i) ZrO_2 pin on the Ti6Al4V as the control group and (ii) ZrO_2 pin on the CDC. Bovine calf serum (BCS) with protein content of 30 g/L was selected as the electrolyte at 37±1°C. A normal load of 83 N was applied, and the pin was controlled to move with an amplitude of 2 µm at 1 Hz for 3600 cycles. A typical protocol was followed to monitor the evolution of open-circuit potential (OCP). After the fretting-corrosion testing, the exposed area was characterized by SEM/EDS.

As a result, friction loops of both groups show a narrow elliptical shape, and the energy ratios of both groups remained below 0.2 throughout the entire stage, indicating a fretting regime of partial slip according to Fouvry et al.[4]. Moreover, CDC possesses higher OCP (-0.076 V) than Ti6Al4V (-0.541 V) during the fretting stage, suggesting that CDC has a higher resistance to corrosion. The fluctuations of OCP caused by fretting motions of CDC is approximately 0.005 mV, which is smaller than that of Ti6Al4V (0.03 mV), suggesting that CDC can provide protection to the substrate under the fretting-corrosion conditions. Based on the SEM images, the main damage showing on the Ti6Al4V disk is abrasive wear with typical ploughing features, which might be because of the higher hardness of ZrO_2 than the Ti alloy. Less damages were observed on the CDC surface and CDC still presents on the surface after the testing, implying that CDC might act as a solid lubricant and get smeared over the surface by the mechanical wear and thus protect the substrate from fretting-corrosion damages. Also, TEM will be utilized in the following study to reveal detailed mechanism and structural information.

[1]S. Yu et al. *J. Clin. Orthop. Trauma* 2020 [2]Sun, Y et al. *Surf. Coat. Technol.,* 2021. [3]J. Geringer et al., *Tribocorrosion Passive Met. Coat,* 2011 [4]S. Fouvry et al., *Wear*, 1995

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E3-1-TuM

Tribology of Coatings and Surfaces for Industrial Applications I

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Dr. Rainer Cremer**, KCS Europe GmbH, Germany, **Dr. Philipp Grützmacher**, Institute of Engineering Design and Product Development, Austria

8:00am **E3-1-TuM-1 Carbon Based Coatings Deposited Over Aisi 4140 to Improve Wear Resistance in Machine Components***, F. Delfin,* UTN, Argentina*; D. Heim,* Upper University of Applied Sciences, Wels Campus, Austria*; **Sonia Brühl,*** UTN, Argentina **INVITED**

Carbon based coatings or DLC are well known to have a low friction coefficient, chemical stability at room or low temperatures, high hardness and also corrosion resistance. Three different carbon-based coatings were deposited over plasma nitrided or non nitrided AISI 4140 mild steel to improve hardness and wear resistance so as tribological properties.

One of them is an amorphous hydrogenated thick Si doped DLC (a-C:H:Si) deposited by PACVD, in a Rübig facility in Austria using a DC pulsed discharge, with acetylene and HMDSO as carbon and silicon precursors, respectively. It will be compared with a Si-free DLC (a-C:H) deposited in the same conditions. The third one is a multilayer film with DLC as top coating deposited by the PVD PEMS technique in a Cemecon facility in Argentina. In this case, the anchor layer consists of CrN and the top layer is a chromium-dopped hydrogenated amorphous carbon (a-C:H:Cr).

Full characterization was carried out by SEM, Raman Spectroscopy and XRD. Mechanical properties were obtained using nanoindentation. Tribological behavior was study with Pin-on-Disk tests, evaluating wear loss and friction coefficient, and complementary SEM/EDS analysis on the wear track and on the counterpart. Adhesion was assessed with variable load Scratch Test and Rockwell C indentation method. Abrasion tests following ASTM G65 standard were also conducted.

All coatings contain hydrogen and a combination of sp^3-sp^2 bonding, with high disorder level caused mainly by the dopants. Low coefficients of friction were obtained with the films, between 0.1 and 0.3, being the lowest the Si-free thick DLC reaching 0.06. Regarding the wear rates with alumina as counterpart, only the Si-free DLC and the duplex nitrided steel plus a-C:H:Cr presented a low volume loss. Adhesion was also improved by the plasma nitriding pre-treatment in this coating, which provided a hardness gradient in the substrate to support the load applied. Meanwhile, Si doping improved DLC wear resistance in the case of abrasion tests.

As a conclusion, the thick and Si-free DLC coating has the lowest CoF and wear rate when deposited over mild steel. On the other hand, the thin PVD Cr doped DLC coating presented the best performance when deposited over nitrided steel. This also improved the adhesion comparing to the other two PACVD coatings. The Si-doped DLC failed in the pin-on-disk test because of the adhesion with the counterpart, but it presented a good wear resistance in abrasion.Tribological mechanisms, and applications of each type of coating will be discussed.

8:40am **E3-1-TuM-3 Tribological Behaviour of Diamond Coated Reaction-Bonded Silicon Carbide Under Dry and Seawater Environment***, R. Kannan, N. C,* Indian Institute of Technology Madras, India*; R. Ganguly, S. Mandal, S. Rao,* Carborundum Universal Limited, Industrial Ceramic Division, India*; **M.S Ramachandra Rao,*** Indian Institute of Technology Madras, India

Ceramic seal materials such as silicon carbide (SiC) and Reaction-Bonded SiC (89%SiC and 11% free Silicon) are widely used in mechanical pumps, compressors, and feed water pumps to prevent the fluid leakage between the two rotating shafts. In a continuously harsh environment, these mechanical seal materials undergo high friction and wear due to the high asperity-to-asperity contact between the two mating parts and generate high frictional heat at the interface. This scenario induces seal failure under high operating conditions. Especially in the corrosive medium such as acids, high pH value solutions and hard abrasive media can cause aggressive seal failure. To reduce production downtime and improve the longevity of the mechanical seal, the surface of the seal material needs to be engineered with a suitable coating that will satisfy the required properties of high hardness, chemically inertness, and low friction coefficient. In this regard, we have come up with a super hard coating material such as diamond (Micro-crystalline) on the surface of Reaction-Bonded SiC using the hot filament CVD (HFCVD) method to meet the above-required properties. In this work, we have carried out a systematic study on the tribological effect of uncoated and diamond-coated seal material against silicon nitride ceramic under a dry and seawater environment. The initial physical characteristics such as surface morphology, surface roughness, and Raman analysis were performed on the samples before and after coating. To understand the friction and wear characteristics, the linear reciprocating tribometer test (Ball on Flat) was conducted on the uncoated (18,000 cycles) and diamond-coated (36,000 cycles) samples using a universal tribometer. The experimental results show that the diamond-coated sample exhibits a low friction coefficient (0.05 ± 0.01) compared to the uncoated sample (Friction coefficient (CoF) = 0.24 ± 0.037) at a normal load of 10 N with a frequency of 10 Hz under a seawater environment. Similarly, under dry conditions for the same tribo-test parameters, the diamond-coated sample (CoF = 0.06 ± 0.02) outperforms compared with the uncoated sample (CoF = 0.42 ± 0.17) at a percentage improvement of 85%. From the observed results, we conclude that diamond-coated ceramic seals are considered a suitable alternative to commercially available seals in terms of high operating conditions and durability under both wet (Sea water) and dry running operation. All these results will be presented.

9:00am **E3-1-TuM-4 Friend or Foe? The Role of Oxygen in the Tribological Performance of Solid Lubricant MoS_2***, **Andrey Bondarev,*** Czech Technical University in Prague, School of Engineering, Bernal Institute, University of Limerick, Ireland*; I. Ponomarev, T. Polcar,* Czech Technical University in Prague, Czechia

MoS_2 is a solid lubricant used in various forms, such as a dry lubricant by itself, or as a component of a more complex coating. In both these forms, the effect of oxygen contamination on the sliding properties of MoS_2 coatings is traditionally considered detrimental, resulting in expensive technological processes to produce pure MoS_2.

The interaction of the film with oxygen can be split into three phases. First, during magnetron sputtering, oxygen is incorporated into the growing film from the residual atmosphere. Then, storing the film in the open air can cause oxidation. Finally, the coatings experience a negative influence of molecular or atomic oxygen from the surrounding atmosphere on their tribological properties. Despite the origin, a formation of a noticeable amount of molybdenum oxides on the sliding surface has been reported as the reason behind the poorer tribological properties.

The Mo-S-O coatings were fabricated by unbalanced magnetron sputtering. It was found that hardness, elastic modulus, and wear resistance can all be enhanced with the addition of oxygen. The Mo-S-O coatings were tribologically tested under vacuum, ambient air, and nitrogen. A high oxygen content, up to 38 at.%, does not prevent the formation of a lubricious crystalline MoS_2 tribofilm, which is formed through triboactivated segregation of the deposited Mo-S-O amorphous coatings into a crystalline MoS_2-based phase and an amorphous S-depleted Mo-S-O phase. By means of advanced TEM and EELS studies, it was shown that an ultra-thin crystalline MoS_2 tribolayer incorporates some amount of oxygen. Such an imperfect tribolayer was found to reduce the coefficient of friction to 0.02, a value lower than that of pure MoS2 under vacuum (0.05). Molecular dynamics simulations performed using a newly developed Mo-S-O force field confirmed that such an imperfect tribolayer can mitigate friction in a manner comparable to MoS_2. Results of DFT simulations support the experimental findings and show that partial substitution of S atoms to O atoms in the MoS_2 crystal structure does not increase shear modulus. Tribological tests of the Mo-S-O coatings after 1-year storage under ambient air (RH = 35 ± 5%) revealed the same trends as freshly deposited samples – the Mo-S-O coatings outperform pure MoS_2 coatings demonstrating lower values of friction coefficient.

In this work it is shown that contradictory to common knowledge, adding oxygen to a solid lubricant MoS_2 coating could be beneficial. Since eliminating oxygen in MoS2-based solid lubricants is extremely costly, our findings can significantly reduce the production and storage cost for aerospace and other vacuum applications.

9:20am **E3-1-TuM-5 Tribological Properties MoS_2-WC Duplex Coatings in Low Viscosity Hydrocarbons***, **Euan Cairns**,* University of North Texas, USA*; S. Dixit,* Plasma Technology Inc., USA*; D. Berman, S. Aouadi, A. Voevodin,* University of North Texas, USA

Emerging applications using low-carbon emission fuels, such as ethanol and dodecane, lead to a growing need for lubricious materials that can improve the tribological behavior and increase the wear life of fuel pump components. In our previous studies we found that MoS_2 spray-coat on 52100 steel had the potential to be used in low-viscosity hydrocarbon fuels as a protective coating. The best results were observed in dodecane fuel, where a coefficient of friction of less than 0.1 was maintained for 100 m of sliding. In this report, we extend the understanding of MoS_2 spray coating performance in low viscosity hydrocarbons to a duplex coating with a hard, wear-resistant underlayer made of coated and ground finished High Velocity Oxygen Fuel (HVOF) thermal spray tungsten carbide (WC) combined with the lubricious MoS_2 top layer to create synergistic tribological protection of 52100 steel substrates from the sliding wear. Tribological tests were performed under the reciprocating sliding condition in dodecane and ethanol, followed by investigations with scanning electron microscopy equipped with an energy dispersive spectrometer, Raman microscopy, and x-ray photoelectron spectroscopy for microstructural and compositional analysis.The effects of substrate roughness and composition on the wear life of the coatings were examined using optical profilometry and microscopy of wear tracks. The results were used to identify lubrication and sliding wear protection mechanisms when using MoS_2-WC duplex coatings prepared by spray methods.

9:40am **E3-1-TuM-6 Modification of Diamond Like Carbon (DLC) to Improve Specific Tribological Characteristics for Automotive Applications***, **Denis Romagnoli**, F. Lavalle,* STS srl, Italy **INVITED**

Carbon-based materials play an important role in today's science and technology. Carbon is a very versatile element whose two most interesting allotropic forms are Diamond (sp3) and Graphite (sp2). In recent years, there have been continuous and important advances in carbon science, such as the chemical vapor deposition of diamond, the discovery of fullerenes, carbon nanotubes, and the single layer of graphene. At the same time, the DLC has consolidated all its applications in the automotive, mechanical in general but also fashion sectors. An amorphous carbon layer can have different ratios between diamond C and graphitic C. The management of these fractions but above all the architecture of the layer generates different types of DLC that allow to enhance the hardness, contain friction and improve the corrosion resistance of the component.

The demand for the application of DLC on components for endothermic and hybrid engines (pins, valves, camshafts) is constantly growing; about the novelties in the field of mobility, the need to protect the gears of electric motors from wear or corrosion the bipolar plates of hydrogen propellers are increasingly pressing. DLC can increase surface hardness, reduce friction and protect against corrosion; for racing this means an improvement in terms of overall engine performance, and for the automotive sector an improvement in yield with the consequent possibility of reducing emissions into the atmosphere, allowing the use of certain components in non-standard conditions (e.g. rotation constantly at a maximum number of revolutions in an electric motor) and use different materials (for example steel compared to graphite in a Fuel Cell). The possibility therefore of being able to manage hardness, coefficient of friction, and corrosion resistance in the same DLC layer is determined for the application.

In this presentation, the DLC deposited with hybrid technology PVD-PaCVD (Physical Vapor Deposition- Plasma assisted Chemical Vapor Deposition) will be examined. The modification of the layers, the thicknesses, the compositions, and the containment of surface defects allow enhancing the characteristics of hardness, reduction of friction, and resistance to corrosion of the layer. These characteristics can therefore be objectified with laboratory instruments such as nanoindenter, contact tribometer, and salt spray chamber. The next step is the bench test to then move on to the final validation and production launch.

10:20am **E3-1-TuM-8 Fabrication and Tribological Behaviors of DLC Coatings Embedded with Graphene Nanoplatelets***, **Guizhi Wu**, R. Brittain, A. Morina,* University of Leeds, UK*; E. Broitman,* SKF Research & Technology Development Center, Netherlands*; L. Yang,* University of Leeds, UK

Graphene has garnered widely interests in tribology due to its nature of reducing friction. The lamellar structure endows graphene a weak shearing stress, and thus a low friction. Utilizing graphene platelets to wrap around nanodiamond particles to form nanoscrolls at a sliding interface would decrease coefficient of friction (COF) significantly by achieving an incommensurate contact on diamond-like carbon (DLC) coatings. However, such complicated design containing too many additives will reduce the stability of the system. COF of TiN ceramic film will decrease by simply driping down a graphene aqueous dispersion on the slding interface, by which a smooth sliding interface promoted by graphene are formed. Nevertheless, the most concern is that graphene might be easily pushed out of the friction interface at the beginning of sliding, thus may not affect the friction test. Graphene nanocrystallites can also be fabricated by vapor deposition method and embedded in the carbon film matrix to form a nanocomposite carbon film, of which the COF decreases significantly. But it remains to be further demonstrated whether the synthesized carbon crystallites is graphene.

In this study we report the synthesis and tribological behaviors of DLC coatings embedded with Graphene nanoplatelets (GNP), namely DLC-GNP nanocomposites. GNP layer was deposited by two methods, namely, spin-coating and spray-coating. The DLC layer was deposited on top of the GNP coated coupon by plasma enhanced chemical vapour deposition. The effect of GNP on the lubricated tribological response under elevated temperature was discussed. The results show that GNP has a tendency to agglomerate for higher GNP coverages by using spin-coating, which would lead to removal of the GNP more easily and negate the friction reduction effect of the GNP. The tribotests show decrease in friction and wear of the DLC-GNP nanocomposites in various GNP coverages, with the lowest friction (COF ~0.03) and wear (~1.6×10^{-19} m^3/Nm^{-1}) achieved, which might be due to a highly graphitic transfer film featuring low shearing stress formed in the friction interlayer. This study might contribute to energy conservation and emission reduction, and also promote the development of green tribology under the global 'Carbon net zero' aim.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-1-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderator: Prof. Olivier Pierron, Georgia Institute of Technology, USA

8:40am **H2-1-TuM-3 Multifunctional Characterization of Nanomultilayers***, **Andrea Maria Hodge**,* University of Southern California, USA **INVITED**

Nano multilayers (NMs) films consist of alternating layers of materials with thicknesses on the order of nanometers and typically display many attractive properties which are attributed to the fact that, as the layer thicknesses decrease, the individual layer behavior changes and the interface volume increases. In this presentation, I will discuss how to synthesize and characterize systems of nanostructured multilayers, leveraging nanoscale features to enhance properties and function. To address this, samples with a wide range of composition and layer thicknesses were synthesized via DC/RF and reactive magnetron sputtering. Multilayer configurations of metal/metal, ceramic/metal and ceramic/ceramic systems were designed as model systems for either optical optimization or thermal studies. A comprehensive microstructural and mechanical evaluation of selected metal and ceramic multilayers are presented in order to elucidate on the role of their interfaces for properties and function.Several NMs configurations including SiO_2/TiO_2, AlN/SiO_2, AlN/Ag, Fe/W, and Mo/Au be discussed. The role of bilayer thickness and composition are evaluated and related to final microstructure and behavior.

9:20am **H2-1-TuM-5 Effects of Radiation Damage on the Critical Resolved Shear Stresses in Zirconium Alloys for Nuclear Applications***, **James Gibson**, C. Grovenor, A. Wilkinson,* Oxford University, UK

Nuclear power provides 10% of the world's electricity and is likely to expand as countries seek to provide low-carbon energy in the future. Of the current operating 442 commercial nuclear reactors, 96% are water cooled and thus have their uranium oxide fuel contained within a zirconium alloy cladding. This cladding limits fission product release into the primary water loop, as well as acting as the main transport medium for neutrons and heat.

Under irradiation, like most metals, these zirconium alloys exhibit strong hardening effects. Typically, the yield stress of Zr-alloys doubles during the early stage of irradiation while a dramatic loss of strain-to-failure is observed. Irradiation hardening is currently qualitatively described by <a> loops being barriers for dislocations during mechanical loading. This hardening is also supplemented by irradiation-induced precipitates, but their effect on irradiation hardening in Zr-alloys is currently unknown.

Like most of other hexagonal close packed (HCP) materials, zirconium deforms anisotropically via plastic slip on the basal, prismatic and pyramidal planes. As loop formation is also crystallographically influenced, a full picture of the radiation damage effects in zirconium must be gathered on a piece-by-piece basis, with the influence of damage levels, strain rate and temperature being determined on each slip system.

We present here the first steps towards painting this picture of radiation damage effects in zirconium. Nano-indentation testing using spherical and Berkovich tips correlated with indented grain orientations from EBSD has been used for initial rapid screening of irradiation hardening and strain softening effects, as required by complementary CP-FEM models. Subsequently identified "interesting" samples have been selected for more quantitative micro-mechanical investigation to determine critical resolved shear stresses on specific slip systems.

9:40am **H2-1-TuM-6 Link between Cracking Mechanisms of Trilayer Films on Flexible Substrates and Electro-Mechanical Reliability Under Biaxial Loading***, **Shuhel Altaf Husain**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; P. Kreiml,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; P. Renault,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; C. Mitterer,* Montanuniversität Leoben, Leoben, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Faurie,* CNRS, France

Flexible electronics is a technological innovation that involves the use of flexible polymer substrates as the basis structure for the assembly of electronic circuits [1–3]. Currently, flexible electronic devices have new emerging applications, especially for foldable displays and even in biology for integration on skin [4,5]. Flexible polymeric substrates show the advantages of low cost, light weight, mechanical compliance and bendability [6]. Nonetheless, these systems suffer from limited durability, both mechanically and electrically due to the multi-cracking phenomenon during loading [7]. Many works have studied the mechanical behavior of multilayers in order to profit from interfaces and mechanical contrasts (ductile/brittle, stiffness) between each layer to improve the durability [8].

In this work, the propagation of cracks from a top layer in trilayer systems (Cr/Cu/Mo) on a polyimide substrate is studied experimentally by in situ synchrotron X-ray diffraction under equi-biaxial loading (see figure 1). The results show that depending on the thickness of the ductile Cu middle layer (100 nm or 500 nm), the propagation can be a direct vertical path through all layers or a more complex path. These effects are analyzed by monitoring the individual stresses of each layer along with electrical resistance and resulting crack patterns. Cracks starting from the upper Cr layer propagate instantaneously through the whole system for a 100 nm Cu layer, but are strongly deflected in a 500 nm Cu layer, thus delaying the global fracture of the system measured by the increase of electrical resistance. Mechanisms are proposed and allow to anticipate the electro-mechanical performances of stretchable systems constructed of several layers.

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10:00am **H2-1-TuM-7 Effect of Nanometric Stacking on the Magneto-Mechanical Properties of Thin Films on Flexible Substrate***, H. Ben Mahmoud, **Damien Faurie**,* CNRS-LSPM, France*; P. Renault,* CNRS-Pprime, France*; F. Zighem,* CNRS-LSPM, France

Flexible or stretchable magnetic systems are of growing interest in the scientific community, on the one hand for the fundamental aspects of magnetomechanical couplings in low dimensional objects and on the other hand for the numerous applications they can generate (magnetoelectric deformable devices for media, textiles or the human body, etc). Thus, it is important for the community to acquire numerical and experimental means to better understand the evolution of the physical properties (magnetic and electrical) of these flexible systems when they are subjected to deformations [1-2].

Regarding the experimental means, it is essential to be able to evaluate the evolution of the magnetization curves at strain levels comparable to those of a real use (a few ten of percent). Indeed, these strains applied at the macroscopic scale can have repercussions at the microscopic level on the organization of the material (in this case magnetic) and affect the functional properties. In the case of nanometer-thick films on deformable substrates (such as polymers), this can in most cases be characterized by cracks that multiply during the mechanical test. This multi-cracking phenomenon can be complex and involves, by the creation of new surfaces, a strong heterogeneity of stress (and strain) at the scale of the inter-crack fragments, but with a rather weak evolution of the stress averaged on the whole thin film.

However, the links between these mechanical phenomena and magnetic properties have been little explored. Currently, the most ambitious in situ developments have been either at small strains (piezoactuation or bending, up to 1-2%), or at large strains for the properties of giant magnetoresistance. Actually, there is a lack of measurements of magnetization curves at large strains.

In this presentation, we present in situ magneto-mechanical experiments carried on 50 nm Co and NiFe thin films deposited on a polyimide substrate in order to highlight links between damaging of these nanometric films and their magnetic properties. Moreover we will show that the addition of weak layer (W) in the systems affects on the one hand the pattern of cracks and consequently the magnetomechanical properties (evolution of coercive and saturation field, magnetic anisotropy and remanent magnetization).

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10:20am **H2-1-TuM-8 Influence of the Aspect Ratio of the Micro-Cantilever on the Determined Young's Modulus Using the Euler-Bernoulli Equation***, F. Konstantiniuk,* Montanuniversität Leoben, Austria*; M. Krobath, W. Ecker,* Materials Center Leoben Forschungs GmbH, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; **Nina Schalk**,* Montanuniversität Leoben, Austria*; M. Tkadletz,* Montanuniversitat Leoben, Austria

Micro-cantilever bending experiments can be used to determine fundamental material properties, such as fracture stress and fracture toughness. Furthermore, the Young's modulus can be calculated from the slope of the load-displacement curve using the classical Euler-Bernoulli equation. However, in literature it can be frequently found that applying this technique, the Young's modulus is significantly underestimated, especially when using micro-cantilevers with aspect ratios (bending length/width) < 6. In order to investigate the influence of the aspect ratio on the determination of the Young's modulus, SiO_2 and single crystalline α-Al_2O_3 micro-cantilevers with aspect ratios ranging from ~3.5 to 6.5 were fabricated using focused ion beam milling and subsequently tested with a nanoindenter system. In addition to the quasi-static tests, dynamic micro-cantilever bending tests were performed by using an excitation frequency on top of a quasi-static loading and the results of both techniques were compared to each other. Finally, finite element analysis was used to simulate the static-micro-cantilever bending experiments and investigate the influence of shear deformation, flexing of the support and the geometry of the micro-cantilever on the load-displacement curves.

10:40am **H2-1-TuM-9 Engineering Metal-MAX Phase Multilayered Nanolaminates for Tunable Strength and Toughness***, **Skye Supakul**, S. Pathak,* Iowa State University, USA*; K. Yaddanapudi,* University of California at Davis, USA

Metal-Ceramic nanocomposites have long been of interest to combine the high strength of ceramics with the toughness in metals. To achieve this combination, metal-ceramic multilayers have relied on significantly reduced bilayer thickness (few nm's) and crystalline components, leveraging improved plastic co-deformation for the improved mechanical properties. Here, we discuss the process of designing metal-MAX phase multilayered nanolaminates (MMN) which leverages the unique combination of metallic, covalent, and ionic bonding in MAX phases to enhance the threshold thickness for improved plastic co-deformation and enhanced toughness. Furthermore, with the atomically layered structure of MAX phase coupled with the metal and MAX phase layers, we engineer a hierarchical layered microstructure – where the metal and MAX phase layers are in direct competition with the internal interfaces within the MAX layers and atomically layered structure – taking advantage of the mechanisms of confined layer slip, Hall-Petch strengthening, and the competing deformation mechanisms to improve the strength of the system. By adjusting the combination of individual layer thicknesses, we can tune the mechanical properties of the metal-MAX phase multilayered nanolaminate system.

We begin by discussing the challenges associated with synthesizing MAX phase, followed by preliminary depositions on a Nb and Ti2AlC metal-MAX phase system which prefaced the overarching challenge of diffusion in the metal-MAX phase multilayered nanolaminates. To investigate and understand the diffusion, the next set of depositions focus on Ti and Ti2AlC metal-MAX phase multilayered nanolaminates to simplify the material system, as well as improve the plastic co-deformation between the metal and MAX phase systems. We utilize conventional direct current (DC) magnetron sputtering physical vapor deposition as well as a unique twin chamber deposition system, capable of automated atomic layer deposition and direct current magnetron sputtering physical vapor deposition without breaking chamber vacuum. We implement high temperature deposition, mixed low and high temperature deposition, as well as combined ALD-PVD depositions with amorphous Al2O3 layers to investigate the pathways to fabricate continuous metal-MAX phase multilayered nanolaminates. The multilayered depositions are characterized with XRD and TEM, and their mechanical properties are evaluated using nanoindentation and micropillar compression.

Topical Symposia

Room Town & Country A - Session TS1-3-TuM

Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications III

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Klaus Böbel**, Bosch Manufacturing Solutions, Germany

8:20am **TS1-3-TuM-2 High-Performance Rechargeable Zinc Ion Batteries: From Surface Modification of Zn Anode and Structural Engineered Cathode to Deep Eutectic Solvent (DES)-Based Electrolytes***, **Yu-Lun Chueh**,* National Tsing Hua University, Taiwan

Rechargeable metal ion batteries have been widely studied as efficient energy storage systems for portable devices, such as electric vehicles, which have become the trend in the future. Among these candidates, zinc ion batteries exhibit superior advantages because of the abundance of zinc compared with lithium, while the cost of zinc is lower than that of lithium. Moreover, zinc has been characterized by multivalence in an ionic state, which provides approximately three times higher volumetric capacity than lithium. For Zn ion batteries, the uncontrollable dendrite growth and side reactions existed on the Zn anode seriously restrict the cycle stability of zinc ion batteries. In my talk, different strategies on the design of low dimensional materials on the surface metal anode or cathode for high-performance rechargeable Zn ion batteries will be reported. For example, organic hydrophobic polyvinylidene fluoride and inorganic Santa Barbara Amorphous-15 (PVDF-SBA15) hybrids were designed as a surface modification layer to stabilize the Zn anode, leading to an optimized Zn/electrolyte interface with large-scale feasibility.[1] In addition, an alternative electrolyte system based on the deep eutectic solvent (DES), because of their low cost, high stability, biodegradability, and non-flammability, making them optimal candidates for sustainable batteries, was demonstrated.[2] *Ex-situ* Raman, XPS, and TEM characterization results of the electrodes under different states confirm the reversible alloying conversion and intercalation hybrid mechanism during the discharge and charge cycles for Zn ion batteries. All possible chemical reactions were proposed by the electrochemical curves and characterization.

Reference:

1. Nano Energy 103, 107805, 2022

2. ACS Applied Materials & Interfaces 14, 7814-7825, 2022

8:40am **TS1-3-TuM-3 Electrochemical Performances of LiNi0.8Co0.1Mn0.1O2 Synthesized by Hydroxide Coprecipitation Method***, **Chia-Hsin Lo**, J. Huang,* National Cheng Kung University (NCKU), Taiwan*; C. Chang,* National University of Tainan, Taiwan

To meet the rising demand of electric vehicles, cathode materials of rechargeable lithium-ion batteries with high energy density and long cycle life are investigated. Lithium nickel cobalt manganese oxide ($LiNi_xCo_yMn_zO_2$) is a promising candidate to be the next generation cathode materials. A series of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was successfully prepared by hydroxide coprecipitation method and calcination. The crystal structures and microstructures were characterized by X-ray diffraction and scanning electron microscopy. Charge/discharge cycling were also employed to investigate their electrochemical behaviours. XRD results show that pHvalue have an impressive effect on the crystal structure of the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder. Among all the samples, the one prepared at pH=11.5 possessed the lowest degree of Li^+/Ni^{2+} disordering and the . Scanning electron microscopy with element mapping tests reveal that the homogeneous $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ solid solution has been achieved via this synthesis method. The $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder prepared at pH=11.5 can deliver a high initial discharge capacity of 182.9 mAh/g with coulombic efficiency of 66.0% at 0.5C-rate in the voltage range of 2.8−4.3 V.

9:00am **TS1-3-TuM-4 Pb-Free Halide Perovskite/TiO_2 Heterostructure for Enhanced Solar-Driven PFC***, **Yong Yu**, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Photocatalytic fuel cell (PFC) isa promising technology that can simultaneously treat wastewater and generate electricity. Upon solar light irradiation, the photoanode generates electron–hole pairs, the holes degrade organic pollutants by formation of reactive oxidative species and the electrons go through the circuit to the cathode for oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER), depending on the oxygen concentration in solution. Regarding the photoanode, TiO_2 is commonly used due to its low toxicity, low cost, and high stability. However, there are still problems need to be solved, such as low visible light absorption and fast electron-hole recombination rate.

In the present study, we use all-inorganic lead (Pb)-free halide perovskite to form a heterostructure with TiO_2 to tackle the above issues. The heterostructure increases the absorption of visible light, reduces the recombination of electron–hole pairs, and improves the efficiency of PFC. Halide perovskite is chosen due to the easy synthesis, narrow energy gap, and high carrier mobility. The Pb is replaced by bismuth. The photodegradation performance is investigated using tetracycline antibiotic as organic pollutant and reported.

9:20am **TS1-3-TuM-5 Inline PVD Coating of Bipolar Plates for Electrochemical Energy Converters***, K. Böbel, M. Mueller,* Bosch Manufacturing Solutions, Germany*; D. Beisenherz, S. Huebner,* Singulus Technologies AG, Germany*; J. Jiao, S. Wetzel,* Bosch Automotive Products (Suzhou) Co., Ltd., Germany*; **Rafael Gryga**,* Matthias Mueller, Bosch Manufacturing Solutions, Germany

Electrochemical energy converters are key components for a broad establishment of green hydrogen economy. The relevant technologies have been applied for decades in several niche applications. Recently many countries and companies pursue the mass production of fuel cells and electrolyzers. Hence, great efforts are made towards cost efficient systems, components and fabrication methods.

In practice single fuel cells and electrolyzer cells are stacked to a powerful system consisting of up to several hundred cells. The single cells are separated and electrically connected via bipolar plates. Those plates must withstand different electrochemical and temperature conditions without significant deterioration of their performance. Widely applied performance indicators are interfacial contact resistance and corrosion current. Those properties can be perfectly controlled by means of noble metal coatings applied onto steel or other bipolar plate materials. In order to replace this expensive solution, many coating systems and a wide variety of coating techniques have been suggested so far.

The paper reports on the optimization of both, bipolar plate properties as well as production efficiency based on PVD coating technology. Different coating designs have been tested and promising candidates have been optimized in terms of process parameters and coating thickness. The coating process has been transferred from batch to inline systems with a cycle time of a few seconds. This results in a competitive solution for the mass production of cost efficient bipolar plate coatings.

9:40am **TS1-3-TuM-6 Studies on the TiO_2 Thin Film on the Silicon Nanowire Arrays using Taguchi - Grey Method for Heterojunction Solar Cell***, A. Chiou, H. Liao,* ***Jun-Luo Wei,*** National Formosa University, Taiwan

In recent years, the problem of energy has become more and more serious, and renewable energy is the most important.Among the renewable energy sources, solar energy is the best developed. Many different materials have been applied to solar cells by scholars. One way to produce large-area, easy-to-process thin films is to use radio frequency magnetron sputtering. In this study, P-layer silicon nanowire arrays were prepared by electroless etching method to replace the previous multilayer films. TiO_2-SiNW Arrays heterojunctions were formed by preparing TiO_2 as N layer by magnetron sputtering method. In this paper, the Grey-Taguchi method was used to analyze and optimize PN heterojunctions with TiO_2 films. The effects of sputtering process parameters (RF power, process pressure, deposition temperature and deposition time) on surface morphology, material structure, photoelectric conversion efficiency and reflectivity were investigated.An AZO window layer is then added and annealed.

The gray correlation analysis shows that the reflectivity is reduced from 8.02225% to 7.72081%, and the photoelectric conversion efficiency is increased from 0.01915% to 0.082%. In the confirmation runs, the TiO_2 film was amorphous and wound around an array of silicon nanowires.After adding the AZO window layer, the reflectivity increased to 18.04712%, and the photoelectric conversion efficiency increased to 0.124%.Confirmation runs show that the AZO film is polymorphic. The experimental results demonstrate the effectiveness of the RF magnetron sputtering method, which provides good reflectivity and photoelectric conversion efficiency.

10:00am **TS1-3-TuM-7 Impacts of Mutual Phase Interactions on Crystal Polarity and Photocatalytic Hydrogen Evolution Reactions***,* ***Jrjeng Ruan,*** National Cheng Kung University (NCKU), Taiwan

The secondary molecular interactions are well known able to influence the organization behaviors and electrooptical responses of dispersed molecules. Whereas, for dispersed phase domains of organic and inorganic components, including amorphous and crystalline phases, mutual polarization/interactions are much less recognized. In general, the interactions among phases, especially crystalline phases, have not been envisaged yet as a factor of crystal engineering and the electrooptical features of phase domains.

Upon the coalescence and mutual drawing behaviors, arrayed stacking of PVDF-TrFE ferroelectric lamellar crystals has been achieved, and, with activated mutual polarization, the dielectric constants of a monolayer of oriented lamellar crystal are able to be enhanced above 80 at room temperature. As the roughness of FTO substrate is tailorable upon the deposition of PMMA molecules, various degrees of coalescence and thus thickening of PVDF-TrFE lamellar crystals are achievable. Following this result, crystal surface potentials and piezoelectric responses of lamellar crystals were found critically dependent on reached lamellar thickness, exhibiting the relationship between crystal dimension and crystal polarity for the first time. Surprisingly, simply with the spread of P3HT-wrapped MoS2 or graphene quantum dots on PVDF-TrFE ferroelectric lamellar crystals, the piezoelectricity of stacked ferroelectric polymer crystals has been dramatically enhanced. These results have been viewed to unveil mutual interactions between the ferroelectric lamellar crystals and deposited 2D materials. Furthermore, depending on reached crystal polarity/surface potentials of underneath ferroelectric polymer crystals, the capability of P3HT-wrapped MoS2 in catalyzing hydrogen evolution upon water splitting under the irradiation of visible light is able to be activated and enhanced. The mutual polarization between dispersed ZnO nanorods crystals and nearby polymer ferroelectric lamellar crystals has been identified also, which causes one order of magnitude increases of piezoelectric responses, and dielectric constants of hybrid thin films. The antiparallel interactions of crystal dipole have been realized able to serve as a new type of phase interactions, which gradually decay with the increase of separation distance between interacting crystals.

The impacts of phase evolution and dispersion on phase interactions have been investigated in this research, which are expected to indicate a new direction for the preparation of hybrid crystalline materials capable to overcome the current bottlenecks of materials applications.

10:20am **TS1-3-TuM-8 Systematic Investigation of the Piezocatalysis–Adsorption Duality of Polymorphic Mos_2 Nanoflowers***,* ***Hsun Yen Lin,*** National Tsing Hua University, Taiwan

This study theoretically and experimentally investigates the piezocatalytic and adsorption effects of different phases of polymorphic MoS_2 NFs. To verify whether the polymorphic MoS_2 NFs would exhibit adsorption or piezocatalytic effects, the electrostatic surface charge of these NFs and the RhB solution is varied using sodium hydroxide and nitric acid solutions. The cationic dye is adsorbed on the surfaces of the 1T MoS_2 NFs; however, the few-layer 2H MoS_2 NFs generate a considerable quantity of hydroxyl species for degrading RhB molecules through the mechanical-force-induces piezopotential. This study discovers that the polymorphicMoS_2 NFs exhibit a piezocatalysis–adsorption duality.

10:40am **TS1-3-TuM-9 Improving Urea Oxidation Reaction Performance by Enhancing Gas Releasing***,* ***Ming Feng Tsai****, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Urea electrolysis, or urea oxidation reaction (UOR) on nickel is considered to be one of the high overpotential routes for water splitting. However, the rate determining step (RDS) during the reaction is related to the release of gas molecule from the active site. In this study, we aim to directly release the creamy gas at the anode via investigating a group of metal organic framework (MOF) electrocatalysts based on nickel.We demonstrate an Ni-based MOF electrocatalyst having a current density of 1 $A\cdot cm^{-2}$ at 1.48 eV (vs. RHE), which is comparable to that of the commonly used noble metal catalyst like Rh and Pt. A mechanism is proposed to explain the excellent performance of the Ni-based MOF electrocatalyst.

Exhibitors Keynote Lecture
Room Town & Country A - Session EX-TuM

Exhibition Keynote Lecture
Moderator: Dr. Samir Aouadi, University of North Texas, USA

11:00am **EX-TuM-1 Future Requirements for Advanced Surface Modification and Coatings Technologies for Turbine Engine Applications***, **David Furrer**,* Pratt and Whitney, USA **INVITED**

Evolution of engineered product designs and associated system requirements have given rise to increased challenges for materials and components. These challenges are in part being overcome through the development and application of surface related technologies. Surfaces are critical features that drive the ultimate behavior, capabilities and value of highly engineered components and systems. Surfaces provide for a means of protection for structural materials from extreme environmental conditions, such as elevated temperatures, corrosive and reactive materials, interfacial contact and loading, and erosion and wear. Turbine engine designs are continuing to evolve to meet the need for ever increasing energy efficiency and reduced environmental impact. Traditional efforts of increasing turbine engine efficiency are aimed at increased core temperatures and increased thermodynamic efficiency. Architecture changes for future turbine engines are bringing new challenges from the introduction of new thermodynamic cycles, hybrid energy systems and alternate fuels. These system-level design changes are increasing the need to advance surfaces to mitigate these new challenges and to support required component durability. A review of potential future system design changes and their potential impact on various materials and components will be reviewed. The requirements for advanced surface modification and coating technologies will be discussed in terms of future product-level requirements. In addition to the requirements for the surface modification or coating of components, the requirements for the manufacturing processes also need to be considered as we embrace and implement Industry-4.0 technologies.

Coatings for Use at High Temperatures
Room Pacific E - Session A2-1-TuA

Thermal and Environmental Barrier Coatings I

Moderators: Dr. Sabine Faulhaber, University of California, San Diego, USA, **Dr. Kang N. Lee**, NASA Glenn Research Center, USA

1:40pm **A2-1-TuA-1 Influence of Microstructure on Phase Transformation of Plasma Sprayed YSZ Coatings Under Thermal Gradient Cycling Conditions***, **Simon Schöler**, D. Mack, Y. Sohn,* Forschungszentrum Juelich GmbH, Germany*; M. Rudolphi,* DECHEMA, Germany*; M. Adam,* TU Darmstadt, Germany*; R. Vassen, O. Guillon,* Forschungszentrum Juelich GmbH, Germany

The efficiency of gas turbines depends to a large extent on the gas inlet temperature. Thus, increasing the temperature capability of thermal barrier coatings (TBCs) represents a major scientific challenge, especially since segregation of yttria occurs in the t' phase of yttria partially-stabilized zirconia (8YSZ) at temperatures above 1250 °C in conventional use. For a more precise understanding of resulting critical phase transformations from tetragonal into the monocline phase, gradient tests were carried out on burner rigs in the present paper. The influence of different microstructures of YSZ TBCs on phase transformations at constant cooling rates in the range of 1-10 K/s from aging temperatures as high as 1600 °C were examined for two layer systems.

A porous YSZ layer was sprayed with high deposition efficiency using atmospheric plasma spraying (APS). A second layer system consisted of a porous APS-sprayed YSZ intermediate layer and a columnar YSZ topcoat, which was applied using suspension plasma spraying (SPS). Both systems were sprayed onto In738 substrates with bond coat. Due to the low corrosion resistance of the substrate at temperatures above 1300 °C, the TBC systems were tested in free-standing conditions in order to study in phase composition prior and after thermo-cyclic exposure at the high temperatures in comparison to former experiments conducted on substrate. For this purpose, the sprayed layers were detached from the bond coat using the method of electrochemical detachment and laser cut to the required sample geometry. The microstructures and phase composition of the free-standing specimen were characterized in the as-sprayed conditions and after the cycling tests using high-resolution scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2:00pm **A2-1-TuA-2 A New Method to Diagnose Early Stages of CMAS Infiltration in Thermal Barrier Coatings***, **Vladimir Pankov**, K. Chen, P. Patnaik,* National Research Council of Canada

Siliceous particles such as dust, sand, volcanic ash, and runway debris represent a serious threat to hot section components coated with thermal barrier coatings (TBCs) in modern gas turbine engines operating at elevated temperatures. Due to a high content of calcium magnesium alumino-silicates (CMAS), these particles melt, adhere to the coating and infiltrate its open voids causing various modes of degradation. TBCs fabricated by electron beam physical vapor deposition (EB-PVD) are especially vulnerable to CMAS infiltration because of their columnar structure and open porosity. In this work a new non-destructive method has been proposed for detecting early stages of CMAS infiltration in TBCs and loss of their thermal stress tolerance. The method is based on analyzing the evolution of in-plane stresses in CMAS-infiltrated TBCs as a function of temperature using the $\sin^2\psi$ technique. The method was implemented in a modified industrial X-ray stress analysis facility. The TBCs with the composition of ZrO_2+7wt%Y_2O_3 were deposited on Hastelloy X substrates by EB-PVD and then infiltrated by volcanic ash from Mount Mazama. The TBC infiltration process was analyzed by weighting, scanning electron microscopy, and energy dispersive spectroscopy. The acquired experimental data demonstrated that visually undetectable amounts of CMAS result is a severe loss of thermal stress tolerance in EB-PVD TBCs while can be easily detected by the developed method. A model was proposed to explain the observed evolution of in-plane thermal stresses in TBCs infiltrated with different amounts of volcanic ash.

2:20pm **A2-1-TuA-3 Mechanical Behavior of a Nial Coating: Effect of Thermal Aging on the Brittle-to-Ductile Transition Temperature***, **Capucine Billard**, V. Maurel,* Mines ParisTech, PSL Research University, France*; D. Texier,* Institut Clement Ader (ICA), France*; D. Marquie,* Safran Aircraft Engines, France*; N. Bourhila,* Safran aircraft engines, France*; L. Marcin,* Safran aicraft engines, France

Nickel-based superalloys are high performance materials used for turbines blades. Due to the long duration of use of these structures and the complex thermomechanical load during a cycle of operations, a coating with an adequate resistance to corrosion and oxidation is essential. The material studied is a polycrystal nickel-based superalloy coated with an aluminure (NiAl) designs as a local aluminum reservoir to form a protective alumina film. NiAl coatings exhibit a brittle behavior up to 650-750°C. This brittle-to-ductile transition makes it sensitive to cracking during service, especially at low temperatures. Such cracking in the coating can lead to premature failure of the coated blade, then propagating under cyclic thermomechanical loading.

The objective is to link the microstructure specificities, with respect to the material's thermal history, to the mechanical response of the coating in temperature. Thermal treatment up to 1100°C, leads to progressively transform β-NiAl phase in γ'-Ni_3Al with the decrease of the Al content in the coating coupled with the diffusion of Ni from the substrate. It has been reported in NiPtAl coatings that thermal aging delayed the apparition of the first crack. This improvement in the ductility, observed at room temperature, is attributed to the γ' phase formation in aged specimens. From these results, our aim is to better understand how the brittle-to-ductile transition occurred in NiAl coatings and how thermal aging will impact it. The experimental approach is twofold. First, to study the crack onset, tensile tests have been carried out on dedicated specimens up to 900°C. The same protocol has been applied on thermal-aged specimens. Several thermal treatments conditions have been explored. As for NiPtAl coatings, results show a gain in ductility at room temperature. To assess the aging impact in the vicinity of the brittle-to-ductile transition temperature, attention has been paid on short time treatments. Mechanical results coupled with a detailed microstructure characterization from post-mortem materials will be presented. Then, micromechanical tests have been carried out using ultrathin bond-coating specimens, after thermal treatment or not. Indeed, due to the thickness of the coating, the direct thermomechanical measurement properties of the coating is not trivial. Assessing local properties within the gradient of microstructure may be useful for the understanding the effect of thermal treatment.

The presentation will compare the experimental results from these two campaigns to discuss the effect of thermal aging on the thermomechanical behavior of NiAl coating.

2:40pm **A2-1-TuA-4 Failure Mechanisms of Conventional Thermal Barrier Coatings and Development of Alternate Coating Systems for IGT Applications***, **Prabhakar Mohan**, B. Cottom,* Solar Turbines Inc., USA **INVITED**

Actively-cooled hot section components of industrial gas turbine (IGT) engines such as combustor liners, turbine blades and turbine stationary vanes continue to benefit from use of thermal barrier coatings (TBC). Zirconia stabilized with 7-8 wt.% yttria (YSZ) topcoat applied with an alumina-forming metallic bond coat system has been the TBC system of choice for many decades. An overview of successful long-term field experience of YSZ TBC from IGT components will be presented. In addition, life-limiting coating failure mechanisms documented for YSZ TBC applied by air plasma spray (APS) and electron beam physical vapor deposition (EBPVD) will be presented using field experience of stationary and rotating engine components such as combustor liners and turbine blades, respectively. Emphasis will be given to environmental degradation mechanisms of TBC by corrosive combustion byproducts as well as air-ingested CMAS-like deposits (calcium magnesium aluminosilicate sand). An overview of alternate TBC systems explored for lower thermal conductivity, higher temperature capability and / or enhanced thermal cyclic durability than conventional TBC will also be presented. Yttrium Aluminum Garnet (YAG) TBC applied by solution precursor plasma spray (SPPS) process demonstrated higher temperature capability and lower conductivity than APS YSZ TBC. In the case of EBPVD TBC, minor addition of a reactive element such as hafnium to platinum-modified diffusion aluminide bond coat demonstrated significant improvement in thermal cyclic durability of TBC when compared with baseline TBC bond coat. Ongoing coating testing and development efforts are targeted towards identifying promising lower conductivity (low-k) TBC systems for higher firing temperature applications.

4:00pm **A2-1-TuA-8 Manufacturing and Performance of a Three-Layer Environmental Barrier Coating System for SiC/SiC CMCs by Magnetron Sputtering***, **Ronja Anton**, V. Leisner, U. Schulz,* German Aerospace Center (DLR), Germany

When implemented in an aero-engine, SiC/SiC CMCs require environmental barrier coating (EBC) systems in order to withstand the atmospheric conditions. Physical vapour deposition processes enabled advanced design concepts of the EBC systems since its advantages lie within the precise control over microstructure and chemistry. A favourable EBC system consists of an Si-based bond coat followed by a rare earth, Y or Yb, disilicate as intermediate layer and finalised by a rare earth, Y or Yb, monosilicate top layer which protects the component against water vapour attack.

The EBC systems presented in this talk were manufactured by using magnetron sputtering for the bond coat and reactive magnetron sputtering for the intermediate and top layer. The X-ray amorphous coating system underwent a subsequent crystallization treatment. The macroscopic homogenous surface as well as local defaults like buckling or spallation of the silicate layers was defined during the crystallization process. Afterwards, the three layered EBC system was tested under cyclic oxidation at 1200 °C up to 1000 cycles where no major macroscopic changes appeared to the EBC system. For comparison, an uncoated SiC substrate and a SiC substrate with the bond coat as single layer were tested as well. The microscopic development in terms of phase stability, layer density and interface reactions were examined by SEM, XRD and TEM at different cycle numbers. While the bond coat and the disilicate remained hermetic dense, the monosilicate forms horizontal pores which agglomerated during long term testing. The disilicate and monosilicate remained phase stable while the bond coat started to form a SiO_2-based TGO layer on top. The oxidation kinetics of the bond coat within the EBC system was compared to the single layer bond coat during the thermocyclic testing. The behaviour of the EBC system in water vapour was investigated first as short-term experiment under aggressive conditions in 100 % water vapour steam with a gas velocity of about 10^{-1} m/s and secondly for a longer duration in about 30 % water vapour steam with a gas velocity of about 10^{-2} m/s at 1200 °C. The degradation behaviour was analysed and correlated to chemistry and morphology of the PVD coatings.

4:20pm **A2-1-TuA-9 EBC Multi-Layer Coatings on SiC-CMC Substrates Synthesized in a Continuous Vacuum Deposition Process***, **Xavier Maeder**, D. Casari,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; D. Chen,* Oerlikon Metco (US) Inc., USA*; K. Glaentz,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; H. Schoech, B. Widrig, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

The mechanical stability at high temperatures of Ceramic Matrix Composites (CMC) material based on SiC compounds in combination with low density is the key concept to replace the Ni-based superalloys utilized in today's aircraft engines. However, the surfaces of these materials react with high pressure water vapour at high temperatures and volcanic ash (CMAS) and show instability due to volatilization, oxidation and diffusion. We present the capabilities of using a combined PVD-CVD technology in a continuous vacuum process to produce Environmental Barrier Coatings (EBC) to stabilize the surface of the CMC against chemical erosion processes and structural degradation. The approach for the coating design is based on a combination of adhesion layer and a chemical barrier dedicated for the CMC for the conditions of application in the turbine. Results for Si bond coat and Yb2Si2O7 barrier coating will be presented, with tests in water vapor up to 510h at 1316°C. SEM, TEM and XRD investigations were done to fully characterize the TGO growth and the diffusion along the interfaces. In addition to Si bond coat, other thin film interfaces have been tested in annealing experiments up to 1400°C in vacuum and in water vapour at 1316°C.

4:40pm **A2-1-TuA-10 Developments of the Slag-Based Geopolymer Coatings by the Flame Spray***, **Wan-Ting Huang**, I. Huang, W. Lee, Y. Yang,* Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, TAIWAN

Geopolymer materials are an emerging environmentally friendly material, due to the easy availability of raw materials, low carbon emissions and good physical properties such as high strength, fire resistance and thermal insulation properties, corrosion resistance, durability, etc. Powder application alkalization to increase its fluidity and reactivity, resulting in a powder form suitable for flame spraying. Therefore, in this experiment, the surface modification technology of flame spraying was used to prepare geopolymer coating on the surface of 304 stainless steel substrate to improve the corrosion resistance and fire resistance of the substrate, and the geopolymer was tested by salt spray test and fire resistance test. The resistance of the coating in high temperature or corrosive environments and the ability to protect the substrate. The experimental results show that the geopolymer coating has no cracks and large-scale spalling after the salt spray test for 7 days, which proves that the geopolymer coating has corrosion resistance and protects the substrate as the coating thickness increases. the better the effect; After 30 minutes of fire damage, the geopolymer coating did not peel off or burn, and the heating curve and the highest temperature measured on the substrate surface (temperature measuring surface) were significantly lower than those without coating. The exposed substrate of the coating proves that the geopolymer coating has the effect of fire resistance and thermal insulation. Therefore, the application of geopolymers material to the protective coating of steel components has great potential for development.

5:00pm **A2-1-TuA-11 Thermal Spray Coating with Ceramic Microspheres for Acoustic Absorption Applications***, **Ting-Ya Chuang**, W. Lee, Y. Yang,* National Taipei University of Technology, Taiwan

Several studies point out that noise contributes to hearing impairment and poor mental health. With the advancement of technology, the continuously increasing noise is unbearable, and it needs to be solved. To solve the noise problem, this research uses the technique of thermal spray to prepare the polyethylene coatings with different concentrations of ceramic microspheres, which we expect to increase the noise immunity.

The results show that the noise immunity of the coatings and substrate varies at different frequencies. Ceramic microspheres in the polyethylene coatings makes structural of coating changes, and the structure, the thickness and the mass density will affect the noise immunity. This research shows that the polyethylene coating with ceramic microspheres can make the higher sound transmission loss effect than the polyethylene coating without ceramic microspheres, because ceramic microspheres change the structure of coatings.

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 toresidual 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_x 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_2O_3-based coatings for these applications deposited using plasma spray/ electrolytic oxidation. However, Al_2O_3 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 µ-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_2 gases were used to deposit SiO_x coatings at varying gas flow ratios (1:12, 1:16, 1:20), µ-powers (2 and 4kW) and coating thicknesses (3 - 10 µm) 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 (µ-power) and 1:12 (HMDSO:O_2) 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_3 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_3 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 »10^6 and a saturated field-effect mobility of 288 $cm^2 \times V^{-1} \times s^{-1}$. 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_3 films for usein 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)N_x 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)N_x films were prepared through co-sputtering with four sputter guns. The stoichiometric ratio x of (TiZrHfTa)N_x films was varied by adjusting the reactive gas ratio of f_{N2} (N_2/(N_2 + Ar)) at 0, 0.4, and 0.7. With an f_{N2} of 0, the fabricated metallic $Ti_{0.23}Zr_{0.22}Hf_{0.30}Ta_{0.25}$ 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 [$(Ti_{0.22}Zr_{0.30}Hf_{0.17}Ta_{0.31})N_{0.83}$] and N07 [$(Ti_{0.33}Zr_{0.34}Hf_{0.13}Ta_{0.20})N_{0.88}$] films were prepared whenf_{N2} 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)N_x 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.

Coatings for Biomedical and Healthcare Applications
Room Pacific D - Session D3-TuA

Biointerfaces: Coatings to Promote Cell Adhesion while Inhibiting Microbial Growth

Moderators: Dr. Valentim A.R. Barão, University of Campinas (UNICAMP), Brazil, **Dr. Sandra E. Rodil**, Universidad Nacional Autónoma de México

1:40pm **D3-TuA-1 Chemical Vapor Deposition of Tantalum for Enhanced Cell Adhesion*, Jessica DeBerardinis,*** Ultramet, USA **INVITED**

Tantalum is a refractory metal with demonstrated strength, ductility, resistance to corrosion and oxidation, and biocompatibility. It has long been used as a biomaterial for medical devices such as pacemaker electrodes, contrast media and markers, and cell growth matrices, and for decades Ultramet's open-cell tantalum foam has been used in orthopedic implants. The use of chemical vapor deposition (CVD) has enabled these biomedical applications of tantalum. Biocompatibility research has demonstrated the following:

- CVD tantalum coatings can enhance the binding of collagen and proteoglycans because of their surface roughness and tension [1,2].
- CVD tantalum has antioxidant properties, which limit the negative effects of reactive oxygen species on osteogenic differentiation [1,3].
- CVD tantalum can up-regulate integrins, which are transmembrane adhesive proteins that enhance cell adhesion and reduce apoptosis [1,4].
- In the presence of CVD tantalum, cells demonstrate enhanced proliferation and autophagy, promoting cell survival in the presence of an implant [1,5].
- Porous tantalum increases cell proliferation and enhances osseointegration in comparison with porous titanium substrates [6].

CVD allows small amounts of metallic material, such as tantalum, to be evenly applied over three-dimensional structures. CVD is not line-of-sight limited, so it can be used to uniformly coat and infiltrate extremely complex three-dimensional structures, such as Ultramet's reticulated (porous) carbon foam (Figure 1). A thin film of CVD tantalum can be applied over less expensive and/or less biocompatible materials to create a biointerface that promotes cell adhesion. Furthermore, Ultramet can modify its CVD processing to deposit tantalum such that it forms a diffusion bond, which occurs at the atomic level, so the tantalum cannot peel or delaminate from the substrate (Figure 2). Ultramet's CVD processing can also be modified to grow a textured tantalum surface (Figure 3), which has been demonstrated to affect the adhesion of human bone marrow stromal osteoprogenitor cells. Examination of the microscale topography of textured tantalum showed increased cell spreading with significant growth of actin fibers, and metabolic activity was also notably higher than with the bare substrate and untextured tantalum.

Ongoing research of textured CVD tantalum coatings at Ultramet involves modifying the texture according to tissue type and incorporating other bioactive layers. Process development continues to improve the application of CVD tantalum coatings to various medical grade substrates to create more economical orthopedic and dental implants.

2:20pm **D3-TuA-3 The Functionalization of N95 Masks Using Atomic Layer Deposited Silver Nano-Islands to Induce Antimicrobial Activity*, Harshdeep Bhatia*,** *C. Takoudis,* University of Illinois, Chicago, USA

Due to the recent COVID-19 pandemic, the demand and use for antimicrobial textiles has increased. This demand saw a similar surge in these textiles during the SARS-COV-1 outbreak, resulting in many patents, after which the use of Silver as a potential material to give a material some antibacterial/antiviral properties was popularized. Additionally, the use of disposable N95 masks has become popularized as the safest and easily available barrier against these viral outbreaks. In this study, a novel strategy to deposit nano-islands of Silver on N95 masks using ALD is developed to give it some antibacterial properties. X-ray Photoelectron Spectroscopy (XPS) and X-ray adsorption fine structure (XAFS) were used to characterize the as-deposited silver nano-islands. The size and roughness of the nano-islands was calculating using atomic force microscopy (AFM). Furthermore, inductively coupled plasma mass spectrometry (ICP-MS) was used to study the leaching of these Silver nano-islands in standard 1x phosphate buffer over predetermined times to simulate the effect of biological fluids such as saliva or mucus. A microbiological assay was also conducted to study the effect Ag- coated N95 had on *Staphylococcus Aureus*. The films grown at the two temperatures, 90 °C and 120 °C, were stable in ambient conditions. The deposited silver nano-islands were stable on the N95 filter media against washing. A comparison of the characteristics of the films grown at different temperatures has been made.The functionalization of materials using ALD of silver provides a repeatable method to impregnate textiles and induce antimicrobial activity which releases silver at a slow rate.

2:40pm **D3-TuA-4 Cold Atmospheric Plasma Jets Generated from Flexible Sources***, C. Corbella,* ***Sabine Portal****, H. Solomon, M. McCraw, M. Keidar, S. Solares,* George Washington University, USA **INVITED**

Atmospheric pressure plasma jets (APPJs) are excellent resources for a myriad of applications in energy and healthcare industries, being cancer therapy a major breakthrough. Their working principle is based on the generation of a rich plasma chemistry and photon emission in open air, which can gently modify surfaces of different materials at room temperature. APPJs originated from a flexible source are able to adapt to complex topologies and to treat delicate samples, like soft matter and organic tissues. Stable and reproducible operation of a flexible multi-jet array has been proven in sources set with planar (concave and convex modes) and radial (cylindrical source) configurations. Also, plasma plumes with different shapes have been achieved by conveniently modifying the nozzle geometry, thereby demonstrating the wide control over plasma performance. The participation of reactive oxygen and nitrogen species (RONS) in combination with energetic UV photons emitted by flexible APPJs as a function of the nozzle-sample distance are crucial aspects that need thorough characterization. Indeed, the action of these plasma species must be considered for the sake of APPJ safety in applications that require proximity of sensitive samples, especially in medical practices. Here, we demonstrate methods to estimate macroscopic parameters of relevance at the plasma-surface interaction region, namely local temperature, relative humidity (RH), pH variations, electric field (jet potential), and UV dose irradiation including shortest vacuum-UV wavelengths (VUV<100 nm). Portable platforms of flexible APPJ arrays exhibiting specific configurations and nozzle geometries will constitute the next generation of plasma devices aimed at biomedical applications.

4:00pm **D3-TuA-8 Multifunctional Coating Approach Integrating Visible-Light Driven Photodynamic Therapy and Photocatalytic Activity for Controlling Biofilm Accumulation and Reinforcing Wear Protection***,* ***Bruna Nagay***[1]*, C. Dini, R. Costa, A. Santos,* University of Campinas (UNICAMP), Brazil*; J. Cordeiro,* Centro Universitário das Faculdades Associadas de Ensino, Brazil*; B. Gomes,* University of Campinas (UNICAMP), Brazil*; E. Rangel, N. Cruz,* Sao Paulo State University, Brazil*; J. van den Beucken,* Radboud University Medical Center, Netherlands*; V. Barão,* University of Campinas (UNICAMP), Brazil

The accumulation of biofilm and further establishment of infections on implant devices is one of the major concerns in the biomedical industry and clinical management. Among current therapies, although antimicrobial photodynamic therapy (aPDT) has been considered effective, inconsistencies regarding its outstanding performance in battling the burden of growing peri-implantitis prevalence have raised concerns towards the development of novel strategies. To overcome these drawbacks, we proposed an integrated coating strategy combining visible-light-driven photocatalytic activity and aPDT to simultaneously face titanium implant infections and optimize the implant biointerface for biomedical and dental implant applications. A multifunctional bismuth (Bi)-doped TiO_2 coating was synthesized upon titanium (Ti) substrate using plasma electrolytic oxidation (PEO). Polished Ti and pure TiO_2 coating were used as controls. PEO produced a crystalline, rough coating on Ti surface with superhydrophilicity features. The incorporation of Bi into the TiO_2 matrix was confirmed by X-ray photoelectron spectroscopy. UV-vis diffuse reflectance spectroscopy revealed that Bi effectively narrowed the band gap of TiO_2, making Bi-TiO_2 promising to exhibit photocatalytic activity under visible-light irradiation, which was confirmed by the methylene blue (MB) degradation assay. In addition, because the visible light used herein has a wavelength compatible with the MB used in aPDT, we hypothesized that the combination of reactive oxygen species generated by the photocatalysis mechanism along with MB-mediated aPDT could potentiate the eradication of microorganisms. As such, in vitro experiments using human saliva as inoculum revealed that Bi-TiO_2 potentiated the polymicrobial biofilm reduction mediated by aPDT, and that 1 min of light exposure had similar antimicrobial effects when compared to 5 min. Furthermore, the Bi-TiO_2 coating was not cytotoxic to human bone mesenchymal stem cells and human gingival fibroblasts, even under light exposure. Finally, PEO coatings presented higher wear resistance, hardness, and albumin adsorption than control groups, indicating their outstanding properties to optimize the implant biointerface. The proposed proof-of-concept research holds great promise to face peri-implant infections by using a visible-light-driven photocatalytic coating and aPDT in a smart and safe manner to reduce biofilm while maintaining the propertiesthat affect the longevity of biomedical devices (e.g., wear resistance, cell-material interactions). This opens a new perspective for the development of effective antimicrobial surfaces by the implant industry.

4:20pm **D3-TuA-9 ZnO_X Nanolayers as Antimicrobial Surfaces***, L. Reyes-Carmona,* Universidad Nacional Autónoma de México*; O. Sepulveda-Robles,* Instituto Mexicano del Seguro Social, Mexico*; A. Almaguer-Flores, C. Ramos-Vilchis,* ***Sandra E. Rodil****,* Universidad Nacional Autonoma de Mexico

The regular use of disinfectants is not an ecologically friendly solution to control the transmission of viruses and bacteria, and it could promote antibacterial resistance. Antimicrobial surfaces are a plausible solution applicable to rigid and flexible surfaces, as well as to protective equipment for healthcare personnel.

In this work, we investigated the antiviral and antimicrobial properties of sputtered ZnO_X nanolayers deposited on polypropylene (PP) fabrics for their use in respiratory protection equipment. Because of the fast traveling of respiratory drops containing viruses and bacteria, our study emphasizes the effect of contact time on the antimicrobial response. Since the substrate cannot be heated, the films were substoichiometric and amorphous.

Two methods were developed to test the antimicrobial response as a function of contact time. The shortest contact time was simulated using a bactericidal/virucidal filtration system where the material was exposed to an aerosol loaded with microorganisms (bacteria and surrogate viruses). Larger contact times between 0.5 and 24 hr. for the viruses and 24 hr. for the bacteria were tested by placing a drop containing the microorganisms on the surface for the specified contacting time. After such time, the virus was recovered, and the infectivity was evaluated by counting the plaque-forming units. Colony-forming unit determination was used for the bactericidal tests to evaluate the survival of aerobic and anaerobic bacteria.

Virus viability assays were used to study the survival of PaMx54, PaMx60, PaMx61 (ssRNA, Leviviridae), and PhiX174 (ssDNA, Microviridae) as surrogates for non-enveloped viruses. An approximate 40% PFUs reduction was obtained after 12 hr. for the RNA viruses, but only 12% was achieved for the DNA virus compared to the uncoated PP. For larger contacting times, the RNA viruses were completely reduced after 12 hr. in the ZnO-coated fabric, but no reduction was observed for the DNA virus or the uncoated PP.

For the aerosols containing the anaerobic bacteria, which are typically found in the oral environment, inhibition ratios between 53-96% were obtained, depending on the strain. Similarly, for the aerobic bacteria aerosols, the inhibition was between 26 and 90%, being slightly more resistant. However, after 24 hr of direct contact between the bacteria and the ZnO-coated surface, most strains were inhibited (80-90%).

These results suggest that ZnOx nanolayers deposited by magnetron sputtering reduce the infectivity of non-enveloped RNA respiratory viruses and inhibit the growth of anaerobic and aerobic pathogen bacteria.

4:40pm **D3-TuA-10 Cytocompatibility of Chitosan-Silver Coated Titanium Coupons***, E. Coleman Montgomery,* ***J. Amber Jennings****, M. Atwill, J. Bumgardner,* University of Memphis, USA

Introduction

Titanium is commonly used in orthopedics due to its strength, resistance to corrosion, and bone-like mechanical properties. Silver ions affect microbials by blocking transport in and out of the cell, inhibiting the production of energy, and interacting with DNA to prevent replication. These characteristics lead to broad spectrum antimicrobial properties against bacteria and fungi and therefore support the advantage of silver ions as an

[1] **Graduate Student Award Finalist**

implant coating using chitosan biopolymer as a complexing agent and coating to localize silver.

Methods

Treated Coupons: Titanium coupons were polished with 400, 600, 800, and 1200 grit sandpaper before being sonicated in soapy water, acetone, and ethanol to remove oil and residue for 10 minutes each. The coupons were then soaked in 5M NaOH for 24h to allow accumulation of hydroxide reactive groups on the titanium surface and rinsed with deionized (DI) water twice. The coupons were treated with a linking agent and dried for 10 minutes in a 110°C oven. Chitosan-silver solution (Chitozan Health) was added and left to dry overnight. The coated coupons were immersed in phosphate buffer for 1 hour, rinsed with DI water, and dried fully.

Untreated Coupons: Titanium coupons were polished with 400, 600, 800, and 1200 grit sandpaper before being sonicated in soapy water, acetone, and ethanol to remove oil and residue for 10 minutes each. The uncoated coupons were rinsed with DI water and dried fully.

Cytocompatibility: Coupons were UV-sterilized for 20 minutes and washed in cell medium. Soas-2 cells were seeded at 90,000 cells/well in a 12-well plate before exposure to 3 test groups: treated coupons, untreated coupons, and tissue culture plastic (TCP) control. After 24 hours, cell viability was determined using CellTiter-Glo Viability Assay (n=3), and cell morphology was determined using Live/Dead staining (n=1).

Results

The Saos-2 cell viability for treated coupons was not statistically different than untreated coupons and was about 70 percent of the TCP control. Live/Dead staining also produced similar results, with mostly living cells in all groups.

5:00pm **D3-TuA-11 Nonsurgical Decontamination Protocols for 3D-Printed Implant Surfaces***, **Valentim Barão**, R. Costa, T. Takeda, C. Dini,* University of Campinas (UNICAMP), Brazil*; M. Bertolini,* University of Pittsburgh, USA*; M. Feres, J. Shibli, J. Souza,* Guarulhos University, Brazil

There is still a lack of a predictable nonsurgical protocol for effective dental implant decontamination, including for 3D-printed surfaces. Therefore, this study aimed to scrutinize the deleterious effects of different mechanical and chemical decontamination treatments on titanium (Ti) surface, electrochemical properties, biofilm cleaning potential, and cell behavior. 3D-printed Ti discs obtained by direct metal laser sintering were used. These samples were coated with polymicrobial biofilm from human saliva *in vitro*. Biofilm-covered surfaces were decontaminated with mechanical [Ti curette, plastic curette, Ti brush, water-air jet device, and Er:YAG laser] and chemical [amoxicillin; minocycline; tetracycline; H_2O_2 3%; chlorhexidine 0.2%; NaOCl 0.95%; and hydro-carbon-oxo-borate-based formula antiseptic] protocols isolated. Negative control using 0.9% NaCl was adopted and PVPI 0.2% as a biofilm matrix-degrading agent applied before all chemical protocols. Surface deterioration and corrosion were analyzed before and after mechanical instrumentation as well as fibroblast adhesion on these degraded surfaces. The best *in vitro*mechanical/chemical protocol was tested in combination using *in situ* biofilm model. Er:YAG laser treatment displayed optimum surface cleaning by biofilm removal with minimal deleterious changes on the surface, smaller Ti release, anti-corrosion performance, and improved cell spreading. NaOCl 0.95% was the most effective chemical agent to reduce *in vitro* and *in situ*biofilms when applied isolated and more prominent results when associated with PVPI as pre-treatment to disrupt biofilm matrix. The combination of mechanical and chemical treatments promoted an optimum mechanical cleaning ability with biofilm matrix disruption and killing remnants *in situ* biofilms (~99% biofilm eradication). We conclude that Er:YAG laser + PVPI 0.2% + NaOCl 0.95% is considered an optimized decontamination protocol by demonstrating a potential to eliminate *in vitro* and *in situ*biofilms with minimum deleterious effects on 3D-printed Ti surfaces, opening new perspectives to improve implant-related infection therapies.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room Town & Country B - Session E1-1-TuA

Friction, Wear, Lubrication Effects, and Modeling I

Moderators: Noora Manninen, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Prof. Dr. Andreas Rosenkranz**, Universidad de Chile, **Dr. Manel Rodriguez Ripoll**, AC2T Research GmbH, Austria

1:40pm **E1-1-TuA-1 Chemistry and Mechanical Properties of 2D Transition Metal Carbides and Carbonitrides (MXenes)***, **Vadym Mochalin**,* University of Missouri S&T, USA **INVITED**

A large family of two-dimensional transition metal carbides and nitrides (MXenes) raises interest for many applications due to their high electrical conductivity, mechanical properties [1], potentially tunable electronic structure [2], nonlinear optical properties [3], and the ability to be manufactured in the thin film state [4]. However, their chemistry that is key to development of these applications, still remains poorly understood [5-8]. In this presentation we will discuss recent progress in understanding fundamental MXene chemistry and harnessing it for suppressing unwanted reactions and prolonging stability of these materials.

Mechanical properties of MXenes, including their adhesion to other materials, 2D materials, and other MXenes will be discussed. Adhesion plays an important role in assembly of 2D heterostructures. Data on tribological properties of MXenes, including superlubricity, will also be presented and discussed.

Selected examples illustrating connections between MXene chemistry and their mechanical properties will also be considered.

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2:20pm **E1-1-TuA-3 Tribocorrosion Behaviours of VNbMoTaWCr High Entropy Alloy Coatings***, **Ismail Rahmadtulloh**, C. Wang, W. Wang,* National Taiwan University of Science and Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Recently, tribocorrosion has become an interesting research topic for academic researchers and industries. The deep understanding of tribocorrosion behaviour has become important in development of alloys having good wear resistance and corrosion protection. In this work, four VNbMoTaWCr high entropy alloy (HEA) coatings with different Cr contents were fabricated by a pulsed DC magnetron sputtering system. For tribocorrosion tests, the HEA coatings were immersed in a 3.5 wt.% NaCl aqueous solution at room temperature under 1 N load using a pin-on-disk tribometer. The potentiodynamic polarization tests were performed to investigate the corrosion potential, corrosion current density, and polarization resistance for each coating before and during the tribocorrosion test. The effect of Cr concentrations on the tribocorrosion behaviours of four VNbMoTaWCr HEA coatings was explored. The synergism between wear and corrosion was studied based on ASTM G119 standard. The change of corrosion loss due to wear and the change of wear loss due to corrosion were calculated. The total material loss rate and corrosion-wear map were explored to understand the extent of the wear and corrosion augmentation factors. We can find out that the VNbMoTaWCr coating with 11.7 at.% Cr content had the lowest total material loss rate of 9.2162 mm/yr, which is better than that of 304SS, 18.0009 mm/yr. It showed that the transitions between wear and corrosion for four VNbMoTaWCr coatings and 304SS were all lower than 0.1

indicating synergistic effects dominated and corrosion was affecting wear to a great extent than wear was affecting corrosion.

2:40pm **E1-1-TuA-4 Fundamentals of Phototribology**, *B. Perotti,* UCS, Brazil; *A. Cammarata,* Czech Technical University in Prague, Czech Republic; *F. Cemin,* Nantes Université, France; *S. Sales de Mello,* Université Grenoble Alpes, CNRS, France; *L. Leidens,* UCS, Brazil; *F. Echeverrigaray,* UNICAMP, Brazil; *T. Minea,* Université Paris-Saclay, France; *F. Alvarez,* UNICAMP, Brazil; *A. Michels,* UCS, Brazil; *T. Polcar,* University of Southampton, UK; ***Carlos Figueroa,*** UCS, Brazil

Friction phenomenon is a ubiquitous manifestation of nature originated in the dissipation of energy after stochastic interactions of particles from two surfaces. There are several ways to set up the friction behavior of tribological systems by means of surface finishing, liquids and gases, all of them nonreversible processes. Thus, the active control of friction through external sources is a challenge in tribology. Electric and magnetic fields were proposed to control friction remotely. It is a new paradigm in tribology where radiation fields can tune friction. In our case, we used a photoactive material (TiO_2) to active control of friction forces at the nanoscale as a function of the presence or absence of UV illumination (λ = 365 nm and variable luminous flux) by friction force microscopy (FFM). We could determine that the light can tune friction forces in a reversible, stable, reproducible and reliable way. The UV light induces surface rearrangements of atoms in a similar way of those processes for degradation of organic molecules on activated TiO_2 surfaces. Indeed, the half-life of the pseudo-first order kinetics is roughly the same of those well stablished degradation processes of organic molecules in aqueous suspension with TiO_2 particles. Moreover, the reduction of friction under UV illumination follows a sigmoidal behavior with the luminous flux. These findings contribute to a new conceptual framework in tribology where light may be defined as a fourth body and the integration of tribology with photonics and optoelectronics providing a promising direction for applications in micro- and nano-opto-electromechanical systems.

3:00pm **E1-1-TuA-5 Ultra-thin nanotwinned (CoCrNi)$_{100-x}$ W$_x$ Medium Entropy Alloy Film: Role of Nanotwin in Mechanical and Tribology Behaviors**, ***Jhen-De You,*** National Taiwan University, Taiwan; *P. Yiu,* Ming Chi University of Technology, Taiwan; *C. Hsueh,* National Taiwan University, Taiwan

A significant amount of materials are lost each year as a result of wear-induced damages. Meanwhile, small-scale medium entropy alloy films (MEAFs) have attracted much attention recently due to their superior mechanical properties over their bulk counterparts. In this work, we aim to investigate the plastic deformation characteristics (hardness, strain rate sensitivity and tribology) and structure evolution of nanotwinned (CoCrNi)$_{100-x}$W$_x$ (x = 0, 0.9, 3, 5.3, 7.2 and 9.8) MEAFs. The (CoCrNi)$_{100-x}$W$_x$ MEAFs were fabricated using magnetron co-sputtering. The tungsten content increased from 0 to 22.01 at.% with the increasing power applied on the W target. Microstructures of thin films thus prepared were examined by the atomic force microscope, scanning electron microscope and transmission electron microscope. The structure evolution and mechanical properties were investigated in this work. The W addition in CoCrNi matrix resulted in transition from FCC solid solution to amorphous structure. Nanotwins were observed in FCC grains for x≤9.8, and the W$_{7.2}$ MEAF showed the thinnest twin thickness of ~1 nm, the superior wear-resistance and hardness, and the lower coefficient of friction via nano-scratch, nano-wear and nano-indentation tests. Although the amorphous W$_{22.01}$ MEAF showed the higher hardness than W$_{7.2}$, its wear resistance was inferior to crystalline W$_{7.2}$ MEAF. Our work demonstrated the structure evolution, mechanical properties, and wear performance of (CoCrNi)$_{100-x}$W$_x$ MEAFs, also gave insight of wear-mechanism in nanotwinned CoCrNi-based system.

4:00pm **E1-1-TuA-8 Understanding the Tribology Behavior of Carbon Thin Films Deposited by the HiPIMS Technique in Ar+Ne Atmospheres**, ***Cesar D. Rivera Tello,*** Universidad de Guadalajara CUCEI, Departamento de Ingeniería mecánica eléctrica, Mexico; *L. Flores Cova, A. Guerrero de León, J. Pérez Alvarez, M. Flores Martínez,* Universidad de Guadalajara CUCEI, Mexico

This investigation focusses in the effects of using Ne + Ar mixture in the plasma of the HiPIMS discharges in the deposition process of diamond like carbon thin films and in the tribological tests. The plasma deposition process was analyzed by mass quadrupole spectroscopy obtaining the ion energy distribution for C^+ ions from different gas composition discharges (20, 40, 60, 80, 90 and 100% Ne). Derived from these processes, a carbon thin film was obtained for each gas composition discharge, where the bond-structures of them were analyzed by Raman spectroscopy. The tribology behavior of all the samples was studied by friction coefficients and analyzing the images of the wear track obtained by reciprocating ball-on-plate configuration of the tribological tests. Furthermore, these Ne +Ar mixture thin film were compared to similar films without Ne to observe mainly differences. The results showed slight increment on the ionization with the %Ne gas composition discharge. Besides, a significant reduction of wear in comparison to the films without Ne was shown, derived from lower sp^3 content in the carbon films in comparison to the carbon films without Ne. Finally, we observe a significant increment on the deposition rate for the films deposited with Ne.

4:20pm **E1-1-TuA-9 Effect of Sizing on the Adhesion Properties of Reclaimed Fiberglass Composites**, ***Nour Halawani,*** Composite Recycling and LPAC - EPFL, Switzerland; *M. Anderson, P. Gallo, G. Perben,* Composite Recycling, Switzerland; *V. Michaud,* LPAC - EPFL, Switzerland

Recycling Glass Fiber Reinforced Plastics has been a challenge for decades. Currently, the most common solution for composite disposal is landfilling, which is the case for more than 90% of GFRP disposal worldwide. We have developed a thermal treatment based on pyrolysis which separates the fibers from the resin without the need for grinding or chopping the feedstock. The reclaimed fibers are then treated and integrated into new composites. To ensure a clean surface free from carbon impurities, the fibers are treated with a thermal cleaning method. After this process the resin, sizing, and the binder are removed from the surface and thus the surface still has impurities at the microscale which requires further treatment. The treatment of fibers requires additional cleaning, surface activation to increase the density of hydroxyl groups (-OH) on the fiber surface, and sizing application.

Sizing formulations are applied in a thin homogenous coating on fiberglass in the commercial production step. The main reason is to protect the fiber surface during the production and post processing steps while creating different kind of fabrics. Additionally, the sizing is adapted to ensure good adhesion between the fibers and the matrix. In this work we aim to use the reclaimed fibers to produce new composites maximizing the mechanical properties in comparison with the initial composite, while keeping the treatment as minimal and benign as possible. We also aim to valorize the reclaimed fiberglass without losing their length.

For the sizing treatment, we apply two different kinds of sizing based on alkoxysilanes on fiber surfaces in order to study their effect on the adhesion as well as the final mechanical property of the obtained composite. A special combination of surface cleaning, surface activation and sizing application are applied and controlled using SEM and FTIR. The surface of the fibers are seen to be clean homogenously. The flexural strength of the composite made up of untreated reclaimed fibers showed a decrease of 60 % whereas, when applying our surface treatment, we can see an improvement with a decrease of only 5 to 25% depending on the process and the sizing used. The adhesion of the treated fibers to the matrix is controlled using single fiber pull-off test validating our treatment procedure.

4:40pm **E1-1-TuA-10 The Effect of Core Crystallographic Orientation on the Dislocation Dynamics of Core-Shell Nanostructures: A Molecular Dynamics Study**, ***Robert Fleming***, Arkansas State University, USA

Core-shell nanostructures, composed of a metallic core with a hard amorphous shell, are known to exhibit unusual dislocation dynamics which subjected to compression loading. Experimentally, this behavior manifests as substantial deformation recovery beyond the elastic limit, enhanced fatigue resistance, and improved durability. However, the fundamental physical mechanisms that enable the underlying dislocation dynamics in these nanostructures are still poorly understood. In this study, the role of crystallographic orientation of the confined metallic core is investigated for 2 FCC metals (Al, Cu) and 1 HCP metal (Mg), all with a-Si shells. Along with supporting stress calculations, understanding the interplay between crystallographic orientation, active slip systems, and core-shell interface structures will provide insights into the unique mechanical behavior of these nanostructures, with an ultimate goal to design material systems with controllable dislocation dynamics.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F3-TuA

2D Materials: Synthesis, Characterization, and Applications

Moderators: Prof. Ying-Hao Chu, National Tsing Hua University, Taiwan , **Prof. Chih-Yen Chen**, National Sun Yat-sen University, Taiwan , **Dr. Yi-Cheng Chen**, National Tsing Hua University, Taiwan

1:40pm **F3-TuA-1 Tellurene Electronics and Sensors*, Wenzhuo Wu,*** Purdue University, USA **INVITED**

Emerging technologies such as distributed computing and the internet of things (IoT) necessitate the implementation of high-speed, energy-efficient devices. Various technological paths are being actively pursued to synthesize and integrate high-performance channel materials for these applications. Specifically, 2D semiconductors have been intensely explored as promising channel materials for related ultra-scaled technologies. However, there has been a lack of synthetic strategies for the scalable, substrate-agnostic production of large-area, high-quality 2D crystals with a low thermal budget for back-end-of-line (BEOL) compatible applications. In this talk, I will discuss our recent progress in the scalable nanomanufacturing of tellurene, an emerging 2D multifunctional material pioneered by my group, for high-performance nanoelectronics and optoelectronics applications. Our results show that the air-stable tellurene exhibits a plethora of intriguing properties appealing for applications in electronics, optoelectronics, energy, sensors, and quantum devices.

2:20pm **F3-TuA-3 Phase/Structure-Engineered Two-Dimensional Layered Materials for Innovative Nanoelectronics*, Yu-Lun Chueh,*** National Tsing Hua University, Taiwan **INVITED**

Novel condensed matter systems can be understood as new compositions of elements or old materials in new forms. According to the definition, various new condensed matter systems have been developed or are under development in recent years. 2D layered materials, including graphene and transition metal dichalcogenides (TMDs) allow the scaling down to atomically thin thicknesses and possess unique physical properties under dimensionality confinement. The chemical vapor deposition (CVD) process is the most popular approach for all kinds of 2D materials due to its high yield and quality. Nevertheless, the need for high temperature and the relatively long process time within each cycle hinders commercial development in terms of production cost. However, the transfer procedure has become one of the major limitations of the overall performance. In my talk,an inductively coupled plasma (ICP) was used to synthesize Transition Metal Dichalcogenides (TMDs) through a plasma-assisted selenization process of metal oxide (MO_x) at a low temperature. Compared to other CVD processes, ICP facilitates the decomposition of the precursors at lower temperatures.We create the phase/structure-engineered-1T/2H 3D-hierarchical 2D materials derived from the MOx 3D-hierarchical nanostructures through a low-temperature plasma-assisted selenization process with controlled shapes grown by a glancing angle deposition system (GLAD). The applications, including (1) water splitting, (2) gas sensors, (3) batteries, and (4) resistive change memory, will be reported.

3:00pm **F3-TuA-5 Tellurene-Based Wearable Biosensor for Real-Time Longitudinal Monitoring of Neurotransmitters in Human Sweat*, Ruifang Zhang***, *W. Wu,* Purdue University, USA

Metabolic biomarkers provide direct indicators of physical and mental health status. However, the state-of-the-art tools for monitoring metabolites in body fluids are expensive, time-consuming, and often require invasive procedures to collect the samples. Non-invasive wearable sensors for monitoring metabolites in sweat, the most accessible human secretion, are promising alternatives to costly diagnostic tools. Moreover, existing wearable sensors have limited sensitivity, selectivity, and lifetime for measuring disease-specific metabolic markers (e.g., neurotransmitters) from human sweat. Wearable sweat sensors that can monitor the dynamics of neurotransmitters directly from human sweat have yet to be developed. Here, the applicant reports a wearable biosensor based on tellurene that can enable, for the first time, the selective and sensitive longitudinal quantification of dopamine (DA) and norepinephrine (NE) concentrations in real human sweat. The applicant also evaluated and validated the concentrations of neurotransmitters in human sweat using high-performance liquid chromatography/mass spectrometry (HPLC/MS) for the first time. This research could create unprecedented diagnostic tools for improving the experience and outcomes of patient care. The development of non-invasive wearable sensors capable of longitudinal measurement of disease-specific metabolic markers from sweat will positively impact erroneous or delayed diagnoses, enable affordable and ubiquitous diagnostic tools, and foster data-driven precise mobile health monitoring with translational applications in patient care and beyond.

4:00pm **F3-TuA-8 A Two-Dimensional $Ti_3C_2T_x$ MXene/Mesochannel Ionic Diode Membrane for High-Performance Osmotic Energy Harvesting*, Wen-Hsin Hung,*** National Taiwan University of Science and Technology, Taiwan*; C. Chu,* Feng Chia University, Taiwan*; L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Osmotic energy has attracted explosive attention in recent year because of its advantages of clean and sustainable. Osmotic energy can be harvested via the reverse electrodialysis technique and it can convert chemical potential stored in an ionic concentration gradient into an electrical energy by using an ion-selective membrane. The osmotic power generation, however, is still restrained due to the inherently limited ion flux in such a small nanochannel. Here, we report a subnano-on-meso architecture (named as MXene@MC), realized by deposition of an ultrathin layer of two-dimensional $Ti_3C_2T_x$ MXene on a single conical PET mesochannel (MC) (Fig. 1). The introduction of the asymmetries in pore geometry gives the MXene@MC outstanding ion current rectification property, which can amplify ionic current at a degree of up to 25.6 times (Fig. 2). We therefore probe the application of the subnano-on-meso ionic diode device in osmotic energy harvesting. The results show that a single MXene@MC can achieve a record osmotic power as high as 343 pW at a 1000-fold KCl gradient, exceeding all the state-of-the-art single-pore devices (Fig. 3).We expect that this study can provide an emerging platform towards high-performance osmotic energy generator.

4:20pm **F3-TuA-9 Discussion on the Growth Parameters and Oxygen Evolution Reaction Performance of Copper Sulfide*, Li-Wen Lin***, *C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

With the advancement of science and technology, energy demand is increasing day by day. People began to look for alternative energy sources in order to solve the problem of insufficient energy. Hydrogen fuel cells have become one of the most notable research projects because of their environmentally friendly and renewable characteristics. One of the cleanest ways to generate hydrogen is through electrochemical water splitting, which can be divided into two parts: Hydrogen evolution reaction (HER) at cathode and oxygen evolution reaction (OER) at anode. Among them, OER is known to be more complicated and thus became the biggest hinder to water splitting.

In this work, Cu_2S microplates were successfully synthesized with non-toxic chemicals via a one-step solvothermal method. The as-prepared samples were then applied as working electrodes for OER electrochemical measurements. The results turned out that the as-prepared Cu_2S/CF electrodes have excellent OER performances with a low overpotential of 269.2 mV (at a current density of 10 mA cm^{-2}) and a Tafel slope of 102.1 mV dec^{-1}. These outstanding results indicated that Cu_2S microplates could be developed as excellent OER electrocatalysts.

4:40pm **F3-TuA-10 Cation and Anion Co-Doped Iron Oxide Toward Efficient Hydrogen Peroxide Formation and Electro-Fenton Degradation of Organic Pollutant*, Yemima Purba***, *J. Ting,* National Cheng Kung University (NCKU) Tainan, Taiwan

Nowadays, electrochemical advanced oxidation processes, Fenton process, have attracted a lot of attention as compared to conventional degradation. Regarding the Fenton catalyst, iron oxide has been known as an efficient catalyst and demonstrated in degradation of organic pollutants. The metal doping into iron oxides has been shown to enhance the degradation rate due to rich redox reactions. However, there are only a few studies on the anion doping. It is known that anion doping is able to enhance the electrical conductivity of the oxide. In this study, novel cation and anion co-doped iron oxide has been firstly demonstrated for electron-Fenton catalyst. The synergistic effect of cation and anion doping is favorable to improve the selectivity of hydrogen peroxide, which thus can be utilized for electro-Fenton degradation of organic pollutants. The electro-Fenton degradation performance has been evaluated through degradation of tetracycline at different conditions. At the optimized condition, the obtained material generates hydrogen peroxide and tetracycline degradation efficiency of 98% within 2-h. This novel oxide catalyst can be regarded as a promising catalyst for wastewater treatment.

5:00pm **F3-TuA-11 Molten Salt Synthesis of Highly Dispersible Hexagonal Boron Nitride Nanosheets for Ultrafiltration***, Neon Vicente III Rosell,* National Cheng Kung University (NCKU), Taiwan, Philippines*; K. Chang,* National Cheng Kung University (NCKU), Taiwan

Hexagonal boron nitride (hBN) is a key material analogue for graphene. It is best known for its use by industry as a chemically-inert, refractory material for use in harsh environments. Conversely, it is this same robustness that make it difficult for researchers to synthesize hBN in the lab without the use of exotic setups and reagents. Molten salt synthesis affords researchers a facile method to synthesize quantitative amounts of hBN for research. In this research, hBN was synthesized in a LiCl-KCl molten salt eutectic at 900°C under nitrogen atmosphere. Boric acid and melamine were used as the boron and nitrogen source respectively. Recovery of bulk hBN from the cooled melt was done with washing with deionized water and centrifugation. The resulting powders were then subjected to materials characterizations such as XRD, FT-IR, Raman, and TEM-EELS that confirm the synthesis of hBN powders. The resulting powders has been shown to have high dispersibilty in water when subjected to exfoliation techniques such as ultrasonication. This hBN dispersion was then used as basis for an ultrafiltration membrane that demonstrates excellent separation efficiency for organic dyes (i.e. Rhodamine B, Methylene Blue, Methyl Orange). Regeneration of this ultrafiltration membrane has been demonstrated through the use of advanced oxidation processes where either exposure to hydrogen peroxide solutions, or decoration of P25 titania nanoparticles was used under xenon lamp illumination.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Town & Country A - Session H3-1-TuA

Characterization of Coatings and Small Volumes in Extreme and Cyclic Conditions I

Moderators: Prof. Dr. Peter Hosemann, University of California, Berkeley, USA, **Prof. Dr. Barbara Putz**, Montanuniversität Leoben, Austria

1:40pm **H3-1-TuA-1 Local Deformation Mechanisms under Ambient and Non-Ambient Conditions Tested via Advanced Nanoindentation***, Verena Maier-Kiener,* Montanuniversität Leoben, Leoben, Austria **INVITED**

Nanoindentation over the recent years established itself as a versatile tool for probing local mechanical properties beyond hardness and modulus. By adapting and improving standard nanoindentation testing methods, reliable protocols capable of probing thermally activated deformation processes can be accomplished. Abrupt strain-rate changes within individual indentations allow determining the strain-rate dependency of hardness at various indentation depths. For probing lower strain-rates and excluding thermal drift influences, long-term creep experiments can be performed by using the dynamic contact stiffness for determining the true contact area. From both procedures hardness and strain-rate, and consequently quantities such as strain-rate sensitivity, activation volume and activation energy can be reliably deducted within individual indentation tests, permitting information on the locally operating thermally activated deformation mechanism.

This presentation will first discuss various testing protocols including possible challenges and improvements, with particular emphasis towards testing at higher temperatures and under hydrogen atmosphere. Second, it will showcase different examples highlighting the direct influence exerted by microstructure, phase transformations and environmental conditions on the underlying deformation behavior in pure and highly alloyed material systems.

2:20pm **H3-1-TuA-3 Extracting High-Temperature Stress-Strain Curves and Assessing Transformation Pressures: The Spherical Indentation of Silicon***, Gerald Schaffar,* Montanuniversität Leoben, Austria*; D. Tscharnuter,* KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; V. Maier-Kiener,* Montanuniversität Leoben, Austria

In the past nanoindentation with spherical tips has already been extensively employed to characterize the mechanical properties of silicon. This work aims to combine advances in spherical indentation testing [1], [2] with the idea of using continuous stiffness measurement (CSM) during the unloading of silicon [3]. Combining both advanced methods allows directly the calculation of the compression flow behavior, including the acquirement of the pressure-induced phase transformations in silicon. Therefore, the use of CSM during the indentation unloading process permits the measurement of the phase transformations during unloading. These transformations can, at room temperature, be seen as "elbows", "pop-ins" or mixes thereof in the load-displacement curve [4]. In the current work, this combined approach is applied to both room-temperature and high-temperature indentations up to 950°C. Subsequently, confocal Raman spectroscopy is used to identify the phase transformations occurring at lower testing temperatures. Further, confocal laser scanning microscopy is used to check the remaining indentations for irregularities, such as pronounced pile-up behavior. Indentation tests using self-similar Berkovich tips, performed beforehand across this entire temperature range, revealed that the plastic deformation behavior is controlled by phase transformations up to ~ 400 °C. At even higher temperatures dislocation plasticity dominates the plastic deformation underneath the indenter. This transition between phase transformations and dislocations as the main mechanism of plasticity when indenting silicon is in good agreement with previous observations from high-temperature indentation testing [5].

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2:40pm **H3-1-TuA-4 Micro-Impact Tests of Novel Thermal Barrier Coating Systems and >1000C Nanoindentation on Ni-Base Superalloy***, Ben Beake,* Micro Materials Ltd, UK*; C. Chalk,* Cranfield University, UK*; S. Goodes, A. Harris,* Micro Materials Ltd, UK*; L. Isern, J. Nicholls,* Cranfield University, UK

Thermal barrier coatings (TBCs) with improved erosion resistance are needed to increase the efficiency of gas turbines in aero-engines by enabling them to operate at higher temperatures. Rare earth zirconate (REZ) TBCs have potential as low-conductivity TBCs permitting higher temperature operation by more effectively thermally shielding the Ni-base superalloy turbine blade material. Although they have much lower thermal conductivity than current yttria-stabilised zirconia (YSZ) TBCs they have lower toughness making them susceptible to erosion. Nanomechanical tests are used to streamline the development of advanced multilayered TBC systems that can combine optimum thermal and mechanical properties.

The micro-scale impact test capability in the NanoTest has been modified to closely simulate real erosion conditions. The resistance of single-layered YSZ coatings and bilayer TBC coatings comprising a top layer of the REZ $Gd_2Zr_2O_7$ and YSZ sub-layer of similar total thickness to repetitive high strain rate contacts has been studied in detail. YSZ showed almost identical impact behaviour in 75 and 90 degree impact tests but in contrast the REZ coating was more resistant in angled impact than normal impact. The performance of the coatings in the novel micro-impact tests correlated with that in conventional erosion tests.

The nanomechanical behaviour of the Ni-base superalloy substrate (Nimonic 75) has been assessed at temperatures above 1000 °C for the first time. The critical role of the nanoindentation load-time profile to mitigate the enhanced creep at these temperatures and obtain more accurate measurements of hardness and elastic modulus is investigated.

Funding support from Innovate UK is acknowledged ("High temperature tools for designing sustainable erosion resistant coatings" Project#10020751).

3:00pm **H3-1-TuA-5 Influence of Si on the Mechanical Properties and High-temperature Fracture Toughness of Cr-Si-$B_{2\pm z}$ Coatings***, L. Zauner, **Rainer Hahn**,* CDL-SEC at TU Wien, Austria*; O. Hunold, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* CDL-SEC at TU Wien, Austria

Si-alloyed diboride systems show outstanding oxidation resistance compared to their unalloyed binary or ternary counterparts. This allows operating temperatures up to 1200 °C, further extending the possible applications of such systems, such as protective coatings in turbines. In addition to the necessary oxidation resistance, adequate mechanical protection is also of great interest. This work investigates the impact of Si segregates on the structural and mechanical properties of Cr-Si-$B_{2\pm z}$ thin films from ambient to elevated temperatures. Overstoichiometric, AlB_2-structured Cr-Si-$B_{2±z}$ thin films with Si-content up to 15 at.% were synthesized on Ti-6Al-4V substrate by magnetron sputtering using a substrate bias of -120 V.

Enhanced surface diffusion of film constituents promotes the growth of mechanically superior, (001)-oriented coatings with a hardness of H~30 GPa up to a Si content of 3 at.%. Higher Si concentrations result in a significant hardness loss to H~20 GPa related to a bias-independent solubility limit in the CrB_2 structure, causing the formation of mechanically weak Si grain-boundary segregations. The as-deposited hardness of all Cr-Si-$B_{2±z}$ compositions is maintained after annealing up to 800 °C despite the initiation of material recovery. In addition, minimum interdiffusion and excellent adhesion are observed on the Ti-6Al-4V-alloy.

In line with the room temperature hardness, an increasing Si content is accompanied by a decreasing fracture toughness, reducing from K_{IC}~2.9 ($Cr_{0.28}B_{0.72}$) to ~1.7 MPa√m ($Cr_{0.24}Si_{0.10}B_{0.66}$), respectively. High-temperature cantilever bending up to 800 °C revealed a brittle-to-ductile-like transition for $Cr_{0.28}B_{0.72}$, resulting in a fracture toughness increase to K_{IC}~3.3 MPa√m. Similar behavior is observed for Si-alloyed coatings up to 400 °C, whereas beyond this temperature, Si-segregates enable high-temperature plasticity and, thus, a significantly increased damage tolerance.

4:00pm **H3-1-TuA-8 Nanoindentation Measurements at Combined High Sustained Strain Rates and Elevated Temperatures***, **Benoit Merle,*** University of Kassel, Germany **INVITED**

Constant strain rate nanoindentation is a versatile method well suited for measuring the microscopic mechanical properties of materials within a wide range of temperatures. Recent developments have focused on increasing the permissible strain rates beside the typical ~0.1/s threshold present in most commercial systems. The current limitation primarily derives from the plasticity error of the continuous stiffness measurements (CSM) and has recently been overcome with a custom evaluation method avoiding the need for a measurement of the contact stiffness. With this improvement, the experimental upper strain rate limit is only limited by the hardware time constants of the system.

Based on a study of an intermetallic alloy, the presentation will demonstrate that nanoindentation is a potent technique for systematic investigations of changes in mechanical properties as a function of the testing temperature and deformation rate.

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Topical Symposia
Room Pacific F-G - Session TS2-TuA

Sustainable Surface Solutions, Materials, Processes and Applications

Moderators: Justin Cheney, Oerlikon Balzers Coating, USA, **Prof. Fan-Bean Wu**, National United University, Taiwan

1:40pm **TS2-TuA-1 Application of High Entropy Spinel Oxides on Photodetector***, **Jyun-Yi Li**, K. Kuo,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; P. Hsiao, C. Chen, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Photodetector as a widely use application in daily life, such as environmental monitoring, biological /chemical analysis, and communication, is often to be constricted to work in the certain wavelength due to the materials inside. Recently, a new concept of high entropy oxides (HEO) has been proposed, which is consisted of more than five metals with concentration of each metal in range of 5-35% and having a calculated configurational entropy ΔS ≥1.5R. Although there have been many studies on high entropy oxides, few of them have focused on photodetectors. Herein, we synthesized a series of high entropy spinel oxides with hydrothermal method and apply on photodetector. The crystal structure of materials were confirmed using X-ray diffraction (XRD). The morphology was characterized with scanning election microscope (SEM). Besides, the material were also characterized using inductively coupled plasma (ICP), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), …. .The optical performance of HEO photodetector were evaluated by UV-VIS-NIR, responsivity(R), external quantum efficiency (EQE), detectivity (D), rise time and decay time.

Keywords: high entropy oxide(HEO), spinel,photodetector, responsivity, EQE, detectivity

2:00pm **TS2-TuA-2 Euro 7/VII – Challenges for Surface Solutions in ICEVs and EVs***, J. Vetter,* Oerlikon Balzers Coating Germany GmbH, Germany*; **Justin Cheney**,* Oerlikon Balzers Coating, USA*; J. Becker,* JB, Germany*; M. Esselbach,* Oerlikon Surface Solutions AG, Liechtenstein

The upcoming Euro 7 standards are aimed to further reduce pollutant emissions from vehicles and improve air quality. Euro 7 is valid not only for passenger car but also for heavy-duty vehicles. The proposed standard will influence the development of internal combustion engine vehicles (ICEVs) and electric vehicles (EVs) alike.

After all the drivetrain of ICEVs and EVs is quite similar and the requirements with respect to improved long-life performance and reduced particle emission may be even more challenging with EVs. Surface solutions are ready to work as an enabler to reach the goals. E. g. coatings allow a longer lifetime of drive train components which otherwise suffer from the higher torque of an electric motor.

Besides the well-known tribological coatings for engines and drive-train other coatings are of interest. Examples are coatings which allow to measure stress, pressure, or temperature, insulating coatings or conducting coatings for connectors of batteries.

Coatings for hydrogen applications will be discussed. Hydrogen applications can be found in fuel cells, the periphery of fuel cells, but also in hydrogen ICEs.

Whatever coating solution may come up, the requirements of a circular economy need to be an integral part of a system.

2:20pm **TS2-TuA-3 Surface Technology as a Key Technology for New Energy Systems***, **Yashar Musayev**, L. Dobrenizki,* Siemens Energy Global GmbH & Co. KG, Germany **INVITED**

Siemens Energy is one of the world's leading energy technology companies. The company works with its customers and partners on energy systems for the future, thus supporting the transition to a more sustainable world. With its portfolio of products, solutions and services, Siemens Energy covers almost the entire energy value chain – from power generation and transmission to storage. The portfolio includes conventional and renewable energy technology, such as gas and steam turbines, hybrid power plants operated with hydrogen, and power generators and transformers. More than 50 percent of the portfolio has already been decarbonized. An estimated one-sixth of the electricity generated worldwide is based on technologies from Siemens Energy.

Using renewable electrical energy like wind or solar power for "green electrons" from the power sector to decarbonize energy across all sectors unlocks enormous environmental and business benefits. Through Power-to-X technologies, sectors beyond power generation will benefit from renewable power and become increasingly green over the total chain from production to application.

Siemens Energy will provide optimum solutions in order to contribute to the realization of a carbon-neutral society in countries and regions around the world by utilizing our hydrogen related technologies, business and global network. The joint vision of the two companies is to advance the technology to produce green hydrogen from innovative PEM (Proton Exchange Membrane, Fig.1) water electrolysis using renewable energy systems. PEM water electrolysis (Fig.2) enables the production of high-purity green hydrogen. The resulting green hydrogen can not only be used for large-scale power generation and other electric power applications, but also for sector coupling such as heat, transport, and industrial applications.

An PEM-electrolysis cell consists of a MEA (Membrane Electrode Assembly; Catalyst Coated Membrane) as well as porous structures (gas diffusion layer & fleece) on both sides for the distribution of product gases. The cells are separated in the segment by bipolar plates. The PEM-systems have been further developed regarding efficiency, service life and cost-effectiveness. The key performance indicators (KPIs) of an electrolysis stack can be derived from the current-voltage and voltage-time curves.

4:00pm **TS2-TuA-8 Progress on Piezoelectrocatalysis for Hydrogen Production and Environmental Science*, Jyh-Ming Wu,*** National Tsing Hua University, Taiwan **INVITED**

Continual technological advancements have substantially improved peoples' quality of life; however, excessive energy consumption and improper waste management have caused tremendous environmental disruption. Unrestricted fossil fuel exploitation contributes to greenhouse gas emissions, precipitating climate change, and the discharge of large amounts of industrial wastewater has deteriorated natural ecologies and contributed to severe health problems. Solutions involving the remediation of water pollutants, water splitting, and clean energy alternatives have been widely investigated. Specifically, electrocatalytic and photocatalytic water splitting are potentially promising strategies for hydrogen gas production and polluted dye decomposition.

This talk will report how 2D transition metal dichalcogenides can be used for piezocatalyts for highly efficient wastewater treatment and hydrogen production without applied light irradiation. Furthermore, we will report that a new generation of piezocatalyts — A self-powered photoelectrochemical microsystem comprising quartz prism microrods assembled with TiO_2 nanoparticles or MoS_2 nanosheets developed and demonstrates a marked catalytic effect on organic dye degradation and hydrogen evolution through a piezopotential sensitized catalytic activity. The induced piezopotential not only tilted the band structure to accelerate the separation of photoexcited carriers but also restrained their recombination, contributing to a more efficacious catalytic reaction. A self-poweredelectrochemical microsystem realizes the remarkable coupling effect of piezocatalysis and photocatalysis on different applications, introducing a potential material and strategy to environmental science and renewable energy fields.

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4:40pm **TS2-TuA-10 Visible Light Activated Photocatalytic Coatings by Reactive Magnetron Sputtering for Environmental Applications*, Peter Kelly,*** John Dalton Building, Chester Street, UK*; M. Ratova, J. Redfern,* Manchester Metropolitan University, U.K.

Photocatalytic coatings and materials have many potential applications, such as removal of organic pollutants in water and air supplies, antimicrobial and anti-viral surfaces, self-cleaning glass and building materials and the production of hydrogen via water splitting. However, the most widely known photocatalytic material, titanium dioxide in the anatase form, is limited by its low quantum efficiency and wide band gap (3.2 eV), which means it requires UV light for activation. Band gap narrowing can be achieved by doping the anatase, but this can increase the recombination of the holes and electrons produced by exposure to ultra band gap radiation and lead to an overall reduction in activity.

We report the development of a series of bismuth oxide and bismuth oxide-based coatings with band gaps in the 2.4 to 2.6 eV range and, consequently, significant visible light activity. The coatings were produced by reactive magnetron sputtering and have been deposited onto planar substrates and also particulates including PC500, P25 and 2mm diameter glass beads to demonstrate the flexibility of the deposition process and to allow a wide range of applications to be explored. Coating types investigated include bismuth oxide, bismuth tungstate and bismuth molybdate. The coatings were analysed using SEM, EDX, XRD, XPS, and UV–vis spectroscopy. The photocatalytic properties have been determined by dye degradation tests under visible light irradiation and an acetone degradation test. The antimicrobial efficiency of the coatings was tested via inactivation of E. coli.

It was found that the performance of bismuth oxide for both dye degradation and bacterial inactivation experiments under visible light was superior to that observed for either bismuth tungstate, bismuth molybdate or titanium dioxide coatings also produced for comparison purposes. Additional tests have been carried out against cyanobacteria and free-floating genomic DNA to demonstrate the water treatment potential of the bismuth oxide coatings. Further trials have demonstrated the capability of selected coatings to breakdown microplastics in water.

5:00pm **TS2-TuA-11 A Covalent Organic Framework-Based Ionic Diode Membrane for Ultrahigh Blue Energy Generation*, Yu-Chun Su,*** *L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Blue energy has recently attracted significant attention due to the growing energy demand and increasing awareness on environmental protection. Electric eels can convert ionic concentration gradients into a high-efficiency electric power when facing enemies via sub-2 nm biological transmembrane channels, which can exhibit high ion selectivity and strong diode-like ion rectification property. Inspired by this, a heterogeneous ionic diode membrane, composed of an ultrathin (~110 nm) two-dimensional covalent-organic framework (COF) membrane with well-oriented sub-2 nm ion transport channels and a highly ordered alumina nanochannel membrane (ANM), is reported for highly efficient blue energy harvesting. Higher ionic flux can be obtained due to well-ordered ion transport channels which achieves lower membrane resistance. Moreover, as verified by our experimental and simulation results, the heterostructured COF/ANM membrane is capable of strong ionic diode behavior due to asymmetric charges and pore sizes in two aligned COF (1.1 nm) and ANM (100 nm) channels that can enhance current density. Thus, an unprecedented power density of up to 27.8 W/m^2 is achieved by mixing the artificial salt-lake water and river water. This study will open new avenues of using the rectified ion channel-mimetic nanofluidic membrane as a new platform towards the exploration and development of an ultrahigh osmotic power generator.

Special Interest Talks
Room Town & Country A - Session SIT2-TuSIT

Special Interest Session II
Moderator: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

7:00pm **SIT2-TuSIT-1 Functional Nitride and Oxide Thin Films – the Key to Our Digital World**, ***Joerg Patscheider,*** Evatec AG, Switzerland **INVITED**

Modern telecommunication depends heavily on assemblies of integrated devices that are composed of most intricate combinations of functional thin films. Nitrides and oxides present an important category among these functional thin films, as their electrical properties allow for tailoring electric currents to build logical elements such as transistors, RF filter devices and memory architectures, to name just a few applications. Moreover, the bandgap of many of these materials may be tuned by alloying with additional elements to tune their electrical and optical properties.

This contribution will present examples from different fields of importance for applications that are driven by the ever-increasing market for handheld devices such as smartphones and smartwatches. We will look at piezoelectric films of AlN and AlScN for frequency filters, shed light on integrated transformers consisting of multilayered ferromagnetic films with intercalated insulators and dive into the world of multilayered oxide coatings for various optical filter applications.

These examples with their respective technological challenges necessitate corresponding equipment concepts for volume manufacturing. Advanced control of thickness and residual stress uniformity, prevention of cross-contamination and parallel processing solutions will be explained. Manufacturing techniques to produce thin films on 8” and 12” wafer level meeting the stringent requirements of today’s semiconductor and optical industry will be presented.

Coatings for Use at High Temperatures
Room Pacific E - Session A2-2-WeM

Thermal and Environmental Barrier Coatings II

Moderators: Dr. Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Dr. Pantcho Stoyanov**, Concordia University, Canada

8:00am **A2-2-WeM-1 On the Suitability of MoNbTaW Based Thin Films to Act as Diffusion Barriers*, Georg C. Gruber*[1]**, Montanuniversität Leoben, Austria*; A. Lassnig, S. Zak,* Austrian Academy of Sciences, Austria*; M. Kirchmair,* Montanuniversität Leoben, Austria*; S. Wurster, C. Gammer, M. Cordill,* Austrian Academy of Sciences, Austria*; R. Franz,* Montanuniversität Leoben, Austria

To further improve the performance of diffusion barriers between Cu and Si, several new approaches were developed, such as the use of high entropy alloys (HEAs). HEAs are alloys with a configurational entropy of at least 1.5R, where R is the gas constant. On the one hand, HEA thin films can be deposited with amorphous microstructure which can be beneficial for their use as diffusion barriers. On the other hand, the lattice distortion within HEAs leads to an increase of the strain energy as well as the cohesion energy leading to an increased activation energy for the Cu diffusion. Within the current study, six different HEAs, based on the MoNbTaW system and alloyed with Ti, V, Cr, Mn, Zr or Hf, have been deposited by high power impulse magnetron sputtering (HiPIMS) as diffusion barrier layers between Cu and Si. The thickness of the HEA layers on the Si substrate was 20 nm, followed by a 150 nm thick Cu layer also deposited by HiPIMS. X-ray diffraction (XRD) investigations found that the MoNbTaW layers alloyed with Ti and V showed a body-centered cubic microstructure while the other alloys showed an amorphous microstructure. Subsequently, the bi-layers were annealed at temperatures ranging from 550 to 800 °C in a vacuum furnace. After annealing, the bi-layers were investigated by XRD, resistance measurement and laser-scanning-microscopy, to check for potential barrier failure. The lowest onset temperature for barrier failure of 600 °C was found for amorphous MoNbTaWZr, whereas the highest of 700 °C was observed for CrMoNbTaW. The obtained results are discussed in terms of strain and cohesive energy as well as the enthalpy of mixing between the fifth alloying element (Ti, V, Cr, Mn, Zr or Hf) and Cu. Within the study, the great potential of these HEAs for future diffusion barriers was demonstrated.

8:20am **A2-2-WeM-2 Improvement of EBC Performance by Controlling Driving Forces for Mass Transfers in Oxides*, Satoshi Kitaoka*,** JFCC, Japan*; T. Matsudaira, T. Ogawa, M. Wada,* Japan Fine Ceramics Center, Japan **INVITED**

Environmental barrier coating (EBC) systems typically have a multilayer structure that consists of complex oxides such as silicates and aluminates to achieve the required performance through the use of layers with different characteristics. Such coatings with highly dense layers exhibit excellent gas shielding performance when they are exposed to a high oxygen potential gradient (dμO) at elevated temperatures.

In the case of Yb2Si2O7 (YDS) and Yb2SiO5 (YMS) layers that constitute the oxide-EBC systems, the application of dμO results in the inward diffusion of oxide ions and outward diffusion of Yb ions along grain boundaries (GBs), according to the Gibbs-Duhem equation. In the case of Al6Si2O13 (mullite) layer, inward GB diffusion of oxide ions and outward GB diffusion of Al ions occur. Cation transport induces decomposition of the complex oxides that comprise the layers, which leads to collapse of the multilayer structure. Hence, suppression of the outward diffusion of cations under dμO is extremely important in the design of robust EBC systems.

In this study, an EBC design to improve both the structural stability and environmental shielding properties of multilayer structures was investigated based on mass transfer mechanisms in the individual layers. The oxygen and cation fluxes at the outflow side in single-layer EBCs such as YMS, YDS, and mullite were significantly larger than those at the inflow side, in accordance with dominant cation transport under a high oxygen potential (μO) region near the surface, and dominant oxygen transport under the low-μO region in the vicinity of the interface between the oxide-EBC and Si-based bond coat or SiC/SiC substrate. This suggests that several different ions interdiffuse within multilayer EBC systems and can be separated into a single species according to the layer configuration by control of the GB densities and thicknesses of the layers. In addition, the interface between the YDS and YMS layers acts as an energy barrier for the outward GB diffusion of Yb ions. Therefore, the structural stability and oxygen shielding properties even for an common three-layer EBC system consisting of a YMS top layer, a YDS intermediate layer, and a mullite bottom layer are considered to be significantly improved by unifying the main diffusion species in each layer and simultaneously utilizing an energy barrier against the outward diffusion of cations.

Key Words: Diffusion, Grain boundary, EBC, Oxygen permeability, High temperature

9:00am **A2-2-WeM-4 Steam Oxidation Kinetics of Si / Modified $Yb_2Si_2O_7$ Environmental Barrier Coatings on SiC/SiC Ceramic Matrix Composites at 1250 °C – 1350 °C*, Kang Lee*,** *J. Stuckner, M. Presby, B. Pulio,* NASA Glenn Research Center, USA*; W. Jennings,* HX5, USA

Environmental barrier coatings (EBCs) have enabled the implementation of SiC/SiC ceramic matrix composites (CMCs) in gas turbines by protecting CMCs from H_2O-induced volatilization. Improving the reliability of CMC components requires long-life EBCs and accurate EBC lifing. Steam oxidation-induced failure is the most frequently observed EBC failure mode. NASA previously reported that modifying Si / $Yb_2Si_2O_7$ EBC by adding Al_2O_3 or Al_2O_3-containing compound, such as mullite ($3Al_2O_3{\cdot}2SiO_2$) and YAG ($Y_3Al_5O_{12}$), in $Yb_2Si_2O_7$ reduces the EBC parabolic oxidation rates by up to about 20 times at 1316°C in steam. Oxidation is a thermally activated process and therefore the oxidation rates vs. temperature relationship typically follows the Arrhenius equation. This paper reports the results of follow-on studies that expanded the test temperature to 1250 °C and 1350 °C to understand the temperature dependency of oxidation rates, which is a key component for EBC lifing.

9:20am **A2-2-WeM-5 Oxygen Permeability, Failure Analysis and Life Prediction of Environmental Barrier Coatings Under Adverse Environments*, Prakash Patnaik*,** Aerospace Research Centre, National Research Council Canada*; A. Kumar,* TECSIS Corporation, Canada*; K. Chen,* Aerospace Research Centre, National Research Council Canada

Environmental barrier coatings (EBCs) are typically used to protect ceramic matrix composites (CMCs) substrate against a harsh environmental attack such as high-temperature water vapour-induced recession in aero-engines achieving lower density, higher temperature tolerance capability and higher engine thrust-to-weight ratio. Under adverse service operations, the oxygen permeability of ytterbium disilicate (YbDS) topcoat and thermally grown oxide (TGO) silicon dioxide in EBCs plays a key role in determining EBCs durability and life span. Using physics-based model and thermodynamics calculations along with defect reaction formulae, oxygen permeabilities under dry oxygen and water vapour conditions, as well as different temperatures, partial pressures and top coat modifiers, are investigated. The results show that oxygen permeability for topcoat YbDS is an order of magnitude higher than for TGO, indicating that TGO hinders the oxidant diffusion stronger, proving to be the diffusion rate controlling layer. Moreover, water vapour strongly increases the oxidant permeation, with the defect reaction playing an important role. It is suggested that the mass transfer through the topcoat is primarily by outward ytterbium ion diffusion and inward oxygen ion movement, with the latter being dominant, particularly in water vapour environments.

The heterogeneous multi-layers designed for EBCs offer specific functions. High thermal strain and stress could develop due to materials mismatch and thermal gradient, leading to an accelerated degradation limiting EBCs durability and performance. Multi-physics/mechanics approaches were used to establish thermal and residual stress models for multi-layer EBCs considering the theory of composite elastic beam bending due to thermal gradient under force–moment equilibrium and stress-strain-curvature relationship. Residual stress distributions along the layer thickness were obtained for selected EBCs. Results are then compared with the test data, and the model exhibits a consistent variation in stress values across different coating layers. Specifically, thermal and residual stresses were evaluated within topcoats YbDS and ytterbium mono silicates (YbMS). Higher stress in YbMS makes it unsuitable as the topcoat despite its thermochemical compatibility between components and very low steam volatility. Finally, the lifetime prediction was explored for selected EBCs under specific water vapor contents and thermal cycle conditions based on the developed stress models.

[1] **Graduate Student Award Finalist**

9:40am **A2-2-WeM-6 Raman Spectroscopic Investigation of SiO_2 TGO Phase Transformation and Si and SiC Substrate Stress***, Michael J. Lance,* Oak Ridge Natinal Laboratory, USA*; M. Ridley, T. Aguirre, B. Pint,* Oak Ridge National Laboratory, USA

SiC ceramic matrix composites (CMCs) are desired for use in combustion environments to achieve higher turbine operating temperatures, although CMCs require environmental barrier coatings (EBCs) for protection from the gas environment. EBC systems are known to primarily fail through coating delamination via growth of a thermally grown oxide (TGO) at the EBC – silicon bond coat interface. The TGO undergoes a phase transformation during thermal cycling, which results in stresses that may encourage EBC spallation. Uncoated Si and SiC substrates were exposed to air and steam to form cristobalite TGOs of a thickness that remained intact upon cooling to room temperature. These TGOs were then thermally cycled across the phase transformation temperature for cristobalite and characterized with Raman microscopy to map the α↔β transformation. The stress in the silicon and SiC was simultaneously measured with Raman microscopy. Finite element modeling was used to predict the CTE mismatch stress and transformation stress in the TGO which was compared to the measured Raman stress. This research was funded by the Advanced Turbine Program, Office of Fossil Energy and Carbon Management, U.S. Department of Energy.

11:00am **A2-2-WeM-10 Hot Section Coating Technology as an Enabler for Sustainable Propulsion***, Eli Ross,* Pratt & Whitney, USA **INVITED**

Continued growth within the aviation sector is often seen as running counter to the shared objective of carbon-neutral flight. That growth trend brings not only higher demand and corresponding emissions, it also brings exposure to more aggressive and challenging operating environments for gas turbine engines. Accordingly, sustainable propulsion systems must build on recent learning from harsh environmental exposure while provisioning for a future state of more efficient, lower carbon engine technology sets encompassing a suite of higher thermal efficiency, hybrid-electric, and alternate fuel solutions. A common thread across this complex future turbine engine landscape is the need for continued improvement and development of thermal and environmental barrier coatings used in the hottest areas of the engine to enable both performance and durability. An overview and historical perspective of Pratt & Whitney work in this area will be presented, along with a system-level vision for the continued role of coating development in helping to deliver on a more sustainable net-zero future.

11:40am **A2-2-WeM-12 Development of Tantalum Coating by the Cold Spray***, **Sheng-Wei Zeng**,* Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan*; Y. Chung, W. Li,* National Chung Shan Institute of Science and Technology, Materials and Electro-Optics Research Division, Long-tan, Taiwan*; Y. Yang,* Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan

In the coating technology, cold spray(CS) is different from the traditional thermal spraying technology. The cold spray coating is formed by plastic deformation without high temperature melting, which can keep the original characteristics of the material during the spraying process and have a denser coating. Refractory metals, tantalum(Ta), has good performance at high temperature, used in the electronics industry, aviation, defense and medical treatment. This study used cold spray to prepare refractory metals, tantalum(Ta) coating, discusses the cold spray under different process parameters (chamber pressure, chamber temperature, working distance) affected the microstructure changes of the coating and its mechanical properties, such as porosity, hardness, tensile strength, etc.

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 Lümkemann**,* Platit AG, Switzerland*; J. Kluson, M. Ucik,* 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 sp3 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/cm2.

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 sp3 to sp2 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 occurs 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.

Functional Thin Films and Surfaces
Room Pacific F-G - Session C1-1-WeM

Optical Materials and Thin Films I

Moderators: Dr. Silvia Schwyn-Theony, Evatec AG, Switzerland, **Dr. Juan Antonio Zapien**, City University of Hong Kong

8:40am **C1-1-WeM-3 High-Rate Deposition of Calcium Fluoride Coatings Using Radio-Frequency Magnetron Sputtering***, **Sharon Waichman**, I. Zukerman, M. Buzaglo, S. Barzilai,* NRCN, Israel

Calcium fluoride (CaF_2) is a ceramic material that exhibits versatile properties such as broadband transparency, lubrication behavior at high temperatures (up to 900 °C), high mechanical stability, and hydrophobicity. CaF_2 can be utilized as an antireflective (AR) coating for different optical needs and applications. Due to its enhanced transmission, mainly in the UV and IR regime, a broader transmission range can be achieved, greater than the common oxide-based coatings (SiO_2, TiO_2, or their combination). Moreover, CaF_2 as a constituent in composite-based coatings can effectively reduce wear and friction in mechanical devices and working tools that are subjected to heavy loads and high temperatures. One of the challenges in CaF_2 sputtering concerns with the low stability of the target under high sputtering power (above ~ 2 W/cm^2). Therefore, CaF_2 deposition is usually characterized by low deposition rates. In the current research, CaF_2 coatings were deposited on silicon (Si) substrates by means of a radio frequency (RF, 13.56 MHz) magnetron sputtering technique in an argon atmosphere, and fixed power of 4.4 W/cm^2, whereas the substrate bias voltage (V_b) was varied from 0 to - 150 V. The role of V_b is to enhance the adatoms' mobility and to increase their probability of residing in permanent binding sites. This lowers the roughness and increases the layer density. The coatings were characterized using SEM/EDS, XRD, and XPS. A spectrophotometer was utilized to study the optical properties of the deposited films. The residual stress was studied using the Stoney formula, while the adhesion was studied by a scotch-tape method. In this research, we report a high deposition rate of 8-25 nm/min, depending on the V_b value, with a maximum deposition rate at the low voltages applied, 0 and - 30 V, as expected. To the best of our knowledge, this high deposition rate of CaF_2 coatings, using RF magnetron sputtering technique, is reported for the first time. The morphology of the surface was changed with increasing V_b, from a rough surface obtained at the low V_b regime to smoother at - 50 to - 75 V, which finally became rougher again at high V_b of - 150 V, because of pits and holes that were generated by the excessive ion bombardment. Moreover, at - 150 V, coatings were delaminated from the Si substrate immediately after deposition. Due to preferential sputtering of the light fluorine, the composition of the CaF_2 coatings turned fluorine deficient with increasing V_b.

9:00am **C1-1-WeM-4 Reactive Sputter Deposition of Nanoporous Black Zinc and White Zinc Oxide Coatings***, **Jakub Zawadzki**,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Faculty of Materials Science and Engineering - Warsaw University of Technology, Poland*; M. Borysiewicz,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

A group of metallic materials characterized by low reflectivity is known as black metals. The transition of the metal from being highly reflective to nearly black can be achieved by its preparation in a way providing a highly porous structure . This phenomenon has been widely applied to the synthesis of macroscopic black metal materials based on Ag [1], Au [2], Al [3], Cr [4], Ni [5], Mo [6], P [7], Zn [8] etc. The dominant applications of black metals are in solar cell collectors [9], optical sensing10, electrochemical sensing11 and decorative coatings12. On the other hand, white coatings can find applications where a high degree of specular light reflection is required – e.g. in cooling coatings [13] or decorative coatings [14]. Depending on the function, several properties must be considered, such as absorbance of electromagnetic radiation in specific wavelengths, thermal emittance, thermal stability and wear resistance.

Our study presents a way to make thin porous zinc and zinc oxide nanosystems obtained by reactive sputter deposition with additional postdeposition annealing as functional black coatings. We show that a wide array of morphologies from highly porous nanocoral and branched structures to densely-porous ones can be obtained by addition of oxygen to inert working gas [15,16]. The purely Zn films are characterized by a wide degree of black or off-black colours. They can be oxidized at an elevated temperature to form matt white ZnO nanoporous films. We show the strategy to increase the mechanical stability and the optical quality of the films, by applying additional protective overcoats. We show that the doping with Al increases the thermal stability of the Zn films for harsh applications. We investigate creating patterns in the black and white films. The influence of morphology, crystal structure and chemical composition on the optical and mechanical properties of the films is discussed.

The comprehensive approach allowed us to achieve highly functional black and white coatings based on zinc with the use of a solvent-free deposition technique widely spread in large-scale thin film industries.

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[4] 10.1016/j.proeng.2013.09.123

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[14] 10.1016/S0257-8972(99)00076-6

[15] 10.1002/pssa.201228041

[16] 10.1016/j.apsusc.2016.07.098

9:20am **C1-1-WeM-5 High Hall Mobility W-Doped In_2O_3 Conductive Films with Thicknesses of Less Than 10 Nm Deposited on Glass Substrates***, **Tetsuya Yamamoto**, R. Palani, H. Makino,* Kochi University of Technology, Japan

We have achieved polycrystalline W-doped In_2O_3 (*p*-IWO) films with thicknesses ≤ 10 nm showing high Hall mobility ≥ 50 cm^2/(Vs). Amorphous IWO (*a*-IWO) films with thicknesses in the range from 5 to 50 nm were deposited on glass substrates without intentionally heating of the substrates by reactive plasma deposition with dc arc discharge (RPD). Then, the *a*-IWO were subjected to under-vacuum solid phase crystallization in the RPD chamber at a pressure of 5×10^{-4} Pa without any additional gas for 30 min at 250 °C, to realize *p*-IWO films. Structural, electrical, and optical properties are characterized by X-ray diffraction and reflectivity (Rigaku SmartLab), Hall-effect combined with the van der Pauw geometry (Nanometrics HL5500PC), and spectrometer measurements (Hitachi U-4100), respectively. For obtaining high Hall mobility *p*-IWO films, flat surfaces of the IWO films and reduced roughness of film/substrate interface are essential. Resolutions to the above issue are follows: (1) control of the energy of flying particles such as positively charged indium (In^+) ions of less than 25 eV; (2) to prevent the generation of low-melting-point In metals at the early growth stage of the films, optimization of the flow rates of oxygen (O_2) gasses introduced into the deposition chamber during the film growth. In this talk, we discuss thickness-dependent electrical and optical properties and elucidate the cause of the high carrier transport, on the basis of the analysis of the data obtained by high resolution Rutherford back scattering and hydrogen (H) forward-scattering spectroscopy measurements and combined with classical size effect theoretical models.

9:40am **C1-1-WeM-6 The Effects of Growth and Post-Annealing Temperatures on MoS_2 Thin Films Deposited by Magnetron Sputtering**, *C. Chao,* National Dong Hwa University, Taiwan*; P. Tsai,* National Chung-Shan Institute of Science & Technology, Taiwan*; P. Wu,* Stone & Resource Industry R&D Center, Taiwan*; **Ing-Song Yu,*** National Dong Hwa University, Taiwan

Molybdenum disulfide (MoS_2), one of two-dimensional semiconductors, can be applied in various fields such as electronics, optoelectronics, energy storage, catalysis, etc. In our work, large-area and highly-continuous MoS_2 thin film was prepared by magnetron sputtering process at different growth parameters. Then, a post-deposition annealing process was conducted in ultra-high vacuum and in the nitrogen-plasma environments in order to improve the crystallinity and optical properties of the MoS_2 layers. After the deposition and annealing process, MoS_2 thin films were characterized by reflection high-energy electron diffraction, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy. The phase transformation of MoS_2 layers was studied by differential scanning calorimetry. The optical properties of MoS_2 thin films were further investigated by photoreflectance spectroscopy. From the observations, the crystallinity of MoS_2 films can be significantly improved after annealing at 300 °C for 45 minutes in ultra-high vacuum. The increase of the annealing temperature did not further improve the crystallinity, but the surface chemical composition ratio of sulfur and molybdenum decreased at higher temperatures. Moreover, the enhancement for crystallinity of MoS_2 can be also achieved by the deposition temperature of 150 °C.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E1-2-WeM

Friction, Wear, Lubrication Effects, and Modeling II

Moderators: Noora Manninen, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Dr. Michael Chandross**, Sandia National Laboratories, USA, **Prof. Dr. Andreas Rosenkranz**, Universidad de Chile

8:20am **E1-2-WeM-2 Coatings and Composites for Extreme Environments Lab (CE)2**, ***Achyuth Kulkarni,*** *T. Ansell,* Naval Postgraduate School, USA

The Aluminum (6xxx.x) series alloys have gained widespread use across several industries, including aerospace, marine, structural, and automobile, primarily due to their impressive characteristics, such as low density, high specific strength, formability, and good corrosion resistance. However, despite these advantages, these alloys are susceptible to poor mechanical strength and wear resistance when exposed to challenging environmental conditions. To tackle these shortcomings, the development of Aluminum Metal Matrix Composites (MMC) has emerged as a crucial advancement in improving the properties of commercial Al alloys without compromising the ductility of their substrate material. The use of MMCs offers the potential to enhance the mechanical properties of Al alloys significantly, including tensile strength, hardness, wear resistance, and fatigue strength, thereby expanding their application range in harsh environments. Moreover, the incorporation of various reinforcing materials, such as ceramic particles, whiskers, fibers, and nanotubes, into the Al matrix can further augment its mechanical properties.

This study presents the synthesis of novel nanocomposite aluminum-based coatings reinforced with boron carbide (B_4C) microparticles and Graphene Nanoplatelets (GNPs) using a dual-reinforcement approach. The combination of the two reinforcing materials activates synergistic interactions between particles, resulting in improved dispersion and enhanced strengthening efficacy. To evaluate the efficiency of the dual-reinforcement approach, coatings containing 4 vol.% of GNPs and 4 vol.% B_4C are compared with unreinforced Al coatings and coatings reinforced with either 4 vol.% BNNT or 4 vol.% B_4C. The mechanical properties of the coatings are evaluated using adhesion testing, and nanoindentation. The structural characterization is done using Optical Microscopy, and Field Emission Scanning Electron Microscope (FE-SEM). Moreover, the elevated temperature (300ºC) dry sliding wear characteristics are studied. The worn surfaces are further analyzed using FESEM and a 3-D non-contact type optical profilometer. These findings have significant implications for the development of high-performance nanocomposite coatings in various industries, including aerospace, automotive, and structural applications.

8:40am **E1-2-WeM-3 Tribological Behavior of Mos_2 Based Coatings Under Different Sliding to Rolling Lubricated Contact Conditions**, ***Newton Fukumasu,*** *I. Machado,* University of São Paulo, Brazil*; R. Rego,* Aeronautics Institute of Technology, Brazil*; A. Tschiptschin, R. Souza,* University of São Paulo, Brazil

Powertrain components, such as gears and bearings, are used in a variety of sectors, including automotive, aerospace, energy conversion and manufacturing. These parts are subjected to high torque, cyclic loading and variable sliding to rolling ratio (SRR), which can induce sliding wear and/or rolling contact fatigue damage. Strategies to mitigate those failures include the use of advanced 2D coating materials, such as molybdenum disulfide, which may exhibit excellent solid lubrication properties under high contact stresses and pure sliding conditions. In principle, higher SRR conditions would demand coatings with higher hardness to mitigate sliding wear while lower SRR conditions would require more ductile coatings to improve RCF life. Given those demands, adaptive coatings that can change their properties in response to local contact conditions would improve component performance and durability. One mechanism to provide such local adaption is the shear-induced crystal orientation (SCO) promoted by high contact sliding condition, in which the highly oriented stresses and elevated local temperatures may lead to the formation of nanocrystalline regions on the surface of the material, resulting in improved mechanical properties, including increased hardness, fracture toughness and/or lower friction. In this work, MoS_2 based coatings were deposited by pulsed direct current magnetron sputtering technique and submitted to 1 GPa contact pressure under variable SRR (10% and 100%) to evaluate conditions more prone to promote the SCO mechanism. SAE 52100 steel discs were coated and tested in a ball-on-disc configuration using a Mini Traction Machine (PCS Inc.) equipment, in which both disc and ball tangential velocities were controlled to provide different SRR levels, maintaining a low average velocity to provide a boundary lubrication condition. Numerical simulations of tested configuration, using the Finite Element Method, indicated no significant correlation between shear stress developed at contact region and SRR values, while shear stress peak values were obtained for higher coefficient of friction. Experimental results indicated elevated coefficient of friction in the running in part of the test for all SRR conditions, decreasing to a lower stable COF along the test. The lower COF was achieved for highest SRR condition, in which Raman spectroscopy indicated the existence of a crystalline MoS_2 phase inside the wear track, not present initially in the as-deposited condition. These results support the SCO mechanism, adapting local coating properties that may improve wear and RCF resistance.

9:00am **E1-2-WeM-4 Catalytic Transformation of Lubricants to Wear-Protective Tribofilms on Selected Steel Surfaces During Sliding**, ***Yip-Wah Chung,*** *A. Khan, J. Ahmed, T. Martin, S. Liu,* Northwestern University, USA*; S. Berkebile,* Army Research Laboratory, USA*; Q. Wang,* Northwestern University, USA

We report here the impact of different alloying elements in steels on friction and wear behavior by performing ball-on-flat lubricated reciprocating tribotesting experiments on 52100 ball on steel flats with different compositions heat-treated to give similar hardness and microstructure, with polyalphaolefin (PAO-4) and/or *n*-dodecane as the lubricant. The major observation is that steels containing high concentrations (>= 5 wt.%) of Cr, Mo, V, or Cu/Ni give rise to markedly reduced wear compared with 52100 or plain carbon steels, with D2 steel, which contains 11.5 wt.% Cr, as the major alloying element being the most wear-resistant. The wear resistance is strongly correlated with the efficiency of formation of carbon-containing oligomeric films at surfaces as determined by Raman spectroscopy. Given the strong affinity of chromium to oxygen, chromium should exist as Cr_2O_3 at the steel surfaces during testing. We have performed molecular dynamics simulation on Cr_2O_3 and demonstrated its ability to catalyze the formation of carbon-containing oligomeric films from hydrocarbon molecules, consistent with its known catalytic activity in other hydrocarbon reactions. We believe that chromium-containing alloys, such as D2, and coatings, such as CrN, derive their wear resistance in part from the efficient *in-situ* formation of wear-protective carbon tribofilms at contacting asperities.

9:20am **E1-2-WeM-5 Aromatic Compounds as Sustainable Lubricants for Iron**, ***Sophie Loehlé,*** TotalEnergies, France **INVITED**

The present work will focus on one type of aromatic compound, Hypericin, as a nature constituent of St. John's wort, which is commonly known as anti-depressant, anti-virus, and anti-biotic agents. Besides its functions in medical treatment, the present work reveals its potential as an original friction modifier. Indeed, amazing tribological properties were observed by adding hypericin to glycerol in order to lubricate a steel/SiC tribopair. A hypericin concentration as low as 0.3% reduces friction coefficient (CoF) from ~ 0.02 to a value below 0.01 (the so-called superlubricity regime) under boundary lubrication. The excellent friction reduction property of hypericin derives from its hydroxygen functionalized carbopolycyclic structure, which achieves surface protection by forming a nanometer-thick hypericin-like tribofilm on both steel and SiC surfaces. The tribologically-induced polymerization of the molecules into graphene is detected by high resolution transmission electron microscopy (HRTEM) on a focused ion beam cross-section. First-principles calculations elucidate the thermodynamic driving force for the process, monitored in real time by *ab initio* and classical, molecular dynamics simulations. This work suggests an exciting and unconventional way to promote the formation of graphene by mechanical stresses and uncovers the great potential of many aromatic molecules derived from the pharmacopoeia, such as hypericin, as lubricants for industrial applications.

11:00am **E1-2-WeM-10 How Efficient Is the Self Adaption Concept for Low Friction with TMD-Based Sputtered Coatings***, **Albano Cavaleiro,*** University of Coimbra, Portugal **INVITED**

In last decades a huge amount of research was dedicated for further improvement of the frictional behaviour of sputtered coatings based on transition metal dichalcogenides (TMD). It is currently accepted that the low friction achieved with this type of coatings is based on the development of a tribolayer in the contact formed by a self-adaption process. The sliding process gives rise to the establishment of contact conditions which are able, by a reorientation / recrystallization process, to transform the material in the contact leading to the formation of a tribolayer with the required low friction characteristics. Whatever are the initial structure and phase composition in the sputtered deposited coatings, the transformation can occur in the contact if specific conditions of sliding exist.

In this talk, the conditions for activating the self adaption process will be presented and discussed. Sliding and contact parameters such as, the number of cycles, the temperature and the contact pressure, will be related with the type of TMD-based sputtered coatings and antagonist materials with the supporting of several practical examples. Tribological testing, using different experimental rigs, and detailed characterization of the materials in the contact are in the basis of the interpretation of the results to be presented.

11:40am **E1-2-WeM-12 Self-Lubricating Titanium Alloys: Design and High Temperature Tribological Performance Up to 800 °C***, H. Torres, K. Pichelbauer, S. Budnyk,* AC2T Research GmbH, Austria*; T. Schachinger, C. Gachot,* TU Wien, Austria*; **Manel Rodriguez Ripoll,*** AC2T Research GmbH, Austria

Titanium and its alloys are extensively used in aerospace and biomedical applications thanks to their high strength-to-weight ratios, excellent corrosion resistance or good biocompatibility. However, a general widespread of these alloys to other applications, such as machine elements is severely limited by their poor tribological properties.

With the aim of improving the performance of titanium alloys and spreading their applicability to new fields, the present work deals with the development of self-lubricating titanium alloys, with an emphasis on high temperature applications performance. The alloy developed is deposited by means of laser melting using a direct diode laser system, as laser deposition processes can be readily used for additive manufacturing techniques that offer a great flexibility and efficiency compared to traditional subtractive manufacturing processes.

A mixture of Bi with Ni powder (70:30) is pre-placed on a Ti6Al4V plate and melted with the direct diode laser. The melting process results in the presence of a 300 µm thickness coating on top of the Ti6Al4V plate. The microstructure and phase composition of the deposited self-lubricating titanium alloy coating is characterized using X-ray diffraction, scanning and transmission electron microscopy. The results reveal the presence of three distinct phases, a Ti6Al4V matrix with Bi-Ti-rich inclusions that are surrounded by a Ni-Ti-rich phase. Afterwards, the friction and wear performance of the developed self-lubricating coating is evaluated using high temperature tribological tests at temperatures ranging from room temperature up to 800 °C. The tribological experiments are performed against Ti6Al4V pins in reciprocating sliding.

The results reveal that the self-lubricating laser deposited titanium alloy is able to significantly decrease friction in the 400 to 800°C range, when compared to conventional Ti6Al4V. In terms of wear, the resulting self-lubricating alloy was also able to clearly outperform the reference Ti6Al4V in all the evaluated temperature ranges, from RT to 800°C. The friction reduction mechanism in the 400 to 600°C temperature range has been linked to the transfer and smearing of bismuth-rich phases to the counter body. At the highest temperature of 800°C, friction reduction could be linked to the formation of the ternary oxide $BiVO_4$, which could act as an effective solid lubricant. This overall tribological performance makes the presented self-lubricating alloy a potential candidate for numerous high temperature applications in the aerospace and energy sectors.

12:00pm **E1-2-WeM-13 Electrodeposited of Silver Nano-Particules Plant Based to Improve Lubrication of Composite Films***, **Pierre-Antoine Gay,*** Haute Ecole Arc Ingénierie, Switzerland*; I. Markovic Milosevic,* HEPIA Institut inSTI, Switzerland*; T. Journot,* HE ARC Ingénierie, Switzerland*; J. Maurer,* Faculty of Biology and Medicine. Clinical pharmacology, Switzerland

Electrodeposition of silver and nanoparticles plant based like TiO_2 and Al_2O_3 has been successfully demonstrated for the first time in silver electrodeposit composite films. Their tribological properties and wear resistance were investigated by a pin-on-disk type friction testing using an electrical system to also measure the resistivity of the composite coatings.

The friction coefficient of silver/TiO_2composite films decreased with increasing TiO_2content. Plating parameters, nanoparticles concentration and zeta potential were systematically investigated in order to found a relationship between incorporation rate *Vp and* friction coefficient. Ag – $TiO_2$with 60g/L of nanoparticles composite film showed the minimum friction coefficient value, with wear resistance 40% better. A comparaison with electrodeposit composit coatings was discussed with traditional nanoparticles.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session G1-WeM

Advances in Application Driven Research: New Methods, Materials, and Equipment for PVD, CVD, and PECVD Processes

Moderators: Ladislav Bardos, Uppsala University, Sweden, **Vikram Bedekar**, The Timken Company, USA

8:00am **G1-WeM-1 Improve Cutting Performance of Carbide Cutting Tools with Multilayer TiAlxN-Based Arc-Cathodic PVD Coating for Industrial Applications***, **Fernando Santiago,*** SADOSA, Mexico*; D. Melo,* ITESM, Mexico

Multilayer TiN/TiAlxN coating deposited by arc-cathodic PVD method evaluated in this work. The adhesion of the single or multiplayer coating was studied and stress formation as the function of bias voltage during the deposition process in solid carbide. Industrial Arc-cathodic PVD with a balanced magnetron was used to coat end-mills carbide. The samples coated were tried in slotting operation in the CNC machine center using extreme cutting parameters.

8:20am **G1-WeM-2 Correlation between Deposition Conditions, Properties and Cutting Performance of Al-Rich AlCrN Wear Protective Coatings Produced by Reactive Arc Evaporation***, **Alexandre Michau,** D. Kurapov, I. Iovkov, S. Fabbro,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; L. Zauner, H. Riedl,* CDL-SEC at TU Wien, Austria*; D. Cahill,* University of Illinois at Urbana-Champaign, USA

Due to its outstanding wear protective properties, the AlCrN system is used in a broad range of cutting and forming tools. For many wear protective applications, AlCrN layers with higher Al content are of particular interest. This might be attributed to a combination of excellent mechanical properties, oxidation resistance, phase stability at high temperatures as well as low thermal conductivity. Having a tool coated with a low thermal conductivity layer during a cutting operation is crucial, as it provides thermal barrier properties. More heat can be dissipated into the chips, preventing the substrate from overheating, improving significantly tool performance.

The reactivity of the arc-deposited AlCrN system is mainly governed by the Al/Cr ratio. If a fcc lattice can be obtained for lower ratios, <70/30 at.%, incorporating more Al triggers gradually the appearance of a hcp-AlN phase. This crystalline transition is accompanied by several other transitions. If the hcp phase exceeds a critical amount, the morphology shifts from columnar to fine-grained and mechanical properties start to decline, with lower values of Young's modulus (E), hardness and residual stress, degrading the wear resistance. Typically, for wear protective applications, AlCrN coatings with fcc crystal structure and E above 400 GPa are preferred.

In this work, AlCrN was deposited by cathodic arc with targets having an Al/Cr ratio from 70/30 to 90/10. Magnetic field configuration as well as bias voltage were varied to adjust the energy influx into the growing film. Influence of the Al/Cr ratio on the morphology, crystal structure, composition and mechanical properties of deposited coatings was investigated at room temperature and after a series of vacuum annealing up to 1200°C, by scanning electron microscope, x-ray diffraction and nanoindentations. Thermal conductivity of the coatings was evaluated by time-domain thermoreflectance as a function of the Al content. It was found that the AlCrN system reactivity towards the bias voltage is independent of the magnetic field configuration, an increasing bias voltage leading to less Al in the films. However, a proper adjustment of the magnetic field configuration allows the deposition of AlCrN films, containing up to 80 at% Al, maintaining fcc crystal structure with columnar morphology and E above 400 GPa. The magnetic field on the cathode surface significantly influences the plasma conditions near the substrate. The coating analysis shows strong dependence of the plasma characteristic on the coating structure and properties. The correlation between the growth conditions of the coatings and their cutting performance is discussed.

8:40am **G1-WeM-3 Designed for Impact: Successful Forming of 3rd Generation Advanced High Strength Steels in Electric Vehicles' Body-in-White**, ***Tobias Brögelmann***, *T. Hurkmans,* IHI Ionbond Netherlands B.V., Netherlands; *J. Owens-Mawson, G. Savva,* IHI Ionbond LLC, USA

The main goals of the mobility driven global energy system transformation are to increase the efficiency and environmental compatibility of conventional and renewable energy to reduce the global CO_2 footprint. More than 60% of all product innovations are based on the development of new and improved high-performance materials, which requires continuous optimization of associated production technologies and manufacturing processes. Here, the right coating solution produced by physical vapor deposition (PVD), chemical vapor deposition (CVD) and plasma-assisted CVD (PACVD) can increase productivity and ensure excellent product quality while minimizing production downtime and scrap rate in forming and molding tool applications.

Within the automotive sector, there is a prime example of continuous development of new materials in the use of press hardened steels (PHS), martensitic and multi-phase ultra-high strength steels (UHSS), dual phase advanced high strength steels (AHSS) and aluminum alloys in the automotive body-in-white. The associated forming applications cover a broad stress profile that results in complex demands on the forming tools, e.g. a high resistance to impact fatigue and crack formation under cyclic loading and a high resistance to abrasive and adhesive wear. One encouraging way of forming these materials is to reduce the frictional forces between the die and the workpiece to obtain an optimum material flow, and to reduce stresses on the die by extending the work-hardening of the workpiece material. The optimum friction state while minimizing costly and environmentally harmful lubricant usage can be set by incorporating the lubrication properties into the coating.

This paper deals with the investigation of hard coatings with self-lubricating properties for industrial forming applications. Three different lubricant concepts in the as-deposited state are discussed, i.e., solid lubricants with layer-lattice structure such as sulfides (MoS_2) and diamond-like carbon (DLC) as well as oxides. Current R&D needs and the preferred coating solutions are introduced based on the performance during industrial field tests. The gap between basic analysis of the coating solutions and time- and cost-intensive field tests is closed by application-oriented model tests. In collaboration with industrial associations and academia, these cover a strip-pull test and an impact fatigue test. Results from the impact fatigue test demonstrate the importance of plasma nitriding to improve the load-carrying capacity for the PVD coating. The improved impact fatigue behavior of such duplex coatings is also reflected in improved performance in the forming application.

9:00am **G1-WeM-4 In-Situ Incorporation of Nanocontainers During Plasma Electrolytic Oxidation**, *S. Al Abri, A. Rogov, A. Matthews, B. Mingo,* ***Aleksey Yerokhin***, The University of Manchester, UK

Plasma electrolytic oxidation (PEO) is a surface treatment technique employed to light metals to enhance their properties such as heat, wear, and corrosion resistance. The coating comprises of inner thin layer and a porous outer layer. The inner layer provides passive protection separating the substrate from the surrounding environment. However, the presence of the porous outer layer allows the propagation of aggressive ions toward the substrate initiating localized corrosion.

This study aims to functionalise PEO coating by incorporating corrosion inhibitors encapsulated into nanocontainers in a single-step process. The inhibitors will be released when detecting electrochemical activity associated with corrosion initiation, providing corrosion protection on demand. The incorporation of nanocontainers in a single step allows the homogenous distribution of the nanocontainers through the coating matrix, but the integrity of the nanocontainers might be compromised due to the high temperatures developed at microdischarge sites. To prevent this, the thermodynamic conditions of the plasma process will be optimised by establishing the soft spark regime at the earliest stage of the PEO process, which allows the non-reactive incorporation of nanocontainers.

The presence of nanocontainers in PEO coating was confirmed by scanning electron microscopy and the corrosion behaviour of PEO coating was assessed by electrochemical impedance spectroscopy.

9:20am **G1-WeM-5 High-Resolution Investigation of the Microstructural Features and Crystal Forms of Industrial Ti(C,N) CVD Thin Hard Coating**, ***Idriss El Azhari***, Saarland University, Germany; *J. García,* Sandvik Coromant R&D Materials and Processes, Sweden; *C. Pauly, J. Barrirero, M. Engstler, F. Soldera,* Saarland University, Germany; *L. Llanes,* Universitat Politècnica de Catalunya, Spain; *F. Mücklich,* Saarland University, Germany

In metal cutting industry, Ti(C,N) is one of the most used thin hard coating during the last two decades. Recently, the authors carried out a multi-scale testing and characterization campaign in which industrial cutting tools coated with Ti(C,N) is contrasted to Zr(C,N). The objective was to reveal the microstructural features that influence their mechanical behavior for milling applications. The more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, better cohesive strength at the grain boundaries and plastic deformation were found to assign to the Zr(C,N) better structural integrity and fracture toughness during intermittent cutting in comparison to the inserts coated with Ti(C,N). In the present work, light is shed on unexplored other characteristics related to the grain boundary complexions and crystal shapes of Ti(C,N). State of the art characterization techniques were used such as atom probe tomography (APT), high-resolution secondary ion mass spectrometry imaging (nano-SIMS) and 3D electron backscatter diffraction (EBSD). Approaches to tailor the microstructure of these compounds to enhance the ductility and maintain the strength are suggested.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific F-G - Session G2-1-WeM

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications I

Moderator: Jan-Ole Achenbach, KCS Europe GmbH, Germany

11:00am **G2-1-WeM-10 Enhanced Tool Surface Properties Against Adhesion in Aluminum Forging**, ***Hanno Paschke***, *T. Brueckner,* Fraunhofer IST am DOC, Germany; *A. Thewes,* Institute for Surface Technology, TU Braunschweig, Germany; *J. Peddinghaus,* Institute of Forming Technology and Machines, Leibniz University Hanover, Germany

The occurring wear during aluminum processing in warm bulk forming limits the economic potential of this highly productive process. Mainly due to the occurring adhesive mechanisms during contact between aluminum and hot working steel, a reconditioning of the forging dies is necessary. A tribological optimization of the system is necessary. Compared to steel forging the investigations in aluminum forging are still limited to a simplified level so far. The presented work aims at filling this gap introducing a holistic analytic approach. Different prospective surface modifications are tribologically characterized in a tribometer with ball-on-disc test. Processing level is approximated with ring compression tests and serial forging tests as well. This investigation route allows the identification of influencing factors during material processing such as lubrication effects and the role of anti-adhesive surface chemistry. Thus, it is possible to evaluate the suitability of different tool coatings based on CrXN (X representing dopant), Ti-B-X multiphase systems (X representing additional elements like Si, C and N) and DLC coatings. Diffusion treatments including a boriding treatment were investigated as well.

The general findings reveal adhesive effects caused by the material flow during processing. When the material flow is deflected at obstacles or by high friction, the passive layer breaks and uncovers pure aluminum. Thus, an enlargement of the active surface of the aluminum occurs. An additional superposition of the contact pressure increases this effect. The presented work tries to focus on the industrial application in order to reveal the potential of coated tools to achieve a significant reduction of aluminum adhesion. Thus, an economic processing is possible by extended service life time and reduced downtime.

11:20am **G2-1-WeM-11 Evaluation of Permanent Thin-Film Coatings Applied to Die Surfaces to Reduce Lubricant Use during Aluminum Forging Operations***, J. Vazquez Gonzalez,* ***Stephen Midson****, A. Korenyi-Both, K. Clarke,* Colorado School of Mines, USA

During the forging process, conventional lubricants such as oils and graphite are applied to the faces of the forging tool, to reduce friction and to minimize transfer of the forged material to the die faces. Although currently required for successful forging operations, there are a number of disadvantages associated with the use of such lubricants, including reduction in part quality, decreased die life, higher costs, increased cycle time, and environmental issues associated with the cleanliness of the workspace. The objective of the research described in this presentation is to reduce or eliminate the need for conventional lubricants during forging through the use of permanent thin-film lubricious coatings applied to the faces of the forging die. Rather than using conventional pin-on-disk type testing to measure friction, this study utilized a functional ring forging test (RFT), where the deformation characteristics of a ring-shaped sample provide an estimate of the level of friction developed during forging. The samples used for forging were rings of aluminum alloy 6061, 25 mm OD, 12.5 mm ID, and 8.4 mm tall. Forging was performed using an instrumented 100 kip forging press. Various thin-film coatings have been evaluated, and testing has been performed at both room and elevated temperatures, and in the lubricated and un-lubricated conditions. The results have shown that two classes of coatings can significantly reduce friction during un-lubricated laboratory ring forging operations, diamond-like carbon (DLC) and a commercial coating containing both graphitic and molybdenum disulfide particles. The results of the testing will be reported, along with analytical testing of the structure and compositions of the coatings.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country D - Session G3-WeM
Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderator: Dr. Christoph Schiffers, CemeCon AG, Germany

8:00am **G3-WeM-1 A Novel AlCr-Based PVD Coating Design for Threading Operation of Super Duplex Stainless Steel***,* ***Qianxi He****, J. M. DePaiva, T. K. Filho,* McMaster University, Canada*; F. L. Amorim, R. D.Torres,* Pontificia Universidade Católica do Paraná, Brazil*; G. Fox-Rabinovich, S. C. Veldhuis,* McMaster University, Canada

The application of PVD coating is largely employed in industry to improve the tool performance of cutting tools designed to perform cutting in several distinguished materials. As a result, there is a sharp increase in demand for innovative materials with remarkable qualities. Current developments in unconventional cutting materials show the potential of different coating combinations. Based on recent finds PVD Hard coatings based on Al, Cr and Ti are recommended for the machining of super duplex stainless steel (SDSS). In this work, three different PVD coatings systems were applied for the threading process of SDSS. Monolayer Al50Cr50N, Al60Cr40N, and multilayer Al50Cr50N/Al50Ti45Si5N were deposited on cemented carbide inserts. The present article highlighted the effect of alloying and coating architecture design on the mechanical properties, and wear performance of the cutting tools. Adhesion and oxidation were observed as predominant wear mechanisms, and the tool life was superior once the system was coated by the novelmultilayer Al50Cr50N/Al50Ti45Si5N. In order to understand these results, the effect of different parameters on the mechanical properties of the coatings was presented and discussed.

8:20am **G3-WeM-2 Property and Deposition Technology for Highly Al-Containing AlCrN Coatings by Arc Ion Plating***,* ***Ryosuke Takei****, T. Takahashi, S. Kujime,* Kobe Steel Ltd., Japan

AlCrN coating is one of the most widely used hard coatings in cutting tool applications. The cutting performance of the coating is dependent on its Al content. The mechanical hardness, wear resistance as well as oxidation resistance at high temperature are known to be increased with the Al content, and hence exhibits a good performance even at a severe machining condition. This feature is generally accepted at an Al content, i.e., fraction of metallic element of Al and Cr, of about up to 70 at.% for AlCrN coatings deposited by physical vapor deposition such as sputtering and cathodic arc, also referred to as arc ion plating. This is mainly linked to the crystallographic structure and characteristics thereof, in which the metastable cubic phase with the favorable mechanical and thermal properties can be sustained at Al content up to 70 at.% while the more thermodynamically stable hexagonal phase with the poor properties tends to form at a higher Al content above 70 at.%. A deposition technique of highly Al containing AlCrN keeping the cubic phase is believed to be a key for further improvement of the coating performance and hence the tool life of cutting tools.

There are some practical challenges for highly Al-containing AlCrN coatings. As compared to typical transition metals of Ti and Cr for nitride coatings, Al has a low melting temperature of 660℃. Therefore, the use of a binary compound target with a high fraction of Al usually results in emission of a large number of macroparticle, which creates internal defects during film growth and adverse effect on the surface quality of the coatings. Another practical point is to ensure the sufficient adhesion of the coating. Coating adhesion of highly Al-containing AlCrN coating appears to be intrinsically poor as compared to those at less Al content.

In this work, we demonstrate the newly developed coating system of arc ion plating equipped with the deposition technology particularly for highly Al-containing AlCrN coatings. With the combination of a newly developed arc source, etching technology and optimization of deposition process parameters, AlCrN coating at Al content above 70 at.% still exhibiting a good surface quality and adhesion were successfully deposited. The coating deposited were characterized in terms of crystallographic structure, surface morphology, chemical composition, and mechanical properties by XRD, SEM-EDX, and nanoindentation, respectively. In order to investigate the performance of the coatings in application, the coatings were also deposited on typical cutting tools such as end-mills and milling inserts and the cutting performance and wear resistance thereof were evaluated.

8:40am **G3-WeM-3 Challenges and Target-Oriented Paths to Maintenance-Free High-Performance Progressive Dies Using HiPIMS-Coatings***,* ***Martin Hess****,* Robert-Bosch-Str., 5, Germany **INVITED**

Being able to economically manufacture precision contacts in large-scale production of 10 million units or more requires more than just having the correctly designed systems.

In such a challenging environment, it is not only the current trend towards electromobility that is driving up the quantities of electrical components and connectors demanded by the market. The consequence for the stamping tool manufacturers is the demand of continuously increasing tool efficiency with increasing stroke rates of currently up to 3000 strokes per minute. In order to achieve the wear resistance of the progressive dies required for this purpose, low-wear active elements (punches, dies, bending and coining tools, clamps, sliding guides, etc.) are essential for the shortest possible stamping press downtimes. Since wear and tear on a single active part of a complex progressive die can already lead to a, time-consuming and therefore costly, maintenance intervention, wear-resistant coatings of active parts are an even more relevant key factor for the production of electrical contact components with outputs of several millions parts per day, respectively up to several billion (!) parts (e. g. connectors, cellphone parts, etc.) per year and progressive die. In addition to general coating challenges as known from micro tools for machining, topics specifically related to stamping applications such as micro cavities, influence of cutting air, parallel machining of different materials with strongly different strengths in one tool, low artifact coated surfaces etc. will be addressed.

The presentation places a special emphasis on HiPIMS, as the latest HIPIMS coatings used for machining high-strength stainless steel strip (Rm > 1400 N/mm²) achieve for the first time comparable wear resistance or part yield compared to active parts machining high-performance copper alloy strip in parallel in the same progressive die. As a result, the goal of the maintenance-free progressive die – which can contain more than 1000 PVD-coated active parts – is also achieved for tools that produce complex electrical contacts with contact securing high-strength oversprings in one progressive die for production lots in the higher two-digit million range.

9:20am **G3-WeM-5 Oxidation and Wear Behavior of CrAlMoN with Varied Mo-content for Cutting $TiAl_6V_4$**, *K. Bobzin, C. Kalscheuer, **Nina Stachowski,*** Surface Engineering Institute - RWTH Aachen University, Germany*; W. Hintze, J. Dege, C. Möller, P. Ploog,* Institute of Production Management and Technology - Hamburg University of Technology, Germany

The cutting of difficult to machine materials such as titanium is still challenging for the machining industry. Materials properties lead to accelerated tool wear and premature failure. In case of the titanium alloy TiAl6V4, the low thermal conductivity of λ = 5.8 W/mK and the low Young's modulus of 110 GPa ≤ E ≤ 140 GPa combined with the high yield strength $R_{p0.2}$ = 870 N / mm² cause high temperatures, mechanical loads as well as self-excited vibrations at the cutting edge. The use of uncoated carbide tools is currently state of the art. However, temperature active, self-lubricating physical vapor deposition (PVD) coatings like CrAlMoN already showed first promising results to reduce friction and wear during turning of TiAl6V4. In order to develop an effective coating, it is important to understand the wear development and oxidation behavior as a function of the chemical composition of the coating. In the present study, self-lubricating CrAlMoN coatings with x_{Mo} = 20 at.-%, x_{Mo} = 30 at.–% and x_{Mo} = 40 at.–% in the metal content were investigated on cemented carbide tools. The coatings were deposited by hybrid process combining dcMS and HPPMS. Coating morphology, thickness, chemical composition, indentation hardness, indentation modulus at ϑ = 20 °C, ϑ = 200 °C ϑ = 400 °C and ϑ = 600 °C as well as the oxidation behavior were analyzed. Moreover, wear development after cutting tests using a computer numerical controlled (CNC) lathe with a cutting velocity of v_c = 80 m/min and a feed rate of 0.12 mm were analyzed, after defined cutting intervals of t_c = 5 s, t_c = 10 s, t_c = 20 s t_c = 40 s, t_c = 80 s, t_c = 120 s. Independent of the amount of Mo, all coating variants possessed a dense morphology and a smooth surface topography, as well as a coating adhesion class of HF1 to the cemented carbide tools in Rockwell indentation tests according to DIN 4856. The tests were conducted in the initial state and after heat treatments up to ϑ = 800 °C. With increasing amount of Mo, heat treatment temperature and time, more self-lubricating molybdenum oxides such as MoO_3 and Mo_4O_{11} were detected by Raman spectroscopy subsequently. Therefore, the coating with x_{Mo} = 40 at.–% in the metal content possess the highest amount of molybdenum oxides. After cutting tests on the tool flank surface, also molybdenum oxides were found by Raman spectroscopy. Additionally, it was observed, that the areas of tribochemical reactions at the rake faces show a growing trend with higher amount of Mo in the coating. The level of flank wear land width decreases with increasing amount of Mo.

11:00am **G3-WeM-10 The Significance and Application Area of CVD $TiCN/Al_2O_3$ based Coatings for Today's Cutting Tools**, ***Christoph Czettl,*** CERATIZIT Austria Gesellschaft m.b.H., Austria*; M. Pohler,* CERATIZIT Austria GmbH, Austria*; N. Schalk, M. Tkadletz,* Montanuniversität Leoben, Austria*; F. Konstantiniuk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leobon, Austria **INVITED**

Chemical vapor deposited (CVD) coatings are frequently used for metal cutting applications, especially on indexable inserts. Beside coating systems like TiAlN, TiB_2 or other innovative CVD systems, the $TiCN/Al_2O_3$ based coatings still play an important role. For turning and milling of cast materials, low carbon steels and martensitic steels these architectures are still the first choice. Thus, recent progress in the development of microstructures and architectures as well as improvements of the deposition techniques are summarized. With their first introduction, in the mid of the 1970's, a huge step in cutting performance could be reached. In the following decades, several optimizations of architecture and deposition techniques were introduced, including the medium temperature process for TiCN, defined growth of α-and κ-Al_2O_3 and highly textured α-Al_2O_3 layers. Modern analytical techniques as well as simulation methods were necessary to create a comprehensive understanding of this coating system and explain why they are still indispensable in industry today. This talk gives an historical overview of the development process of the $TiCN/Al_2O_3$ coating system until reaching the current state of the art.

11:40am **G3-WeM-12 Indentation and Sliding Contact Testing of Three Laser-textured and PVD-coated Cemented Carbide Tools**, ***Shiqi Fang,*** Saarland University, Germany*; C. Colominas,* Flubetech, S.L., Spain*; C. Pauly,* Saarland University, Germany*; N. Salán, L. Llanes,* Universitat Politècnica de Catalunya, Spain

In this study, a new concept cemented carbide tool is presented with laser-generated abrasive-like protrusions on their machining surfaces that mimic the surface features of diamond or cubic boron nitride abrasives commonly used on honing tools. The novel tools were first surface textured by a picosecond laser, and then the new surface structure was protected by three different PVD ceramic hard coatings. All three nitride-based coatings, i.e., TiSiN-TiAlN, TiSiN-TiAlN-CrN and AlTiN-CrN, differ in the adhesion layer and coating structure. The coating-substrate systems were assessed by means of indenting and sliding contact testing. Experimental methodology included (1) 'passive' Vickers indentation hardness tests, and (2) 'active' machining tests. In both cases, the resulting surface integrity was inspected by using FIB/SEM/EDS. It is found that both laser texturing and coating deposition significantly increased the hardness of the coated cemented carbide. The tool coated by the two-layer film (TiSiN-TiAlN) achieved the best performance, in terms of both hardness enhancement and damage prevention experienced under both tests. Meanwhile, improvement was much less pronounced by the two-layer (AlTiN-CrN) coated tool. Here, cracks appeared under the Vickers indentations and the film was completely or partially spalled-off at some protrusion tops (cutting fronts), due to the concentrated stress during the machining. Finally, the three-layer coating with the TiSiN on the top (TiSiN-TiAlN-CrN) exhibited an intermediate response, where moderate hardness increase was combined with some wear – although less severe than for AlTiN-CrN film - taking place at critical points, such as cutting fronts.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session G4-WeM
Hybrid Systems, Processes and Coatings

Moderators: Hana Barankova, Uppsala University, Sweden, **Sang-Yul Lee**, Korea Aerospace University, Republic of Korea

11:00am **G4-WeM-10 Water-Repellent and Low Emissivity Coatings on Fabric Prepared by Roll-to-Roll Hollow Cathode PECVD and Magnetron Sputtering**, *J. Jolibois,* AGC Interpane Demonstration Center, Germany*; G. Arnoult,* AGC Plasma Technology Solutions, Belgium*; N. Koyra,* AGC Interpane Demonstration Center, Germany*; **John Chambers,*** AGC Plasma Technology Solutions, USA*; H. Weis,* AGC Interpane Demonstration Center, Germany*; H. Wiame,* AGC Plasma Technology Solutions, Belgium

Thin film deposition appears to be a suitable process for textile finishing at a time when environmental protection is a global concern. It enables textile functionalization without the wet processing drawbacks, such as hazardous wastewaters. Moreover, thin film technology limits the use of chemicals, water, etc., and do not require a drying system resulting in low energy consumption. Water and oil repellent finishes by PECVD are among the most studied treatments for fabrics. While recently there is a growing interest in metallizing textiles using the magnetron sputtering method.

In this work, we demonstrate the successful use of the hollow cathode (HC) technology to impart water repellent property on polyolefin fabric with silicone precursor. The effects of parameters such as power, pressure and gas mixture on waterrepellencyare evaluated according to international standards such as the resistance to surface wetting. The water repellent finish has a resistance surface wetting of 4.5 and decreases steadily after several wash cycles.

In addition, we show the deposition of low-emissivity coatings prepared by roll-to-roll on a 1.6-m wide fabric. The low-E property is obtained by magnetron sputtering of metal layer (*e.g.* aluminium) and silicone polymer by HC-PECVD. Here, the silicone polymer is used as a corrosion protection barrier. The low-E layer displays an emissivity of 0.2 and 0.25 after 48h in saline water.

11:20am **G4-WeM-11 Amorphous Carbon Coatings on Glass for High Voltage Protection**, ***Hana Barankova,*** *L. Bardos,* Uppsala University, Sweden

Radio frequency Hollow Cathode based hybrid process integrating both Physical Vapor Deposition and Plasma Enhanced Chemical Vapor Deposition was used for deposition of amorphous carbon directly on glass, without using any interlayer. The films grown at 0.25 – 0.5 % of acetylene in the mixture with argon were subjected to high voltage pulses and the performance was compared with uncoated glass samples to test the protection ability of the films, the ability to prevent the deteriorating effects of corona flashovers/arcs. In contrast to the uncoated glass the well adherent carbon films with thicknesses between 3.5 and 17 µm exhibited an excellent protection of the glass substrate against the flashovers/arc damages in both polarities of the electric field with voltages up to 300 kV.

11:40am **G4-WeM-12 Plasma Pretreatment of Small Parts and Granular Materials in Bulk Vacuum Coating*, Heidrun Klostermann*,** *B. Krätzschmar, F. Fietzke,* Fraunhofer FEP, Germany

Bulk coating seems to be an intriguing variant of vacuum coating for small mass parts. Compared to individual part coating, the handling effort is considerably reduced. This applies to indirect and direct labor such as the production and maintenance of adapted fixtures and the charging and de-charging of individual parts. Furthermore, the utilization of processing volume can be maximized, avoiding void space between the parts. This benefit turns into a drawback during plasma etching due to the competitive processes of sputter cleaning and re-deposition on the parts. However, plasma pretreatment of the surfaces is an indispensable step also in bulk vacuum coating. Otherwise, the permanent mechanical impact during agitation will entail delamination defects due to interface imperfections. Identification of appropriate plasma pretreatment regimes is as important as the coating step itself.

In case of granular materials, the aspect of an effective removal of adsorbents before the coating step is a major issue. It becomes more and more challenging with decreasing grain size, hence increasing outer surface area of an ever bigger number of grains, and even more difficult if the grains consist of porous material, where inner surfaces are loaded with adsorbates as well.

Fraunhofer FEP is developing coating equipment and technology for an efficient coating of small parts and granular materials. Depending on the application, adapted plasma pretreatment steps based on a hollow cathode plasma source are established. In this contribution two applications will be presented: 1. the plasma pretreatment of small metallic parts, 2. The plasma heating of hygroscopic porous granular material. In both cases, the pre-treatment steps are essential for the whole processing and have a big effect on the resulting coating. To establish such processes, many aspects have to be considered: 1. Generation of a sufficiently dense plasma close to the bulk of substrate material to be treated, 2. Identification of parameters for effective material removal, 3. Verification of a sufficient and uniform treatment of the batch, 4. Qualification of etching efficiency, 5. Coating qualification including the indirect approval of the pretreatment step. The presentation will give insight into procedures and results along this sequence.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-2-WeM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II

Moderator: Dr. James Gibson, University of Oxford, UK

8:40am **H2-2-WeM-3 The Nature of Defects and their Dynamics Characterized using Scanning Electron Microscopy Approaches*, Dan S. Gianola,*** University of California Santa Barbara, USA **INVITED**

The past several years has witnessed a surging popularity of two techniques for defect characterization in crystalline materials: (*i*) scanning transmission electron microscopy (STEM) using diffraction contrast imaging, and (*ii*) electron back-scattered diffraction (EBSD) mapping.Here, we link these capabilities by employing a field emission SEM equipped with a transmission detector for defect characterization – termed transmission SEM (TSEM).Imaging modes that are similar to conventional CTEM bright field (BF) and dark field (DF) and STEM are explored, and some of the differences due to the varying accelerating voltages highlighted.We further demonstrate how the richness of information encoded in EBSD patterns is amplified by a new generation of direct electron detectors that enable high speed mapping and acquisition of high-fidelity patterns that can be used for statistically-meaningful defect analyses.Using this new system, we quantify the sharpness of EBSD patterns obtained from several additively manufactured metallic alloys, which reveals sub-grain dislocation structures with high fidelity.Our results demonstrate that the dislocation cell walls produced during fast solidification do not always possess measurable misorientations, and thus do not reflect a geometrically necessary defect organization.Finally, we will show how these techniques can be employed for *in situ* tensile experiments to study the nature of dislocations dynamics in several structural alloys.

9:20am **H2-2-WeM-5 Measurement of Hardness and Elastic Modulus by Depth Sensing Indentation: Improvements to the Technique Based on Continuous Stiffness Measurement*, Warren Oliver,*** KLA-Tencor, USA*; P. Sudharshan,* ARCI, India*; G. Pharr,* Texas A&M University, USA

The method to measure hardness and elastic modulus of small volumes of material by instrumented indentation presented in the seminal works of Oliver and Pharr in 1992 and 2004, has revolutionized the field of small scale nanomechanical testing. Several recent advances in measurement electronics have enabled testing over a wider range of test conditions (speeds) using methodologies that were developed earlier, which requires a critical assessment. In the backdrop of the latest developments in instrumentation and test methodologies, an overview of the various factors affecting the precision and accuracy of the nanoindentation test results at different test conditions with specific focus on Continuous Stiffness Measurement (CSM) technique will be presented. The CSM technique has also been used to explore the time dependence of material properties.In particular, the stiffness of the contact together with the modulus of the material being characterized gives a direct way of calculating the contact area at any instant that is relatively insensitive to thermally driven displacement drift rates.One of the parameters used to calculate the hardness being measured in such experiments is the load being exerted on the sample by the indenter.The CSM technique requires that the load on the sample be modulated to some degree at a specific frequency.The question arises what value of the load should be used to calculate the hardness when the load is being modulated.Results indicating how the load could be chosen will be presented.

9:40am **H2-2-WeM-6 Ultrasonically Induced Nanofatigue During Nanoindentation*, Antanas Daugela,*** Nanometronix LLC, USA*; J. Daugela,* Johns Hopkins University, USA

In the era of fast product development thin film developers are looking for quick and efficient methods of characterization.This is especialy true in a semi-conductor industry where advanced multilayered chip/MEMS develpment process needs advanced characterization techniques. Nanoindentation based multi-cycle loading is offering insides into the real-time contact fracture dynamics [1]. A nanofatigue phenomenon can be observed on thin sub-micrometer films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves where post-test imaging helps in identifying materials' behavior [2, 3].In addition, clasical Mason-Coffin and racheting fatigue models derived for the nanoscale contact can be utilized in the predictions and correlate reasonably well with nanofatigue cycles obtained experimentally.

A newly developed ultrasonic nanoindentation tip operates at hundreds of kHz, therefore, inducing milions of load cycles within seconds.The resulting nanofatigue induces different thin film fracture modes such as radial, sink-in and produce unique acoustic signatures.The ultrasonic nanoindentation tip monitors associated waveforms, which can provide additional inside into nanofatigue process dynamics via advanced acoustic waveform analysis.Following our previous study [4], acoustic waveforms were processed using a combination of wavelet based signal decomposition and Deep Learning. The proposed Deep Learning technique yields a reliable classification of acoustic signatures obtained during fracturing ofsub-micrometer thick coatings.

References:

1. B. D. Beake et al, *Materials Science & Engineering A*, 7**80** 139159 (2020)

2. H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

3. Y. Matsuda et al, Wear, **259**, p. 1497–1501 (2005)

4. A Daugela et al, *Materials Science & Engineering A*, **800** 140273 (2021)

11:00am **H2-2-WeM-10 Comparison of Electrical and Image-Based Sensing for Quantitative in Situ TEM Nanomechanical Testing***, S. Stangebye, L. Daza, X. Liu, J. Kacher,* ***Olivier Pierron,*** Georgia Tech, USA

This presentation describes a microelectromechanical system (MEMS) based, quantitative in situ TEM nanomechanical testing technique to measure the mechanical properties of thin film specimens and characterize their plastic flow kinetics, while observing their deformation mechanisms. The MEMS is comprised of a thermal actuator and load sensor. Two types of sensing techniques, electrical (capacitive) and image-based, are compared in term of their accuracy and precision. The advantages and drawback of each sensing technique are also discussed. The mechanical properties of Al and Au thin films, with a range of thickness (from 25 to 200 nm) and average grain size (from ~50 to 350 nm), and their deformation mechanisms are characterized, and the associated size effects are investigated.

11:20am **H2-2-WeM-11 Understanding the Interface Strain Induced hcp-to-bcc Phase Transformation in Nanolaminate Mg***, K. Jacob,* Iowa State University, USA*; K. Yaddanapudi,* University of California, Davis, USA*; M. Jain,* University of Nevada, Sandia National Laboratory, USA*; J. Michler,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Sid Pathak**,* Iowa State University, USA

In this work, we strive to answer fundamental questions related to the hcp-to-bcc pseudomorphic phase transformation of Mg in Nb/Mg nanolaminates. Mg and its alloys attract immense attention for being one of the most promising lightweight structural materials, and are of growing interest to automobile and aircraft industries due to their low density, being 35% lighter than aluminum and 78% lighter than steel . The constituent Mg phase is plastically anisotropic and not ductile due to its inherent hexagonal closed pack (hcp) structure. However, by encouraging a pseudomorphic phase transformation of Mg within the Mg/Nb multilayers, the hcp structure of Mg was transformed to a less anisotropic and more ductile body center cubic (bcc) structure at ambient pressures. The critical layer thickness for stabilizing the pseudomorphic bcc Mg phase (above which the metal reverts back to its traditional hcp structure under ambient conditions) was found to be around 7-8 nm from experimental observations. However this value is significantly larger than the critical layer thickness of 4.2 nm for Mg predicted using an analytical model with density functional theory (DFT) information, or 5 nm from direct thermodynamic calculations. This large discrepancy between experimental and theoretical values clearly indicates that a complete understanding of the underlying mechanisms involved during the phase transformations is still lacking.

This work aims to investigate the following questions: (a) What are the operative mechanisms that control the critical layer thickness of pseudomorphic bcc Mg in a Nb/Mg nanolaminate? In particular, can the discrepancy mentioned above between the experimental and theory/modeling results be explained by considering the effects of the bottom (substrate) vs. top Nb layers separately in a Nb/Mg multilayered structure? (b) What would be the effects of the Nb volume fraction on the resultant structure?

We utilize a novel deposition strategy where bi-layers of Nb/Mg will be terminated/protected by an amorphous coating before further deposition in order to isolate the effects of the bottom (substrate) vs. top Nb layers on the pseudomorphic phase transformation of Mg. We also use micro pillar compression tests to investigate the effects of layer thickness vs. crystal structure (Mg bcc vs. hcp) on these fine-tuned microstructures.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Town & Country A - Session H3-2-WeM

Characterization of Coatings and Small Volumes in Extreme and Cyclic Conditions II

Moderators: Prof. Dr. Peter Hosemann, University of California, Berkeley, USA, **Prof. Dr. Barbara Putz**, Montanuniversität Leoben, Austria

8:00am **H3-2-WeM-1 Characterizing Interfacial Straining Mechanisms Using High Temperature *in situ* Tem***, **Shen Dillon**,* University of California Irvine, USA **INVITED**

Thin film stress relaxation can depend strongly on interfacial strain mechanisms, particularly at grain boundaries within the film and at the film-substrate interface. Diffusion dependent strain, i.e that requiring atomic fluxes, is typically assumed to be diffusion rate limited, and in some cases, rate limited by the emission and absorption of point defects at sources and sinks. The process could also be rate limited by the nucleation of interfacial line defects that mediate climb during the atomic flux. This latter process has largely been ignored within the literature, since it is assumed to require large stresses. The nucleation rate limited kinetic mechanism can stabilize large stresses and exhibits discontinuous stress relaxation. The other mechanisms, diffusion and point defect emission/absorption limited, relax stress continuously. Appropriately identifying the correct mechanism is, therefore, of significant importance for understanding stress evolution in thin films. The work presented in this talk demonstrates the use of high temperature *in situ* transmission electron microscopy (TEM) based mechanical testing applied to characterizing the strain mechanisms active at bicrystal grain and phase boundaries. These experiments indicate that interfacial strain kinetics are nucleation rate limited up to large stresses, and that creep at low stresses in polycrystals results from stress concentration effects. Models for bulk and local interfacial creep are discussed. The strain behavior at and around metal-oxide interfaces is discussed as an example relevant to many thin film applications. These systems are interesting because metal-oxide tensile strain is extremely unfavorably, while interfacial sliding is facile. Such factors must be accounted for to understand microstructural changes occurring during interfacial stress relaxation.

8:40am **H3-2-WeM-3 Quantitative in Situ TEM Observations of a Grain-Boundary-Migration-Assisted, Radiation-Damage Healing Mechanism in Ultrafine Grained Au Thin Films***, **Lina Daza**, S. Stangebye, K. Ding, X. Liu, T. Zhu, J. Kacher, O. Pierron,* Georgia Tech, USA

The plastic deformation mechanisms of ultrafine grained gold thin films (average grain size of 150 nm) irradiated with 2.8 MeV Au+ ions at three different levels (0.1, 1 and 5 dpa) have been studied using quantitative *in-situ* transmission electron microscopy (TEM) nanomechanical testing. This technique allows for the simultaneous observation and comparison of the active deformation mechanisms, measurement of mechanical properties and true activation volume.Some of the observed deformation mechanisms include dislocation nucleation at grain boundaries (GB), dislocation pinning/de-pinning at irradiation induced defects, and stress-induced GB migration. During the early stages of deformation, dislocation nucleation and GB migration occur simultaneously. However, the dense populations of irradiation-induced defects prevent transgranular dislocation motion. As the deformation levels increase, GB migration leads to defect-free zones which then provide avenues for unimpeded dislocation glide. The true activation volume increases from ~10b^3 in unirradiated specimens, to ~22b^3 in irradiated specimens at 1dpa, for flow stresses ranging from 400 to 550 MPa.

Special Interest Talks
Room Town & Country A - Session SIT3-WeSIT

Special Interest Session III
Moderator: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

1:00pm **SIT3-WeSIT-1 Thin Film Sputtering Technologies Enabling Manufacturing of Functional Devices for Smart Society*, Koukou Suu,*** ULVAC, Inc., USA **INVITED**

Functional materials from thin film technology are finding new applications. Sputtering is one of the critical processes to deposit thin films. Industry needs reliable and reproducible sputtering solutions. ULVAC has been developing sputtering equipment and technology using Radiofrequency (RF) for functional materials deposition. Sputtering has a wide range of applications in BST, STO, PCM Memory, Electrolyte Materials of Lithium Ion Battery and PZT. Piezoelectric PZT thin films, one of ULVAC's leading technologies, have been used to fabricate advanced piezoelectric MEMS (Piezo-MEMS) devices, such as gyro/acceleration sensor, microphone, piezoelectric micro-machined ultrasonic transducer (pMUT), µ-mirror and pyroelectric sensor. These devices have been identified as key enabling technologies for "Smartphones," "Wearable devices," and "Autonomous cars," which are rapidly becoming one of the most important components of a modern "Smart Society's" "Smart infrastructure." ULVAC provides CMOS-compatible solutions for Piezo-MEMS device integration in order to realize next-generation IoT applications for smart societies. A brief overview of how we developed an original sputtering module and stable advanced process technologies, including the low temperature crystallization technique of PZT, will be presented in this talk.

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 α-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 α-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 <110> oriented crystal texture are obtained as compared to <111> 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 σ = 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 σ = 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 μΩcm) for the Kr sputtered tungsten films. Moreover, we showed a very low resistivity of 13.9 μΩcm at an ultra-thin thickness of ~10 nm grown on 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 $J_{D,peak}$ in the range 0.33 - 0.73 A 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^+ and C^+ 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 Trzewiczyński**, 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 Id (Ud) 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.

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. Thank to isotopic oxidation tests with sequential time duration $^{16}O/^{18}O$ 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 TiO_2-rutile nearer the surface, followed by the Al-rich oxide, then mixed oxide region of $(AlCr)_2O_3$ with small islands of TiO_2 and an amorphous 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 TiO_2 top-layer and also promotes the formation of Al-rich protective oxide layer.

Functional Thin Films and Surfaces
Room Pacific F-G - Session C1-2-WeA

Optical Materials and Thin Films II

Moderators: Dr. Silvia Schwyn-Theony, Evatec AG, Switzerland, **Dr. Juan Antonio Zapien**, City University of Hong Kong

2:00pm **C1-2-WeA-1 Perovskite Stannate $BaSnO_3$ Films for Near- and Mid-Infrared Plasmonic Applications**, ***Heungsoo Kim****, A. Piqué,* Naval Research Laboratory, USA

Recently, ternary perovskite oxides have attracted great attention as alternative transparent conducting oxides (TCOs) because their structures are compatible with many other perovskite oxides that allow devices to be fabricated comprised entirely of perovskite oxides. Among these perovskite oxides, $BaSnO_3$ has gained considerable attention as a promising TCO because of its high mobility at room temperature (~320 $cm^2V^{-1}s^{-1}$ in bulk single crystals and ~100 $cm^2V^{-1}s^{-1}$ in epitaxial thin films) and high temperature stability in oxygen atmospheres compared to other TCOs, such as Sn-doped In_2O_3, Al-doped ZnO, and F-doped SnO_2. We have grown epitaxial La-doped $BaSnO_3$ (LBSO) thin films on (001) $SrTiO_3$ and (001) MgO substrates by pulsed laser deposition and investigated their structural, electrical, and optical properties as a function of the oxygen pressure and substrate temperature during deposition. By adjusting the oxygen pressure and substrate temperature during deposition, we were able to control the film crystallinity and strain, which modified the electrical and optical properties. The LBSO films grown at the optimum conditions (780 °C and 100 mTorr of oxygen) show the highest conductivity (3.6 x 10^3 S cm^{-1}) with a carrier concentration of 3.5 x 10^{20} cm^{-3} and a carrier mobility of 65 $cm^2V^{-1}s^{-1}$. This observed high conductivity corresponds to the film with the best crystallinity and the lowest strain state. The permittivity of the LBSO films can also be modified as a function of the oxygen pressure and temperature during deposition allowing tuning of their epsilon-near-zero (ENZ) wavelength from 2 µm to 6 µm. We will present details of the deposition conditions on the properties of LBSO films and the ability to tune the permittivity in infrared range.

This work was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory basic research program.

2:20pm **C1-2-WeA-2 2-Dimensional Growth of GaS_x Crystal by Low-Pressure Vapor Phase Deposition**, ***Yijia Chen,*** National DOng Hwa University, Taiwan*; C. Huang,* National Dong Hwa University, Taiwan

GaS_x is a promising material with band gap of less than 3 eV, which could be used for novel 2-dimensional nano-electronics and nano-photoelectronics. We successfully prepared GaS_x thin film on silicon substrate by low-pressure vapor phase deposition. The examination of the microstructure reveals the evolution of the 2-dimensional GaS_x crystal growth. We found that the GaS_x platelets are just sprouting out of the substrate from those dots coincidently aligned along some crystallographic direction of the Si substrate. The edges of the platelets show preferred directions, confirming the occurrence of preferred-orientation growth of GaS_x from the substrate. It is very interesting to find that the edges of the platelets are accumulated with the dots similar to those found further downstream on the substrate as the nucleation sites for GaS_x. Apparently, the dots not only signify the remnant for GaS_x nucleation, but also reveal their involvement of the lateral growth of GaS_x crystals. Recall that the dots are where GaS_x is abundant. It is most likely that sulfur is first dissolved in the Ga liquid, then reacts with Ga and precipitates as GaS_x on the existing edge of GaS_x platelets to expand the crystal size. These crystals were later exfoliated into GaS sheets, as evidenced by x-ray diffraction analysis. From this study, a major leap forward is provided toward the realization of 2-D GaS preparation.

2:40pm **C1-2-WeA-3 Hysteresises on Voltage-Current Characteristics and Optical Responses of PEDOT:PSS/ZnO Nanorods/ZnO:Ga Heterojunctions**, ***Tomoaki Terasako,*** Graduate School of Science and Engineering, Ehime University, Japan*; M. Yagi,* National Institute of Technology, Kagawa College, Japan*; T. Yamaoto,* Materials Design Center, Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) with a wide bandgap energy of ~3.37 eV is expected to be applied to ultraviolet (UV) detectors. In general, ZnO exhibits *n*-type conduction because unintentionally doped native defects and/or residual hydrogen (H) atoms act as donors. On the other hand, it is difficult to obtain *p*-type conduction with good reproducibility by intentional impurity doping. Therefore, we have fabricated the UV detectors composed of the heterojunctions between the ZnO nanorods (NRs) and poly(3,4-ethylenedioxythiophne) poly(styrenesulfonate) (PEDOT:PSS) instead of those of ZnO *pn* homojunctions. In this paper, generation mechanisms of both hysteresises on the voltage-current (V-I) curves and optical responses of the PEDOT:PSS/ZnO NRs/ZnO:Ga (GZO) heterojunctions will be discussed.

The GZO seed layers were deposited on alkali-free glass substrates by ion-plating (IP) with a DC arc discharge using a sintered ZnO pellet containing Ga_2O_3 powder of 4.0 wt.%. Preparations of ZnO NRs layers were done by chemical bath deposition (CBD) using the mixed aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine. The PEDOT:PSS layer was spin-coated on the surface of the ZnO NRs layer at 3000 rpm for 30 s, followed by thermal annealing in air at 80 °C.

The V-I curves of the PEDOT:PSS/ZnO NRs/GZO heterojunctions exhibited a rectification behavior with hysteresis loops both in forward and reverse voltage regions. Under the irradiation of the ultraviolet (UV) light of 360 nm, the hysteresis loop area in the forward voltage region decreased, but that in the reverse voltage region increased. Both the ln V vs. ln I plots and Fowler-Nordheim (F-N) plots, 1/V vs. ln (I/V^2) plots, for the voltage increase in the forward voltage region in a dark state can be clearly divided into three characteristic regions. The V-I curve showed an ohmic characteristic in the low voltage region, whereas the current was approximately proportional to the fourth power of the forward voltage in the high voltage region. Therefore, the possible transport mechanisms in the low and high voltage regions are direct tunneling and F-N tunneling, respectively. In the medium forward voltages, the current was approximately proportional to the square of the forward voltage, which is characteristic of space-charge-limited conduction. The increase in repetition number of V-I measurement under the forward voltage (0→3→0 V) in a dark state led to the increase in maximum forward current.

This work was supported by JSPS KAKENHI Grant Number JP22K04220.

3:00pm **C1-2-WeA-4 Effective Ways to Enhance the Performance of n-MoS_2/p-CuO Heterojunction Based Self-Powered Photodetectors*, Krishan Kumar*,** *D. Kaur,* Indian Institute of Technology Roorkee, India

In the present study, two effective routes to improve the response time and the detection range have been investigated for the n-MoS_2/p-CuO (a conventional p-n heterojunction). Initially, an insulating Aluminium nitride (AlN) layer was inserted in between the Molybdenum disulfide (MoS_2)and Cupric Oxide (CuO) layer, which eventually converted the conventional p-n heterojunction to Semiconductor-Insulator-Semiconductor (SIS) with a superior carrier tunneling mechanism. Here, the n-MoS2/p-CuO and n-MoS2/AlN/p-CuO (SIS) heterojunctions have been fabricated using the dc magnetron sputtering technique. The responsivities of the n-MoS_2/p-CuO and n-MoS_2/AlN/p-CuO (SIS) heterojunction are found to be 3.88 mA/W and 20.22 mA/W for the visible radiations (532 nm) and 4.47 mA/W and 26.28 mA/W and NIR radiations (1064 nm), respectively. The response time (rise time and decay time) of the fabricated n-MoS_2/p-CuO heterojunction decreases from 93.35 ms and 102.68 ms to 11.31 ms and 12.73 ms with the insertion of ultrathin insulating AlN Layer. The higher current and ultrafast photoresponse in n-MoS_2/AlN/p-CuO (SIS) heterojunction can be ascribed to the carrier tunneling mechanism through the ultrathin insulating layer. Furthermore, the range of detection of the photodetection can be enhanced up to the UV region with the addition of a layer of MoS_2 quantum dots on the surface of the MoS_2 layer in the fabricated heterostructure. The fabricated n-MoS_2 QDs/n-MoS_{2-}/AlN/p-CuO heterostructure shows photoresponse in a broad range from UV to NIR radiations. The recorded values of responsivity for the fabricated n-MoS_2 QDs/n-MoS_{2-}/AlN/p-CuO heterostructure are 4.97 mA/W, 20.22 mA/W and 26.28 mA/W for the incident of UV (376 nm), visible (532 nm) and NIR (1064 nm) radiations, respectively. The obtained results demonstrate the n-MoS_{2-}/AlN/p-CuO (SIS) heterostructure with the addition of MoS_2 QDs shows excellent potential for next-generation ultrafast optoelectronics applications.

3:20pm **C1-2-WeA-5 Femtosecond Laser Ablation (FESLA) XPS – A Novel XPS Depth Profiling Technique for Optical/Electrical Thin Films and Multi-Layered Structures*, Mark Baker*,** *S. Bacon, S. Sweeney,* University of Surrey, UK*; A. Bushell, T. Nunney, R. White,* Thermo Fisher Scientific, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers through the use of argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed which employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (10s - 100s microns) and is much faster than sputter XPS sputter depth profiling. FESLA XPS results will be shown for selected bulk, thin film and multi-layered materials employed in optical and electrical applications.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Pacific F-G - Session E3-2-WeA

Tribology of Coatings and Surfaces for Industrial Applications II

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Dr. Rainer Cremer**, KCS Europe GmbH, Germany, **Dr. Philipp Grützmacher**, Institute of Engineering Design and Product Development, Austria

4:20pm **E3-2-WeA-8 Hard MoSC Solid Lubricant Coating*, Tomas Polcar*,** *I. Ponomarev, T. Vitu,* Czech Technical University in Prague, Czech Republic

Doping of transition metal dichalcogenides with carbon results in coating with much better mechanical properties (adhesion, hardness) than that of pure MoS2. Solid lubrication is achieved through tribochemical reaction during sliding, which produces a thin MoS2 tribolayer with basal planes parallel to the coating surface. The coating is a superb lubricant in a vacuum and provides a very low coefficient of friction (lower than typical DLC) in the humid air. However, MoSC prepared by d.c. sputtering is still a relatively soft coating with a hardness of 2-4 GPa, and chemical composition (e.g. carbon content) cannot be further optimized due to an insufficient understanding of tribolayer formation.

We deposited amorphous MoSC coating by co-sputtering MoS2 and C targets in HiPIMS mode, leading to enhanced hardness close to 8 GPa and improved adhesion on steel substrates. Special attention has been paid to tribological testing in various environments (vacuum, humid air) and a formation of a low-friction MoS2 tribolayer. Experimental results are compared with molecular dynamics simulations of sliding thanks to our recently developed force fields for Mo-S-C material combinations. It seems that the sliding induces the segregation of the carbon phase facilitating the formation of a solid lubricant tribolayer.

4:40pm **E3-2-WeA-9 Coating Solutions for Wind Turbine Bearings*, Esteban Broitman,*** SKF - Research and Technology Development, Netherlands*; T. von Schleinitz,* SKF GmbH, Germany

Wind power, a clean and affordable alternative to fossil-fuel power generation, is becoming one of the most the preferable choices around the world thanks to novel technical and engineer advances, and also costs drops.

The operational challenges for wind turbines are enormous, like the permanent demand to increase turbine power and size, the work in extreme weather conditions, increasing heavy loads, need of installation in remote locations, etc. In turn, significant advances in rolling bearing designs, materials and heat treatments engineering, and coating technologies have helped to achieve enhanced performance, reliability, and increased service life at many parts of the wind turbines.

In this presentation, we will introduce three kind of coatings used at different bearing locations of the wind turbine: aluminum oxide INSOCOAT®, SKF tribological black oxide, and carbon-based NoWear®. The deposition, mechanical, tribological and electrical properties of the coatings will be discussed. Results will illustrate how far the use of coated bearings have evolved in meeting operational demands and improving the productivity and profitability of wind turbines.

5:00pm **E3-2-WeA-10 Scratch Testing and Tribology Combined with Integrated 3D-Profilometry for in-Depth Characterization of Damage Modes in PVD Coatings*, Philippe Kempe,*** Rtec-Instruments SA, Switzerland

Scratch testing has been used to characterize the adhesion of PVD and CVD coatings. It has been normalized to different standards (ISO 20502 and ASTM C1624) which are in much use now in different industries.

The principles of the method are based on a extremely high stress at the interface between coating and substrate which generates strong damages and potential delamination in the material structure. For the development of new coatings, the correlation with real situations is not necessary straightforward and is discussed.

The integration of a 3D profilometer (confocal microscopy and white-light interferometry) combined with mechanical testing (scratch tests and tribology) allows to visualize different damages in the coating structure. It can be used with advantages in R&D projects. Different modes of testing with scratch tester are explained and could foresee various automated modes for quality control.

5:20pm **E3-2-WeA-11 Structural, Electrochemical, and Tribological Evaluation of Silver - Hydroxyapatite Multilayer Coatings Obtained by Magnetron Sputtering with Potential Application in Implants*, Julián Andrés Lenis Rodas,*** University of Antioquia, Politécnico Colombiano Jaime Isaza Cadavid and Servicio Nacional de Aprendizaje - SENA, Colombia

In the present study, silver-hydroxyapatite multilayer coatings were obtained by magnetron sputtering. The structure of the coatings was evaluated by scanning electron microscopy and transmission electron microscopy. Chemical composition and phases were determined by energy-dispersive X-ray spectroscopy, micro Raman spectroscopy, and X-ray diffraction. The corrosion resistance was evaluated using electrochemical impedance and polarization techniques, while the wear resistance of the coatings was evaluated using a pin-on-disk tribometer.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-1-WeA

Boron-Containing Coatings I

Moderators: Dr. Marcus Hans, RWTH Aachen University, Germany, **Prof. Helmut Riedl**, TU Wien, Institute of Materials Science and Technology, Austria, **Prof. Johanna Rosén**, Linköping University, Sweden

2:00pm **F4-1-WeA-1 Improving the Oxidation Resistance of TiB_2 Coatings by TM-silicide Alloying (TM = Ti, Ta, Mo)***, **Ahmed Bahr**[1], O. Beck, T. Glechner, A. Grimmer, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

TiB_2 is considered a promising candidate among the family of transition metal diborides (TMB_2) to be applied in several high-performance applications under extreme conditions. In particular, the unique strength of TiB_2 is based on its high melting temperature (~3225 °C), high thermal shock resistance, and chemical inertness. However, the wide applicability of TiB_2 as a protective coating is still limited due to its poor high-temperature oxidation resistance by forming volatile, non-protective Ti- and B-based oxide scales. Si-alloying of TMB_2 provides a successful route to enhance the high-temperature oxidation resistance up to 1200 °C [1, 2]. Yet, the high Si content usually leads to the deterioration of the mechanical properties of these films [3].

Here, we investigated new alloying routes for sputtered TiB_2 coatings based on $TMSi_2$ secondary phases (TM = Ti, Ta, Mo) for achieving the challenging compromise between good mechanical properties and high oxidation resistance. We employed DC magnetron sputtering technique to synthesize TiB_2 alloyed coatings with different $TMSi_2$ phases from compound targets. The alloyed coatings were characterized in terms of chemical composition, phase constitution, and mechanical properties using high-resolution characterization techniques.Moreover, the oxidation kinetics within the alloyed Ti-(TM)-Si-B were studied at different temperature regimes up to 1400 °C, accompanied with detailed morphological characterization of oxide scales formed.

Keywords: Diborides; TiB_2; PVD; Protective Coatings; Oxidation; Mechanical Properties;

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2:20pm **F4-1-WeA-2 Quaternary CrTaBN: Experimental and Theoretical Insights Into a Novel Coating Material with Promising Mechanical Properties and Exceptional Thermal Stability***, **Christina Kainz**,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; L. Patterer, D. Bogdanovski,* Materials Chemistry, RWTH Aachen University, Germany*; H. Krüger,* Institute of Mineralogy and Petrography, University of Innsbruck, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; I. Letofsky-Papst,* Institute for Electron Microscopy and Nanoanalysis and Center for Electron Microscopy, Austria*; M. Pohler, C. Czettl,* Ceratizit Austria GmbH, Austria*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; C. Mitterer,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Austria **INVITED**

Owing to their combination of excellent thermal stability, outstanding oxidation resistance and beneficial mechanical properties, ternary CrTaN coatings have recently received increasing interest for use in demanding applications. Although the addition of B to ternary transition metal nitride coatings is an effective strategy to improve their mechanical properties and thermal stability, studies on quaternary CrTaBN coatings are not available in literature. The present work provides a comprehensive overview on the microstructure, phase composition and thermal stability of $Cr_{0.69}Ta_{0.20}B_{0.11}N$ coatings grown by cathodic arc evaporation. Lab–scale X–ray diffraction yielded only the fcc-$Cr_xTa_{1-x}N$ solid solution being present as crystalline phase of the coating. X–ray photoelectron spectroscopy, however, confirmed the presence of B–N bonds. A combination of atom probe tomography and transmission electron microscopy showed that B forms nanoscale segregations, which seem to be preferably located at the grain boundaries. The thermal stability of CrTaBN was investigated by complementary application of X-ray photoelectron spectroscopy, atom probe tomography and *in–situ* high–temperature synchrotron X-ray diffraction. Annealing the coating at 1000 °C provokes no change in the crystalline phase composition, but induces a reduction of the B content and the formation of B–metal bonds. These findings on phase composition and thermal stability of the coating were furthermore compared to density functional theory calculations. Finally, *in-situ* high–temperature synchrotron X-ray diffraction and nanoindentation confirmed that CrTaBN allows for an exceptional oxidation resistance up to 1100 °C with simultaneous high hardness (32±2 GPa). The thorough investigation of phase composition and microstructure of CrTaBN at ambient and elevated temperatures provides the basis for a fundamental understanding of this novel coating system.

3:00pm **F4-1-WeA-4 Transition Metal Diboride Superlattices: Combination of *Ab Initio* and Experimental Approach for Investigation of Ceramic Thin Films with Improved Ductility and Fracture Toughness***, **Tomáš Fiantok**,* Comenius University, Slovakia*; N. Koutná,* Linköping University, IFM, Sweden*; V. Šroba,* Comenius University, Slovakia*; M. Meindlhumer,* Austrian Academy of Sciences, Austria*; T. Roch, M. Truchlý, M. Vidiš, L. Satrapinskyy, M. Gocník,* Comenius University, Slovakia*; D. G. Sangiovanni,* Linköping University, IFM, Sweden*; M. Mikula,* Comenius University, Slovakia

Demanding high temperature mechanical applications create an opportunity to exploit the potential of transition metal diboride based thin films (TMB_2, TM = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W) due to their very high hardness and temperature stability. However, the industrial use of these materials is limited by their brittle behavior under high-temperature mechanical loads which results in the initiation and propagation of cracks leading to permanent failure.

One of the approaches to suppress the inherent brittleness of TM diboride films is the concept of superlattices (SL) – i.e., formation of alternating chemically and/or structurally modulated nanolayers. Such SL structures ensure efficient dissipation of accumulated energy in the vicinity of an already formed crack due to its deflection, blunting and stopping at the interface between the flexible and stiff layers.

In our work, using density functional theory (DFT) calculations, we predict the structural stability and theoretical ductility of 184 TMB_2 SL systems, where we search for suitable candidates exhibiting improved fracture toughness.

In the next step, we experimentally focus on the magnetron co-sputtered TiB_2 – TaB_2 films with different bi-layer period where we performed micromechanical bending tests on the film cantilevers which confirmed the

[1] **Graduate Student Award Finalist**

positive superlattice effect on improving the fracture resistance. In addition, for a more detailed explanation of the obtained results, the films are investigated using X-ray diffraction, and transmission electron microscopy. Mechanical properties (hardness and indentation modulus) are measured by nanoindentation techniques.

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The calculations were carried out using the resources by the Swedish National Infrastructure for Computing (SNIC)—partially funded by the Swedish Research Council through Grant Agreement (VR-2015-04630)—on the Clusters located at the National Supercomputer Centre (NSC) in Linköping"

3:20pm **F4-1-WeA-5 Tissue Phase Affected Fracture Toughness of Nano-Columnar TiB_{2+z} Thin Films***, **Anna Hirle**, C. Fuger, R. Hahn, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, A-1060 Vienna, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Despite being intensively investigated and already established in industry as protective coatings for aluminium machining [1] or diffusion barriers [2], Titanium-Diboride (TiB_2) is still not fully understood. In particular, for the fracture behaviour and the corresponding material characteristic (intrinsic fracture toughness, K_{IC}) the literature presents only little descriptions. So far it is known that the mechanical properties (H and E) of TiB_2 are highly dependent on the crystal orientation [3] and the amount of tissue phase present [4], which in turn can be influenced by the choice of coating parameters. To figure out, if this also affects the fracture behaviour, we synthesized a broad stoichiometric variation from $TiB_{2.07}$ up to $TiB_{4.42}$ by DC magnetron sputtering and thoroughly determined their structural, morphological and mechanical properties. By using micro-mechanical test set-ups (in-situ microcantilever bending tests) the intrinsic fracture toughness was investigated in relation to the chemical and hence morphological variation. In addition, information about the stress states within the thin films were obtained by nanobeam (synchrotron) experiments. The presence of a B-rich tissue phase was confirmed by HR-TEM analysis, showing that the grain size is decreasing with increasing B content, which is accompanied by an increase in tissue phase fraction. The dominance of the tissue phase is progressing with increasing B, also forcing smaller column sizes (from ~10 to < 5 nm) [5]. A change in Boron content from $TiB_{2.22}$ to $TiB_{4.42}$ leads to a decrease in fracture toughness from 3.55 ± 0.16 MPa√m to 2.51 ± 0.14 MPa√m of these superhard films. In summary, this study underlines the influence of stoichiometry and the potential of tissue phase engineering on the mechanical properties of TiB_{2+z} based thin films.

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3:40pm **F4-1-WeA-6 Characterization of Ti-Al-La-B-N Hard Coating and Cutting Tool Application***, **Shin Takayama**, T. Ishigaki, M. Takahashi,* Mitsubishi Materials Corporation, Japan **INVITED**

Current machining applications require new developments in the field of hard coatings to achieve excellent precision and effective processes. TiAlN thin films are well established due to their good thermo-mechanical properties. Recently, we reported TiAlLaBN films by sputtering. In the report the addition of La into the TiAlN lattice was shown to increase film hardness and H/E which correlates with film toughness. The microstructure of the film composes fine grain crystals with a size of 5 nm. However, the relationship between the microstructure of the TiAlLaBN film and its mechanical properties is still unclear. It is necessary to understand the relationship to maximize the cutting performance. The microstructure of the film can be varied by changing the deposition rate. Increasing the deposition rate may change the crystal grain size, leading to coarse grain microstructure. In this study, we investigate the changes in microstructure and mechanical properties by changing the deposition rate in order to improve the cutting performance.

Two different deposition approaches of sputtering and CAE (Cathodic Arc Evaporation) were used for changing the deposition rate. Ti-Al alloy added with 2 mol% LaB_6 was used as metal target. So as to prepare the metal target including unstable La, it was stabilized by combining with boron to form the LaB_6 compound. The deposition rate in CAE was 144 nm/min which was faster than in sputtering, 104nm/min. From the cross-sectional SEM observation and TEM images, the TiAlLaBN film of 144 nm/min was found to be a fine columnar structure with a width of 10 nm and length of 30 nm. The film hardness H and H/E of the fine-grained TiAlLaBN were H=40.1 GPa and H/E=0.095, then those of columnar structure were H=35.3 GPa and H/E=0.096, where E is elastic modulus. Both increased compared to H=31.3 GPa and H/E=0.065 for conventional TiAlN by CAE. The hardness of the TiAlLaBN film with fine-grained structure was found to be larger than that of columnar structure, while film toughness H/E was almost the same regardless of their different structures.

Milling cutting performance of TiAlLaBN with columnar structure was evaluated on ductile cast iron that was widely used for automobile parts. The TiAlLaBN with columnar structure showed 1.25 times better performance than TiAlN by CAE. The observation of the cutting edges indicated that TiAlLaBN with columnar structure reduces crack damage on the rake face by 20%. This is because the addition of La improves the film toughness and oxidation resistance. TiAlLaBN coatings deposited by stabilization with boron is expected to be an important material for future cutting.

4:20pm **F4-1-WeA-8 Mechanical Properties and Thermal Stability of ZrBSiTaN Films***, **Kuo-Hong Yeh**,* National Taiwan Ocean University, Taiwan*; L. Chang,* Ming Chi University of Technology, Taiwan*; Y. Chen,* National Taiwan Ocean University, Taiwan

ZrBSiTaN films were fabricated on silicon and AISI 420 stainless steel substrates through direct current magnetron co-sputtering. ZrB_2, Ta, and Si targets were used. The power applied on the Si target and the nitrogen flow ratio of the reactive gas were the variables in the sputtering processes. The effects of Si and N contents on the mechanical properties and thermal stability of ZrBSiTaN films were investigated. The results indicated that all the as-deposited ZrBSiTaN films formed amorphous structures. The supplement of reactive gas with a nitrogen flow ratio of 0.4 resulted in that the ZrBSiTaN films exhibited a high N content of 60 at.%. The increase of Si content from 0 to 42 at.% in ZrBSiTa films decreased the hardness and Young's modulus values from 19.1 to 14.3 GPa and 264 to 242 GPa, respectively, whereas the increase of Si content from 0 to 21 at.% in ZrBSiTaN films increased the hardness and Young's modulus values from 11.5 to 14.0 GPa and 207 to 218 GPa, respectively. The amorphous BN and SiN_x phases played the vital role in the variations of structural and mechanical properties of ZrBSiTaN films. The thermal stability test was conducted at 800 °C for 10 min within purged Ar gas in a rapid thermal annealing furnace. The ZrBSiTa films oxidized with the residual oxygen in the vacuumed furnace, which was accompanied with the formation of ZrO_2, Ta_2O_5, and $TaSi_2$ phases, whereas the ZrBSiTaN films maintained amorphous structures. Further exploration on the oxidation behavior of ZrBSiTaN films will be studied.

4:40pm **F4-1-WeA-9 Formation of Orthorhombic MAB Phase $Mo_{1-x}Cr_xAlB$ Solid Solution Thin Films***, **Peter J. Poellmann**, D. Bogdanovski, S. Lellig, M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; D. Holzapfel, P. Zoell, S. Karimi Aghda,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

$Mo_{1-x}Cr_xAlB$ thin films were deposited by combinatorial magnetron sputtering at temperatures between 450 °C and 700 °C. Subsequent analysis by XRD, EDX, ERDA, and TEM revealed the compositional phase formation range to be between $0.38 \leq x \leq 0.76$ for orthorhombic MAB phase $Mo_{1-x}Cr_xAlB$, consistent with previous ab initio predictions, and can hence be rationalized by composition-induced changes in chemical bonding. For samples with lower x, the formation of Cr_2AlB_2, Cr_3AlB_4, and Cr_4AlB_6 side phases has been observed, again in accordance with theoretical and experimental literature data.

5:00pm **F4-1-WeA-10 Application of AlTiBN Coating for Cutting Tools for Exotic Materials Machining**, ***Yuta Suzuki***, *H. Kanaoka,* Sumitomo Electric Hardmetal Corporation, Japan

In recent years, the machining of difficult-to-cut materials, such as heat-resistant alloy and titanium alloy, has been increasing for aircraft, energy and medical markets. When cutting exotic alloys, the workpiece material is likely to adhere onto the cutting edge of a tool, resulting in a sudden fracture of the cutting edge of the tool. The tool life is significantly shorter than that of tools for cutting general steel. This study was intended to investigate the mechanical property and cutting performance of AlTiBN coating in order to solve the serious problems. AlTiBN coating was deposited on cemented carbide by arc ion plating method using nitrogen as reaction gas and Al-Ti-B alloys with B contents of 0, 2, 5 and 10 at. % were used as target materials. The mechanical properties of the coatings were measured by nano-indenter and the microstructure was evaluated by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The cutting performance was evaluated by milling test of Ni-based heat-resistant alloy, and then tool life and damage to the coating at the early stage of machining were evaluated.In conventional PVD coatings for cutting tools, Cr and Si has often been added to AlTiN in order to increase hardness and heat resistance, achieving high wear resistance. However, these methods increase hardness as well as Young's modulus, which reduces toughness of coating. In heat-resistant alloy and Titanium alloy milling, coatings with a high Young's modulus tends to develop internal cracks, leading to early destruction of the coatings. In this research, we developed an innovative coating with high hardness and low Young's modulus for difficult-to-cut materials milling. Optimizing B content of AlTiBN coating, we realized low Young's modulus of 504 GPa while maintaining high hardness of 38 GPa. This is probably because the pure AlTiN changed to a mixed crystal structure of cubic and hexagonal by the addition of B. When the cutting performance of this AlTiBN coating was evaluated in milling for Ni based super alloy, material equivalent to Inconel 718, it was found that internal cracks were suppressed at the initial stage of processing. As a result, cemented carbide tool with the AlTiBN coating achieved approximately 1.6 times longer tool life than that with B-free AlTiN coating. As described above, the AlTiBN film with high hardness and low Young's modulus has not only excellent wear resistance but also excellent toughness, so it is expected to contribute to the improvement of productivity in aircraft, energy and medical markets.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific D - Session G2-2-WeA

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications II
Moderator: Dr. Jan-Ole Achenbach, KCS Europe GmbH, Germany

2:20pm **G2-2-WeA-2 Effect of Different Diffusion Treatments on the Surface Properties of Austenitic Stainless Steels**, ***Phillip Marvin Reinders***, *P. Kaestner, G. Bräuer,* Technische Universität Braunschweig, Germany

The aim of the present study is to investigate the influence of plasma diffusion treatments with different process gases on the surface properties of austenitic stainless steels. This is necessary to functionalize austenitic stainless steels as a material for hydrogen applications, such as bipolar plates in the proton-exchange membrane fuel cell (PEMFC).

For this purpose, the austenitic stainless steel X2CrNiMo17-12-2 (AISI 316L) was modified by low temperature plasma diffusion treatment. The experimental investigations focus on improving the corrosion behavior and the interfacial contact resistance (ICR) of the modified boundary zone. Nitrogen and carbon as well as the combination of both were used as process gas in a temperature window from 390 to 450 °C.Own preliminary work has shown that temperatures above this could lead to an increase in corrosion current, which can be explained by the formation of chromium nitrides. While lower treatment temperatures can possibly lead to inhomogeneous nitriding zones.

In order to evaluate the properties with respect to corrosion resistance, the samples were exposed to potentiodynamic polarization measurements. The ICR was determined under surface pressure between two copper electrodes coated with gold. The diffusion zone was analyzed by X-ray diffraction (XRD) and Glow Discharge Optical Emission Spectroscopy (GDOES). In addition, standardized surface analytics, like Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray spectroscopy (EDX) have been applied.

The results show a clear influence of the treatment temperature and the process gases on the studied properties. Plasma diffusion processes based on nitrogen show a significantly higher influence of the treatment temperature than those based on carbon. The plasma carbonized samples show a corrosion rate up to two orders of magnitude lower than the nitrided samples (between 10^{-4} and 10^{-5} A/cm²) in potentiodynamic measurements. But the IRC is significantly increased after the corrosion measurement from lower than 20 up to more than 100 mΩ*cm². The nitrocarburized samples combine the properties of both individual processes and show a comparatively low corrosion rate at low temperatures in combination with low IRC values at increased temperatures.

2:40pm **G2-2-WeA-3 Fine-Tuning of PVD Conditions for Tools Used in Automotive and Manufacturing Applications**, ***Miha Cekada***, *A. Drnovsek, M. Drobnic, M. Panjan, P. Panjan,* Jozef Stefan Institute, Slovenia **INVITED**

Tools used in automotive and manufacturing applications come in different shapes and sizes. The deposition of a protective PVD coating is relatively straight-forward for shank tools (drills, mills, reamers) since a standard planetary mounting enables to set up a more or less uniform batch. Other types of tools (stamps, saw blades, powder compaction tools) have more complex shapes, which complicates mounting and reduces the uniformity of the batch. Thus a standard protocol for a uniform batch of shank tools may have to be adapted depending on the specific collection of tools.

There are several features that influence the coating properties on the surface of tools, despite having been coated in the same batch. The tool shape and size dictate the rotation type (single, double, triple rotation) which in turn strongly influences the microstructure. In high ionization rate processes, such as cathodic arc evaporation, electric field concentration on sharp edges can substantially locally increase the coating thickness; that can be a critical issue in reaming when micrometer-sized tolerances are required. Yet another parameter is the vertical position of tools in the chamber with border areas (top/bottom) where the thickness quickly decreases. A similar effect is observed at shaded areas which are often the working surfaces of some tools, such as dies. In addition to new tools, reground tools can be coated too, which requires more steps to prevent subsequent re-coating.

These features will be addressed based on daily experience in our job coating activities. We will show the dependence of coating thickness, roughness, growth defect density and microstructure. These observations should serve as a guide to reduce unwanted influences and optimize the local coating properties. Our own results will be supported by results published by other authors; nevertheless, these data are relatively scarce since they are often retained as secret know-how within a job coating facility.

3:20pm **G2-2-WeA-5 Development of Al_2O_3-B_2O_3-SiO_2 Glass for Space Shuttle Coating**, ***Jun-Yan Qiu***, *Y. Lee, C. You, G. Hung,* Ming Chi University of Technology, Taiwan*; R. Montecillo,* Ming Chi University of Technology, Taiwan, Philippines*; P. Chen, C. Tu, K. Feng,* Ming Chi University of Technology, Taiwan

The development of space technology, which includes information transmission, secure communication, and defense protection, will soon play an important role in every country. At present, the team is mainly engaged in the research and development of outer glass coatings for space shuttles. When space shuttles pass through the atmosphere, high temperatures up to ~1350 ℃ are generated on its surface resulting in thermal cracks, Thermal protection failure. Thus, the glass coating can protect the inner porous ceramic layer and act together as thermal insulation to form a thermal protection system (TPS). Borosilicate glass has a high softening point to achieve a wetting effect fit fiber brick and achieve a self-healing effect. In this study, we developed the Al_2O_3 added in the B_2O_3-SiO_2 glass coating.

The experimental results show that the transition temperature (Tg) of the B_2O_3-SiO_2 glass system (BS system) increases from 650 ℃ to 750 ℃ when the SiO_2 content increases. However, the XRD results show that the devitrification reaction occurs when the B_2O_3-SiO_2 glass with high silicon performance is sintered between 800 ℃ and 1200 ℃. Furthermore, when the sample was sintered at 1200 ℃, the crystal peak shifted from (101) to (004) orientation, which was confirmed in TEM. The FESEM microscopic images showed thermal cracks caused by devitrification transformation. Therefore, the proportion is adjusted by the ternary phase diagram of aluminum boron silicon. Adding Al_2O_3 to B_2O_3-SiO_2 glass suppresses devitrification, reduces thermal cracking, and increases glass transition temperature. DSC analysis observed that Tg increased from 750 ℃ to 950 ℃. The XRD results showed unstable α-cristobalite traced to be in the mullite phase, which proved that the addition of Al_2O_3 can suppress the formation of α-cristobalite, inhibit devitrification, and increase Tg. The FESEM microscopic images also showed a smooth morphology without cracks on the surface, indicating that the Al_2O_3-B_2O_3-SiO_2 glass system (BSA system) has stable properties.

In the past, thermal insulation aluminum-silicon fiber bricks were used, so the development of Al_2O_3-B_2O_3-SiO_2 glass is expected to match the thermal expansion coefficient of the substrate to achieve a stable bonding effect. Subsequent analysis of structural changes, microscopic images, thermal properties, and mechanical properties was performed. It is expected that glass coating materials with high glass transition temperature and Thermal shock resistance can be developed and can be applied as a coating for space shuttles.

3:40pm **G2-2-WeA-6 Analysis of the Temperature Variation of Bizarre Thermal Barrier Coatings and Their Impacts on Engine***, **Thirunavukkarasu Raja**,* P.S.V College of Engineering and Technology, India*; P. Sivanandi,* Government College of Technology, Coimbatore, India*; S. Dhandabani, V. Murugan,* Sri Ramakrishna Institute of Technology, India

The automotive industry today focuses on reducing the effects of global warming, supposedly caused by engine exhaust emissions. Ansys simulation and experimentation were used to study the TBC effects on engine performance and emissions. The two different novel thermal barrier coating compositions were identified in this study, and the same materials were coated on the engine pistons. According to transient thermal analysis, it is found that the temperature distributions on the coated surface were reduced by 35 % and 18 % for TBC-1 and TBC-2, respectively. Compared to conventional engines, TBC-1 and TBC-2 coated engines increased brake thermal efficiency (BTE) by 8.7% and 7.52% at full load. A decrease in brake-specific fuel consumption of 27.03 % and 18.91 % is identified for TBC-1 and TBC-2 coated engines. Based on the heat balance sheet, the energy conversion rate and useful work are increased by 3.5% and 2%, which ultimately decreases the emission of CO and HC due to complete combustion.

4:00pm **G2-2-WeA-7 Novel High-Entropy Alloy Powders and Their Thermal-Sprayed Coatings for High-Temperature Applications***, **Shih-Hsun Chen**,* NTUST, Taiwan

With our experience in the research and development of metal materials, we will continue to develop various multi-principal high-entropy alloy powder materials and establish their technical capabilities for additive manufacturing. The alloy powders prepared by gas atomization method can ideally present the characteristics of homogeneous high-entropy alloy through the rapid solidification process, and achieve the most suitable process technology for high-entropy alloy products. Combined with the selected additive manufacturing technologies, such as plasma spraying process, it could implement the application and promotion of high-entropy alloys. The above-mentioned process is common and important technology in the industry. Although material research continues to innovate, there are not many researchers engaged in the development of thermal spray process technology. Therefore, this research will rely the established high-entropy alloy powder manufacturing technology, and the development experience of thermal spraying process, focusing on the development of new high-performance AlCrFeNiSi high-entropy alloy powder products and their applications via additive manufacturing technology. This project integrates high-entropy alloy composition design and powder manufacturing, and practical additive manufacturing of high-entropy alloy workpieces.The goal is to develop industrially applicable products and promote them into the industry.

4:20pm **G2-2-WeA-8 A Facile Fluoride Sealing Treatment to Improve Corrosion Resistance of Magnetism Alloy (AZ31B) Micro-arc Oxidation Layer***, C. Lee,* National Defense University, Republic of China*; J. Lee,* Lung Hwa University of Science and Technology, Taiwan*; S. Jian,* Ming Chi University of Technology, Taiwan*; **Ming-Der Ger**,* National Defense University, Republic of China

In this study, MAO treatment was used to generate a high corrosion resistance MAO layer on AZ31B magnesium aluminum alloy,During the MAO treatment, the coating will be solidified and contracted owing to thermal stress gradient, resulting in structural defects such as microcracks on the surface . Unfortunately, corrosive ions (such as Cl− and H+) will penetrate into the substrate through these structural defects, which deteriorates the protective performance. The porosity, pore size distribution and connectivity with the substrate play an important role in the performance of corrosion resistance.In order to maintain the integrity of the MAO layer, the surface of the MAO layer is sealed with a fluorine (NaF) compound containing, so that the MAO surface covers NaMgF3. The protective NaMgF3 cubic lattice fills the defects to optimize the corrosion resistance of magnesium aluminum alloys.

Scanning electron microscopy (SEM) microscope equipped with Energy Dispersive Spectrometer (EDS) was used to observe the surface of the MAO and fluoride post- sealing treatment coatings,and to detect the corrosion performance of the coating by the polarization curve (PDP), with salt spray test (SST) for a long time observe the occurrence of pitting corrosion in sealing treatment over time, decide the optimization degree of post-treatment. According to the surface morphology, the number of NaMgF3 by low-concentration short-term fluoridation post-treatment is small and only locally distributed, and the surface structure of the micro-arc itself does not change significantly. After high-concentration fluoridation for five mins The NaMgF3 particles are evenly distributed, and more particles go deep into the hole to achieve proper protection.

The relationship between the concentration of the fluorinated post-treatment solution and the soaking time has an extreme value on the corrosion efficiency of the micro-arc layer. The corrosion resistance is the best at a certain concentration. After soaking in 0.5 M fluorinated sealing solution for five mins. According to the polarization curve, icorr 1.08 x10-9, in SST, compared with the MAO layer without sealing treatment, the storage time can extend double, and after sealing, it can be stored for more than 480 hours without surface discoloration and pitting. Based on the above experimental results, can understand about fluoride sealing post-treatment, the appearance of pitting can be delayed, and it is confirmed that the fluoride sealing post-treatment by simple immersion can get crack free MAO coating on AZ31B magnesium alloy, raise up corrosion resistance optimization.

4:40pm **G2-2-WeA-9 Chemical Vapor Infiltration Technology for Coatings of Fibers and 3D Porous Bodies***, **Dennis Zywitzki**, H. Strakov,* IHI Bernex AG, Switzerland

With the increasing demand for fiber reinforced materials, chemical vapor infiltration (CVI) as a means to fabricate protective layers between the reinforcement and the matrix, is of increasing industrial interest. These layers can enhance the thermal stability of composites, for example in heat shields, or can be designed to strengthen or weaken the adhesion of the reinforcement to the matrix and thus tailor the mechanical properties. One main requirement to this technology is high infiltration rates and homogeneity. That's why batch and continues coating concepts are developed and optimized.

In this context newly developed infiltration processes will be presented and the impact of the equipment design will be discussed. The reactor designs allows for example continuous processing of fiber tows of variable length and stable operation for complete infiltration of 3D porous bodies. Additionally, the modular concept allow a high flexibility in terms of gas feeds and deposited materials, and the extensions for industrial upscaling. CVI processes for the deposition > 1 µm thick BN, PyC and SiC films on SiC fibers were developed and show promising characteristics with regard to the infiltration rate and homogeneity.

Topical Symposia
Room Town & Country B - Session TS3-WeA
Processes of Materials for Printed and Flexible Film Technologies

Moderators: Prof. Panos Patsalas, Aristotle University of Thessaloniki, Greece, **Dr. Demosthenes Koutsogeorgis**, Nottingham Trent University, UK

2:00pm **TS3-WeA-1 Upscalable Nanomanufacturing of Thin-Film Electronics***, **Thomas Anthopoulos**,* King Abdullah University of Science and Technology (KAUST), Division of Physical Sciences and Engineering, Saudi Arabia **INVITED**

Adapting existing manufacturing methods to emerging forms of large-area nanostructured electronics presents major technological and economic challenges. Despite the difficulties, however, a number of new processing concepts have been gaining ground, transforming the broader marketplace and relevant manufacturing infrastructure. In this talk, I will discuss our recent efforts toward scalable manufacturing of emerging forms of large-area nanostructured electronics. I will show how the development of innovative patterning technologies in tandem with engineered nanomaterials, can lead to more sustainable forms of optoelectronics with high-performance characteristics. Particular emphasis will be placed on the development and evolution of adhesion lithography (a-Lith) and self-forming nanogap lithography techniques and their use in an expanding range of applications from ultra-fast optoelectronics to new forms of chemical reactors.

2:40pm **TS3-WeA-3 Plasma Technologies for Sustainable Packaging Materials***, **Glen West**,* Manchester Metropolitan University, U.K.*; T. Cosnahan, C. Struller, N. Copeland,* Bobst Manchester Ltd., UK*; P. Kelly,* Manchester Metropolitan University, U.K.

The sustainability drive in the plastics packaging market has, in recent years, been propelled to public attention and incorporated into corporate strategies. In response, most major market players, from resin producers to brand owners and retailers are aligned to have only fully recyclable packaging by 2025, and to reduce carbon dioxide emissionsfor this 141 MTonne market. Other requirements in development from various regulatory and statutory bodies present an environment of increasing demand on producers throughout the sector. From an equipment manufacturer perspective, these environmental sustainability pledges will require technological development.

The industry is moving away from multi-layer, multi-chemistry structures which were used to adhere various coating layers to each other, as mono-material plastic packets are being targeted due to their recyclability. Substantial research attention is focused on promoting the surface energy of polyolefin materials, including the utilization of plasma in the early converting steps. Plasma techniques are favored within the industry, as they are operator independent processes. The plasma surface treatment of kilometers-long reels of polymer to prepare them for subsequent deposition steps is now understood to be vital to achieve the required interfacial bond strength. This is understood to promote barrier and adhesion performance to parity with historical non-recyclable structures (i.e. <1 cc/m2.day oxygen transmission and > 3 N/15mm adhesive failure).

Within the flexible film packaging market, thin film SiOx and diamond-like-carbon are deposited using plasma enhanced chemical vapor deposition – as these thin films create robust environmental barriers to oxygen and water vapor on plastic packaging for food and medical products, although one drawback of DLC is the use of acetylene which comes with various safety hazards. One of major issues when using plasma is the control of arcs that can damage the polymer web. For successful plasma enhanced chemical vapor deposition, two key parameters required: high enough ionization percentage of large input gas flow, and sufficient energy of deposition. These create the high reaction rates required and the energy for surface reorganization (and reaction) of the deposit on the surface to create a correctly reacted and structured bonding which has the balance of properties of barrier, flexibility and toughness. The plasma technologies for achieving effective surface treatment and consistent barrier film deposition on large areas with sufficient processing speed will be discussed in this paper.

3:00pm **TS3-WeA-4 Transition Metal Nitride Colloids: From PVD Targets to Laser-Ablated Nanoparticles***, N. Pliatsikas, S. Panos, I. Fekas, S. Kassavetis, **Panos Patsalas**,* Aristotle University of Thessaloniki, Greece

Transition metal nitrides (TMN), such as TiN, ZrN, HfN, VN, NbN, TaN, MoN, WN, have been the cornerstone of hard coating industry for several decades. Some of them have been considered as electronic materials of substantial importance, mostly as diffusion barriers in transistors. Recently TMN have been revisited as important plasmonic materials and biomaterials for emerging applications in the printed electronics and biomedical sectors. TMN share unique traits such as refractory character, electronic conductivity, notorious chemical stability, and miscibility among them facilitating the formation of ternary (e.g. $Ti_{1-x}Zr_xN$, $Ti_{1-x}Ta_xN$, and $Ti_{1-x}Sc_xN$, among others) and quaternary (e.g. $Ti_{1-x-y}Zr_xAl_yN$, $Ti_{1-x-y}Ta_xAl_yN$, among others) alloys. TMN collectively cover a wide range of values for their electron conductivity, work function and plasmon resonance spectral location. While they are routinely produced in thin-film form by PVD (mostly sputtering) and CVD/ALD, the formation of colloidal nanoparticles of TMN has been proven exceptionally challenging, especially for the case of ternary TMN. In this work we exploit the knowledge of various sputtering variants (including HIPIMS) to produce thick TMN films to be used as targets for laser ablation in liquids (LAL) to produce TMN colloids and inks. We attempt to correlate the crystal structure and chemistry of the film materials with the LAL conditions (laser wavelength, pulse duration, liquid solvent), and with the traits of nanoparticles by implementing a variety of experimental techniques such as optical transmission spectroscopy, AFM, SEM, XPS, and Raman spectroscopy.

3:20pm **TS3-WeA-5 Fully Inkjet-Printed Gas Sensing Antenna Based on Carbon Nanotubes for Wireless Communication Applications***, **Hsuan-Ling Kao**,* Chang Gung University, Taiwan*; L. Chang,* Ming Chi University of Technology, Taiwan*; Y. Tsai,* Chang Gung University, Taiwan

Sensors have been widely used in wearable electronic devices for various detection such as gas, strain, or temperature. The sensor incorporates wireless transmission to reduce the bulkiness and inconvenience caused by the cable. Wireless sensors that embedded sensing film into wireless communication devices such as resonators or antennas has been proposed to achieve small size, simple fabrication, high energy efficiency, and low cost for real-time remote monitoring. In order to embedding sensing film into wireless devices, the conductivity of sensing film is important. Fully inkjet printing technology promotes the green process using by digital controlled pattern in required location due to the advantages fast fabrication, material saving, low cost, high substrate selectivity, and low annealing temperature, which is one of the green process technologies. Carbon nanotubes (CNTs) have been attention for gas sensing applications owing to their high specific surface area and high structural porosity, which enable fact response, high sensitivity and low operating temperature. Inkjet printing technology can precisely control the density carbon nanotubes by droplet spacing (DS) and multi-pass to provide various resistive-type samples to study gas response. However, the relationship between the density of carbon nanotubes and gas sensing response has not been discussed yet. In this work, various DSs and passes were used to control the density of CNTs by pattern rotation. The sensing film and conductive film were printed by commercially carbon nanotube ink (Nink-1000, Nano Lab.) and nanoparticle silver ink (DGP-40LT-15C, Advanced Nano Products Co., Ltd.), respectively. The gas sensing properties were studied by resistance response to validate its feasibility, repeatability, and reversibility. After optimize the CNTs sensing film, wireless sensing antenna composite was designed and fabricated. The appropriate carbon nanotube sensing film was embedded into the dipole antenna by changing the transmission characteristics of antenna. The CNT films allows the electromagnetic transduction of antenna during gas sensing. The appropriate carbon nanotube sensing film was embedded in the dipole antenna to use microwave characteristics to obtain multi-dimensional values for providing high precision detection, which is also more stable than DC resistance value. In addition, it can also reduce the connection-induced loss and the area required for matching to obtain compact area and low power consumption. The wireless antenna sensor can be used in portable electronic products for its light, thin, and compact size and detection in anytime and anywhere.

3:40pm **TS3-WeA-6 Characterization and Evaluation of PVD-Coatings on Bipolar Plates for PEMFC***, **Julian Kapp**, V. Lukassek, V. Mackert, J. Wartmann, H. Hoster,* ZBT Zentrum für BrennstoffzellenTechnik GmbH, Germany*; R. Cremer, P. Jaschinski,* KCS Europe GmbH, Germany

As a result of the steadily increasing demand for energy and the associated need for the responsible use of global energy resources, efficient and sustainable energy conversion and storage is becoming increasingly important. Promising solutions in this context are new developments in fuel cell technology. Here, the chemical energy of an energy carrier (e.g. hydrogen) is directly converted into electrical energy, resulting in high efficiency.

The development of novel techniques for improvement of Proton Exchange Membrane fuel cell (PEMFC) components has to be addressed. One of those components is the bipolar plate (BPP) which has various functions within the PEMFC, such as cell separation, fuel and oxidant gas distribution, collection and transport of generated electricity as well as water and heat management. Therefore, with respect to all those functions, an ideal BPP has to fulfill a number of material requirements, such as high compressive strength, sufficient electrical and thermal conductivity, along with good electrochemical stability. Although metal-based BBPs meet all necessary requirements, the main weak point of these is their susceptibility to corrosion in acid environment, as during PEMFC operation. While formation of the passive layer prevents further corrosion, it often results in electrode catalyst poisoning and contamination of the membrane. Furthermore, an increase in electrical resistance is a typical behavior induced by a passivation process of the metallic surface.

One goal of this work is the suitable series production of corrosion protection coatings with an excellent electrical conductivity on metallic BPP from a PEMFC. The Physical Vapor Deposition (PVD) processes arc and sputtering are used to generate these layers. When selecting the material for the BPP, attention is paid to inexpensive steel and aluminum alloys. The coating material is completely deposited without precious metals for cost reasons. At the same time, the task is to develop a continuous coating process that meets the demands for large-scale production of BPPs.

The developed coating systems were investigated using material characterization (XPS, SEM/EDX, CLSM and Contact Angle Measurements) and in-situ electrochemical analysis. Interfacial-electrical contact resistance (ICR) of coated BPP samples were measured before and after they were exposed to electrochemical corrosion testing. The ICR values and the corrosion rate were compared to United States Department of Energy (DOE) values. Promising coating systems were finally subjected to in-situ diagnostic studies.

4:00pm **TS3-WeA-7 Towards Large Area Scalable Organic Solar Cells using Solution Processing*, S. Ravi P. Silva,*** Advanced Technology Institute, University of Surrey, UK **INVITED**

The rise in global energy consumption and demand requires a faster expansion in renewable energies. The world at present is powered from energy generated by burning coal/oil and gas to sustained industry, domestic heating and electricity [1]. The world now needs to change from the fossil fuels and march towards a net carbon zero position, with changes urgently needed to the energy mix, all manufacture, including the electronic device industry as well as powering devices during its operational lifetime.

Electronic devices have evolved into nanoscale architectures that could be powered via mW power management systems. The envisioned future sustainable societies will be intrinsically inter-connected: humans to transport to homes to cities etc. driven by inexpensive nano-scale electronics, most likely in the form of inexpensive flexible devices that are connected to everything – the Internet of Everything (IoE) -.This lends itself to delocalized power sources, that can operate under variable conditions. Plastic electronics are ideally suited to produce such devices with some of the lowest carbon footprints. We will examine next generation designs for sustainable nanodevices and renewable energy harvesting systems to help reduce the impact on the carbon foot-print. This will include energy harvesting systems such as plastic photovoltaics and Triboelectric generators.

Hybrid organic-inorganic halide perovskite solar cells (PSCs) show great potential for future solar, due to their incredible efficiency growth in last decade, which now reached as high as 25.7%, competing with the commercially available Si solar cells. Perovskites benefits from superior light absorption coefficient, long carrier diffusion length, high mobility, low exciton binding energy, and high defect tolerance. The solution processability of perovskite materials to form high-quality polycrystalline thin films provides the possibility of low-cost fabrication of PSCs on both rigid and flexible substrates. This can significantly cut the final price of solar energy harvesting. Roll-to-roll (R2R) production of flexible solar cells can also reduce the cost of transferring and storing and makes it possible to easily deliver the solar cells to less developed regions in the world with higher needs for energy.

[1] Silva, S.R.P. (2021), EDITORIAL: Now is the Time for Energy Materials Research to Save the Planet. Energy Environ. Mater., 4: 497-499. https://doi.org/10.1002/eem2.12233

4:40pm **TS3-WeA-9 Rational Design of Perfluorocarbon-Free Oleophobic Textiles*, Sadaf Shabanian,*** University of British Columbia, Canada*; K. Golovin,* University of Toronto, Canada

Water- and oil-repellent fabrics have global applications within the textile industry and as technical apparel. Fabric finishes utilizing perfluoro compounds (PFCs) are known to render textiles both water and oil-repellent uniquely. However, PFC-based finishes are not sustainable because they compromise environmental and human health, and garment factories have accordingly begun to phase out PFC usage. This is problematic, as all previous studies on fabric finishes indicate that oil repellency cannot be achieved without perfluorination. Here we develop design parameters for fabricating oil-repellent textile finishes using PFC-free surface chemistries. In this work, we demonstrate that oil repellency is possible using PFC-free finishes by controlling a finish's texture size, porosity, and surface chemistry, based on a design framework rooted in wettability theory. For example, a PFC-free, oil-repellent jacket fabric is fabricated that exhibits oleophobicity towards canola, olive, and castor oil in addition to synthetic sweat. The textile remains non-wetted for liquids with surface tension as low as 23.9 $mN\,m^{-1}$. The equations developed in this work allow for the rational design of oil-repellent textile finishes that do not utilize perfluorinated substances.

Awards Ceremony and Honorary Lecture
Room Town & Country A - Session HL-WeHL

Bunshah Award Honorary Lecture

Moderator: Dr. Ivan G. Petrov, University of Illinois at Urbana-Champaign, USA

6:05pm **HL-WeHL-2 R.F. Bunshah Award and ICMCTF Lecture Invited Talk: What TEM, XRD, STM, AFM, HIM, LEED, 3DATP, DSC, Nanoindentation, DFT, and MD Tell You About Functional Nanostructured Ceramics***, Lars Hultman*[1]*,* Linköping University, Sweden **INVITED**

This presentation reviews strategies for characterizing diverse nanostructures that form in functional nitride thin films during vapor deposition intended to enhance mechanical and electronic properties. Material design is obtained by self-organization during surface- and bulk-driven segregations and phase transformation in metastable TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN alloy model systems, and analyzed by a suite of materials science tools. Density functional theory (DFT) calculations are employed to assess phase stability and decomposition from lattice mismatch and electronic band structure effects. The concept of age hardening is discussed for isostructural systems whereby spinodal decomposition is established for TiAlN by the formation of cubic-phase nm-size domains in a checker-board-pattern of TiN and AlN during annealing, as studied by XRD, TEM, atom probe tomography (APT) and differential scanning caloriometry (DSC). 2-D-nanolabyrinthine structuring in ZrAlN is obtained from the intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110}║{11-20} interfaces. Focused-ion beam (FIB) is used to prepare cross-sectional TEM samples of TiN-based films with nanoindents to study plastic deformation from dislocation slip. Superhardening in TiN/Si_3N_4nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN_x tissue phase, which is a vacancy-stabilized cubic-SiN_x layer, as shown by STM, LEED, and annular-bright-field STEM.Si segregation is demonstrated in APT using ^{15}N isotopic substitution to resolve mass spectral overlap between Si and N. DFT is combined with molecular dynamics (MD) simulations to study growth of TiN with a competitionfor preferred crystallographic orientation (001) vs (111). High fluxes of low-energy (~20 eV) nitrogen ions control atomic layer roughening and yield low-temperature sputter epitaxy, as adatoms diffusing on an upper terrace require an additional energy (the Ehrlich barrier) to cross descending step edges. The barrier asymmetry at step edges leads to up-hill flux resulting in kinetic roughening.Step-flow growthof ductile inherently nanolaminated MAX phases like$Ti_3AlC_2$is confirmed by atom force microscopy (AFM) and helium ion microscopy (HIM). Scanning TEM/EDX elemental mapping reveals a new growth phenomenon - transmorphic heteroepitaxy – which takes place between CVD-grown AlN epilayer and SiC(0001) wafer substrates. The atomic chemical configuration transits over two atomic layers from SiC to AlN. The resulting AlN layer enables growth of high-quality thin GaN HEMT heterostructures.Finally, curved-lattice epitaxial growth of $In_xAl_{1-x}N$ core-shell nanospirals is presented.

[1] **R.F. Bunshah Awardee**

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 4th 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 µm and s = 3.5 µm, were deposited on HS6-5-2C susbstrates. 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 = ~ 9.7 GPa and frequency f = 50 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 σ > -3 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 $(Ti_{1-y}Al_y)_{1-x}W_xN$ Thin Films Grown with no External Heating***, **Xiao Li**, A. Pshyk, B. Bakhit,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; M. Johansson Jõesaar, 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 ≤ 130 °C in a hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS/DCMS) setup involving a high mass (m > 180 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 $Ti_{0.50}Al_{0.50}N$

based thin films is reviewed. Three series of $(Ti_{1-y}Al_y)_{1-x}Me_xN$ (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 Cr^+ irradiation exhibit porous nanostructure, high oxygen content, and poor mechanical properties. In contrast, $(Ti_{1-y}Al_y)_{1-x}W_xN$ 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_s) 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 $(Ti_{1-y}Al_y)_{1-x}W_xN$ 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)n/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 / N2 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 40N 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^2 for the overall power of 25 kW have been achieved. We then produced a series of the novel (Al,Cr)N coatings by sputtering $Al_{60}Cr_{40}$ and $Al_{70}Cr_{30}$ targets (Ø110x510 mm) and compared them to the benchmark CAE (Al,Cr)N coatings. Most of the sputtered coatings have astoichiometric 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_2.

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 MoS2 and WS2. 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 MoS2 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.

11:40am **B1-1-ThM-12 Mechanical and Electrochemical Properties of AlCrN/FexN 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 Insitute, 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_xN) 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_xN] and only nitrided substrate [Fe_xN]. 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_xN, respectively; whereas for Fe_xN it was 10 µm. The mechanical properties were obtained by cross-sectional Berkovich indentation tests, where the Fe_xN interlayer in the duplex coating AlCrN/Fe_xN 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_xN 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_xN duplex coating exhibited better behaviour under same testing conditions as compared with the AlCrN and Fe_xN coatings, due to the presence of the iron nitrides interlayer.

12:00pm **B1-1-ThM-13 Mechanical and Electrochemical Properties for SiC_xN_Y 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_xN_y) 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_xN_y). The a-SiC_xN_Y 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_xN_y, 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_2O_3 layer in the early stage, Ta slows down the rate of inward diffusion of O through the TiO_2 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 friciton 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_2 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. Lümkemann,* Platit AG, Switzerland

Titanium diboride dopped by vanadium (Ti,V)B_2 coating as well as pure TiB_2 due to their densely packed hexagonal structure with strongly covalently bonded boron atoms separated by metallically bonded metal layers exhibits very high hardness H ≥ 40 GPa, high elastic modulus E ≥ 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_2 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_2 is becoming a good alternative to hard tetrahedrally amorphous carbon (ta-C) with high amounts of diamond bounds (sp^3), due to its high deposition rate, low roughness, and cleaner process. Moreover, both TiB_2 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_2 [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_2 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. Lümkemann, M. Morstein, P. Polcik, *Synthesis and characterization of sputtered (Ti,V)B_2 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.

10:00am **B5-ThM-7 Development of TiB2 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_2) coatings exhibit excellent combination of hardness and low adhesion to cutting metal alloys such as these based on Ti, Al or Ni, and it has been used since a decade on cutting tools in the aerospace sector. TiB_2 is well known to exhibit low moderate toughness, which limits it applicability under complex 3D shaped cutting tools, or tools subject to very high loads. Pulsed DC sputtering as well as other conventional vapor deposition techniques are being developed to this purpose. In our approach, a hybrid 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 TiB2 coating formulations.

TiB2 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 TiB2 coatings are tested against aluminium. A test matrix of variables such as temperature (RT-300ºC) and sliding-speed (10-50 cm/s) has been set in order to identify the mild-to-severe galling threshold conditions at the TiB2 - Aluminium interfaces. The comparison of the frictional properties of the deposited TiB2 coatings with benchmark TiN and CrN HIPIMS sputtering coatings sliding against aluminium clearly indicated that the TiB2 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 nano-bubbles 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_2 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_2-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 ^{4}He and ^{3}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.

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[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. Feria, 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***, **Moishe Azoff-Slifstein**,* Rensselaer Polytechnic Institute, USA*; S. Lee,* University of Connecticut, USA*; D. Gall,* Rensselaer Polytechnic Institute, USA

Superlattices of 1-µm-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_2 and Ar/CH_4 mixtures to obtain TiN-TiC superlattice films with equal nitride and carbide fractions and a variable superlattice bilayer period Λ = 1.5-30 nm, as measured using X-Ray diffraction (XRD) ϑ-2ϑ superlattice peaks. XRD ω-rocking curves indicate strong crystalline alignment with a peak width increasing from 0.1 - 0.6° with decreasing Λ. Reciprocal space maps confirm a cube-on-cube epitaxy of alternating rock-salt structure TiN(001) and TiC_x(001) layers and indicate fully-strained TiN(001)-TiC(001) superlattices which are coherent with the MgO(001) substrate for Λ = 3 and 30 nm but are partially relaxed for Λ = 6 and 13 nm. Scanning electron microscopy analyses show surface protrusions due to misoriented grains which increase in density from ρ = 0.4 to 1.0 µm^{-2} for Λ = 1.5 to 3 nm but then decrease back to ρ = 0.06 µm^{-2} for Λ = 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 Λ = 1.5, 6, and 30 nm, respectively. Accounting for these deviations allows to determine H and the elastic modulus E as a function of Λ: The TiN-TiC superlattice system demonstrates an increase in H from 23 to 34 GPa with increasing Λ = 1.5 to 6 nm, followed by a decrease to H = 30 GPa for Λ = 30 nm. Similarly, E increases from 450 GPa for Λ = 1.5 nm to a maximum of 750 GPa for Λ = 6 nm and a subsequent drop to E = 450 GPa for Λ = 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 technique 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 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_3N_4 phases, which are highly resistant against oxidation, act as diffusion barrier for O_2, 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 canswith 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^2) 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 ~ 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 $H_\alpha$and H_β emissions *via* theStark 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 rareafaction 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^{-8} mm^3/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 Θ-2Θ measurements. Typically, in deep Silicon etched vertical vias of 5µm diameter and 25µm 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 10µm diameter and 100µm 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***,* ***Arutiun P. Ehiasarian,*** 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 HIPMS 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).

[3] Babu *et al.,* Plasma Sources Science and Technology **31**, 065009 (2022)

Functional Thin Films and Surfaces
Room Pacific D - Session C3-1-ThM

Thin Films and Novel Surfaces for Energy I

Moderators: Dr. Clio Azina, RWTH Aachen University, Germany, **Prof. Carlos Tavares**, University of Minho, Portugal

8:40am **C3-1-ThM-3 Tailoring Surface Reactivity of Perovskite Oxides for Water Oxidation***,* ***Kelsey Stoerzinger,*** Oregon State University, USA**INVITED**

The intermittent nature of renewable energy sources requires a clean, scalable means of converting and storing energy. One Earth-abundant storage option is water electrolysis: storing energy in the bonds of O_2 and H_2, and later extracting electricity by the electrochemical reaction of gasses in a fuel cell. Nickel oxides are notably active for oxygen electrocatalysis in alkaline solutions, and the perovskite structure ($ANiO_3$) in particular. I will present studies of model oxide electrodes grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) on single crystal substrates that display a known crystallographic orientation, strain, surface area, and path for charge transport. Electrochemical measurements on these heterostructures can establish the intrinsic activity of oxide catalysts in a way that cannot be realized with polydisperse nanoparticle systems, and we use these findings to rationally design the nickelate composition and structure to maximize activity. Additional insight into the mechanism of the oxygen evolution reaction (OER) is obtained from spectroscopic probing of adsorbates with ambient pressure X-ray photoelectron spectroscopy (AP-XPS), pH dependence of activity, and measurements of oxygen isotope exchange. This fundamental understanding aids in the design of active, earth-abundant electrocatalysts for efficient conversion of renewable energy into chemical fuels.

9:20am **C3-1-ThM-5 The Influence of Sb Doping on the Local Structure and Disorder in Thermoelectric ZnO:Sb Thin Films***, J. Ribeiro, F. Rodrigues, F. Correia,* University of Minho, Portugal*; A. Kuzmin,* University of Latvia*; E. Alves, N. Barradas,* University of Lisbon, Portugal*; O. Bondarchuk,* International Iberian Nanotechnology Laboratory, Portugal*; A. Welle,* Karlsruhe Institute of Technology (KIT), Portugal*; **Carlos Jose Tavares**,* University of Minho, Portugal

Thermoelectric transparent ZnO:Sb thin films were deposited by magnetron sputtering, with Sb content varying between 2-14 at.%. As evidenced from X-ray diffraction analysis, the films crystallize in the ZnO wurtzite structure for lower levels of Sb-doping, developing a degree of amorphization for higher levels of Sb-doping. Temperature-dependent (10-300 K) X-ray absorption spectroscopy studies of the produced thin films were performed at the Zn and Sb K-edges to shed light on the influence of Sb doping onthelocal atomic structure and disorder in the ZnO:Sb thin films. The analysis of the Zn K-edge EXAFS spectra by the reverse Monte Carlo method allowed to extract detailed and accurate structural information in terms of the radial and bond angle distribution functions. The obtained results suggest that the introduction of antimony to the ZnO matrix promotes static disorder, which leads to the partial amorphization with very small crystallites (~3 nm) for large (12-14 at.%) Sb content. Rutherford backscattering spectrometry (RBS) experiments enabled the determination of the in-depth atomic composition profiles of the films. The film composition at the surfaces determined by X-ray photoelectron spectroscopy (XPS) matches that of the bulk determined by RBS, except for higher Sb-doped ZnO films, where the concentration of oxygen determined by XPS is lower near the surface, possibly due to the formation of oxygen vacancies that lead to an increase in electrical conductivity. Traces of Sb-Sb metal bonds were found by XPS for the sample with the highest level of Sb-doping. Time-of-flight secondary ion mass spectrometry obtained an Sb/Zn ratio that follows that of the film bulk determined by RBS, although Sb is not always homogeneous, with samples with lower Sb content (2 and 4 at.% of Sb) showing a higher Sb content closer to the film/substrate interface. From the optical transmittance and reflectance curves, it was determined that the films with the lower amount of Sb doping have higher band-gaps, in the range of 2.9 – 3.2 eV, while the partially amorphous films with higher Sb content have lower band-gaps in the range of 1.6-2.1 eV. Albeit the short-range crystalline order (~3 nm), the films with 12 at.% of Sb have the highest Seebeck coefficient (~56 mV/K) and a thermoelectric power factor of ~0.2 $mW\cdot K^{-2}\cdot m^{-1}$.

9:40am **C3-1-ThM-6 An Economic Experimental Approach to Optimize the Microstructure and Thermoelectric Performance of ZnSe Thin Films***, **Khalid Mahmood**,* Department Of Physics, Government College University Faisalabad, Pakistan

Current study demonstrated the growth of good quality, smooth surface ZnSe thin films by an economic and safer thermal evaporation method. The quality of grown thin films was modulated by varying the source to substrate distance (SSD) from 5-15 cm with a step of 5 cm during the thermal evaporation process. XRD scans indicated the pure phase formation and SEM analysis has confirmed the uniformity and smooth surface growth of these deposited thin films. Crystallite size is found to be increased from 28.73-40.18 nm with the increase in source to substrate distance. Raman analysis has further confirmed the cubic phase crystalline nature of these films. Transport properties such as the electrical conductivity, Seebeck coefficient [https://www.sciencedirect.com/topics/physics-and-astronomy/seebeck-effect] and power factor were observed to be varied with source to substrate distance. The highest values of Seebeck coefficient, electrical conductivity and power factor (260 µV/C, 4.1 S/cm and 2.21344 x 10^{-6} W/mK^2 respectively) were achieved by varying SSD.

10:00am **C3-1-ThM-7 The Influences of Plasmonic Resonance and Coupling Effect on Photocatalysis of MoS_2/Gold Hybrid Nanoparticles for Hydrogen Production***, **Yi-Hsueh Chen**, J. Ruan,* National Cheng Kung University (NCKU), Taiwan

Hydrogen energy is clean and more friendly to our environment, which drives scientists around the world to look for materials able to catalyze hydrogen production. MoS_2 has been recognized as the most efficient photocatalyst for hydrogen evolution among non-noble metals. In particular, MoS_2 nanosheets exposed lots of active sites for the attachment of proton and later reduction reactions, and the efficiency is better than other bulk materials. Unfortunately, the absorption wavelength of MoS_2 nanosheets is only within the UV region. Visible light accounts for 95% of sunlight and UV light occupies only 5%. It is vital for photocatalysts to be able to efficiently harvest visible light. The absorption of visible light is able to cause strong localized surface plasmon resonance (LSPR) of gold nanoparticles (AuNPs), which has been widely investigated able to promote the performance of MoS_2 as a photocatalyst. However, the desired dispersion patterns of AuNPs for the optimization of surface plasmon resonance are less achievable. As an approach to maximize the amount of energy absorbed from the sunlight, we aim to design and fabricate hybrid particles composed of AuNPs and MoS_2 nanosheets with the control of coupling effect of among AuNPs. Through the achieved adjustment of separation distances among AuNPs, we are able to clarify the required condition for the best effect LSPR to absorb visible light and thus to optimize the efficiency of electron transition from AuNPs to MoS_2 nanosheets, which largely enhances desired hydrogen production.

To prove the influence of local surface plasmonic resonance and coupling effect to achieve hot electron transfer and reflect in hydrogen production, we fabricated a plasmonic nanostructure with gold nanoparticles (Au NPs) / MoS2 nanosheets. The distribution of Au NPs fabricated by a steric hindrance of PVP to avoid the characteristic that colloidal particles tend to agglomerate during precipitation. In the MoS_2-generated portion, the PVP segment originally attached to the gold surface is squeezed out by grafting the MoS_2 precursor thiourea, so that MoS_2 grows directly on the gold and maintains a specific spacing between the Au NPs on MoS_2 nanosheets.

10:20am **C3-1-ThM-8 Self-Reconstruction of Sulfate-Containing High Entropy Sulfide for Exceptionally High-Performance Oxygen Evolution Reaction Electrocatalyst***, **Thi Xuyen Nguyen**, Y. Su, C. Lin, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Novel earth abundant metal sulfate-containing high entropy sulfides, $FeNiCoCrXS_2$ (where X = Mn, Cu, Zn, or Al), have been synthesized via a two-step solvothermal method. We show that sulfate-containing $FeNiCoCrMnS_2$ exhibits superior OER activity with exceptionally low overpotential of 199, 246, 285, and 308 mV at current densities of 10, 100, 500 and 1000 mA cm^{-2}, respectively, and surpassing its unary-, binary-, ternary-, and quaternary-metal counterparts. The electrocatalyst yields exceptional stability after 12000 cycles and 55 h of durability even at a high current density of 500 mA cm^{-2}.Various *in-situ* and *ex-situ* analyses were used to investigate the self-reconstruction of the sulfides during the oxygen evolution reaction (OER) for the first time.The resulting metal (oxy)hydroxide is believed to be the true active center for OER. The remaining sulfate also contributes to the catalytic activity. Density function theory calculation is in a good agreement with the experimental result.The extraordinary OER performance of the high entropy sulfide brings a great opportunity for desirable catalyst design for practical applications.

10:40am **C3-1-ThM-9 Hydrothermal-Based Synthesis of Piezo-Composite Thin Films and Their Applications***, **Thi Nghi Nhan Nguyen**, K. Chang,* National Cheng Kung University, Taiwan

Piezoelectric materials have shown key characteristics for engineering and electrochemical applications, such as in sensors and actuators. The heterojunction has been investigated to prove the feasibility of the built-in electric field, which promotes the improvement of photocatalytic efficiency and the piezoelectric nanogenerator (PNGs) applications. In this research, detailed studies focused on piezo-composite thin films and their relative piezo-applications were reported. $BiFeO_3$ (BFO) microplates were grown on the ZnO nanorod array using the hydrothermal method, effectively reducing excess electrons in the ZnO layer. The BFO-ZnO composite act as a power generation source under a force from a motor steeper or external resources such as human hands and a pen. The output voltages and currents of the fabricated PNG were measured. The results clearly demonstrate the effectiveness of the BFO-ZnO heterostructure for realizing high performance, revealing the high durability and stability of devices. The piezo-photocatalytic application such as piezo-photodegradation and piezo-photoelectrochemical water splitting were studied under light irradiation and external stress. Moreover, the piezotronic effect on the performance of the BiOBr/Carbon fibers-based glucose sensor was systematically investigated under various glucose concentrations. The BiOBr/Carbon fibers exhibited a large surface area and low band gap, facilitating improved electrochemical reactivity toward glucose oxidation. The piezo-electrochemical results indicated that the piezotronic effect significantly increased the sensitivity as well as improved the sensing resolution of the BiOBr/Carbon fibers-based glucose sensors. The working mechanism of coupling the piezoelectric effect and photoexcitation in composite has been proposed based on the analysis of the band energies in the heterojunctions. This work demonstrates a promising approach to improve the sensitivity and generally improve the performance of the PNGs, glucose sensors, and the photocatalytic activities of composites.

11:00am **C3-1-ThM-10 A Comparative Study of the Thermochromic Performances of VO_2 Films Obtained by Air Oxidation of V and VN Precursors**, *D. Pilloud, A. Garcia-Wong, F. Capon,* ***Jean-François Pierson,*** Institut Jean Lamour - Université de Lorraine, France

Thanks to its metal-to-insulator transition (MIT) temperature not so far from the ambient one, thermochromic VO_2 exhibits great potentiality in smart coatings devoted to energy purposes. Among the different methods to synthesize thermochromic VO_2 films, reactive sputter deposition remains one of the most suitable for cost-effective industrial-scale production. For a few decades, increasing attention has been paid to a fast and relatively simple approach based on two steps to produce thermochromic VO_2 thin films: synthesis of a vanadium thin film followed by its oxidation at moderate temperatures (often less than 500 °C).Recently, we have revealed that the oxidation of vanadium nitride (VN) thin films also give rise to the formation of thermochromic VO_2. This work aims to compare the thermochromic properties of VO_2 films achieved after thermal air oxidation of V and VN thin films prepared by sputtering deposition from an elemental vanadium target. For both precursors, short-time air annealing (from 60 to 300 seconds) was performed at 550 °C. X-ray diffraction and Raman spectroscopy depicted that the thermal oxidation domain allowing the formation of the thermochromic VO_2 phase was enlarged for VN compared to V precursor films. These results were confirmed by electrical measurements of the resulting oxides in the temperature region that encompass the MIT of thermochromic m-VO_2. Finally, a particular focus was made on the oxides of the VN series in terms of their infrared properties. The results indicate that the oxidation of VN precursor allows the synthesis of monoclinic VO_2 films with high puritydisplaying good thermochromic performances(IR contrast of 63%, electrical switch of ~ 2 decades) with narrower hysteresis widths (< 9.3 °C) as compared to those obtained by vanadium films oxidation, making VN precursor of particular interest for industrial upscaling.

11:20am **C3-1-ThM-11 Revolutionizing Concentrated Solar Thermal Power Technology: Developing Self-Cleaning Mirrors with TiO_2 Films**, ***Nafsika Mouti,*** *V. Terziyska, N. Kostoglou,* Montanuniversität Leoben, Austria*; A. Kaidatzis, M. Arfanis,* National Centre of Scientific Research "Demokritos", Greece*; A. Eliades, K. Milidonis,* The Cyprus Institute, Cyprus*; K. Giannakopoulos,* National Centre of Scientific Research "Demokritos", Greece*; C. Mitterer,* Montanuniversität Leoben, Austria

Concentrated Solar Thermal (CST) technologies constitute a promising approach for harnessing the power of the sun to drive high-temperature thermal processes of interest, such as a power block for electricity generation, high-temperature industrial process heat or high-temperature solar chemistry applications. The Light Collection and Concentration Sub-system (LCCS) of a CST plant is responsible for collecting the direct solar radiation and concentrating it onto the active surface of a receiver system, where the thermal energy conversion takes place. The LCCS use mirrors (usually of parabolic shape) to concentrate the sunlight onto the receiver, however, the accumulation of dust and other particles (e.g. mirror soiling) on the mirrors has a direct effect on the efficiency of the LCCS. To address this issue, the Nano4CSP project with partners from Austria, Greece and Cyprus focuses on the development of self-cleaning CST mirrors using TiO_2 films. TiO_2 is a well-known photocatalyst, capable of breaking down dirt and other contaminants upon exposure to sunlight, making it a suitable material for creating self-cleaning surfaces. Within this study, sputtering has been successfully used to deposit TiO_2 films on CST mirrors at room temperature under various growth conditions. The deposited films with thicknesses in the range of 10 to 1000 nm have been extensively characterized using scanning electron microscopy with energy-dispersive X-ray spectroscopy, X-ray diffraction, Raman spectroscopy, optical measurements, nanoindentation, nanoscratching and field tests. Films with a dominant anatase phase have been found to show self-cleaning properties, thus improving the mirrors efficiency. Additionally, doping of TiO_2 films with N_2 and Zr has been evaluated, to improve the transparency and photocatalytic properties and to maximize the performance of the mirrors. The obtained results indicate that sputter deposition represents a promising method for producing self-cleaning CST mirrors, since it allows a precise control over the thickness and uniformity of the films, as well as the ability to apply them at room temperature, thus reducing costs and increasing efficiency for the necessary large area deposition on mirror surfaces. The findings of this research can have a significant impact on the further development of CST technology and its widespread implementation in larger scales, increasing the cost competitiveness of such plants by reducing the operational and maintenance costs and the associated water consumption for mirror cleaning.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E2-1-ThM
Mechanical Properties and Adhesion I

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Dr. Alice Lassnig**, Austrian Academy of Sciences, Austria, **Dr. Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

8:00am **E2-1-ThM-1 Residual Stress and Interfaces in Optical Coatings for Space Applications**, ***Chelsea Appleget,*** *K. Folgner, V. Jiao, S. Dunscombe, S. Sitzman,* The Aerospace Corporation, USA*; D. White, A. Hodge,* University of Southern California, USA*; J. Barrie,* The Aerospace Corporation, USA **INVITED**

Optical coatings are an enabling technology in the space industry for a variety of applications requiring high reflectance, transmittance, spectral selectivity, or thermal control. Traditional multilayered optical coatings can be designed to achieve virtually any reflectance or transmittance characteristics by tuning layer thickness, material selection, and layer material properties. For space applications, additional multifunctional performance requirements must be considered, including, but not limited to, low residual stress, good durability and adhesion in extreme environments, and tuning of surface structure. The space environment brings increasing demands on the performance of optical coatings and materials, and as such, requires an understanding of the mechanisms leading to maximized multifunctional properties.

In this talk, a discussion on adhesion, stress, and interfaces for optical films for space applications will be presented, with two case studies for residual stress and mechanical properties to follow. The first study will explore multifunctional properties of antireflection (AR) coatings and evaluation of the structure-property relationship in the context of interface character and layer microstructure in crystalline/amorphous and amorphous/amorphous multilayers. Characterization by spectrophotometry, transmission electron microscopy, and nanoindentation showed substantial variations in microstructure and film properties with tuning of layer configurations for improved transmittance. The second case study presents microstructural tailoring in highly reflective, mirrored films for improved surface scatter and residual stress performance. Thick (>1 µm) optical coatings with favorable optical properties are desired in space to protect sensitive substrates, such as radiation sensitive glass. However, traditional high reflectivity optical films, such as Ag, exhibit a degradation in optical properties due to increases in surface roughness with increasing film thickness. To circumvent these traditional limitations, the role of alloying, microstructural progression, and in-situ and ex-situ residual stress evolution is explored.

In summary, the design and fabrication of multifunctional optical coatings for space requires insight into the role of residual stresses, interfaces, delamination behavior, and microstructure, all of which inform the process-structure-property relationship in optical films.

8:40am **E2-1-ThM-3 Increased Adhesion of Mo Films on Polyimide Through Interface Modification**, ***Megan Cordill**, P. Kreiml,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; M. Rausch, C. Mitterer,* Dept. of Materials Science, Montanuniversität Leoben, Austria

Flexible and wearable electronics use metal films on polymer substrates. Here, the adhesion energy of these films to the substrates determines device performance. The interface between film and substrate is critical to adhesion energy. In this work, tensile induced delamination is used to quantify the adhesion energy of various Mo-based films on Polyimide, a common electrode material in thin film transistor displays. The method uses uniaxial straining to cause fracture of the film perpendicular and film delamination parallel to the tensile loading. Three different approaches to modify the interface to alter the adhesion energy will be compared, namely (i) the use of metallic interlayers between Mo and Polyimide (Al, Ta), (ii) the use of alloy interlayers between Mo and Polyimide (MoAl, MoTa), (iii) and the use of an alloyed Mo film (MoAl, MoTa) without an interlayer. Experiments on the different samples were performed with in-situ resistance measurements, confocal laser scanning microscopy (CLSM), and X-ray diffraction (XRD). CLSM allows for the quantification of crack density and delamination dimensions necessary for the adhesion measurement, while XRD provides film stress evolution to understand fracture and delamination mechanisms. The main aspects presented will be the adhesion energy along with the crack and stress evolution under uniaxial tensile loading. Results show that only the use of metallic interlayers between Mo and Polyimide (Al, Ta) provide a difference in the crack and delamination densities as well as a significant increase in the calculated adhesion energy compared to any of the other modification strategies.

9:00am **E2-1-ThM-4 Picosecond Acoustics as a Local and Quantitative Adhesion Technique**, ***Arnaud DEVOS**, A. Vital-Juarez,* IEMN, France*; J. Desmarres,* CNES, France

The study of the bonding at interfaces between thin layers is of crucial importance in numerous applications whether they are related to optics, electronics or space exploration. A large number of methods have been developed to characterize the adhesion of a thin film to a substrate. But most of them are non local and destructive.

Acoustic waves are also sensitive to adhesion defects as they affect the way acoustic waves are reflected at the concerned interface. To address thin-films and complex stacks, ultra-high frequency acoustic waves (typ. greater than 10 Ghz) are needed. Such a range is only reachable to femtosecond laser techniques known as picosecond acoustics following the pioneer work of H. Maris in the 1980's. Recently we reported several studies that show how useful can be the picosecond acoustic technique to detect and quantify adhesion defects[1][2][3].

In this paper, we prepare dedicated samples to demonstrate the local character of the adhesion measurement by picosecond acoustics. For that a fingerprint is deposited between a silicon substrate and a thin metal film. A fingerprint acts as a large adhesion defect since the wafer surface is not clean at that place when the metal film is then deposited.

We then use the picosecond acoustic technique to map the reflection coefficient of ultrahigh frequency acoustic waves along the sample surface. A clear difference is first seen on and out the zone where the fingerprint has been deposited. Second, a high resolution mapping reveals the complete shape of the buried fingerprint: bumps and hollows of the fingerprint are easily discriminated acoustically as such details do not affect the adhesion in the same manner. The acoustic map reveals the fingerprint image and the guilty person can be identified !

References:

[1] A. Devos and P. Emery, "Thin-film adhesion characterization by Colored Picosecond Acoustics", Surface and Coatings Technology 352, 406 (2018).

[2] A. Devos, A. Vital-Juarez, A. Chargui and M. Cordill, « Thin-film Adhesion: A Comparative Study Between Colored Picosecond Acoustics and Spontaneous Buckles Analysis", Surface and Coatings Technology, 421, 127485 (2021).

[3] A. Vital-Juarez, L. Roffi, J.-M. Desmarres and A. Devos, « Picosecond Acoustics Versus Scotch Tape Adhesion Test: Confrontation on a Series of Similar Samples With a Variable Adhesion", 448, 128926 (2022).

9:20am **E2-1-ThM-5 What Controls Size Effects on the Mechanical Properties of Additive Manufactured Polymers**, *K. Shergill, Y. Chen,* ***Steve Bull**,* Newcastle University, UK

3D printed artefacts are becoming more common and the effect of printing parameters on their properties is key to their performance in applications. Although parameters like build orientation and raster direction are well-studied the effect of layer thickness (and its introduction of sizeeffects into the properties of the material) is less well-known. This study determines the influence of layer thickness on the mechanical properties of polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and PETG (Polyethlene terephtalate Glycol) 3D printed specimens made with fused filament fabrication (FFF). Samples were printed with differing layer thickness and tensile tested according to ASTM D638. The study also found that when increasing the layer thickness the mechanical properties of the specimens for both ABS and PLA decreased. When it came to ultimate tensile strength, the effect of layer thickness on PLA was more significant than on ABS with PETG being in between. The differences were attributed to differences in additive layer adhesion and the effect of the structure and defects introduced by the additive layerprocess.

9:40am **E2-1-ThM-6 Mechanical Properties and Microstructure Evaluation of HiPIMS Cu/W and Cu/Cr bilayers with Different Thickness Ratios**, ***Tra Anh Khoa Nguyen**, T. Zhang,* Graduate Institute of Precision Engineering, National Chung Hsing University, Taiwan*; H. Wang, H. Wu,* National Chung Hsing University, Taiwan*; M. Lin,* Graduate Institute of Precision Engineering, National Chung Hsing University, Taiwan

Copper/tungsten and copper/chromium bilayer films with a total thickness of 400 nm deposited using High Power Impulse Magnetron Sputtering(HiPIMS), have been compared with those fabricated by DC Magnetron Sputtering (DCMS). The different thickness ratios of 1:3, 3:5, 1:1, 5:3, 3:1 and sputtering power effects on the surface, microstructure, morphology, the texture of sputtered films, and mechanical properties of the bilayer thin films were investigated. The results show that the HiPIMS sputtered copper/tungsten and copper/chromium bilayers exhibit higher hardness, lower electrical resistance, and lower surface roughness than films deposited under the same deposition conditions as DCMS. These properties can be attributed to the increased peak power density of the target during the HiPIMS deposition process, which increases the ion energy and enables the deposition of highly dense grain structures and changes in texture transformation. Through the results of different thickness ratios, the deposition parameter database can be used for future HiPIMS copper/ tungsten and copper/chromium multilayer deposition.

10:00am **E2-1-ThM-7 Nanoengineered Thin Film Metallic Glasses with Mutual Combination of Large Yield Strength and Ductility**, *F. Bignoli,* CNRS, France*; A. Brognara, J. Best,* Max-Planck Institut für Eisenforschung GmbH, Germany*; P. Djemia, D. Faurie,* CNRS, France*; A. Li Bassi,* Politecnico di Milano, Italy*; G. Dehm,* Max-Planck Institut für Eisenforschung GmbH, Germany*;* ***Matteo Ghidelli**,* CNRS, France

Thin film metallic glasses (TFMGs) are object of intense research due to their a unique combination of mechanical properties involving large yield strength (~3 GPa) and ductility (>10%) [1]. Nevertheless, the synthesis of advanced TFMGs with engineered microstructure and the understanding of their mechanical properties are barely tackled. Here, I will present recent results involving two (2) strategies to develop nanoengineered TFMGs with a controlled microstructure down to the atomic scale, resulting in outstanding and tunable mechanical properties.

In the first case, I will show the potential of Pulsed Laser Deposition (PLD) as a novel technique to synthetize nanostructured $Zr_{50}Cu_{50}$ (%at.) TFMGs. I will show how the control of PLD process parameters enables to synthetize a variety of film microstructures among which compact fully amorphous and amorphous nanogranular, showing lower density and large free volume interfaces [2]. High-resolution TEM reveals a nano-laminated self-assembled atomic structure characterized by alternated layers with different chemical enrichment [2]. This results in an unique mechanical behavior as shown by in situ TEM/SEM tensile/compression tests, reporting homogeneous deformation for nanogranular (cluster assembled) TFMGs in combination with a large yield strength (>3 GPa) and ductility (>9 %) [2].

In the second case, I will focus on the fabrication of multilayers with nanoscale period alternating either fully amorphous or amorphous/crystalline sublayers. I will show how the control of the sublayer thickness (form 100 down to 5 nm) influences the deformation behavior affecting shear bands formation, while tuning the mechanical properties. As an example, alternating CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolayers results in an ultrahigh compressive yield strength (3.6 GPa) and large homogeneous deformation (~15%) [3]. Similarly, I will show the suppression of shear band/crack process in fully amorphous ($Zr_{24}Cu_{76}/Zr_{61}Cu_{39}$ %at.) multilayers with bilayer period < 50 nm, while keeping a mutual combination of large ductility (> 10%) and yields strength (>2.5 GPa).

Overall, our results pave the way to the development of novel amorphous materials with improved mechanical properties and wide application range especially in the field of microelectronics.

References:

[1] M. Ghidelli et al. Acta Mater., 131, 246, 2017.

[2] M. Ghidelli et al. Acta Mater., 213, 116955, 2021.

[3] G. Wu et al., Materials Today, 51, 6, 2021.

10:20am **E2-1-ThM-8 Measurements and Simulation of Mechanical Behavior of Amorphous and Crystalline Zr(–Hf)–Cu Thin-Film Alloys***, **Stanislav Haviar**, T. Kozák,* University of West Bohemia, Czechia*; M. Meindlhumer,* Montanuniversität Leoben, Austria*; M. Zítek,* University of West Bohemia, Czechia*; J. Keckes,* Erich Schmid Institute of Materials Science, Austria*; P. Zeman,* University of West Bohemia, Czechia

Nanoindentation and microbending testing were used to investigate the mechanical properties of Zr(–Hf)–Cu thin-film alloys prepared by nonreactive magnetron co-sputtering. A detailed analysis of nanoindentation data and microscopic images of indents allowed a more precise determination of the effective Young's modulus of the films thanks to taking the pile-up effect into account.

Microbending testing in a scanning electron microscope was performed with microcantilevers fabricated by focused ion beam and the data were evaluated using a finite element method model. As outputs of this elasto-plastic model, Young's modulus, yield strength, elastic strain, apparent yield point and approximate ultimate strength and strain of the films were determined.

From a material point of view, the effect of elemental composition (Cu content and Hf substitution) and structure (glassy and crystalline) was investigated and discussed. It was shown that the substitution of Hf for Zr has less pronounced effect on the mechanical properties than the increase in the Cu content in the films that leads to a pronounced increase in the hardness, Young's modulus, elastic strain, yield strength, apparent yield point and ultimate strength but also to a decrease in the plastic parameter k and ultimate strain. Furthermore, a different atomic ordering in the crystalline and glassy Zr–Cu films of identical elemental composition results in differences in their mechanical properties and deformation behavior. The crystalline film was observed to be harder and stiffer with approximately the same elastic strain but higher yield strength and its plastic deformation was free of shear bands events.

[1] Haviar S., Kozák T. et al. Nanoindentation and microbending analyses of glassy and crystalline Zr(–Hf)–Cu thin-film alloys. *Surf. and Coat. Technol.* 399 (2020) doi: 10.1016/j.surfcoat.2020.126139

10:40am **E2-1-ThM-9 A Nanotwinned CoCrFeNi Medium Entropy Alloy with Ultrahigh Strength Over a Wide Range of Temperature***, **Yun-Xuan Lin**, J. Wang, C. Tsai, S. Chang, F. Ouyang,* National Tsing Hua University, Taiwan

The medium-entropy alloys (MEAs) or high-entropy alloys (HEAs) have many superior properties, including high strength, high ductility, corrosion resistance, oxidation resistance, and high temperature resistance, which can be used in many applications. In addition, nanotwin (NT) structure plays an important role on strengthening mechanism in the microscopic scale because of its special properties, such as great thermal stability, high strain rate sensitivity, low electrical resistivity, and increased mechanical strength. In this study, we combined HEA and nanotwin structure to fabricate NT-MEA thin films and investigated its mechanical properties at different temperature ranges. At first, the NT CoCrFeNi MEA films were fabricated by pulsed DC magnetron sputtering system on Si substrate. The hardness of nanotwinned CoCrFeNi medium entropy alloy films was examined by nanoindentation at varied temperatures from -80 ℃ to 300 ℃. At the same time, the microstructures of the indentation regions were studied by transmission electron microscope (TEM). As-deposited CoCrFeNi medium entropy alloys had a columnar grain structure containing high-density nanoscale growth twins parallel to the substrate with an average twin thickness of 2.4 nm. The results show that NT-MEA was observed to have remarkably high strength, outperforming many other bulk HEAs, MEAs, nanocrystalline HEAs, and conventional NT-metals in the temperature range from -80 °C to 300 °C. The maximum hardness of NT-MEA was measured with a value of 11.3 GPa at cryogenic environment of -80°C and its hardness slightly decreased to 9.4 GPa when temperature increased from -80 ℃ to 300 ℃. Meanwhile, neither cracks nor fractures were observed in all temperatures, suggesting that the NT-MEA was still ductile material, especially in the cryogenic environment. The corresponding deformation mechanism at different temperature ranges would be discussed in details in this talk.

11:00am **E2-1-ThM-10 Material Properties and Mechanics of Eggshells—Nature's Survival Capsules***, **Jia-Yang Juang**,* National Taiwan University, Taiwan **INVITED**

Amniotic eggs emerged over 300 million years ago in tetrapod vertebrates and are now the primary reproductive mode of all terrestrial amniotes. Unlike the simpler, shell-less eggs of amphibians, amniotic eggs are covered with shells, which allow the eggs to develop fully on land without drying out and thus open up new terrestrial habitats for amniotes, including birds and egg-laying reptiles. In birds, eggshells are multifunctional thin-walled structures that protect the embryo from excessive water loss, provide calcium, and sustain the weight of incubating birds. As a load-bearing structure, the eggshell must be strong enough to resist deformation and impact. Meanwhile, it must be breakable for the hatchling to emerge. Those are mechanical design trade-offs that must be adequately balanced. Here, we use combined experimental, numerical, and theoretical methods to analyze the morphology, material properties, and mechanics of 700 freshly-laid bird eggs from 58 species across three orders of magnitude in egg mass (from 1 g to 1459 g). We characterize the mineral content by acid-base titration, the crystallographic characteristics by electron backscatter diffraction (EBSD), and effective Young's modulus *E* by compression test and finite-element analysis (FEA). We find that the mineral content is positively correlated with *E,* with the lowest of 83.1% and 23.28 GPa in Zebra finch and the highest of 96.5% and 47.76 GPa in ostrich in this study. The EBSD shows that eggshell is anisotropic and non-homogeneous, with different species exhibiting different degrees of crystal orientation and texture. The experimental results are consistent with the nanoindentation test and theoretical prediction of linear elasticity. This study provides new data and insights into the material properties and mechanics of eggshells and provides clues for the future development of bioinspired multifunctional thin-walled shells.

11:40am **E2-1-ThM-12 Effects of Cathodic Currents on Mechanical and Corrosion Behaviors of Plasma Electrolytic Oxidation Coatings on 6061 Aluminum Alloy***, C. Tseng,* Department of Materials Engineering, Ming Chi University of Technology. Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; **Xianghe Wang**,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan

In this study, we fabricated the porous aluminum oxide (Al_2O_3) coatings on 6061 aluminum alloy by using plasma electrolytic oxidation (PEO) in alkaline sodium silicate solution under bipolar pulsed power mode with maxima anodic voltage at 500V, maxima cathodic voltage at 100V, duty cycle of 25%, pulse frequency in 1000 Hz, anodic current in 2A and cathodic current in 1~5A.The effects of cathodic current on microstructural, mechanical and corrosion behaviors of PEO coatings on 6061 aluminum alloy were investigated by X-ray diffractometer (XRD), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), scratch test, pin-on-disk wear test and potentiodynamic polarization measurement. The XRD results show that the PEO coatings are mainly composed of a-Al_2O_3 and γ-Al_2O_3. However, the ratios of a-Al_2O_3 and γ-Al_2O_3 in PEO coatings are identical with various cathodic currents applied. The SEM images display that the thickness of PEO coating is increased with increasing cathodic current from 11mm (1A) to 17mm (5A) and surface porosity of PEO coating is decreased with increasing cathodic current from 16.2% (1A) to 9.4% (5A). The potentiodynamic polarization curves show that the PEO coatings, as compared to 6061 aluminum alloy, exhibit higher corrosion resistances in 3.5 wt% NaCl solution. However, the corrosion current density (Icorr) and passivation current density (Ipass) for PEO coatings are decreasing with increasing cathodic current applied. In summary, the thickness, porosity and corrosion resistance of PEO coatings on 6061 aluminum alloy can be significantly improved by controlling cathodic current applied.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-ThM

Boron-Containing Coatings II

Moderators: Dr. Marcus Hans, RWTH Aachen University, Germany, **Prof. Helmut Riedl**, TU Wien, Institute of Materials Science and Technology, Austria, **Prof. Johanna Rosén**, Linköping University, Sweden

8:40am **F4-2-ThM-3 Ternary Tungsten Boride Coatings with Improved Mechanical Properties Deposited by High-Power Pulsed Magnetron Sputtering from One Spark Plasma Sintered Target**, ***Tomasz Mościcki**, R. Psiuk, J. Chrzanowska-Gizynska,* Institute of Fundamental Technological Research of Polish Academy of Science, Poland*; D. Garbiec,* Łukasiewicz Research Network – Poznań Institute of Technology, Poland **INVITED**

Today the deposition of protective coatings with magnetron sputtering is well known in scientific laboratories and in industry also. However, there is an increasing need to coat larger and heavier tools. Also, sometimes substrate materials shouldn't be deposited at temperature greater than 300˚C. This is a problem because some of novel materials like tungsten borides needs high substrate temperature (>400 ˚C) during deposition to obtain special mechanical properties. According to Thornton deposition model the deposition of films at lowered substrate temperature with exceptional mechanical properties (ZONE T) is possible by increasing of the energy of plasma. Such possibility gives a HIPIMS method. Additionally, this method allows to deposit defected by vacancies α-WB_2 structure which according to first-principles calculation possess exceptional mechanical properties.

In this presentation the influence of HIPIMS parameters like the pulse duration, frequency and power and also the bias voltage and substrate temperature on ternary tungsten borides films properties will be shown and discussed. The deposited at 350 ˚C coatings by High-Power Pulsed Magnetron Sputtering from one Spark Plasma Sintered W-Ti-B_{2-x} target are very hard (H>30 GPa) and possess high crack resistance. Additionally, they are thermally stable at temperature below 700 ˚C. The comparison between Titanium and Tantalum as a doping element will be presented also.

This work was financed by the National Centre for Research and Development (NCBR, Poland) under project no. TECHMATSTRATEGIII/0017/2019.

9:20am **F4-2-ThM-5 The Architectural Design of High-Temperature Protective Coatings: Improving the Oxidation Resistance of TMB_2 (TM = Hf, Ti, W) Thin Films**, ***Sophie Richter**, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; B. Widrig, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal (TM)-borides are well known for their high thermal stability, high melting points, and excellent mechanical properties such as high hardness and Young's modulus, making them suitable for a broad field of applications. However, TM-borides suffer from poor oxidation stability at high-temperature ranges. Therefore, improving the oxidation resistance is of great interest for coated high-performance components, where both – a combination of mechanical and oxidative resistance – are particularly desired.

Within this study an architectural approach to protect TMB_2 (TM = Hf, Ti, W) thin films from further oxidation is presented. For this purpose, different materials were investigated as protective layers on top of each boride system. The coatings have been deposited by PVD techniques. The phase formation, morphology, and mechanical properties (e.g., hardness and Young's modulus) of all as deposited thin films were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), and nanoindentation. Thermogravimetric analyses up to 1400 °C in synthetic air was utilized to investigate the barrier function of these coatings with respect to the underlying TMB_2 against oxidation. Subsequently, the long-term oxidation behavior of the synthesized films in ambient air at 1200 °C for 30 h was examined. In particular, the HfB_2 and TiB_2 systems were characterized by their oxidation resistance. High-resolution characterization techniques (i.e. TEM, HR-TEM, EDX) confirmed the good adhesion between the barrier top layers, as well as the unaffected diboride coatings and the sapphire substrates, respectively.

Keywords: Protective coatings; Oxidation resistance; High temperature; PVD; Borides;

9:40am **F4-2-ThM-6 Stoichiometry, Structure, and Mechanical Properties of Superhard Zirconium Diboride Films Prepared by the High-Power Impulse Magnetron Sputtering**, ***Viktor Šroba**, K. Viskupová, T. Roch, L. Satrapinskyy, M. Truchlý, T. Fiantok,* Comenius University, Bratislava, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; B. Grančič, P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of refractory transition-metals (TMB_2) especially from IVB (ZrB_2, TiB_2) are thanks to their excellent mechanical properties like high hardness or wear resistance and high thermal stability, given by high melting temperatures (above 3000 °C), promising ceramic materials for applications in extreme environments. Magnetron sputtering of TM diboride films from compound target is accompanied by the different angular distribution of sputtered boron and metal atoms which leads to the growth of overstoichiometric films $TMB_{2+\Delta}$ (B/TM > 2), The films have a nanocomposite structure consisting of stoichiometric crystalline TMB_2 nanofilaments surrounded by an amorphous boron tissue phase. The presence and volume fraction of the boron tissue phase relative to the crystalline phase significantly determines the mechanical properties and affects behavior of the films during high-temperature exposure in a real environment. The progressive technology of high-power impulse magnetron sputtering (HiPIMS) using pulsed plasma discharges leads to the efficient ionization of the target atoms, whose flux and kinetic energy can then be controlled by appropriate synchronization with the pulsed negative substrate bias. In this way, a better control of the composition (B/TM) of the diboride films can be ensured, which then leads to the formation or absence of the boron tissue phase.

Here in this work, HiPIMS (Hipster 6, Sweden) with synchronized substrate bias is used to prepare ZrB_x films where changes in deposition parameters (pulse width, frequency, phase shift) on stoichiometry, formation of nanostructure and mechanical properties are investigated using X-ray diffraction, scanning and transmission electron microscopic and nanoindentation techniques. All ZrB_x films exhibit understoichiometric composition ratio of B/Zr which vary from 1.5 to 1.9. The films have a crystalline character identified as hexagonal α-ZrB_2. A deeper insight into nanostructure shows changes in nanocomposite character of the films. Hardness of ZrB_x films is up to ~ 45 GPa and indentation Young's modulus of ~ 430 GPa.

This work was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042) Scientific Grant Agency (Grant No. VEGA 1/0296/22), European Space Agency (ESA Contract No. ESA AO/1-10586/21/NL/SC), and Operational Program Integrated Infrastructure (Project No. ITMS 313011AUH4).

10:00am **F4-2-ThM-7 Exploring Phase Evolution and its Consequences on Mechanical Properties of a Novel HfB_2-AlB_2 Coating System**, ***Samyukta Shrivastav**, D. Yun, K. Canova, J. Abelson, J. Krogstad,* University of Illinois at Urbana Champaign, USA

Thin films of ternary $Hf_xAl_{1-x}B_y$ were deposited using low temperature (200-300°C) chemical vapor deposition (CVD), using the precursors $Hf(BH_4)_4$ and AlH_3NMe_3.We hypothesized that the addition of Al would increase the oxidation resistance of HfB_y, which in the absence of Al oxidizes quickly at service temperatures of 700°C. One issue with aluminum alloying would be the formation of a soft phase that may deteriorate mechanical properties of the coating. Here, we report in detail on the phase and properties of $Hf_xAl_{1-x}B_y$ films. Due to the very low growth temperature, only ~ 0.09-0.1 on the homologous scale, it was not known whether the ternary films would be amorphous or crystalline, fully mixed or segregated, nonstoichiometric in B, or include elemental Al. We report that as-deposited $Hf_xAl_{1-x}B_y$ contains only metal diboride and that, remarkably, the films are nanocrystalline with grain sizes ~ 10 nm. This is in sharp contrast to as-deposited HfB_2, which is X-ray amorphous and has a metal sublattice density about half that of the crystalline phase. The concentration of aluminum is uniform throughout the coating thickness, indicating that the CVD reactions at the growth surface are kinetically in steady-state. We qualitatively evaluated the mechanical response using nanoindentation, to compare the effect of alloying on mechanical properties. AFM analysis of the indent on the as deposited $Hf_xAl_{1-x}B_y$ coatings shows elastic recovery, whereas HfB_2 exhibits considerable plastic response with outer pileup. These results show an improvement in mechanical response due to alloying, and negate the presence of a soft elemental Al phase.The improvement in mechanical properties could be due to the presence of an HfAlB ternary, which will be further explored using advanced chemical characterization techniques such as STEM-XEDS. We have also seen that the coatings form a uniform oxide at 700°C, and heat treatments do not seem to bring about any changes in microstructure and microscale phase segregations. We will also be showing our results for any nanoscale compositional fluctuations present due to heat treatments at 700°C, and the impact of such fluctuations and heat treatments on mechanical properties will also be demonstrated.

10:20am **F4-2-ThM-8 Challenges and Perspectives of Wear Resistant Boron-Containing Coatings***, **Jose L Endrino**,* Nano4energy SL, Spain*; J. Rao,* Cranfield University, UK*; T. Brzezinka,* Dell Technologies, UK*; A. Mendez, J. Santiago,* Nano4energy SL, Spain*; J. Molina,* Polythecnic University of Madrid, Spain **INVITED**

This invited talk will present two different cases studies related to the deposition of new generation of boron-containing coatings with highly ionized physical vapor deposition techniques such as filtered cathodic-arc evaporation and positive pulse high power impulse magnetron sputtering (HiPIMS). Although the deposition of boron-based compounds, brings in the prospect of hard coatings exhibiting very useful physical prospects, the brittle nature of borides, high melting points and characteristic compound formation introduces a unique set of challenges as well.

The first case study deals with the use of TiB2 for arc evaporation after first densifying its structure and adding non-metallic sinter additives such as C and TiSi2. Cylindrical cone-shaped cathode configuration is used and coating properties were compared to those obtained from monolithic TiB2 cathodes. Arc spots were found to stick at certain locations, leading to extensive local fracturing of the cathode. TiB2-C required the lowest current setting (40A) to trigger an arc and provided the best arc-spot stability and mobility. Carbon inclusions successfully prevented crack propagation, although they did not stop crack initiation, which resulted in high cathode flaking and poor target utilization. An appropriate distribution of magnetic fields from filtering and focusing coils was found to be essential for maintaining stable and mobile arc spots on TiB2-C and TiB2-TiSi2 cathodes.

The second case study deals with the optimization of nanostructured AlTiBN and AlCrBN coatings by tailoring metal ion fluxes and energies using HiPIMS with positive pulses. In this study, the formation of nanocrystalline grains embedded in an amorphous boron-rich phase provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained using nanoscratch testing.

11:00am **F4-2-ThM-10 TiB_X Thin Film Synthesis from an Industrial-Sized DC Vacuum Arc Source***, **Igor Zhirkov**, A. Petruhins, A. Shamshirgar,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden*; N. Hellgren,* Department of Computing, Mathematics, and Physics, Messiah University, USA*; S. Kolozsvári, P. Polcik,* PLANSEE Composite Materials GmbH, Germany*; J. Rosen,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden

Titanium diboride exhibits outstanding properties promising for the next generation of hard and wear resistant coatings. However, for efficient physical vapor deposition (PVD) through DC vacuum arc, the field is comparatively unexplored due to challenges associated with the materials synthesis process. It is well known that arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This, in turn, can make DC arc deposition a preferred method for sustainable materials engineering, reducing the carbon footprint of the thin film industry. This motivates development and investigation of arc processes for TiB_2 synthesis. Furthermore, previously reported attempts of TiB_2 arc depositions from a TiB_2 cathode mentions process instability, cracking of the cathode, and intensive generation of macroparticles, which in turn limits an evaluation of the process efficiency. In this work, we show consistent analysis of the cathode surface, the plasma composition, the film composition (from XPS) and (micro-)structure (from SEM, XRD), as well analysis of collected macroparticles. The study is done with an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. The cathode weight loss, the amount of the generated droplets and the deposition rate is also measured as a function of process parameters (arc current and pressure). Furthermore, we also investigate tuning of the process efficiency by modifying the cathode composition. Plasma analysis shows average ion energies consistent with the velocity rule, around 115 and 25 eV for Ti and B, respectively. The plasma ion composition shows approximately 40 % Ti and 60 % B, while the deposited films are understoichiometric in B. The film hardness is found to be above 30 GPa for all shown samples. The deposition rate is around 100 nm/min, while the cathode weight loss is around 0.3 gram/min. Altogether, the results show potential for the use of cathodic arc as an efficient and useful method for synthesis of metal borides.

11:20am **F4-2-ThM-11 Oxidation Behavior of Stochiometric $Ti_{0.35}Al_{0.65}B_2$ Coatings***, **Sebastian Lellig**,* Materials Chemistry, RWTH Aachen University, Germany, and Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Navidi Kashani,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, and Lawrence Berkeley Lab, USA*; M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

The oxidation resistance of stochiometric $Ti_{0.35}Al_{0.65}B_2$ coatings is investigated systematically in a TEM study at temperatures of 700 to 1000 °C and annealing times of 1, 4 and 8 h.
In the as deposited state, a native, amorphous aluminum oxide layer covers the surface as well as the grain boundaries of the lamellar structure. The oxidation behavior upon annealing is dominated by the formation of a partly amorphous and nanocrystalline aluminum oxide layer, whereby the crystallinity is increased with higher annealing temperatures. At higher temperatures, spinodal decomposition leads to the segregation of AlB_2 and TiB_2. Ti diffusion through AlB_2 regions is hindered due to the low solubility of Ti in AlB_2. Outdiffusion of Al from binary and ternary regions lead to a homogeneous concentration distribution over the whole film. Simultaneously, the diffusion of Al through the oxide layer is hindered by nanocrystalline and amorphous regions. At temperatures ≥ 920°C, it is evident that AlB_2 phase segregations decompose, whereby liquid Al is formed, leading to the disintegration of the film. It is reasonable to assume that the application temperature range of other AlB_2 segregation containing transition metal borides is restricted by the here identified decomposition process.

Focused Topic Session
Room Town & Country C - Session FTS-ThL

Focused Topic Session

12:20pm **FTS-ThL-1 How to Publish in a Scientific Journal***, D. Biswanath,* Elsevier, USA*; **Allan Matthews,*** University of Manchester, UK

Publishing research articles is of pivotal importance in the scientific career of a researcher. Young researchers with little or no experience of writing research articles often find it challenging to present their research outcome in a structured fashion. In this presentation, I will discuss different areas of scientific publishing such as (i) how to write a research article and (2) how to publish a research article. I will introduce the publication workflow and explain the different stages involved in the workflow. For the choice of journal, I will explain different models of scientific publishing, including subscription and open access models. With the knowledge of best practices of scientific publishing, young researchers would be qualified to write and publish their research work in state-of-the-art scientific journals.

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_2 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_2 addition on the microstructure and the electrical and chemical properties of Ag nanometre-thick films grown on SiO_2 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_2 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_2O) were obtained in varying proportions depending on the O_2 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_2 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_2 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_2N) is regarded as one of the promising coating materials for the tools applied at elevated temperature, because Mo_2N will form a Magnèli 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_2N 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_2N coating. The objective of this study was to investigate the influence of Mo interlayer on the adhesion and tribological properties of Mo_2N coatings on D2 steel substrate. Mo_2N 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_2N coatings on D2 steel will be discussed.

2:40pm **B1-2-ThA-5 Enhanced Adhesion and Thermal Stability of Thick $(Al,Cr)_2O_3$ 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 ≤ 700 °C by modification of the binary Al-O system using Cr. Thereby, High Speed PVD showed a high potential to synthesize crystalline $(Al,Cr)_2O_3$ 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 $(Al,Cr)_2O_3$ 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 µm < d < 11 µm at constant bias voltage. Moreover, two graded $AlCrN_g$ interlayers were deposited at different bias voltages. Deposition of the functional $(Al,Cr)_2O_3$ layer is initially omitted to analyze the adhesion strength between substrate and interlayer. In a next step, compounds of 1.2344 and $AlCrN/(Al,Cr)_2O_3$ with total thickness of 21 µm < s < 30 µm were produced. Hereby, the thickness of functional layer s_f is varied between 16 µm < s_f < 25 µm in order to analyze the effect of functional layer thickness. Moreover, the thermal stability of the $AlCrN/(Al,Cr)_2O_3$ 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 comparision to $(Al,Cr)_2O_3$ coated substrate, the $AlCrN_g/(Al,Cr)_2O_3$ 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 $AlCrN_g$ interlayer increases the adhesion of thick $(Al,Cr)_2O_3$ 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 $AlCrN_g/(Al,Cr)_2O_3$ coatings during annealing up to a temperature of T = 1,200 °C. Therefore, thick $(Al,Cr)_2O_3$ coatings, s ≈ 30 µm, deposited by HS-PVD in combination with a graded $AlCrN_g$ 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 Zítek,*** 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., $Cu_{51}W_{25}Cr_8Ti_{16}$)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, nanoindenation)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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3:40pm **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 $Al_{57}Ti_{35}Ta_8$ 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.

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. $CoCrNiNd_xB_y$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. Ehiasarian**, Sheffield Hallam University, UK, **Dr. Yolanda Aranda Gonzalvo**, 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 µm 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 µN range, can be determined experimentally.

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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_2. 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 unpreceded 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 ExB drift). However, the electron drift shows clear anisotropy and the azimuthal electron drift evolves according to a changing balance of E x 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. Wuu,* 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+ 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^+, Cr^+, N_2^+, and Ar^+ 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^+ and Ar^+ intensity increases at a phase difference of 100 µs, and the hardness and polarization resistance increase. CrN plasma is dominated by Cr^0, and the strength of both Ar^+ and Cr^+ 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. Wieczerzak, 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[1–3]. Different fabrication approaches have been used, including molecular beam epitaxy (MBE), direct-current (DC) and radiofrequency (RF) magnetron sputtering and reactive sputtering[1,4–8], 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_2 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_2 phase exhibit thermally induced switching of electrical conductivity, V_2O_5 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.

This work was supported by the Czech Science Foundation through the project GAČR 22-16667S.

4:00pm **B7-ThA-9 Diagnostics with an Optically Trapped Microparticle in the Sheath of an Asymmetric CCP*, Viktor Schneider,*** *J. Schleitzer, 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 SiO2 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 µPLASMA (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 descrease 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 rediual particle charge.

[1] J. Benedikt, H. Kersten and A. Piel 2021 Plasma Sources Sci. Technol. 30 pp 033001
[2] H. R. Maurer, V. Schneider, M. Wolter, R. Basner, T. Trottenberg and H. Kersten 2011 Contrib. Plasma Phys. 51 pp 218-227
[3] V. Schneider and H. Kersten 2018 Rev. Sci. Instrum. 89 pp 103505

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_2/O_2 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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[2] H. Kersten *et al.,* Vacuum **63**, 385-431 (2001).

[3] L. Hansen *et al.,* PSST **31**, 035013 (2022).

[4] L. Hansen *et al.,* Thin Solid Films **(Submitted)**.

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Functional Thin Films and Surfaces
Room Pacific F-G - Session C2-1-ThA

Thin Films for Electronic Devices I

Moderators: Dr. Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Dr. Jörg Patscheider**, Evatec AG, Switzerland

1:20pm **C2-1-ThA-1 An Imperfect High k Dielectric (O Vacancies, Contamination) Can Give a Perfect MIM Device*, Christophe Vallee,*** *N. Tokranova, K. Beckmann,* SUNY College of Nanoscale Science and Engineering, USA*; N. Cady,* SUNY college of Nanoscale Science and Engineering, USA **INVITED**

The reduction of high k dielectric thicknesses below 10 nm gives rises to new potential application of these materials due to unexpected "resistance switching"which is a phenomenon by which some electrical insulators display a change of resistance upon application of a dc bias voltage.Increasing the voltage across an insulator inevitably leads to breakdown, which corresponds to an abrupt resistance decrease. In some circumstances, it is possible to restore a high value of resistance by applying a voltage of opposite polarity. Switching between a low and high resistance state can be repeated by voltage sweeping, leading to a hysteresis loop in the current-voltage (I-V) characteristic. Resistance switching is observed in a variety of metal oxides thin films. In recent years this phenomenon has attracted interest for the fabrication of memory devices ("resistive memory") and for the fabrication of voltage-controlled resistors ("memristors"). At present, physical mechanisms at the origin of resistance switching are based on field-enhanced electrode diffusion into the oxide (in that case the devices are named "conductive bridging memories" or CBRAM) and voltage-controlled creation and annihilation of oxygen vacancies (named "OXRAM" devices).

Within this presentation we will discuss the use of high k dielectrics and their fabrication for metal-insulator-metal (MIM) devices such as linear MIM capacitors, resistive memories, and MIM diodes. We will also discuss the use of resistive switching for neuromorphic computing and compute-in-memory applications, and the integration of resistive memory devices with CMOS. Whatever the device, due to the very small thickness of the high k dielectric, it seems obvious that the electrode materials as well as the interfaces between the insulator and the metal electrodes must be optimized. But more importantly, we will try to elucidate how impurities (like contamination from precursors used for the deposition process) and defects (O vacancies) can be intentionally added to improve the device properties. Ultimately, optimization of device performance is paramount for adoption of these devices for advanced, highly efficient computing hardware.

2:00pm **C2-1-ThA-3 Optoelectronic and Thermoelectric Properties of New Heterobilayers of Janus-Type Noble-Metal Chalcogenides Materials***, **Mourad Boujnah**,* CINVESTAV-Unidad Queretaro, Mexico

Janus and non-Janus monolayers are one of the transformations of the 2D materials viz present an exceptional opportunity to control and manipulate their physical properties. Herein, we predict the two-dimensional of noble-Metal Chalcogenides (NMCs) materials A_2B (A = Ag, Au and B = S, Se) heterobilayes (HtBLs) through first-principles calculations. The Ab initio molecular dynamics simulations demonstrate that these monolayers possess excellent dynamic and mechanical stabilities. According to that, a combination of Janus and non-Janus of NMCs monolayers (MLs) and HtBLs. High optical absorption of around 4.5×10^5 cm^{-1} and high anisotropic carrier mobility of ~10^5 cm^2 V^{-1}s^{-1} is observed, which indicates that they may shine in the next generation of electronic and optoelectronic devices. All of these explorations not only enhance the types of 2D materials but also provide a structural reference for designing new MLs on the molecular level. The band gap values of αand βphases calculated at the HSE06 level are between 1.35 and 3.70 eV.The calculated lattice thermal conductivity of Ag_2S (about 0.85 W m^{-1}K^{-1}) is low while the electrical conductivities and Seebeck coefficients are high at room temperature. Thus, the properties of these combinations show a high potential for thermoelectric applications.

2:20pm **C2-1-ThA-4 High-Entropy Ba(Ti,Zr,Ta,Hf,Mo)(on)$_3$ Gate Dielectric Films for Zno-Channel Thin Film Transistors***, **Van Dung Nguyen**,* Department of Materials Science and Engineering, National Cheng Kung University (NCKU), Taiwan, Viet Nam*; K. Chang,* Department of Materials Science and Engineering, National Cheng Kung University (NCKU), Taiwan

In this study, high entropy Ba(Ti,Zr,Ta,Hf,Mo)(ON)$_3$dielectric films were fabricated on an ITO/glass substrate via a combinatorial sputtering technique. Favorable compositions were efficiently determined from a wide range of the Ba(Ti,Zr,Ta,Hf,Mo)(ON)$_3$ space. The high entropy oxynitride (HEON) was then incorporated in a metal-insulator-metal (MIM) stack and thin film transistor to investigate dielectric and electrical performance. HEON exhibits high dielectric constant and low dielectric loss, which is promising for MIM and TFT applications. HEON-based TFTs show excellent performance with a high on/off current ratio of 10^8, low threshold voltage (V_T) of 0.14 V, a low subthreshold swing of 0.08 V×dec^{-1} and interfacial defect (D_{it}) of 7 × 10^{10} eV×cm^{-2}. Moreover, the devices exhibited stable performance with small V_T shifts and negligible changes in the maximum drain current under gate bias stress (GBS). HEON-based TFTs outperformed various reported thin film transistors, indicating the great promise of Ba(Ti,Zr,Ta,Hf,Mo)(ON)$_3$ as a dielectric layer in thin film transistors.

2:40pm **C2-1-ThA-5 Hydrothermal Fabrication of The Heterojunction of $BaTiO_3$ Nanorod Arrays with Ag_2O and their Applications***, **Yen-Lun Chiu**, K. Chang,* National Cheng Kung University (NCKU), Taiwan

$BaTiO_3$ (BTO) is an attractive material because of its excellent piezoelectric characteristics. The property can be tailored through morphology control, specifically in the form of nanoparticles or one-dimensional nanorod and nanowire arrays. However, studies on this topic directly through hydrothermal processes for the fabrication of three-element compounds are still lacking. In this study, the nanocomposite, which combined well-aligned BTO nanorod arrays and Ag_2O nanoparticles, were synthesized through a single or two-step hydrothermal reaction by the addition of various surfactants e.g., polyethylene glycol-400 (PEG-400). To study the morphology effect on the junction, hydrothermal parameters, including concentrations of precursor solutions, reaction time, temperatures, different surfactants, and substrate positions in an autoclave, were manipulated. X-ray diffraction and scanning electron microscopy were employed to determine the phase and morphology of the resultant composite samples. In addition, an atomic force microscope was employed to determine the topography of the samples, and the amplitude of the piezoresponse (d_{33}) was measured through a piezoresponse force microscope. The morphology effect on the piezoelectricity and the optoelectronics of the samples was systemically studied and optimized for related applications.

3:00pm **C2-1-ThA-6 Toughening Mechanisms of Al Nanoparticles in Flexible Mo Thin Films Revealed by in-Situ Synchrotron Diffraction Experiments***, **Barbara Putz**, T. Edwards,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Kreiml,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; E. Huszar, L. Pethö,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; D. Többens,* Helmholtz Zentrum Berlin, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The combination of a nanoparticle gas phase condensation source with physical vapour deposition opens up plentiful potential for the fabrication of unique nanocomposite thin films, as it allows incorporation of nanoparticles with tailored size, shape, distribution and volume density without precipitation-related restrictions concerning phase diagrams and solubility. In this work, we use combined magnetron sputtering and nanoparticle (NP) deposition to fabricate Mo thin films (200 nm thickness) with and without incorporated Al NPs (diameter 50 nm) on flexible polymer substrates. Microstructure, NP size and concentrations of our nanocomposites were characterized by cross-sectional scanning (SEM) and transmission electron microscopy (TEM). Pure Mo layers are frequently used as part of the metallization of flexible thin film transistors; however they suffer from inherently brittle electro-mechanical behaviour, with through-thickness cracks forming at very low applied strains. To study deformation mechanisms as a function of Al nanoparticle concentration and test the hypothesis that ductile nanoparticles incorporated into the brittle matrix can introduce toughening effects such as crack deflection, arrest or bridging, the electro-mechanical behaviour of the nanocomposites and pure Mo reference films was studied with X-ray diffraction and four point probe resistance measurements during polymer-supported in-situ tensile experiments. Results indicate a clear toughening of Mo thin films with increasing amounts of incorporated Al nanoparticles, as revealed by the shape of the film stress curves recorded parallel and perpendicular to the loading direction. The less severe degradation of electrical conductivity during straining indicates that the nanoparticles limit the extend of mechanical failure of the Mo matrix. Combined with post-mortem focused ion beam (FIB) and SEM analyses of tensile induced cracks, this shed further light on the role of Al nanoparticles during crack initiation and propagation. In summary, the novel manufacturing approach and resulting nanocomposites are promising candidates for multifunctional thin films in next-generation electronic devices.

3:20pm **C2-1-ThA-7 Fabrication of 5g sub-6 Ghz Antennas on Polyimide Substrates Using Laser Thermo-Responsive Polymer Silver Nanocatalysts***, Y. Chen, J. You,* National Defense University, Republic of China*; M. Youh,* Ming Chi University of Technology, Taiwan, Republic of China*; C. Lee, T. Chiang, **Chang-Pin Chang**, M. Ger,* National Defense University, Republic of China

In the study, laser-activated nanosilver catalyst inks were used to fabricate copper-selective metal patterns for sub-5G-6 GHz antennas. The activity of the catalyst ink can be performed by laser activation treatment. Electroless plating was performed on catalytically active polyimide substrates used to form metallic antenna patterns. PEI-GA was synthesized from polyethyleneimine (PEI) and Glutaraldehyde (GA), followed by a heat-curable Ag composite ink composed of Ag salt and tert-butyl peroxybenzoate (TBPB) to enhance the adhesion between the Cu coating and the PI substrate. After laser activation of the lacquer ink and continuous copper chemical deposition on PI, a layer of copper with good adhesion will be formed on the PI substrate. Copper patterns can be easily prepared by combining laser direct patterning of lacquer inks and electroless copper deposition. This is a way to quickly obtain the best metallic wire patterns on polyimide substrates for fabricating sub-6 GHz antennas for 5G. FTIR-ATR analysis and characterization of monomer and polymer functional group changes before and after cross-linking, and verification of substrate metallization by SEM, EDS, and Cross-cut tester were performed. The laser direct writing process is fast and easy to apply and is expected to replace the existing printed circuit process in the future. The produced metallic wires can also be used in 5G antennas. There is great potential for development in the market. A convincing method and potential solution can be given in this study.

3:40pm **C2-1-ThA-8 Metal-Semiconductor Amorphous Boron Carbide Contacts***, **Vojislav Medic**, N. Ianno,* University of Nebraska - Lincoln, USA

The development of amorphous hydrogenated boron carbide (BC) devices is an increasingly important research topic due to its application in radiation safety and deep space exploration. To improve the device performance research has been conducted in optimization of BC, its fabrication and through it, its electronic properties. However, to our knowledge, a study of metal-semiconductor amorphous boron carbide contacts has not been performed. In addition to understanding and quantifying the effect of contact resistance on device performance, it is important to differentiate metals that form Schottky or Ohmic contacts with BC. The spreading resistance model is used to quantify BC resistivity and metal-BC contact resistance. As the thickness of the deposited BC film is much smaller than the radius of the metal contact area, spreading resistance is linearly dependent on film thickness.

$R_s=\rho*b/(\pi a^2)$

b – film thickness, a – contact radius, ρ – resistivity of BC

Since the total resistance can be calculated from Ohmic measurements, the equation below shows the linear dependence of total resistance on BC thickness.

$R=\rho*b/(\pi a^2)+2*Rc$

R_c – contact resistance on each side of BC films

The linear equation for total resistance can be extrapolated to b=0 from the respective I-V curves of various thickness BC films with identical metal contacts, yielding twice the contact resistance. Once R_c is determined ρ can be calculated from any I-V curve.The I-V curves are collected from varying thickness BC films deposited via PECVD from orthocarborane/Ar or metacarborane/Ar gas mixtures, on a plane of metal with the constant size metal dot top contact deposited in a subsequent step. This effectively forms a BC resistor (Figure 1). Specific metals can be categorized as Schottky or Ohmic type contacts by observing the I-V curve measurements. Figure 2 shows the data collected for Cr contacts and Ti contacts on n-type BC. Both of those metals form a Schottky contact, which results in two diodes in series when a completed device is made. However, in Figure 3 Cr contacts on p-type BC structures show an Ohmic contact, and the resistance of this structure can be analyzed using the spreading resistance model previously discussed.As BC deposited from orthocarborane or metacarobrane polymeric precursors is p-type or n-type respectively, we plan to study how different metals from the same groups in the periodic table interact with either p-type or n-type BC, whether they produce Schottky contacts or Ohmic contacts, with the goal of quantifying losses that occur at the metal-BC junction due to contact resistance.

4:00pm **C2-1-ThA-9 Modifying Oxidation State Distribution in Interfacial Layer of Ge Nmosfet with Pre- or Post- Remote Plasma Oxidation Treatment***, **Pei-Hsiu Hsu**,* National Tsing Hua University, Taiwan*; D. Ruan,* Fuzhou University, China*; K. Chang-Liao,* National Tsing Hua University, Taiwan

In this research, the effect of pre- or post- remote plasma oxidation treatment on interfacial layer (IL) of germanium (Ge) n-type metal oxide semiconductor field effect transistor (nMOSFET) has been discussed in detail. The pre-remote plasma oxidation treatment, which is similar with traditional post IL oxidation annealing, might reduce the unstable oxidation state in the IL. However, the remaining plasma damage may still enlarge surface roughness and induce high gate leakage current. On the other hand, the post-remote plasma oxidation treatment can effectively passivate the oxygen vacancy with well-bonded oxygen atom, instead of a post high-k deposition annealing process. Nevertheless, it seems that IL quality might not be further improved by the post high-k oxidation treatment. After analyzing X-ray photoelectron spectroscopy and electrical characteristics, it is found that the Ge nMOSFETS with pre-remote plasma oxidation treatment exhibits low subthreshold swing and high on-off current ratio. It may provide an important reference for high performance Ge device fabrication.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E2-2-ThA
Mechanical Properties and Adhesion II

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Dr. Alice Lassnig**, Austrian Academy of Sciences, Austria, **Dr. Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

1:20pm **E2-2-ThA-1 Scratching the Surface: Understanding Plasticity Associated with Microscale Asperity Contacts***, **Anna Kareer**,* University of Oxford, UK **INVITED**

When considering macroscale sliding, an understanding of the effect of plasticity is essential. Plastic behaviour directly affects the macroscopic wear processes and provides a quantitative mechanism of energy dissipation in friction. Recent nanotribology studies enable the investigation of sliding contacts at the scale of individual asperities, however, the instruments used to carry out these studies involve extremely low contact forces, which leave the surface unmodified by the sliding process. In this work we carry out nanoscratch experiments using a nanoindenter, in a single crystal copper sample. Nanoscratches are made with a constant normal force of 3 mN, which is sufficient to plastically deform the surface with a scratch penetration depth of approximately 250 nm. The residual deformation fields that surround the scratch are mapped using high resolution backscatter diffraction (HR-EBSD) and are compared to that of a statically loaded indent, in an attempt to understand the mechanisms of deformation. A physically based crystal plasticity finite element model (CPFEM) is used to simulate the lattice rotation fields and provides insight into the 3D rotation field surrounding a nanoscratch experiment as it transitions from a statically loaded indent to a kinetic scratch.

2:00pm **E2-2-ThA-3 Effect of Al/Ti ratio and Bias on Mechanical and Tribological Properties of AlTiN Coatings***, **Jiri Nohava**,* Anton Paar TriTec SA, Switzerland*; J. Sondor,* LISS, a.s., Czechia

The effect of Al content and bias during deposition on to the mechanical and tribological properties of the $(Al_xTi_{1-x})N$ coatings were characterized using nanoindentation, tribology and adhesion testing. The coatings were deposited on HSS steel substrate hardened to 64 HRC by cathodic ARC evaporation at 450°C on an industrial Platit Pl 1011 equipment. This PVD machine allows simultaneous deposition from four targets: two Ti targets were used for deposition of TiN adhesion coating and two Al-Ti targets with three different target compositions (Al0.67Ti0.33, Al0.60Ti0.40 and Al0.50Ti0.50) were used for deposition of monolayer top coating. The deposition parameters were the same for all samples except the DC bias which was set to -40V, -80V and -120V for each target combination.

The thickness of the coatings was 4.0 µm for 50/50 and 67/33 groups and 2.2 µm for the 60/40 group and the TiN adhesion layer was 0.6 µm. The wear tests, done with Ø6 mm alumina ball and contact pressure ~2200 MPa revealed similar friction coefficient of ~0.9 for all 60/40 samples whereas for the 50/50 and the 67/33 groups the friction coefficient was decreasing with decreasing bias: ~0.7 at -40V to ~0.5 at -120V. The wear rates decreased with decreasing bias: the lowest wear rates were obtained on the -120 V bias samples in the 50/50 and the 67/33 groups (up to three times increase in wear resistance at -120V compared to -40V in the 50/50 group). The effect of bias was less pronounced in the 60/40 group where only minor decrease of wear rate was observed. The wear performance seems to be related to the hardness of the sample in each group: hardness in the 50/50 and 67/33 groups increased from ~34 GPa and –40V bias to ~38 GPa for the -120V bias samples of the same group. Within the 60/40 group the hardness was approximately 31 GPa for all bias levels. The scratch test showed that samples with –40V bias from both 50/50 and 67/33 groups exhibited slightly lower critical load than the other bias levels from the same group and all 50/50 and 67/33 coatings showed more extensive scratch damage compared to the 60/40 coatings. This was evidenced by more extensive chipping on the edges of the scratches compared to scratches of the 60/40 group. Such scratch morphology is an indication of better cohesion of the 60/40 coatings.

The results show that the bias affects the hardness and adhesion only slightly but it strongly affects the wear rate: the lower the bias, the lower the wear rate. XRD measurements are currently underway to understand the microstructure and mechanisms leading to better wear resistance of coatings deposited with the -120V bias.

2:20pm **E2-2-ThA-4 Effect of Nb and V Doped Elements on the Mechanical and Tribological Properties of CrYN Coatings***, **İhsan Efeoğlu**, G. Gülten, B. Yaylalı, Y. Totik,* Atatürk University, Turkey*; P. Kelly, J. Malecka,* Manchester Metropolitan University, U.K.

One of the most promising approaches to enhancing the tribological properties of engineering materials isto add transition elements to the structure. In this study, Nb and V doped CrYN thin films deposited by closed-field unbalanced magnetron sputtering (CFUBMS) system.The deposition parameters examined were target current (1, 1.5 and 2 A), deposition pressure (0.15, 0.25 and 0.35 Pa), pulsed frequency (100, 200 and 350 kHz) and duty time (0.43-5 µs). Taguchi L9 orthogonal design was used to arrange deposition process for each doped film. Microstructure, thickness, composition, hardness and tribological properties of Nb and V doped CrYN thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), microhardness and pin-on-disc test, respectively.The bonding strength between the substrate and the film (adhesion) were analyzed by the scratch test. In Nb doped films, the maximum hardness value of 38± 0.5 GPa and the lowest friction coefficient of 0.36 were obtained. On the other hand, in V-doped films, the maximum hardness value was 29 ± 0.5 GPa, while the lowest friction coefficient of 0.11 were obtained. In addition, Nb doped films exhibited lower critical load values than V doped films, depending on the hardness and film thickness.

2:40pm **E2-2-ThA-5 Effect of Mo Interlayer on the Mechanical Properties and Tribology Behavior of Molybdenum Nitride Coatings Deposited by High Power Pulsed Magnetron Sputtering***, **Yu-Che Fang**, J. Huang,* National Tsing Hua University, Taiwan

Transition metal nitride have been widely used as protective hard coatings owing to their superior mechanical properties, good corrosion resistance and high wear resistance. Molybdenum nitride (MoN_x) is one of the candidate materials for protective coating in tool industry due to the formation of self-lubrication Magnéli phases. In our previous study, the single phase γ-Mo_2N coatings were found to have good wear resistance, whereas adhesion issue occurred frequently during wear test. The addition of Mo interlayer may be a good remedy to enhance the adhesion of γ-Mo_2N coatings. Therefore, the purposes of this study were to investigate the effect of Mo interlayer on the mechanical properties and tribological behavior of γ-Mo_2N coatings deposited on AISI D2 steel substrate. The coatings were deposited using high power pulsed magnetron sputtering (HPPMS), where the 200-nm Mo interlayer was deposited by dc unbalanced magnetron sputtering (dc-UBMS). After deposition, the chemical compositions of the specimens were measured using an electron probe microanalyzer. The film thickness, cross-sectional microstructure and surface morphology of the specimens were examined by scanning electron microscopy. X-ray diffraction was used to characterize the structure and the texture of the coatings. The hardness and the elastic constant of the coatings were measured by nanoindentation. The residual stress of the coatings was measured by laser curvature method (LCM) and average X-ray strain (AXS) method. The surface roughness was measured by atomic force microscope (AFM). Scratch test and pin-on-desk test were used to determine the adhesion strength and wear resistance. The major concern of the adhesion strength will be evaluated by introducing different interlayer thickness, and the effect of interlayer on the residual stress and wear resistance will be discussed.

3:00pm **E2-2-ThA-6 Tribological Behavior of TiN Thin Film Deposited by Magnetron Sputtering System on Ti6Al4V with different α/β Grain Sizes***, K. Lan, **An-Jia Chen**,* National Tsing Hua University, Taiwan

Although titanium alloys with excellent corrosion resistance and biocompatibility have been widely used in the field of biomedicine, such as Ti-6Al-4V, their hardness and wear resistance limited the durability in application. Various studies tried to improve the wear resistance of titanium alloys by using different techniques of surface treatment. However, delamination of surface coatings from titanium alloys can be observed easily which is correlated to unsatisfactory abrasion resistance. According to literature, most failure of thin film on Ti6Al4V might be related to a low hardness and a low elastic modulus of Ti6Al4V compare to the properties of the hard coating deposited on the substrate. Moreover, the hardness of Ti-6Al-4V seems to varied with its grain size of α and β phase. Thus, the objective of this study is to investigate the tribological behavior of TiN thin films prepared by magnetron sputtering system on the titanium alloys Ti-6Al-4V with varied grain sizes of α and β phase. The α/β grain sizes of Ti-6Al-4V will be investigated. The structure and the texture of each sample are characterized by X-ray diffraction (XRD). The residual stress is assessed by laser curvature method (LCM) and average X-ray strain (AXS) method. The hardness of each sample composes of the TiN and Ti-6Al-4V substrate is measured by nanoindentation and Vickers hardness. Scratch and Pin-on-disk tests will be carried out on TiN thin film samples to investigate adhesion and wear resistance, respectively.

Keywords: nitride, titanium alloy, tribology, adhesion

3:20pm **E2-2-ThA-7 Tailor the Tribological Behavior of TiN Coatings on D2 Steel by Adjusting Process Parameters during Deposition***, **I-Sheng Ting**, J. Huang,* National Tsing Hua University, Taiwan

The objective of this study was to tailor the tribological behavior of hard coatings by adjusting the process parameters during deposition. High residual stress has been considered as one of the crucial factors leading to the failure of hard coatings. From the perspective of energy, the stored elastic energy (G_S) in the coatings should be as low as possible. Once G_S reaches the fracture toughness of a coating (G_C), cracks may start to propagate and lead to the failure of coating. However, the energy-based theory ignores the stress distribution, especially the in-depth stress gradient in the coating, and cannot fully explain the coating failure. In fact, high compressive stress is conducive to impede the crack propagation. The relation between the stress distribution and the failure of coating has not been well understood. Since the generation of residual stress in hard coatings is closely related to the impingement of plasma species, the stress distribution can be tailored by adjusting the process parameters during deposition. In this study, TiN coating on D2 steel was selected as the model system to investigate the effect of stress distribution on the tribological behavior of hard coatings. TiN coatings were deposited on D2 steel using dc unbalanced magnetron sputtering, where the deposition parameters, working pressure and substrate bias were respectively adjusted during deposition to affect the impingement of plasma species. The stress of TiN coating was measured using the average X-ray strain (AXS) combined with nanoindentation methods [1-3], and the stress gradient was carried out using different X-ray incident grazing angles. The adhesion and wear resistance of TiN coating on D2 steel were evaluated using scratch test and pin-on-disk wear test, respectively. The stress distribution and the corresponding tribological behavior of TiN-coated D2 steel were found to depend on the impingement of plasma species. Tailoring the stress state of hard coatings shows great potential on the control of tribological behavior.

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3:40pm **E2-2-ThA-8 Micromechanics of Hydrogen Barrier Coatings During *in Situ* Hydrogen Charging***, **Maria Jazmin Duarte Correa**, H. Gopalan, J. Rao, P. Patil, C. Scheu, G. Dehm,* Max-Planck Institut für Eisenforschung, Germany

Hydrogen is a strong candidate to be the energy carrier of the future; however, its use also represents a challenge as it might cause material degradation through hydrogen embrittlement. Hydrogen barrier coatings represent, in this regard, an appealing option to prevent and/or slow down the hydrogen ingress into structural alloys that are susceptible to embrittlement. In this work we present our research on a 1-2 µm thick layer of Al_2O_3 and its effect as a hydrogen barrier coating on a Fe-Cr alloy. The mechanical stability of the coating was tested by nanoindentation and nanoscratching tests during hydrogen loading. For this purpose, we used our novel electrochemical cell design, the “back-side” charging approach, developed in-house to perform micromechanical testing during hydrogen charging [M. J. Duarte, et al., J Mat Sci 56 (2021) 8732-8744]. Hydrogen diffusion from the charged back-side towards the testing surface is quantified by permeation tests. Moreover, this unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements with different hydrogen levels monitored over time to consider hydrogen absorption, diffusion and release.

The mechanical behavior of the coating remained unaltered during the performed tests due to the slow hydrogen diffusion Al_2O_3, which is about 9 orders of magnitude slower with respect to the Fe-Cr substrate, measured by the Kelvin probe technique. However, the accumulation of hydrogen at the substrate-coating interface reduces the critical load required for the coating to crack, and might lead to local delamination during scratching. These mechanical analyses were complemented using atom probe tomography, confirming the presence of hydrogen close to the substrate/coating interface, and by transmission electron microscopy, used to reveal the microstructural changes related to hydrogen during scratching.

4:00pm **E2-2-ThA-9 Nano-Scale Mechanical Characteristics of Epitaxial Stabilization Zrtin/Nbn Superlattice Coatings*, Pin-Yuan Lai,* *T. Ku, S. Hsu, P. Chen, J. Duh,*** National Tsing Hua University, Taiwan

Protective hard coatings are widely used in industrial applications, especially under extreme conditions. In this regard, superlattices with epitaxial stabilization have shown to be a potential approach. owing to the similar lattice parameter and crystal structure, the ZrTiN/NbN system was chosen. This superlattice system showed no cracks after indentation, possessing stronger crack resistance than both ZrTiN and NbN monolayers. The wear volume of multilayers was significantly lower than monolithic films. However, phase transformation of c-NbN to h-NbN occured in relative thick sub-layer NbN. This phenomenon would deteriorate the wear resistance and elastic recovery of the coatings. HRTEM images confirmed that h-NbN led to the loss of epitaxial growth, and thus the coatings demonstrated polycrystalline structure. It was demonstrated that epitaxial ZrTiN/c-NbN superlattices can be controlled by adjusting the thickness ratio. The epitaxial structure exhibited not only favorable mechanical performance but also excellent tribological behavior.

4:20pm **E2-2-ThA-10 Mechanical and Tribological Behavior of Nitrided AISI/SAE 4340 Steel Coated With NiP and AlCrN, *Ricardo Torres,*** Pontificia Universidade Católica do Paraná, Brazil*; M. Soares,* Universidade Tecnologica do Parana, Brazil*; P. Soares,* Pontifícia Universidade Católica do Paraná, Brazil

Deterioration by wear and corrosion is a serious problem in the oil and gas industry. The presence of H2S, CO2 and chlorides with abrasive materials such as sand causes severe wear and corrosion. One strategy to mitigate steel surface deterioration is coating the steel surface with electroless NiP. The NiP coating on steel substrates requires an interdiffusion post-heat-treatment to create a metallurgical bonding between the steel substrate and the NiP deposit. However, this heat treatment causes a softening of the steel and the NiP deposit. This work investigated the following surface engineering strategies: i) NiP deposition in steel substrates that were previously nitrided followed by the NiP interdiffusion heat-treatment at 400oC or 610oC; ii) AlCrN PVD coating deposition on NiP layers on steel substrate that was previously nitrided followed by the NiP interdiffusion heat-treatment at 400oC or 610oC. Then, hardness and tribological behavior were determined. The tribological tests were performed in a ball-on-disk mode of tribometer applying a load of 20 N, a tangential speed of 25 cm/s. The counterpart used in the tribological tests was 6 mm diameter cemented carbide spheres; the total sliding distance was 1000 m. The friction coefficient was monitored throughout the tribological tests. The lowest wear rate was for the specimen with AlCrN PVD coating deposition on NiP layers on a previously nitrided steel substrate, followed by the NiP interdiffusion heat treatment at 610oC.

4:40pm **E2-2-ThA-11 Designing Hydrogen-Free Diamond Like Multilayer Carbon Coatings for Superior Mechanical and Tribological Performance*, Muhammad Usman,*** City University of Hong Kong

Diamond like carbon (DLC) coatings are in focus from a last few decades due to its exceptional mechanical and tribological properties. This class of coating borrows mechanical and tribological properties from diamond (sp^3) and graphite (sp^2) respectively. Therefore, high hardness, low coefficient of friction and wear rate are some of the intrinsic characteristics. Due to this unique combination, it finds wide applications in microelectromechanical systems (MEMS), automotive sector (tappet, camshaft, finger roller follower, camshaft sprocket, piston, piston rings), bearings, hip and knee joints, tools and dies, laser barcodes scanners, magnetic storage media. Researchers shifted from monolayer to multilayer architecture in DLC to achieve high hardness and resistance to plastic deformation (high toughness) simultaneously as these are inversely correlated [1-3]. Multilayers provide the optimum solution to this problem. Additionally, multilayers reduce compressive residual stress in the coating compared to hard monolayer [2]. The current research aims to evaluate the impact of bilayer numbers (bilayer thickness) on earlier mentioned properties. Therefore, new multilayer DLC coatings are designed with alternate hard and soft layers using closed field unbalanced magnetron sputtering (CFUBMS). Discrete sharp interfaces are produced by selecting two different bias voltages. Hard to soft layer ratio is kept constant (1:1) for all specimens with fixed total coating thickness of 1µm. 10, 20, 40 and 80 bilayers (shown in supplemental file) are deposited onto steel substrate having Cr/CrC_x interlayer. Raman spectroscopy, nanoindentation, nanoscratch and residual stresses are measured for all the specimens. Raman analysis depicts increasing I_D/I_G ratio and decreasing full width at half maximum (FWHM) trend by increase in bilayer numbers (decreasing bilayer thickness). Moreover, hardness and scratch resistance are directly proportion to number of bilayers. Residual stresses also increase with greater number of bilayers. This implies that graphitization is in direct relation to bilayer numbers and hardness increases potentially due to interlocking of graphitic clusters. 80 bilayers coating exhibited outstanding elastic and plastic deformation resistance. Hence, this design may offer the combination of high hardness and toughness in addition to wear resistance without introducing any other element or complex multilayer architecture, which require further investigations.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F2-ThA

High Entropy and Other Multi-principal-element Materials

Moderators: Dr. Erik Lewin, Uppsala University, Sweden, **Prof. Dr. Jean-François Pierson**, IJL - Université de Lorraine, France

1:20pm **F2-ThA-1 Data Driven Methods Enable Rational Design of High Entropy Materials for Hydrogen Storage*, Matthew Witman,*** *V. Stavila, M. Allendorf,* Sandia National Laboratories, USA **INVITED**

Data-driven modeling in recent years has ushered in a new paradigm for rapid discovery of useful materials across a plethora of domains in the physical and materials sciences. These methods become particularly invaluable when investigating applications of high-entropy materials, where the combinatorial growth of explorable chemical space makes brute-force experimentation or first-principles simulation intractable. To assess the primary figure(s) of merit for 10,000s of possible materials for a given application and down-select only top candidates for more rigorous examination, accurate and efficient machine learning and data-driven techniques are required. This talk will survey a variety of data-driven (high entropy) hydride discovery exemplars representing efforts between Sandia and a large international collaboration group. These range from traditional machine learning approaches for direct hydride thermodynamic property prediction to modern graph neural networks, trained as DFT surrogate models, that feed sampling-intensive first principles simulations. These modeling strategies can rapidly screen hydride thermodynamic properties and therefore experimentally target new materials or rationally tune existing ones for various hydrogen storage or compression use cases. Coupled with additional simple objectives (i.e., raw material costs), multi-dimensional Pareto optimal materials can therefore be identified, targeted, and synthesized.

2:00pm **F2-ThA-3 Effect of Mo Content on the Corrosion and Tribocorrosion Behavior of $(CoCrFeNi)_{100-x}Mo_x$ HEA Thin Films Deposited by HiPIMS*, Alessandro Togni,*** *R. Tinazzi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy*; S. Deambrosis, E. Miorin, F. Montagner, C. Mortalò, V. Zin,* Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council, Italy*; G. Bolelli, L. Lusvarghi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy

Based on a multi-principal-element-design concept, high-entropy alloys (HEAs) feature enhanced mechanical strength, excellent thermal stability, and superior wear and corrosion resistance, making them promising candidates for applications in harsh environments. Moreover, the microstructure and properties of HEAs can be fine-tuned by changing their composition or by alloying them with additional elements, boosting their application potential even further. Therefore, HEA-based protective films with suitably designed compositions could improve the wear and corrosion resistance of low-cost substrate materials under various service conditions. In this work, $(CoCrFeNi)_{100-x}Mo_x$ HEA thin films were deposited on Si and AISI 304 stainless steel substrates by high-power impulse magnetron sputtering (HiPIMS) using pure Mo and equiatomic CoCrFeNi targets. The effect of Mo content on the microstructure, mechanical properties, and corrosion and tribocorrosion behavior of the films was investigated by adjusting the Mo target-to-substrate distance. Higher amounts of Mo favored the formation of a dense microstructure, resulting in higher hardness values. The potentiodynamic polarization curves revealed that the corrosion resistance of the films in 3.5 wt.% NaCl solution is not significantly affected by Mo concentration. Differences were found, however, in terms of tribocorrosion behavior. With increasing Mo content up to 12 at.%, the wear rate of the films gradually decreased. Above this value, further Mo addition resulted in increased material loss. The obtained results aim to contribute to a comprehensive understanding of the corrosion and tribocorrosion behavior of HEA thin films in artificial seawater to broaden their application in marine engineering.

2:20pm **F2-ThA-4 Corrosion Behavior of Sputter-Deposited CoCrNiFeAl High Entropy Alloy**, *A. Korra,* University of Tennessee at Chattanooga, USA*; H. Raji,* Florida Institute of Technology, USA*; **Hamdy Ibrahim**,* University of Tennessee at Chattanooga, USA*; S. Saedi,* Florida Institute of Technology, USA

Multicomponent or High-entropy alloys (HEA) are the new generation of alloys with exceptional properties such as high strength and hardness, excellent thermal stability at high temperatures, and remarkably good fatigue. Recently HEA thin films have attracted significant attention due to their superior corrosion resistance and emerged as potential candidates to meet demanding requirements for selected extreme applications, particularly in the nuclear, turbine, and aerospace industries. Prominent advantages of HEAs are primarily derived from their ability to stabilize as a single-phase crystalline structure when specific alloy design criteria are met. HEA thin films have been fabricated using a wide range of technologies including laser cladding, arc cladding, electrodeposition [https://www.sciencedirect.com/topics/materials-science/electrodeposition], and spraying. However, magnetron sputtering is one of the most desirable fabrication methods due to lower growth temperatures, precise control, good film-forming ability, high efficiency, and good film adhesion. In this work, CoCrNiFeAl (at.%) was deposited by Radio Frequency (RF) magnetron sputtering to evaluate its corrosion behavior. While homogenization is a common post-processing treatment in metallurgy, the process for HEA can be entirely different from regular alloys due to the slow/sluggish diffusion and phase transformation rate in HEAs. To understand the effects of homogenization on the sputter target deposited HEAs, heat treatments in the range of 800-1100 °C were performed and the microstructure, phase stability, hardness, and corrosion behavior were investigated. While the results obtained from both Calphad modeling and experiments showed that homogenization is a strong mechanism for improving the corrosion resistance in HEA composition, it was also concluded that hominization temperature can play an important role in the formation of phases that can significantly deteriorate the corrosion resistance. The conclusion was drawn from the fact that lower homogenization temperatures led to the formation of an undesirable sigma phase in the microstructure that was decomposed to a secondary BCC single phase in the alloys treated at higher temperature ranges.

2:40pm **F2-ThA-5 Mechanical Properties of Low Density Ternary Titanium-rich Medium-entropy Alloy with Heterogeneous Structure**, ***Che-Wei Chang,*** Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan*; P. Chen, S. Jang,* Institute of Material Science and Engineering, National Central University, Taiwan*; C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan

At present, global warming is becoming more and more serious. We plan to reduce the weight of the material to reduce energy loss during transportation. Therefore, we expect the medium entropy alloy to have good mechanical properties, and it can also have low density characteristics, so we choose alloys to carry out. In follow-up studies, the mechanical properties of alloys have always been an important issue for researchers. It is well known that the strength and ductility of alloys compete with each other. It has been pointed out that the heterostructure allows alloys to exhibit good strength and ductility simultaneously. Therefore, we attach our alloys to rolling and annealing and expect to obtain a heterostructure. X-ray diffractometer (XRD) and electron backscatter diffractometer (EBSD) was used to observe the changes in crystal structure and microstructure of the alloy under different annealing time. Finally, we perform tensile tests to obtain the mechanical properties of the alloys and compare the microstructural evolution between them.

3:00pm **F2-ThA-6 Charge Transfer Effects in Multicomponent Materials – Shown by Ab-Initio Calculations and X-Ray Photoelectron Spectroscopy XPS**, ***Barbara Osinger,*** Uppsala University, Angstrom Laboratory, Sweden*; L. Casillas-Trujillo,* Linköping University, Sweden*; R. Lindblad,* Uppsala University, Angstrom Laboratory, Sweden*; B. Alling,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden*; I. Abrikosov,* Linköping University, Sweden*; E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Multicomponent materials have opened a vast landscape for complex compositions and interesting properties. They exhibit complex bonding, due to their diverse chemical environment, as a result of the extensive alloying, typically involving 5 or more elements. Ab-initio calculations, using density functional theory (DFT) and X-ray photoelectron spectroscopy (XPS), were used to investigate the electronic structure of multicomponent thin films based on the HfNbTiVZr system. The charge transfer was evaluated theoretically using relaxed, non-relaxed, as well as elemental reference structures using a fixed sphere size model to quantify the charge transfer. High-resolution XPS spectra were obtained from HfNbTiVZr and (HfNbTiVZr)C magnetron sputtered thin films.

The HfNbTiVZr alloy shows core level binding energy shifts and peak broadening, compared with metal references, which are in good agreement with shifts calculated from DFT simulations, where charge transfer between the metal atoms is observed. The charge transfer follows the general electronegativity trend, and results in a reduced atomic size mismatch and lattice distortion δ, compared with estimates based on tabulated atomic radii. Similarly, the (HfNbTiVZr)C carbide films exhibit core level binding energy shifts and broadening effects, as a result of their complex chemical environment.

This study demonstrates the importance of chemical bonding and environment when discussing multicomponent materials. Moving beyond the concept of an ideal solid solution and considering the bonding in more detail opens up a deeper understanding and the possibility of tuning the electronic structure. This would be especially interesting for the design of multicomponent materials, as many desirable properties are a result of their bond character.

3:20pm **F2-ThA-7 Toughness Estimation of High Entropy Nitride Coatings by Tensile Testing**, ***Martin Kuczyk,*** *T. Krülle,* Technische Universität Dresden, Germany*; M. Zawischa, M. Leonhardt, O. Zimmer, J. Kaspar,* Fraunhofer IWS, Germany*; C. Leyens, M. Zimmermann,* Technische Universität Dresden, Germany

High Entropy Nitrides (HEN) are an interesting material system intended for sophisticated wear and high-temperature applications. Being closely linked to the group of so-called high entropy alloys, which were discovered independently by Cantor and Yeh in the early 2000s [1,2], they consist of five or more nitride-forming constituents in a near equimolar ratio as well as 50 at% nitrogen forming single-phased fcc microstructures. Multiple works have shown that through the use of HEN superior hardness close to or in some cases well into the superhard range (H > 40 GPa) can be achieved while also maintaining high thermal stability [3,4].

For the possible use as protective tool coatings, not only hardness and thermal stability are important factors but also toughness. A method that might be suitable for high throughput screening of coating toughness is tensile testing of coated substrates. The description of critical strains at which first cracks in the coating appear as well as the development of the crack density with increasing applied strain can be used to reasonably estimate coating toughness values.

In this work, three HEN coatings are compared to (AlTi)N via tensile testing. The three coatings are (AlCrTaTiZr)N, (AlCrNbSiTIV)N and (HfNbTaTiVZr)N and were chosen based on previous works of the author [4]. The applicability of that method for the screening of coating toughness is discussed by comparing the results with other more established methods for the estimation of fracture toughness such as micro-beam bending.

It could be shown that tensile testing is a feasible method for high throughput screening of coating toughness.

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3:40pm **F2-ThA-8 Synthesis and Characterisation of (Gd,Hf,Sc,Ti,Zr)-Oxide Coatings***, **Alexander Kirnbauer**, E. Peck, M. Derflinger,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Especially oxides are of great interest as they can serve as oxidation protection coatings at high temperatures. A very common oxidation-protection coating is α-Al_2O_3, usually synthesised by chemical vapour deposition as very high temperatures are required to form the stable α form. Another interesting oxide for use at high temperatures is HfO_2 as it exhibits the highest melting point within the group of oxides besides Thorium oxide. As HfO_2 crystallises, similar to ZrO_2, in three different crystal structures, the desired cubic high-temperature modification is hard to stabilise. Within this work we report on the phase formation and mechanical properties of (Gd,Hf,Sc,Ti,Zr) oxide coatings. High-entropy metal sublattice oxides were synthesised using reactive magnetron sputtering utilising a single equiatomic target consisting of Gd, Hf, Sc, Ti, and Zr. For synthesis of oxide coatings different O_2/(Ar+O_2) flow ratios were used to investigate the influence of reactive gas flow on the structure and mechanical properties. X-ray diffraction analysis show that the coatings crystallise in a single-phase fcc structure. Nanoindentation measurements revealed hardness values of ~20 GPa and an indentation modulus of ~ 250 GPa. Furthermore, transmission electron microscopy investigations were done to get more detailed information about the growth morphology and crystal structure of the oxide coatings. To investigate the structural stability at elevated temperatures, vacuum annealing treatments and subsequent XRD and nanoindentation measurements were done.

4:00pm **F2-ThA-9 Functional Materials for Energy Applications***, **Susan Sinnott**,* Pennsylvania State University, USA **INVITED**

The development of new functional materials for use as battery electrodes, for catalysis, and for electronic devices is an ongoing area of research. Structure-property relationships are determined using a combination of experimental characterization and high-fidelity computational methods. Here, first-principles density functional theory (DFT) calculations are used to investigate functional two-dimensional inorganic materials and high-entropy oxides (HEOs). Two-dimensional materials have properties that strongly depend on composition, defects, and surface structure. This presentation will focus on two-dimensional metal dichalcogenides and metal dichalcogenide/metal carbide heterostructures that have unique properties related to electron confinement within these layered materials. The computational predictions are compared to experimental data to advance design of two-dimensional materials for electronic devices. Similarly, the controlled synthesis of functional HEOs are being investigated, including J14 [(Mg, Co, Cu, Ni, Zn)0.2O] and F1 [Ce, La, Pr, Sm, Y)0.2O2-δ] where δ indicates oxygen vacancies. In this case, DFT calculations are being employed to help explain recent findings of structural dependencies on growth conditions for J14 and to reveal structure-transport composition trends in F1, a leading high-ion conductor. The synergies between experimental synthesis, characterization, and modeling is a focus of the presentation.

Coatings for Use at High Temperatures
Room Golden State Ballroom - Session AP-ThP

Coatings for Use at High Temperatures (Symposium A) Poster Session

AP-ThP-1 Thermal Stability of Thick α- and γ-Al_2O_3 Coatings Deposited by High Speed PVD*, K. Bobzin, **Christian Kalscheuer**, M. Moebius, P. Hassanzadegan Aghdam,* RWTH Aachen University, Germany

Metal oxide coatings such as α- and γ-Al_2O_3 are state of the art for different high-temperature applications T > 800 °C. However, synthesis of stable α-alumina coatings is limited to chemical vapor deposition (CVD), due to its high formation temperature T >1000 °C. Physical vapor deposition (PVD) can realize deposition of aluminium oxide coatings at lower process temperatures T ≤ 600 °C. Nevertheless, metastable or amorphous Al_2O_3 phases can be formed in this case. This leads to a lower thermal stability and limits the application of these coatings at higher temperature. However, previous studies showed that High Speed PVD can realize the synthesis of cristalline α- and γ-Al_2O_3 coatings with high coating thickness of s > 10 µm at T ≈ 780 °C. In this study the thermal stability of α- and γ-Al_2O_3 coatings deposited by means of HS-PVD was investigated. High temperature (HT)X-ray diffraction (XRD) measurements were performed in order to study the phase transformations of the coatings as a function of temperature between T = 700 °C to T = 1,200 °C in vacuum and in atmosphere. Moreover, morphology, indentation hardness H_{IT} and indentation modulus E_{IT} of the coatings were investigated after HT-XRD. HT nanoindentation (HT-NI) measurements were performed to in-situ analyze the indentation hardness H_{IT} and indentation modulus E_{IT} at T ≈ 650 °C and the highest device measurement temperature of $T_{max,NI}$≈ 750 °C. The HT-XRD results show that up to a temperature of T = 1,200 °C neither in vacuum nor in atmosphere any phase transformations of coatings are recognizable. This confirms phase stability of the coatings up to this temperature. Moreover, the morphology of the coatings did not show any changes after HT-XRD, indicating a high structural stability. In addition, the morphology did not show any cracks detectable by scanning electron microscopy after HT-XRD. In situ HT-NI measurements showed a reduction of indentation hardness and indentation modulus compared to measurements at room temperature. However, the indentation hardness and indentation modulus after HT-XRD do not vary from the as-deposited state. The results of the conducted research reveal a high thermal stabillity of crystalline α- and γ-Al_2O_3coatings deposited by HS-PVD up to T = 1.200 °C. This can extend the application of these coatings to higher tempertaures.

AP-ThP-3 e-Poster Presentation: High-Temperature Stability and Mechanical Properties of Non-Reactive PVD-Synthesized $MoSi_2$ Coatings*, **Sophie Richter**, A. Bahr, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

Molybdenum disilicide belongs to the group of refractory transition metal silicides, which are highly attractive as oxidation-resistant materials to be applied in high-temperature regimes (i.e., above 1000 °C). The unique strength of $MoSi_2$ is based on its high melting temperature and the formation of a highly protective silicon-based oxide scale. In relation to the metallic and covalent bonding nature, $MoSi_2$ obtains unique mechanical properties, suggesting this disilicide as a promising candidate for future protective coatings.

Within this study, direct current magnetron sputtering (DCMS) as well as high-power pulsed magnetron sputtering (HPPMS) techniques have been deployed to grow $MoSi_2$ thin films. These coatings were non-reactively deposited in an in-house developed (laboratory-scaled) sputter system using 3’’ compound targets. The influence of the deposition parameters (e.g., substrate bias potential and deposition temperature) on the phase formation, morphology, chemical composition, and mechanical properties (e.g., hardness and indentation modulus) has been investigated systematically by high-resolution characterization methods such as X-ray diffractometry (XRD), scanning and transmission electron microscopy (SEM and TEM), energy-dispersive X-ray spectroscopy (EDS), as well as nanoindentation. Additionally, micro-cantilever bending tests have been performed to determine the fracture toughness of the as deposited thin films. Furthermore, we employed differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to investigate the oxidation kinetics. The formed oxide scales have been analysed for different temperature regimes up to 1500 °C (1 hour in synthetic air). The samples were subjected to long-term oxidation treatments in ambient air at 1200 °C for up to 100 hours. Based on these results, sputter deposited $MoSi_2$ thin films constitute a promising protective coating material applied for challenging environmental conditions.

Keywords: Disilicides; PVD; Protective coatings; Oxidation resistance; Phase stability;

AP-ThP-4 Thermal Stability of Atmospheric Pressure Plasma Jet Deposited YSZ Top Coats and Sputtered Al Bond Coats on Inconel 617*, **Yung-I Chen**, L. Wang, X. Qiu,* National Taiwan Ocean University, Taiwan

In this study, microstructure and oxidation behavior of YSZ-alumina thermal barrier coatings after high-temperature annealing were explored. Ni-based superalloy (Inconel 617) was used as the substrate material. Al bond-coat was deposited by direct current magnetron sputtering. YSZ top-coat were deposited through several iterations of atmospheric pressure plasma jet deposition and rapid thermal annealing at 600°C. Multilayered YSZ/Al coatings were fabricated with various stacking periods. The Al sublayer transformed into a dense Al_2O_3 layer after annealing. The multilayered YSZ/Al_2O_3 coatings were further annealed at 1100 °C in ambient air. The YSZ coatings maintained at a tetragonal phase after annealing at 1100 °C for hundreds of hours.

AP-ThP-5 $Ti_{1-x}Al_xN$ PVD Coatings in Hot-Corrosion Environments*, O. Hudak, **Rainer Hahn**, A. Scheiber,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; L. Shang, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Hot corrosion is an accelerated oxidation process commonly observed in high-temperature settings (650-950 °C), such as gas turbines, coal gasification plants, and waste incinerators. It is a phenomenon where sulfur-rich atmospheres (exhaust gases) react with salt impurities to form high-melting sulfate salts that adhere to machining components. There, the salt deposits elicit an accelerated degradation of the operating parts by forming porous, non-protective oxide scales, drastically reducing the longevity of in-service parts. Ni-, Co-, and Fe-based superalloys, representing the backbone in the previously mentioned applications, are especially prone to hot-corrosion attacks.

This contribution presents $Ti_{1-x}Al_xN$ as a potential candidate as a protective PVD coating for hot-corrosion environments. $Ti_{1-x}Al_xN$ coatings with varying metal content ratios were arc-evaporated on a Ni-based superalloy and tested in an in-house built hot-corrosion testing rig. By applying a sulfate-salt mixture from the alkali and alkaline earth metal groups, we tested coated and uncoated samples in a SO_x-rich atmosphere at 700 and 850°C for a maximum duration of 30 h and subsequently analyzed using a set of high-resolution characterization techniques.

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 $(W,Ta)B_2$ Coatings Prepared by High Power Impulse Magnetron Sputtering HiPIMS*, **Rafał 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 $(W,Ta)B_2$ coatings prepared by HiPIMS. We evaluated the influence of pulse duration, substrate temperature and substrate bias on properties of $(W,Ta)B_2$ 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 corespondent 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. Seville, 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 Universite Paris-Saclay, France*; J. López-Viejobueno, J. Caballero-Hernández, D. Hufschmidt, M. Jiménez de Haro,* Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Seville, 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 ^4He and ^3He 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 ofhigh 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. Lümkemann,* 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 subtrates. Ceramicoin is a TiB2-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 (ϕ2 inch, t: 3 mm) scratched with diamond powder and ultrasonically cleaned with acetone was used as the substrate. CH_4-H_2 mixture gas was used as the reaction gas, CH_4 flow rate: 2, 20 sccm, H_2 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_4 gas was introduced from the upper direction and a convex profile when CH_4 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^{-1} attributed to diamond and a peak at 520 cm^{-1} 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 fabricatedat a fixed Ar/N_2 inlet ratio of 12/8 sccm/sccm and 350°C with tunning 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, γ-Mo_2N, and β-Mo_2N multiple phases. After 750°C vacuum annealing, increase in hardness from 20.1 to 28.4GPa was obtained. Similarly, the H^3/E^2 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 μm³/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_x 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 (orderN) scaling behavior.

Amorphous silicon nitride (a-SiNx) 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-SiNx 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.

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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 VB 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 Poucques,* 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_2 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_2 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^+. 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. Abraha,* 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^3/sp^2 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_2 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_2 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_2 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_2 and Pt-decorated porous Ni/MoS_2 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_2 largely increased the surface area and active reaction site for the HER performance. In addition, the decoration of Pt-nanoclusters on porous Ni/MoS_2 can demonstrate the synergistic effect of the Pt-decorated porous Ni/MoS_2. So, the overpotential (η10) and the Tafel slope of the Pt-decorated porous Ni/MoS_2 are determined in 43 mV and 56 mV/dec, respectively. The promising approach to synthesizing Pt-decorated porous Ni/MoS_2 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_3) 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_3+H_2 plasma treatment exhibits lower subthreshold swing and higher on-off current ratio.

BP-ThP-18 On the High Temperature Oxidation Behavior of AlCrBN/TiAlNbSiNMultilayer 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 ^{o}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_2O_3 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 thang 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_2/SiO_2 Nanolaminates on AlGaN/GaN*, B. Wang, Y. Li, M. Chen, **Duo Cao**, F. Liu, W. Shi,* Shanghai Normal University, China

In the current work, HfO_2/SiO_2 nanolaminates and HfO_2 films were grown on AlGaN/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_2/SiO_2 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_2/SiO_2 nanolaminates, forming an $HfSiO_4$ composite structure simultaneously. The 800 °C annealed HfO_2/SiO_2 shows a low k value and large leakage current density. While the 600 °C annealed HfO_2/SiO_2 possesses an effective dielectric constant of 18.3, a turn-on potential of 9.0 V, as well as a leakage density of 10^{-2} μA/cm^2 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 heterogenous 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.

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.

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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.

Functional Thin Films and Surfaces
Room Golden State Ballroom - Session CP-ThP

Functional Thin Films and Surfaces (Symposium C) Poster Session

CP-ThP-1 Structural and Compositional Analysis of Titanium-Based PVD Coatings*, **Celia Rojo-Blanco**,* Sheffield University, UK, Mexico*; J. Qi,* Sheffield University, UK, China*; G. Wu, L. Yang,* University of Leeds, UK, China*; S. Creasey-Gray, A. Leyland,* Sheffield University, UK

Novel Ti-Al-B and Ti-Al-B-N coatings have been deposited by plasma-assisted sputter PVD, with a view to constructing erosion-resistant metallic/ceramic multi-layered coatings for demanding environments of high humidity or temperature. Sample coatings of 1.2 to 1.6µm thickness were produced on both AISI 316 and Si-wafer substrates, and were studied using optical profilometry, XRD, SEM, TEM and EPMA to analyse their (nano)structure and chemical/phase composition.

TEM samples were prepared in both plan-view and cross-section. It was found that the coatings were constituted primarily of an amorphous solid solution with embedded nanocrystals – of either intermetallic (in the Ti-Al-B films), or boride/nitride (in the Ti-Al-B-N films) compounds. Clear TEM Electron Diffraction Patterns were not formed, even though we could observe some XRD reflections, indicating some degree of crystallisation within the coatings deposited.

it was also observed that the coatings contained a significant amount of oxygen 'contamination', distributed primarily at nanograin boundaries.

CP-ThP-3 Study of Spatial Distribution of Sputtered Al-Doped Zinc Oxide for Optoelectronic Applications*, **Eduard Llorens**, E. Stamate,* DTU, Denmark

Transparent conducting oxides (TCOs) are needed for a wide range of applications in thin film devices such as thin film transistors, solar cells, and smart windows.

Tin doped indium oxide (ITO) is the most commonly used TCO material since it possesses high electrical conductivity and optical transmittance. Nevertheless, indium is scarce and expensive, hence, it would be desirable to find a cheaper and more abundant TCO material that could replace ITO. Aluminum doped zinc oxide (AZO) stands as one of the most suitable candidates due to its earth abundance, high stability, and non-toxicity. Despite its advantages, AZO suffers from low spatial uniformity when it is grown as a thin film using sputter deposition. This issue has been attributed to the bombardment of the film by high-energy negative oxygen ions generated at the sputter target and accelerated in the plasma region between the target and the substrate [1].

In this study, the spatial uniformity of the key properties of sputtered AZO films was studied as a function of the discharge type (DC, pulsed-DC, and RF), and sputtering parameters. A ceramic target containing 2 wt % of Al was used for all experiments. Usually, these kind of depositions are performed using rotation of the substrate to seek uniformity, in this study however, the rotation of the substrate was stopped for a better mechanism growth understanding, obtaining a thickness gradient.

Both pulsed-DC and RF discharges produced films possessing high electrical conductivity ($4x10^{-4}$ Ω.cm) and an average optical transmittance above 85% when the substrate temperature was above 100°C. All films deposited at room temperature presented lower electrical conductivity and lower transmittance. A DC discharge led to inferior film properties for TCO applications.

Films deposited at room temperature and using Pulsed-DC, and DC discharges showed an edge effect with an increase of the sheet resistance in the wafer region that is closer to the target, therefore, low distance from target to substrate (DTS). This undesirable characteristic was improved once the temperature of the substrate increased. Films deposited using RF discharge showed the best performance regarding optical and electrical properties.

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CP-ThP-4 Optical and Electrical Characterization of Thin NiO_x Films Obtained by R.F. Sputtering*, **Francisco David Mateos-Anzaldo**, R. Nedev, E. Osorio-Urquizo, M. Curiel-Alvarez, O. Perez-Landeros, J. Castillo-Saenz,* Universidad Autónoma de Baja California, Instituto de Ingeniería, Mexico*; A. Arias-Leon,* Universidad Autónoma de Baja California, Facultad de Ingeniería Mexicali, Mexico*; B. Valdez-Salas,* Universidad Autónoma de Baja California, Instituto de Ingeniería, Mexico*; N. Nedev,* Universidad Autonoma de Baja California, Instituto de Ingeniería, Mexico

Thin NiO_x films were deposited on crystalline Si (c-Si) and corning glass by r.f. magnetron sputtering at temperatures in the range of 25–250 °C and powers in the range of 40–80 W. After the deposition, the films were thermally annealed at 450 °C to form nanocrystals. Ellipsometry measurements were used to determine the film thicknesses and the optical constants. The size of nanocrystals in annealed layers was evaluated by XRD measurements, while the surface roughness of the as-deposited and annealed films was measured by AFM. Metal/NiO_x/n–Si heterostuctures were prepared by deposition of thin NiO_x layers on n-type Si and evaporation of Au electrodes through a mask. The Au/NiO_x/c-Si structures were electrically characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements. The I-V dependences showed formation p-n heterojunction diodes with properties, which depend on the r.f. power, deposition temperature and annealing. The obtained results indicate that NiO_x films deposited at optimal conditions are promising for application in optical sensors.

CP-ThP-5 Deposition of Lanthanum-Doped Barium Stannate as Transparent conducting Oxides*, C. Liu, Y. Yan, S. Chen, **Yijia Chen**, M. Wong,* National Dong Hwa University, Taiwan

The barium stannate ($BaSnO_3$, BSO) crystal has a perovskite structure, so as the lanthanum-doped barium stannate (LBSO). The LBSO thin film has high light transmittance and high electron mobility, and is considered potential candidate to replace the indium tin oxide (ITO) as conductive glass used for optoelectronics, because the indium in ITO is increasingly depleted in mineral resources and becomes ever expensive. We use the lanthanum metal target and the barium stannate target in the magnetron sputtering deposition system. The barium stannate is sputtered with 80W with radio frequency and lanthanum is sputtered with 10W DC. In the coated lanthanum-doped barium stannate film, a metal thin layer of pure lanthanum is intermittently deposited in between BSO layers to further improve the conductivity of the film. The transmittance of the coating shows periodical oscillation with the wavelength, which is typical of the consequence of interference phenomenon, signifying the flatness of the deposited film. After annealing at 600°C, crystallization occurs, as the x-ray diffraction analysis suggested. The concentration of La doping in the coating is about 10% of that of barium. According to Hall's measurement results, the multi-layerd LBSO coating with inserted La metal layer has a carrier concentration of $1.3x10^{22}/cm^3$ and a mobility of 177 cm^3/V s.

CP-ThP-6 Electrical Evaluation of Micro Water Droplets During Solidification Process Using Galvanic Array with Micro to Nano Gaps*, K. Hirayama,* Chiba Institute of Technology, Japan*; M. Mekawy, J. Kawakita,* NIMS, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

Frost damage can be classified into two types: white frost, which occurs when water vapor sublimates on the surface of an object to form ice, and water frost, which occurs when water droplets condense and solidify. Currently, there are no excellent sensors that can detect frost, and frost can only be observed visually, which makes field observations difficult and makes the actual state of frost damage unresolved. The presenters have developed a sensor that can detect water and adsorbed water molecules by measuring the electric current that flows spontaneously due to galvanic action when an aggregate of water or adsorbed water molecules comes into contact with adjacent arrays of alternating thin wires made of different metals at regular intervals (minimum value 100 nm) on an insulating substrate. Previous results have shown that the current peaks appear before and after the water undergoes a supercooled state and solidifies, indicating that frost formation detection may be possible, and furthermore, the current peaks and microscopic solidification process have been clarified. As a response to water solidification, the current response is decreasing despite the growth of water droplets. The authors believe that the temperature dependence of the conductivity of water is responsible for the decrease in the current response. However, although the temperature dependence of conductivity in water has been clarified, the temperature dependence of conductivity in the supercooled state of water has not been clarified.

In this study, we aim to clarify the temperature dependence of conductivity in supercooled water by cooling the sensor surface temperature step by step from 0°C and by clarifying the sensor response behavior.

CP-ThP-7 Engineered Ionic Diode Membranes Based on Subnanochannel Metal-Organic Frameworks with High Space Charges for Boosted Lithium Ion Transport and Unprecedented Osmotic Energy Conversion in Organic Solution*, **Amalia Rizki Fauziah**, L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Harvesting the Gibbs free energy contained in the salinity gradient of waste organic solutions will not only relieve the environmental burden but also render a new clean energy resource to accomplish the never-ending energy demand. Taking inspiration from the electrocytes in the bioelectricity systems (e.g. electrical eel) which possess numerous subnanoscale rectified ion channels acting as an ion-selective filter allowing unidirectional ion transport, we sought a feasible strategy to design an ionic-diode membrane, ZIF-8/PSS@ANM, consisted of a continuous layer of the subnanochannel zeolitic imidazolate framework-8 (ZIF-8)/polystyrene sulfonate (PSS) and a highly ordered aluminum nanochannel membrane (ANM), as osmotic energy conversion generator. The SEM results indicate that a large-scale, continuous, defect-free ZIF-8/PSS membrane was successfully prepared. Furthermore, the BET result verifies that the as-synthesized MOF membrane possesses subnanoscale (~4.1 Å) channel windows with a high surface area (~1290 m^2/g). The as-developed ZIF-8/PSS_2@ANM demonstrates a vivid diode-like ion current rectification effect even in methanol solutions with a ratio as high as ~5.57 in 1 mM LiCl (Fig. 1a), enabling the ion transport magnification at the subnanoscale confinement, due to the multiple broken symmetries (Fig. 1b). We, thereby, probe the application of this subnanoscale ionic-diode membrane in osmotic energy conversion, and exceptionally, an unprecedented osmotic power density of ~5.28 W/m^2 at 50-fold LiCl gradient in methanol was achieved (Fig. 2a), exceeding the bandgap of commercial benchmark value. The unbelievable osmotic power achieved can be plausibly elucidated to be associated with the space charges carried by PSS enhancing the ionic selectivity and accelerating ion migration, abundant ordered subnanoscale window-cavity channels of the ZIF-8 for screening dehydrated cations (Fig. 2b), and ionic-diode effect for amplifying the generated ionic current. The heterogeneous subnanochannel MOF membrane we designed will likely ignite valuable insight not only to help alleviate the environmental burden but also to open up a new avenue towards a new energy platform for meeting the need of the ever-growing energy demand.

CP-ThP-8 Designing Experimental Determination of Sheet Resistance of a Titanium Self-Aligned Silicide Formation*, **Jau-Shiung Fang**, Y. Chang, Y. Kuo,* National Formosa University, Taiwan

In recent years, metal silicides have been widely used in ultra-large scale integrated-circuit (ULSI). Shallow junction generation has always been a major challenge with ever-shrinking device dimensions, and size effects must be overcome for silicide generation, thermal stability, and electrical properties. Due to the size effects, evolution of metal silicides from $TiSi_2$, $CoSi_2$, to NiSi has been used as the source material for the formation of a low-resistivity form of metal silicide on top of the gate and source/drain for connecting the tungsten contact plug. However, characteristics of $TiSi_2$ have led to it having the potential to be a plug/interconnect material in nanoscale devices.

Because the $TiSi_2$ used in logic device is normally fabricated using a self-alignment silicide process, the process includes Ti/TiN deposition, first-step rapid thermal annealing (RTP-1), strip of unreacted Ti/TiN, second-step rapid thermal annealing (RTP-2), and final-step annealing for smoothing the top-cap dielectric. The process needs to be optimized using a design of experiment method. The influence of arsenic doping dosage, the thickness of titanium, the temperature of rapid thermal annealing on the sheet resistance of a polysilicon gate was experimentally analyzed. Experimental results revealed that thickness of titanium, the temperature of RTP-2, and the interaction between the thickness of titanium and the temperature of RTP-2dominated the sheet resistance of $TiSi_2$. An optimum RTP-2 temperature was also required for reducing sheet resistance of $TiSi_2$. A low sheet resistance was yielded for titanium thickness = 32-35 nm, RTP-1 = 720-750°C for 75 sec, and RTP-2 = 860°C for 20 sec. Heavily doping of the polysilicon gate with arsenic suppressed the formation of C54-$TiSi_2$. The lowest sheet resistance of 3.91 Ω/sq. was obtained with an arsenic dosage of 1´10^{14} /cm^2. The characteristics of the $TiSi_2$ supports its capability as a contact material for next generation devices.

Keywords: Titanium self-aligned silicide, $TiSi_2$, Sheet resistance, Designing experimental

CP-ThP-9 Hybrid Structures of p-n junction for Improving Efficiency of Photovoltaic Devices*, **Paweł Jarka**, T. Tański,* Department of Engineering Materials and Biomaterials, Faculty of Mechanical Engineering, Silesian University of Technology, Poland*; B. Hajduk, H. Bednarski,* Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Poland

The article describes the study of electrical properties investigations of solar cells based on organic p-n junction. Organic layer systems will be produced using spin-coating method with starting material in form of mixture of polymeric materials: Poly[2,6-(4,4-bis-(2-ethylhexyl)-4Hcyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2, 1,3-benzothiadiazole)] - PCPDDTBT) and poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3,6-diyl)-alt-(2.2';5',2'';5'',2'''-quaterthiophene-5.5'''-diyl)] - DPP4T. The p-n heterojunction materials were selected on the basis of gap matching component acting as an electron donor to a wavelength of 700 nm, corresponding to the maximum photon density in the spectrum of sunlight (about 1.8 eV) to the acceptor material. Acceptor material was selected on the basis of the band gap width and the electron affinity energyionization energies suitably greater than the electron affinity of the excited state of the donor, and ionization potential, ensuring dissociation of the exciton and transfer of the electron from the LUMO orbital of the donor into the LUMO orbital of the acceptor. The investigations presented in article included the production of organic solar cells (OSC) with bulk heterojunction (BHj) and determination ofthe structure and morphology of the deposition layers, chemical composition analizses, optical and electrical properties of the BHj thin films and I–V characteristics of created OSC using PV Test Solar Cell I–V Tracer System and Keithley 2410 source meter under Standard Test Conditions (AM 1.5, 100 W/m2). The conducted basic research brings knowledge of controlling the structure and properties of the thin films of the semiconducting organic material (containing bulk heterojunctions). Analysis of the results of electrical properties testing will allow for a thorough examination mechanisms of electronic transitions, electron-electron and electron-phonon interactions in p-n heterojunctions combining organic materials.

CP-ThP-10 The Investigation of Electro-Optical Properties of Hybrid Organic-Inorganic Thin Films*, **Tomasz Tański**,* Department of Engineering Materials and Biomaterials, Faculty of Mechanical Engineering, Silesian University of Technology, Poland

The aim of researchis to present influence of phase composition and manufacturing parameters on structure and electro-optical properties and surface morphology of hybrid nanocomposite thin films. The hybrid organic-inorganic material constitute thin layer of a nanocomposite with a polymer semiconductor matrix and reinforcement of semiconductor nanoparticles. The DPP4T polymer, Poly [2,5-bis (2-octyldodecyl) pyrrolo [3,4-c] pyrrole-1,4 (2H, 5H) -dione -3,6-diyl) -alt- was chosen as the matrix material (2,2 '; 5', 2 ''; 5 '', 2 '' - quaterthiophen-5,5 '' - diyl)] due to its narrow optical band gap and high charge-carrier mobility, as reinforcement were selected TiO2 and ZnO nanoparticles (NPs) with a wider band gap, however ensuring high electrical stability of the inorganic semiconductor - polymer system. Such a hybrid combination of materials has a very perspective application in electronics, with particular emphasis on optoelectronics and photovoltaics. Thin films ofDPP4T / NPs were deposited using spin-coating simple and fast method from solution. The spin-coating processes were carried out with the use of variable deposition conditions, from the point of view of the starting material and using different technological conditions.

In order to identify the structure (with particular emphasis on arrangement of the reinforcing phase) and surface morphology of thin films the Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) were used. Chemical composition analysis was performer with use X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and Fourier-Transform Infrared Spectroscopy (FTIR)

Opto-electrical properties have been performer by UV-Vis absorption spectroscopy and elypsometry. Based on the analysis of the measurement results of produced nanomaterials, the energy band gap (Eg) for the materials, the refractive index, the extinction coefficient, the real and imaginary part of the dielectric constant will be determined. The equivalent electric model of the thin films was determined by impedance spectroscopy (EIS).

The results of the work indicate that the application of the developed thin layers may be a promising solution in optoelectonics and photovoltaics (especially in thin-film heterojunction systems) due to the optical and electronic properties obtained, as well as the speed and simplicity of application.

CP-ThP-11 Multilayer Growth of 2D Layered Material Bi_2Se_3 Through Heteroatom-Assisted Step-Edge Barrier Reduction*, Namdong Kim,* Pohang Accelerator Laboratory, Republic of Korea

Various two-dimensional (2D) van der Waals systems including graphene, hBN, MoS_2, WS_2, and topological insulators form heterostructures with the high quality in atomic-layer scale. Understanding the growth kinetics of the layered heterostructure films is essential to control the atomic layer growth. We studied the growth kinetics of Bi_2Se_3 film on graphene by using AFM images and DFT calculations as well as by in-situ x-ray scattering.

During growth of 2D materials, abrupt growth of multilayers is practically unavoidable even under well-control. Delicate control of growth reaches its limits for complicated crystal structure. In epitaxial growth of Bi_2Se_3 thin film, we observe that the multilayer growth pattern deduced from in-situ x-ray diffraction requires nontrivial interlayer diffusion process. We expect that an intriguing diffusion process occurs at step edges where a slowly downward-diffusing Se adatom having a high step-edge barrier interacts with a Bi adatom pre-existing at step edges. The Se−Bi interaction lowers the high step-edge barrier of Se adatoms. This drastic reduction of the overall step-edge barrier and hence increased interlayer diffusion modifies the overall growth significantly. Thus, a step-edge-barrier reduction mechanism assisted by hetero adatom-adatom interaction could be widely utilized for multilayer growth of 2D heteroatomic materials.

KEYWORDS: heteroatom epitaxial growth, kinetic multilayer growth model, step-edge barrier

CP-ThP-12 Metallic Ground States of Strained Ti_2O_3 Thin Films*, Heungsoo Kim*, *S. Mathews, E. Lock, J. Prestigiacomo,* Naval Research Laboratory, USA*; M. Qazilbash,* William and Mary University, USA*; A. Piqué,* Naval Research Laboratory, USA

Single crystal Ti_2O_3 with a trigonal corundum structure exhibits a metal to insulator transition (MIT) between 400K and 500K without a structural phase transition. Upon cooling Ti_2O_3 undergoes a transition from metallic state to a nonmagnetic insulating state showing a ultranarrow bandgap (~0.1eV). Compared to other MIT oxides such as V_2O_3 and VO_2 that undergoes structural phase transition during MIT, the Ti_2O_3 shows pure electronic MIT process without having a structural transition. This purely electronic MIT is unique and would be useful for many electronic and photonic devices. We have deposited epitaxial corundum structured Ti_2O_3 films on c-plane sapphire substrates using pulsed laser deposition and investigated their structural, electrical, and optical properties as a function of the film growth parameters. We have found that a MIT temperature is varied with a growth temperature and the MIT is suppressed when the films are grown at 480 °C, showing conducting behavior at all temperatures. This metallic ground states were further investigated by X-ray diffraction and spectroscopic ellipsometry measurements to provide crystal structure and broadband optical properties of Ti_2O_3 films. Results show that the electrical properties are governed by the lattice parameter ratio(c/a) of crystal structure and the imposed strain causes an increase in the c-axis length as the temperature is decreased, and thereby suppresses the MIT. We will present details of the deposition conditions on the structural, electronic, and optical properties of Ti_2O_3 films.

This work was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory basic research program.

CP-ThP-14 Rapid Thermal Annealing and Structural Evolution of Sputter-Deposited AlScN Thin Films*, Hongfei Liu*, *A. Yong, N. Gong, R. Karyappa, T. Meng,* Institute of Materials Research and Engineering (IMRE), Singapore

The excellent chemical and mechanical stability, the excellent piezoelectrical properties, as well as the semiconductor compatibility, not only in thin film deposition but also in device processing, of AlN made it widely used in various piezoelectric applications. Recent studies revealed that incorporation of Sc with proper composition to substitutionally replacing Al in the lattice of AlN could dramatically increase its piezoelectric coefficient and electromechanical coupling. The presence of polarity inversion domains in III-nitride could negatively affect the piezoelectric coefficient. In fact, polar-controlled growth has long been studied in III-nitride thin films and heterostructures, e.g., to enhance carrier injections in GaInN/GaN multiple quantum well structures. Post-growth thermal annealing has also been found to reduce the density of polarity inversion domains in III-nitride thin films.

In this work, we have studied the effect of rapid thermal annealing (at T_{ann} = 600-900 °C)on surface chemical and structural evolutions of fiber-textured AlScN thin films deposited on Si (111) substrate by magnetron-sputtering. The film thickness was controlled at 1.0 µm and the Sc composition was controlled at about 15%. By varying the annealing time t_{ann} in periodic cycles from 3 to 48 min, we found that the lattice constant along the (0001) direction tends to be increased, along with a peak splitting of the X-ray diffraction (XRD) peak around the (0002) atomic planes. In this post, we will be presenting the experimental results.

CP-ThP-15 Work Function Enhancement of WO_3 Filamentous Films Obtained by Resistive Heating Evaporation Technique*, Fabien Sanchez*, *L. Marot, R. Antunes, R. Steiner, E. Meyer,* University of Basel, Switzerland

Tungsten trioxide (WO_3) films are of great interest due to their electronic properties, which can be tuned by surface nanostructuring leading to enhanced efficiency for gas sensing, energy storage or electrochromic applications. Resistive heating of tungsten (W) filaments at pressures of few Pa in an oxygen O_2 atmosphere has already demonstrated its capability to form porous, micro/nano-structured, cheap and fast films making it suitable for industrial applications.

In this work, stoichiometric WO_3 films were produced by applying a current into a W filament in an O_2 atmosphere. The pressures were varied from 2 to 20 Pa. The increase of the pressure above 7.5 Pa led to amorphous WO_3 films with a filamentous morphology. As a function of the pressure, the film morphology and the work functions (W_F) were analyzed using Scanning Electron Microscopy (SEM) and in-situ Ultraviolet Photoelectron Spectroscopy (UPS). In addition to the high surface-to-volume ratio of the films, the W_F exhibited an increase from 5.8 eV, for a conventional WO_3 film, to a maximum of 8.7 eV at 20 Pa. This change corresponds to an increase of the W_F of about 50 %, making our films suitable for a large variety of applications.

CP-ThP-17 Controlled Thermal Conduction-based Detection of Dew Condensation on Target Solid Surface by Galvanic Arrays Sensor Chip*, K. Iida*, Chiba Institute of Technology, Japan*; M. Mekawy, N. satoh, J. Kawakita,* NIMS (National Institute for Materials Science), Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

Reliable early detection of dew condensation is considered a bottleneck in surface protection against numerous negative effects such as surface fogging and corrosion. To detect the early stage of dew condensation, we fabricated a thin film-based sensor chip composed of a confined silica surface between two adjacent interdigitated gold and aluminum metal arrays that are arranged alternately at regular intervals varied between 0.5 to 10 mm. Whenever a tiny droplet is bridging between these arrays, a passage of galvanic current could be reliably detected. Imitating the surface condition for dew condensation was carried out in a temperature-controlled scheme employing thermal conduction heat transfer between the solid surfaces of the sensor chip and its contacting heat conductor. However, the effect of the geometrical shape of the heat conductor on the thermal heat conduction rate is yet to be emphasized. In this study, three different fabricated geometrical shapes of aluminum heat conductors (Fig. 1(a)) were attached to the back side of sensor chip and used for a step-wise (static) or direct (dynamic) temperature-cooling heat transfer mechanisms (Fig. 1(b)). The experimental results revealed that the sensor response current (as a measure of dew condensation detection) increased when the sensor surface temperature was dropped below the dew point. Moreover, the rate of thermal conduction was larger at direct temperature-cooling mechanism than at step-wise mechanism as shown in Fig.2. In addition, the temperature difference between the senor surface and each heat conductor was found to follow the order of $DT_{I} > DT_{II} > DT_{III}$. Furthermore, the rate of thermal conduction between the thermally contacted surfaces of sensor and each heat conductor was found to follow the order of I < II < III. This could be attributed to the thermal resistivity of each examined heat conductor which followed the order of $R_{I} > R_{II} > R_{III}$ (listed in table 1). The results were in an agreement with further simulation-based investigations that were also performed to correlate the geometrical shape of contacting heat conductorwith its heat transfer to the sensor surface.These results demonstrated that controlling the temperature of the sensor surface depends on the geometrical shape and the temperature change of its contacting heat conductor. Therefore, it can be concluded that our developed sensor can be beneficially used for the enhanced early detection of dew condensation at the solid substrate surfaces of interest employing the thermal conduction heat transfer mechanism.

CP-ThP-18 Polyimide-Based Gate Dielectrics for High-Performance Organic Thin Film Transistors*, **Yan-Ting Chen**, Y. Yu,* Ming Chi University of Technology, Taiwan

In this study, TiO2-SiO2 nanoparticles with OH group on their surface will be prepared by sol-gel process from TEOS and titanium ethoxide. The particle size and morphology, crystal phase, crystallinity, and the corresponding dielectric constants are investigated. The prepared ST colloids will further react with the fluorine-containing soluble polyimide with side OH group chains to form the PI/ST hybrid thick films on glass and flexible plastic substrate. The prepared high dielectric PI/ST films will be applied to fabricate the high capacitance memory devices with structure Al/PI-ST/ITO-Glass or Al/PI-ST/ITO-PET .The PI/BT films will further be applied to fabricate the OFETs with structure Al/ PffBT4T-2OD /PI-ST/Si on the silicon substrate with the PI/ST hybrid film as the gate insulator. We have systematically investigated the effects of properties of PI/ST films such as dielectric constant, surface roughness, and thickness on capacitance, field-effect charge mobility, on/off ratio, threshold voltage, and leakage current.

CP-ThP-19 Epitaxially Grown Gold (100) Surfaces for Oxygen Reduction Reactions*, **Katharina Kohlmann**, D. Guay,* Institut national de la recherche scientifique, Canada*; A. Sarkissian,* Plasmionique Inc., Canada*; C. Schindler,* Munich University of Applied Sciences, Germany*; A. Rüdiger,* Institut national de la recherche scientifique, Canada

Noble metals have long been known to be an excellent basis for electrocatalysts. While the effectivity of catalysts depends on the reaction they are used for, studies have shown that for the oxygen reduction reaction (ORR), Au (100) is the most active face of Au in alkaline media. This work investigates magnetron sputtered epitaxial Au-films on MgO (100) for electrocatalysis. We show that the deposition parameters and their effect on the surface morphology are a key factor to optimize catalytic activity. We further explore various surface treatment methods to improve the adhesion of Au as well as its surface morphology without the use of a transition metal seed layer. The samples are characterized by atomic force microscopy, X-ray diffraction and cyclic voltammetry to establish a correlation between the surface topography and electrocatalytic activity.

CP-ThP-20 Ion-Selective Capacitive Deionization of Saltwater Using Functionalized Graphene Thin-Film Coated Electrodes*, H. Cheng,* National Cheng Kung University, Taiwan*; J. Wang,* Stanford University, USA*; **Hong Paul Wang**,* National Cheng Kung University, Taiwan

Drinking water shortage is getting worse in recent decades. Desalination of saltwater by capacitive deionization (CDI) with the advantages of relatively low energy consumption and environmental friendly is of increasing importance. To improve the desalination performances, by introducing ion exchange membranes (IEM) on the surfaces of CDI electrodes for weakening co-ion repulsion effect, membrane CDI (MCDI) cell architectures have been constructed. Nevertheless, IEM may suffer from high cost and interfacial resistance. It would be economically attractive to use IEM for selectively moving relatively ions to electrodes for better desalination performances and higher feed rates. Thus, in the present work,sulfonated- and poly(diallyldimethylammonium chloride)-functionalized graphene oxide (SGO and PGO) serves as hydrophilic cation- and anion-exchange membrane (CEM and AEM), respectively to enhance CDI efficiencies. The positively charged PGO thin-film coated on the activated carbon (AC) can selectively transport anions to positive electrodes in the CDI process. The SGO and PGO coated AC electrode pair (AC/SGO ‖ PGO/AC) for CDI of saltwater ([NaCl]=200-500 ppm) under +1.2 V for 1 h reaches a highoptimized salt removal (200 mg/g·day) and electrosorption capacity (9 mg/g). In the reverse voltage desorption operation mode, effective desorption of anions for regeneration with the thin-films can also be achieved. This work presents the feasibility using the high-efficiency, low-cost and facile SGO and PGO ion-selective thin-film coated on AC electrodes to enhance desalination performances.

CP-ThP-21 Research on the Application of the Double-layer Hole Transport Layer of Novel Functional Organic Small Molecule Materials in High-efficiency Inverted-Perovskite Solar Cells*, **Wei-En Wu**, Y. Yu,* Ming Chi University of Technology, Taiwan

This research is divided into two parts. Both use the hydrophobic small molecule as a double-layer hole transport material provided by Professor Yung-Chung Chen from Kaohsiung University of Science and Technology. In the first part, we investigate the effects of the three p-type small molecules (CL-1~CL3) with tetraphenylethylene as the core and different aromatic rings attached to the side chain. The side chains are benzene, naphthalene, and pyrene. The tetraphenylethylene core has highly distorted nature, even without alkyl solubilizing groups, it can still have good solubility, and then through the modification of side chain groups, the energy level and hole mobility can be fine-tuned. Under the condition of AM1.5, NiOX/ CL-3 double-layer hole transport layer has the best power conversion efficiency of 20.15% in the trans-structured perovskite solar cell.

CP-ThP-22 High-Performance non-Fullerene Systems for Organic Solar Cells*, **Chun-Chieh Lee**, Y. Yu,* Ming Chi University of Technology, Taiwan

For the organic photovoltaics (OPVs), the choice of solvent affects the morphology of the active layer blend as well as the device performance and potential commercial applications. In this study, two different solvents, chloroform (CF) and chlorobenzene (CB) with optimal process parameters, were applied to prepare the OPVs with the PM6:BTP-eC9 as the active layer. Atomic force microscopy and grazing-incidence wide-angle X-ray scattering were used to evaluate the blend morphologies of the OPVs, and also examined the optoelectronic properties of the blend films and devices. The power conversion efficiencies could reach up to 17.82% when using CB as the solvent, without any additives. Compared with the CF-based device, the optimized CB-derived OPV exhibited a more suitable phase-segregated domain size with stronger face-on molecular stacking, leading to more efficient carrier transport. Thus, by optimizing the fabrication conditions and selecting a suitable solvent that could improve the the structure of the PM6:BTP-eC9 blend films and thus also improve the OPV performance.

CP-ThP-23 Vanadium Doped Zno Nanorod Array Piezoelectric Pressure Sensor*, **Shu-Yu Lin**, J. Huang, S. Brahma,* National Cheng Kung University (NCKU), Taiwan

ZnO has semi-conductivity and piezoelectricity at the same time that makes it a promising material for piezotronics. Zinc Oxide (ZnO) nanorod array was grown on silicon substrates by a hydrothermal method. From SEM top-view image, well aligned ZnO nanorods were deposited on the silicon substrate. The XRD patterns showed that the nanorods behaved highly (002) oriented. Resonant Raman spectroscopy revealed that the degree of (002) orientation was decreasing with raising the vanadium concentration of growth solution. The Photoluminescence spectrum showed typical ZnO UV emission and the 6% sample has an obvious red shift.

Coatings for Biomedical and Healthcare Applications
Room Golden State Ballroom - Session DP-ThP

Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

DP-ThP-1 Antibacterial Properties of Ag Doped Tetrahedral Amorphous Carbon Coatings Synthesized Using Hybrid Filtered Cathodic Vacuum Arc and Magnetron Sputtering System*, **SangYul Lee**, K. Oh, J. Park,* Korea Aerospace University, Republic of Korea*; D. Kim, J. Kim,* KIMS, Republic of Korea

Tetrahedral amorphous carbon (ta-C) coating is a hydrogen-free carbon coating with the remarkable properties comparable with those of diamond film, such as high hardness, optical transparency and chemical inertness. In this study, as silver (Ag) is known to be a potent antibacterial agent, silver (Ag) doped ta-C coatings with different Ag concentrations were synthesized on the AISI 316Land Ti64 coupons using an hybrid filtered cathodic vacuum arc (FCVA) and magnetron sputtering system. The doping effects of Ag concentration in ta-C coatings on the bacteria biofilms formed on the surface of medical products were examined. Surface condition and its physicochemical properties were investigated using SEM, AFM and XPS and also studied was their antibiofilm efficacy against a multi-drug resistant nosocomial pathogen *Pseudomonas aeruginosa*. In addition the antibacterial activity of Ag doped ta-C was evaluated by bacterial eradication tests with *Escherichia coli (E. coli)* at different incubation times.The result revealed that the synthesized Ag doped ta-C coatings inhibited the biofilm formation of *P. aeruginosa*and the antibacterial activity against *E. coli*in a concentration-dependent manner. Hence, this study demonstrated the possible use of Ag doped ta-C coatingsagainst the biofilm-related infections out of *P. aeruginosa* and antibacterial activity against *E. coli.* Experimental details will be discussed.

DP-ThP-2 Adhesion, Corrosion Resistance, and Blood Compatibility of Mao- Pretreated Magnesium Alloy Coated with Graphene Oxide and Pyrolytic 1,8-Diaminooctane-Incorporated Oxidized Polydopamine*, **Chau-Chang Chou**, S. Chang, H. Lee,* National Taiwan Ocean University, Taiwan*; W. Chen,* Cheng Gung Memorial Hospital, Keelung, Taiwan

Surface treatment and functional coating can effectively reduce the degrading status and promote the blood compatibility of magnesium implants. This study applied micro-arc oxidation (MAO) treatment to improve the corrosion resistance of magnesium alloy. The electrolyte was prepared by using sodium silicate, sodium hydroxide, and sodium citrate. The MAO process was performed by adjusting voltage which was determined by observing the completeness of the ceramic films. Then, Layer-by-layer assembly technique was implemented by dipping the substrates with graphene oxide, oxidized polydopamine mixed with pyrolytic 1,8-diaminooctane sequentially to provide their corrosion resistance, adhesive strength, and anti-clotting capability. The composition of substrate was confirmed by inductively coupled plasma mass spectrometry. Microstructural morphologies and crystallography of the MAO coatings were characterized using X-ray diffraction. Optical microscopy was implemented to observe the topographies of coatings. The samples' surface transition was revealed by water contact angle. Their surface topographies and element were observed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The cross-sectional morphology and the film thickness were evaluated by dual-beam focused ion beam microscopy. The function groups contained in composite multilayers were examined by Fourier transform infrared spectroscopy. The degradation resistance was measured by corrosion polarization curve. The combination of the multilayers was investigated by conducting scratch tests.The hemocompatibility of composite films for original, 7 days, and 15 days were studied according to the activated partial thromboplastin time and the platelet adhesion experiment. The results indicated that the coatings with multilayers of graphene oxide, oxidized polydopamine mixed with pyrolytic 1,8-diaminooctane layers after micro-arc oxidation had the best adhesion strength, corrosion resistance, and anticoagulant ability which can sustain more than 7 days under theorbital shaking tests.

DP-ThP-3 Surface Alloying for Antibacterial Martensitic Stainless Steel Fabrication*, Z. Chen, B. Liu, **Wen-Ta Tsai**,* National Cheng Kung University (NCKU), Taiwan*; C. Huang,* Tung Mung Development Co., Ltd., Taiwan

Stainless steels (SSs) containing antibacterial elements, such as copper element, could be used as antibacterial structural materials. However, the traditional metallurgical processes for the fabrication of copper-containing SSs include melting, casting, rolling and many other steps, which are highly costive and inconvenient for final product manufacturing. Furthermore, for ferritic and martensitic stainless steels, the low copper solubility in these grades of stainless steels makes copper alloying more difficult. Therefore, this study aims to develop a novel method for preparing copper-containing martensitic SS (namely SS 440C) on its surface by incorporating electrochemical plating and thermal diffusion process.

Successful surface alloying of copper onto SS 440C surface was achieved with unique processes consisting proprietary copper electroplating and subsequent thermal diffusion treatment. It generally accepted that stainless steels (normally SS 304) containing 3 wt% copper exhibits effective antibacterial activity. The SEM images and the associated EDS results of the above treated samples reveal that a surface layer with copper concentration greater than 3 wt% and a thickness as high as tens of micrometer could be produced on SS 440C surface by employing the novel technique invented in this investigation, which meets the requirement for antibacterial applications. The effective antibacterial performance of the above mentioned product was confirmed by employing the standard test (JIS-Z2801) for antibacterial activity examination.

DP-ThP-4 Enhancing the Surface Properties of Polymethylmethacrylate (PMMA) by Functionalizing with Atomic Layer Deposited Titanium(Iv) Dioxide*, **Harshdeep Bhatia**, C. Takoudis,* University of Illinois, Chicago, USA

Polymethyl methacrylate (PMMA) is a widely used polymer in applications such as engineering structural plastics, energy storage materials, and biomaterials. However, its poor surface properties lead to fracture and deformation. Functionalization of the PMMA surface can make it more resistant to aggressive environments and prevent it from biodegradation, discoloration, and increased surface roughness. Here, atomic layer deposition (ALD) was used to deposit TiO_2 thin films from tetrakis(dimethylamido)titanium (TDMAT) and ozone on PMMA substrates to improve its surface properties without the need for plasma assistance or another interlayer. Spectroscopic ellipsometry was used for the first time to measure the metal oxide film thickness on thick PMMA substrates. Two different growth regimes were observed, one for initial and the other for later ALD cycles. Initially, the growth rate on PMMA was 1.39 A˚/cycle, which is*3.5 times higher than that on stand-alone silicon (0.4 A˚/cycle); this is attributed to cyclic chemical vapor deposition of TDMAT and moisture within PMMA concomitant with TiO_2 ALD from TDMAT and ozone. However, after the formation of about 30-nm-thick film on PMMA, the TiO2growth rate became similar to that on silicon. Moreover, our results revealed that the presence of PMMA in the deposition reactor affects the TiO_2 growth rate on silicon substrates as well. These findings are discussed and corroborated with residual gas analyzer and X-ray absorption near-edge structure data. The thermal stability of the PMMA samples was examined by thermogravimetric analysis. Chemical composition and surface roughness of coated PMMA were studied by X-ray photoelectron spectroscopy and optical profilometry, respectively. The TiO_2 coating increased wettability by ~ 70% and surface hardness by 60%

DP-ThP-5 Diffusion-Based Plasma Nitriding for Surgical Needle*, **Takao Yamauchi**, P. Abraha,* Meijo University, Japan

Surgical instruments require medical grade and biocompatible materials with good corrosion resistance and tensile strength. Austenitic stainless steels are appropriate materials that can provide a sharp edge for repetitive use in medical procedures. These surgical tools may be cutting and holding tools or closure and hemostatic tools such as suture needles.

This research aims to enhance suture needles for improved ease of use in the repetitive suturing of large incisions. The shape of the needle body and the sharpness of the needle tip determines the force acting on suture needles. Therefore, better ease of use in terms of a smaller resistance force, a smaller body diameter, and a sharper needle tip are preferable. However, as we reduce the body diameter and sharpen the needle tip, the needle strength tends to decrease, and bending of the needle tip and possibly the needle body occurs, resulting in a short useful life span. In this study, surgical suture needles are plasma nitrided to suppress the bending of the needle tip and body for applications in large incisions.

Currently, silicone-coated or metallic glass-coated modified surfaces are the available methods that enhance the durability of surgical tools. However, delamination of the coating while in use may cause an undesirable medical problem for the subject and compromise the sharpness of the needle tip. This study aims to determine the insertion-retraction characteristics of untreated, silicone-coated, and plasma-nitrided suture needles. The results of our experiments show the measured insertion-retraction characteristics curves of plasma nitrided suture needles were superior to those of the silicon-coated and untreated samples tested. Furthermore, since plasma nitriding is a diffusion process, the dimensional changes are minimal and no danger of delamination. The presentation will show the performance of plasma-nitrided stainless steel surgical suture needles.

DP-ThP-6 Development of TiO_2/Ag Multilayer Antibacterial Coatings Using Magnetron Sputtering Technique for Potential Applications in Non-Permanent Implants*, **Sebastián Rodríguez Maya**, M. Restrepo Posada, F. Bolívar Osorio, G. Bejarano Gaitán, J. Lenis Rodas,* Universidad de Antioquia, Colombia

The development of ideal surfaces to be used in metal implants and osseus stabilization devices require the consideration of different phenomena such as the formation of a bacterial biofilm on the surface followed by the usual appearance of infections or the total rejection of the device. On the other hand, the overgrowth of bone material around these devices constitutes a barrier when it comes to removing them when their function has been fulfilled. Due to this, the development of multilayer antibacterial coatings of TiO2/Ag on Ti6Al4V substrates by means of the Magnetron Sputtering technique for its potential use in non-permanent implants were studied. The coatings obtained using this technique exhibit a uniform and densely packed, columnar growth profile and it also offers significant control over the microstructural features. Consequently, the properties of the developed systems were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), tribologic assays and surface properties such as rugosity and contact angle.

DP-ThP-8 Evaluation of Biocompatibility and Corrosion Resistance of Strontium-Calcium Phosphate Coated Magnesium by Electrodepositon*, **Jung-Eun Park**, J. Ji, Y. Kim, S. Byeon, M. Lee,* Chonbuk National University, Korea

This study aims to improve the initial corrosion and biocompatibility of biodegradable magnesium by coating the magnesium surface with calcium phosphate containing strontium by electrodeposition. In this study, calcium phosphate coatings doped with Sr of various concentrations were electrodeposited on the magnesium surface at an applied voltage of 4 V for 1 h. The corrosion behavior and biocompatibility of the modified magnesium surfaces were evaluated.

The surface of the magnesium coated with strontium-calcium phosphate showed a dense dendritic shape and became denser as the strontium content increased. strontium-calcium phosphate coated magnesium showed improved corrosion resistance and lower pH change than pure magnesium. In vitro strontium-calcium phosphate coated magnesium showed enhanced bioactivity. strontium-calcium phosphate coated magnesium showed excellent osteoblast proliferation and differentiation.

Therefore, the strontium-calcium phosphate developed in this study inhibited the initial corrosion of magnesium and effectively formed corrosion products and bioactive materials on the surface. In addition, excellent biocompatibility was confirmed.

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DP-ThP-9 Improvement in Corrosion Resistance and Biocompatibility of Biodegradable Mg Surface with Combination of Calcium Phosphate and Chitosan*, **Seo-young Kim**, Y. Jang, T. Bae, M. Lee,* Jeonbuk National University, Republic of Korea

Metallic implants for bone fixation have been used for healing a fractured bone. For success of implantation, the superior bearing capacity and biocompatibility is needed. Magnesium, which is biodegradable metal, has great mechanical properties than other biodegradable materials, and its biocompatibility can be improved by functional polymer or ceramic coating. in this study, Mg surface was modified with bio-ceramic (apatite) containing chitosan to improve its corrosion resistance and biocompatibility.

For coating, chitosan$_{(sol)}$ was prepared by dissolving 1% chitosan powder in 1% acetic acid (pH 6.0). Calcium phosphate $_{(sol)}$ was prepared by mixing 0.25mol/L Ca-EDTA and 0.25mol/L KH_2PO_4 in DW (pH 5.9). The surface of pure Mg was thermally treated in the different ratio of mixture [Calcium phosphate $_{(sol)}$: chitosan $_{(sol)}$] for 1 h at 90℃. The morphology and composition of the surface were examined by SEM with EDS. The precipitated crystal structure and chemical bonding was analyzed using XRD and FT-IR. The electrochemical corrosion resistance of surface was measured by potentiodynamic polarization. The cytocompatibility on MC3T3-E1 osteoblastic cells was conducted.

After thermal treatment, porous and fine particles were formed on the Mg surface. The particles were uniformly covered on the surface. Increasing the mixing ratio of chitosan contributed to miniaturization of the particles and improvement of the density of the coating layer. The particles in coating layer were composed of Mg, C, O, P, and Ca components, and it was an apatite-based compounds with octacalcium phosphate (OCP) and hydroxyapatite (HA) crystal phase. FT-IR analysis results demonstrated the presence of chitosan in the coating layer. The bio-ceramic (apatite) layer increased the potential of the Mg surface, which improved corrosion resistance. It was effective on the increase of cell's proliferation.

The surface coating technique can form the uniform film consisted with chitosan-apatite particles. The dense apatite layer was effective in improving the corrosion resistance of magnesium and enhancing cytocompatibility.

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DP-ThP-10 Influence of Plasma-Enhanced Chemical Vapor Deposition Associated with Different Finishing Procedure on the Degradation of CAD/CAM Dental Ceramic*, **Aldiéris Alves Pesqueira**, L. Scaion Silva,* São Paulo State University (Unesp), School of Dentistry, Araçatuba, Brazil*; V. Adelino Ricardo Barão,* (University of Campinas (UNICAMP), Piracicaba Dental School, Brazil*; K. Henrique Cruz, V. Alves Nascimento, J. Pedro Justino de Oliveira Limírio,* São Paulo State University (Unesp), School of Dentistry, Araçatuba, Brazil*; B. Egumi Nagay,* University of Campinas (UNICAMP), Piracicaba Dental School, Brazil*; E. Cipriano Rangel,* Sao Paulo State University (UNESP), Laboratory of Technological Plasmas (LaPTec), Engineering College, Sorocaba, Brazil

Acid erosion is common in patients with gastroesophageal reflux disease or eating disorders (nervous bulimia and/or anorexia). Such condition can degrade the mechanical strength of oral restorative materials such as ceramics. Surface treatments have been used to protect or improve the mechanical properties of ceramic materials. In this context, plasma-enhanced chemical vapor deposition (PECVD) is a promising technique for depositing a thin film on ceramics. Therefore, we aimed to evaluate the structural and mechanical characteristics of zirconia/silica ceramic in a CAD-CAM interpenetrating resin matrix (Shofu Block HC) as a function of different finishing procedures associated or not with PECVD after erosive challenge. A total of 120 specimens were divided into 4 groups of surface finishing: only mechanical polishing (MP), only application of light-curing sealant (S), association of MP or S with PECVD (MP+PECVD and S+PECVD). A steel reactor was used for PECVD application and a thin-film was deposited under an atmosphere of 85% hexamethyldisiloxane monomer (HMDSO) and 15% argon (Ar). The erosive challenge was performed with 5% HCl (pH = 2.0) for 273 h. The surface roughness (Ra), surface free energy, Vickers microhardness, flexural strength, and elastic modulus of ceramic material as a function of surface finishing were investigated before and after the erosive challenge. A homogeneous silicon-based thin film was successfully deposited on ceramic surface. The PECVD thin film was able to reduce the surface roughness and increase flexural strength of ceramic when associated with mechanical polishing, even after erosive challenge, while the other groups had an increase in roughness ($p<0.05$). In general, PECVD increased the ceramic surface hardness, and reduced the surface free energy when associated with mechanical polishing or sealant application before and after erosive challenge ($p<0.05$). In conclusion, the PECVD thin film effectively enhanced the roughness, hardness, surface energy, flexural strength, and elastic modulus of zirconia/silica ceramic in an interpenetrating resin matrix, mainly when associated with mechanical polishing. The creating of silicon-based thin films might be a good strategy to reduce ceramic degradation in the oral environmental.

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Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Golden State Ballroom - Session EP-ThP

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium E) Poster Session

EP-ThP-1 e-Poster Presentation: Combinatorial Study of Mo_2N-Cu Coatings to Optimize Tribological Performance in Low Viscosity Fuel Environments*, **Slater Caldwell**, M. Dockins, E. Cairns,* University of North Texas, USA*; S. Berkebile,* US DEVCOM Army Research Laboratory, USA*; A. Voevodin, D. Berman, S. Aouadi,* University of North Texas, USA

Wear-induced failure between sliding mechanical interfaces causes a reduction in component lifespan and subsequently a system failure. These problems are exacerbated when the environment is insufficiently lubricated, such as in the case of low viscosity fuels used in automotive and aerospace engines. In the current study, a combinatorial and high throughput magnetron sputtering method was used to determine the optimum copper content in Mo_2--N-Cu coatings that provides the best tribological response. Mo_2--N-Cu is a tribo-catalytically composite whereby copper promotes the formation of a carbon-based lubricious film at sliding interfaces. More specifically, metal nitride films with copper inclusions provide both strength and wear resistance whereby copper clusters act as catalysts for carbon film formation when paired with synthetic oils. Hence the goal of this study is to understand the interplay between the catalytic activity of copper that improves the lubricity of the interface and the mechanical properties that diminish for high copper and to optimize such properties to minimize wear. Therefore, Mo_2--N-Cu coatings were produced by reactive magnetron sputtering from Mo and Cu targets in a controlled nitrogen environment. The structural and chemical properties of these materials were evaluated using X-ray diffraction (XRD) and an environmental scanning electron microscope (ESEM) equipped with energy dispersive X-ray spectroscopy (EDS). The mechanical and tribo-catalytic properties were tested using a nanoindenter and a high frequency reciprocating rig (HFRR) tribometer in decane.

EP-ThP-2 Triboactive CrAlXN Coatings for Wear and Friction Reduction under Grease Lubrication*, K. Bobzin,* Surface Engineering Institute - RWTH Aachen University, Germany*; C. Kalscheuer,* surface Engineering Institute - RWTH Aachen University, Germany***; Max Philip Möbius,*** Surface Engineering Institute - RWTH Aachen University, Germany*; M. Rank,* Institute of Machine Elements, Gears and Tribology - TU Kaiserslautern, Germany*; M. Oehler, O. Koch,* Institute for Machine Elements, Gears and Tribology, Germany

The continuous development of tribological systems to increase their energy efficiency and sustainability is of increasing social and economic interest. The chain drive as a common machine element offers open potential in this respect. The service life of a chain is determined by its wear-related elongation. The wear of chain pins in the chain joint can be reduced by CrAlN coatings. This component also leads to most frictional losses in a chain drive. When lubricating with greases, friction- and wear-reducing reaction layers are formed in interaction with the steel surface. Interactions of CrAlN coatings with the lubricating greases, however, are limited due to their chemically inert properties. Triboactive CrAlMoN coatings offer a promising solution. In this study CrAlMoN coatings deposited by magnetron sputtering physical vapor deposition (MS-PVD) were tribologically investigated via pin-on-disc tribometer (PoD) and compared to a CrAlN coating and an uncoated reference. All systems were tested with two fully additivated grease references and two basic greases, which exclusively contain a S- or P-additive. To approach the application, selected combinations were then tested in a chain-joint tribometer (CJT), a component test bench for chain drives. The coatings were successfully deposited on chain pins. The incorporation of the triboactive element Mo leads to a lower indentation hardness H_{IT} of the coatings. The CrALMoN coating with a high Mo content achieved a low total wear volume and lead to a stable and relatively low coefficient of friction (CoF) in contrast to the other tested coatings. This coating leads to low levels of friction and total wear in combination with a basic grease +S equivalent to a steel surface in combination with a fully additivated grease lubricant. The results show the high potential of triboactive coatings for wear and friction reduction in chain drives. Additionally, expensive and environmentally dangerous anti-wear and extreme pressure additives can be avoided using the triboactive CrAlMoN coating.

EP-ThP-3 Influence of Nb and Ta Added Elements on the Corrosion and Mechanical Properties of CrYN Coatings*, **İhsan Efeoğlu**, B. Yaylalı, G. Gülten, Y. Totik,* Atatürk University, Turkey*; P. Kelly, J. Malecka,* Manchester Metropolitan University, U.K.

Barrier coatings are applied to many machine elements that are exposed to aggressive/hardservice conditions to prevent corrosion, oxidation and wear at high temperatures. These coatings are widely used to protect structural components of gas/steam turbines in the energy and aerospace industries against aggressive operating conditions. Looking at the usage areas in general terms, it is seen that thermal barrier coatings (TBC) are of vital importance in terms of environmental and socio-economic aspects. With the increase in technological developments, gas/steam turbines and high temperature components such as aircraft/jet engines are expected to operate under supercritical conditions and with minimum losses. In this study, Nb and Ta doped CrYN film was coated on 316L stainless steel (SS) using CFUBMS (Closed Field Unbalanced MagnetronSputtering) technique. Then, the corrosion resistance, structural and mechanical properties of CrYN:Nb/V solid thin films were investigated. Microhardness device was used for mechanical properties. SEM and XRD techniques were used to study the microstructural characteristics of the coatings on the silicon wafer. Corrosion properties were investigated using potentiostat test unit NaCl solution. The highest hardness was found as 38.60 GPa for CrYN:Nb film and 26.47 GPa for CrYN:Ta. The results show that the coated samples have higher corrosion resistance than the uncoated samples. In addition, it has been observed that the corrosion resistance of Ta doped CrYN thin films is relatively better than Nb doped thin films.

EP-ThP-4 Evaluation of the Adhesive Strength of a Nitrided Stainless Steel Under Cyclic Contact Loads*, D. Fernández-Valdés, **Jesús Vidal-Torres**,* SEPI ESIME Instituto Politécnico Nacional, Mexico*; A. López-Liévano,* Universidad Veracruzana, Mexico*; G. Rodríguez-Castro, A. Meneses-Amador,* SEPI ESIME Instituto Politécnico Nacional, Mexico

In this study, the adhesion resistance of a nitrided AISI 316L stainless steel is analyzed by standing contact fatigue. The AISI 316L steel was nitrided by the salt baths process where three nitride layers were obtained. Hardness and Young's modulus values were obtained by nanoindentation testing. The H^3/E^2 ratio was used as an indicator of fracture resistance of the nitride layers. Fracture toughness of the nitride layers was achieved by scratch testing. The cyclic contact loads were applied to nitrided steel by means of an alumina spherical indenter. The layer/substrate systems were evaluated under 50,000 load cycles and maintaining a constant frequency of 5 Hz. The Hertzian stress state caused by the contact loads was obtained using the finite element method. Two different damage zones were observed, one at the periphery of the contact zone, where cohesive damage was caused by the maximum principal stresses and the other inside the contact zone where adhesive damage was caused by the maximum shear stress. The adhesive resistance of the nitride layers was a function of both layer thickness and H^3/E^2 ratio of each system.

EP-ThP-5 Effect of Annealing Treatment on Mechanical Properties of Nanostructured Metallic Films Deposited by Pulsed Laser Deposition*, **Francesco Bignoli**,* CNRS, France*; S. Rashid, E. Rossi,* Università degli studi Roma 3, Italy*; P. Djemia,* CNRS, France*; M. Sebastiani,* Università degli studi Roma 3, Italy*; A. Li Bassi,* Politecnico di Milano, Italy*; M. Ghidelli,* CNRS, France

The design of metallic thin film with controlled composition and microstructure has become increasingly important for industry applications, involving strong mechanical solicitations. Specifically, metallic glasses (MGTFs) and high entropy alloys thin films (HEATFs) have shown a great potential due to their unique combination of large mechanical properties such as yield strength (3 GPa) and ductility (10%) [1,2]. However, the relationship microstructure-mechanical properties are not fully understood since the morphological control is often limited by the most employed sputtering deposition. In this field, Pulsed Laser Deposition (PLD) offers the possibility to widely control the morphology of the films by simply changing the process parameters, affecting the growth mechanisms from atom-by-atom to cluster-assembled growth regimes. Recently, PLD has shown a large potential for the deposition ZrCu MGTFs and CoCrCuFeNi HEATFs reporting large and tunable mechanical properties such as an elastic modulus and hardness of 175 and 11 GPa [2].

Here, we explore the possibility to further nanostructuring PLD deposited ZrCu compact and nanogranular MGTFs by performing annealing treatments from 300 up to 550°C, while investigating the devitrification process and the evolution of the mechanical properties.

Structural characterization shows that compact films remain amorphous up to 420°C, while the crystallization process of nanogranular films is completed at 420°C due to the combination of high interface density, free volume and O content [3]. We show that the mechanical properties increase with the annealing temperature due to the progressive crystallization reaching a plateau upon complete crystallization with elastic modulus and hardness up to 180 and 14 GPa, respectively. Furthermore, we show that compact films have residual tensile stress from 169 to 691 MPa whose magnitude increase as a function of the temperature due to nanocrystalline phase nucleation followed by grain growth. On the other hand, nanogranular films show a maximum residual stress of 1.1 GPa at 420°C followed by a decrease at higher annealing temperatures, indicating a complete crystallization.

Overall, we show that PLD in combination with post-thermal annealing can generate different families of metallic films with varying nanoscale morphologies, resulting in tunable mechanical properties and thermal stability with potential as structural coatings.

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EP-ThP-6 Accurate Measurement of Thin Film Elastic Properties Using Thermal Loading*, C. Trost,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences & Dept. of Materials Science, Montanuniversität Leoben, 8700 Leoben, Austria*; S. Zak,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; **Megan J. Cordill,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences & Dept. of Materials Science, Montanuniversität Leoben, 8700 Leoben, Austria

Measuring the elastic modulus of novel metallic thin films, such as intermetallics or high entropy alloy (HEA) films, can be challenging. Nanoindentation is the most used method to determine the hardness, but has recently been shown that nanoindentation is not a reliable method to measure elastic modulus of films less than 5 µm thick without having an influence from the substrate [1] (especially in case of stiff thin film on compliant substrate). Therefore, another method should be utilized to accurately measure thin film elastic modulus. One approach that has not been considered is to use in-situ stress measurements while heating the film. From the initial slope of the heating and cooling stress-temperature curves, a substrate-free elastic modulus can be calculated. In order to determine if this technique is viable, known metal films of Mo and Al on silicon substrates will first be evaluated and compared to literature and nanoindentation of the same film systems. Then, more complex, metastable MoAg alloys and refractory HEA films, with applications in power electronics, will be evaluated.

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EP-ThP-7 Microstructural, Mechanical and Tribological Properties of TiAlSiN–Cu Superhard Nanocomposite Coatings Deposited by Filtered Cathodic Arc Ion Plating Technique*, **In-Wook Park**, S. Heo, W. Kim, J. Kim, E. Choi, S. Choe,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; J. Lim,* BMT Co., Ltd, Republic of Korea

The effects of the Cu content on the microstructural, mechanical and tribological properties of the TiAlSiN–Cu coatings were investigated in an effort to improve the wear resistance with a good fracture toughness for cutting tool applications. A functionally graded TiAlSiN–Cu coating with various copper (Cu) contents was fabricated by a filtered cathodic arc ion plating technique using four different (Ti, $TiAl_2$, Ti_4Si, and Ti_4Cu) targets in an argon-nitrogen atmosphere. The results showed that the TiAlSiN–Cu coatings are a nanocomposite consisting of (Ti,Al)N nano-crystallites (~5 to 7 nm) embedded in an amorphous matrix, which is a mixture of TiO_x, AlO_x, SiO_x, SiN_x, and CuO_x phase. The addition of Cu atoms into the TiAlSiN coatings led to the formation of an amorphous copper oxide (CuO_x) phase in the coatings. The maximum nanohardness (H) of ~46 GPa, H/E ratio of ~0.102, and adhesion bonding strength between coating and substrate of ~60 N (L_{C2}) were obtained at a Cu content ranging from 1.02 to 2.92 at.% in the TiAlSiN–Cu coatings. The coating with the lowest friction coefficient and best wear resistance was also obtained at a Cu content of 2.92 at.%. The formation of the amorphous CuO_x phase during coating growth or sliding test played a key role as a smooth solid-lubricant layer, and reduced the average friction coefficient (~0.46) and wear rate (~10 × 10^{-6} mm^3/N·m).

EP-ThP-8 Adhesion of WTi to Polyimide Measured by Complementary Methods*, D. Gutnik, **Alice Lassnig**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; A. Kleinbichler,* Infineon Technologies AG, Austria*; P. Imrich,* KAI Kompetenzzentrum Automobil- und Industrieelektronik, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Adhesion of metal films to polymers is an increasing area of research. Not only are metal-polymer interfaces found in flexible and foldable electronics, but also in rigid microelectronics. While several methods to quantify the metal-polymer interface adhesion are available, a direct comparison of the available methods on the same interface has not been performed yet. In this work, the adhesion of the WTi-Polyimide (PI) interface was evaluated with methods, using spontaneous buckles and the tensile induced delamination model. One unique aspect of the samples is that all fabrication processes were performed at the wafer level and testing performed on released WTi-PI dogbone shaped tension samples. After being released from the rigid wafer, spontaneous cracking and buckling occurred due to the release of residual stresses in the WTi film. The results show that both models lead to similar adhesion energies. The similarity of adhesion results indicate that both methods are suitable to assess interface strength and that the two methods can be confidently compared.

EP-ThP-9 On the Use of Integrated 3D-Profilometry to Bring New Insights on Mechanical Characterization of PVD Coatings by Scratch and Tribology Tests*, **Philippe Kempe**,* Rtec-Instruments SA, Switzerland

Coatings bring advantages for functional surfaces on different relevant mechanical performances: higher wear resistance for a longer lifetime or lower friction coefficient for a reduced energy consumption. The physical phenomena involved at the surfaces under stress conditions represent a key part in understanding the performances of some coatings. Scratch testing characterizes the scratch resistance and adhesion of coatings. Tribology testing characterizes the wear resistance and friction of surfaces in relative contacts. The unique combination of mechanical testing with 3D-profilometry (confocal microscopy and white-light interferometry) provides new insights into the visualization of surface damages occurring in scratch testing (cracks, plastic deformation and delamination of coatings) and tribology (modes of wear and deformation). Examples of characterization with 3D imaging on PVD coatings are shown.

EP-ThP-10 Typical Gaffes During the Nanoindentation of Coatings*, **Esteban Broitman**,* SKF - Research and Technology Development, Netherlands

Nowadays, nanoindentation has become a routinely technique for the mechanical characterization of thin films and small-scale volumes. Thanks to the development of friendly analysis software and advances in high sensitive instrumentation, it feels like the measurement and calculation of hardness and elastic modulus can be easily done by just *"the pushing of one button."* However, the consequences of easy procedures have led many researchers to multiple publications with erroneous data.

Recently, we have reviewed the nanoindentation hardness of materials at macro, micro, and nanoscale (E. Broitman, Tribology Letters, vol. 65, 2017, p. 23). Some misconceptions in the nanoindentation technique were highlighted, and solutions to errors were proposed. In this paper, five typical mistakes in the measurement and data analysis during the nanoindentation of thin films will be critically reviewed, and the possible ways to correct them will be discussed: (1) the wrong area selection to calculate instrumented indentation hardness; (2) the wrong data conversion from Vickers microindentation to Berkovich nanoindentation; (3) the confusion of thermal drift with creep and viscoelastic effects; (4) the wrong correlation of hardness with tip penetration; (5) the preconceptions about a direct relationship between elastic modulus and hardness.

The origins of the aforementioned mistakes will be elucidated from the lack of understanding on contacts mechanics theory, the limits and validation of the Oliver and Pharr's method, and preconceptions transmitted from generation to generation of nanoindenter users. At the whole, it will be stressed that it is not enough to know *"how to push the button"* in order to measure the nanoscale mechanical properties of coatings.

EP-ThP-11 High Temperature Tribological Behavior of TiAlN Coatings with Different Ti/Al Ratios*, C. Pereira, F. Amorim,* Pontifícia Universidade Católica do Paraná, Brazil*; G. Souza,* UEPG, Brazil*; P. Soares, M. Meruvia, **Ricardo Torres**,* Pontifícia Universidade Católica do Paraná, Brazil

Dry machining is an advanced process that places higher demands on machine tools, as the temperature at the interface between a cutting tool edge and a metallic workpiece can vary from 200°C to over 1,300°C. This requires the tool material to have extremely high hardness and thermal toughness besides good wear and adhesion resistance. The use of coatings which act as coolant, isolating the tool from the heat of the cut, improve tool performance and increase the tool lifespan. TiAlN, a currently used coating with high hardness at high temperatures and good wear resistance, has properties that depend greatly on its crystal structure, which are Al content and annealing temperature dependent. Thermal annealing at 700-900°C causes decomposition of $Ti_{1-x}Al_xN$ solid solution into stable c- or w-TiN and AlN, which affect the coating microstructure and, consequently, its properties. Therefore, this work aims to investigate the effect of the Ti/Al ratio on the tribological behavior of $Ti_{1-x}Al_xN$ coatings when submitted to wear conditions at 20 °C, 500 °C and 800 °C. For that samples of Futura Nano® TiAlN ($Ti_{0,56}Al_{0,44}N$) and the Latuma® AlTiN ($Ti_{0,37}Al_{0,63}N$) coatings, deposited on tungsten carbide (WC) hard metal discs by cathodic arc physical vapor deposition (CAE/PVD) by Oerlikon Balzers Revestimentos Metálicos LTDA, were used. The coatings were physico-chemically analyzed by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron (XPS) and Raman spectroscopy; their hardness and elastic modulus were determined, the adhesion evaluated and the tribological performance investigated at 20 °C, 500 °C and 800 °C temperatures performing pin-on-disk wear testing. The results show that for both coating, the annealing up to 800 °C gradually induces the solid solution to decompose in c-TiN and AlN, followed by formation of TiO_2 and Al_2O_3, that lead to decrease in hardness, more pronounced in TiAlN 800 °C (35%) than in AlTiN (18%), and in elastic modulus. COF in the same trend show a more pronounced increase in COF for TiAlN than for AlTiN when the temperature is raised up to 500 °C, followed by a sharp decrease in COF with increasing temperature. For both coatings the wear mechanism changes from abrasive to oxidative with temperature raise and, while no change in failure mechanism is observed in TiAlN, that buckles under compression, for AlTiN it changes from delamination at 20 °C to spalling at 800 °C.

EP-ThP-12 Structural, Phase, Electrochemical, and Tribological Evaluation of TiO_2 and SiO_2 Multilayer Coatings Obtained by Reactive Magnetron Sputtering with Potential Biomedical Applications*, **Julián Andrés Lenis Rodas,*** University of Antioquia, Politécnico Colombiano Jaime Isaza Cadavid and Servicio Nacional de Aprendizaje - SENA, Colombia

In the present study, TiO2 and SiO2 multilayer coatings were obtained by reactive magnetron sputtering using Ti and Si targets in the presence of a mixture of Argon and oxygen. The cross-sectional structure of the coatings was evaluated by scanning electron microscopy, while the chemical composition was determined by energy dispersive X-ray spectroscopy. The phases present in the coatings were analyzed by micro Raman spectroscopy and X-ray diffraction. Additionally, corrosion resistance tests were performed using electrochemical impedance and polarization resistance techniques. Finally, the wear resistance of the coatings was evaluated using a pin-on-disk tribometer.

EP-ThP-13 Tribological Performance of Sliding Pads Against Ti_6Al_4V for Aeronautic Applications*, **Manel Rodriguez Ripoll**, A. Ventura,* AC2T Research GmbH, Austria

The extension and retraction of flaps in commercial aircrafts relies on the displacement of rolling elements along a flap trap made of titanium alloy. A typical flap support relies on 2 sets of 4 rollers to transfer flight/ground and lateral loads from the flap panel into the wingbox. These rollers are part of the carriage assembly and need to be re-greased every C-check (~7500 flight cycles).

With the aim of extending the maintenance intervals of rollers, the present work evaluates the possibility of replacing the sets of rollers by sliding pads. To this end, prospective sliding pad materials are evaluated under reciprocating sliding against Ti6Al4V plates using a flat-on-flat configuration. The experiments are performed under contact conditions similar to those encountered by the rollers in actual flap configurations.

The selected materials comprise a self-lubricating nickel base coating, a high-performance cupper nickel alloy and a diamond-like carbon coating. After the experiments, the total wear volume on the titanium plate is measured using 3D microscopy. Both, the pin and the plate are investigated using scanning electron microscopy in order to elucidate the dominating wear mechanism. Based on the results obtained, the best performing candidates will be upscale via component tests.

New Horizons in Coatings and Thin Films
Room Golden State Ballroom - Session FP-ThP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-ThP-1 Fabrication of Chemical Bath Deposited ZnO Nanorods Layer Based Ultraviolet Light Detectors and Their Device Properties: Influences of Solution Concentration and Thermal Annealing*, **Tomoaki Terasako**, T. Fujikawa, K. Hirota, K. Kobayashi,* Graduate School of Science and Engineering, Ehime University, Japan*; M. Yagi,* National Institute of Technology, Kagawa College, Japan*; T. Yamamoto,* Materials Design Center, Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) has a bandgap energy of ~3.37 eV which enable to realize ultraviolet (UV) light detectors. In addition, the enhancement of specific surface area by nanosizing the ZnO crystallites is expected to improve the performances of the ZnO based UV light detectors. Among the various techniques for preparing ZnO nanorods (NRs), we have paid attention to chemical bath deposition (CBD) because of its simple procedure, cost-effectiveness and low deposition temperature.

The UV light detectors studied in this paper have a structure of PEDOT:PSS/ZnO NRs/ZnO:Ga(GZO) Schottky junction. To clarify influences of the morphologies and surface states of the NRs on the performance of UV light detecting, the PEDT:PSS/ZnO NRs/GZO Schottky junction UV light detectors with the ZnO NRs layers grown from the CBD solutions with the different concentrations and those annealed under the different conditions are fabricated and characterized.

The GZO seed layers were deposited on alkali-free glass substrates by ion-plating with a DC arc discharge. The ZnO NRs layers were grown by CBD using the mixed aqueous solutions of zinc nitrate hexahydrate (ZnNit) and hexamethylenetetramine (HMT) with the different concentration ratios of HMT to ZnNit ([HMT]/[ZnNit]). The [HMT]/[ZnNit] value was changed in the range of 0.24-3.78. The bath temperature and growth time were ~86°C and 60 min, respectively. Thermal annealing was done to some of the NRs layers in the air. The annealing temperature and time were changed in the ranges of 150-450 °C and 20-60 min, respectively. The PEDOT:PSS layer was spin-coated on the surface of the NRs layer, followed by thermal annealing.

Values of diode ideal factors (n), rectification ratios (I_F/I_R) and potential barrier heights at the PEDOT:PSS/ZnO NRs heterointerfaces (Φ_b) were determined from the voltage-current characteristics taken in a dark. The n values smaller than 2 were obtained in the [HMT]/[ZnNit] range of 0.94-2.83. Both the I_F/I_R and Φ_b increased with increasing [HMT]/[ZnNit]. The UV light detector with the NRs layer grown from the CBD solution with [HMT]/[ZnNit]=0.94 exhibited the maximum ratio of photocurrent (PC) to dark current of 92.6. PC spectra were composed of bands with peaks at ~360 and ~380 nm. The intensity ratio of the 360 nm peak to the 380 nm peak (I_{360nm}/I_{380nm}) showed a maximum at [HMT]/[ZnNit]=0.94. The I_{360nm}/I_{380nm} value decreased along with the change in [HMT]/[ZnNit] from 0.94 towards both the lower and higher sides. The increase in annealing temperature led to the decrease in forward current, resulting in the decrease in I_F/I_R.

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FP-ThP-2 Advances in Nanosynthesis by Atmospheric Pulsed Arc Discharges*, C. Corbella, **Sabine Portal**,* George Washington University, USA*; M. Kundrapu,* Tech-X Corporation, USA*; M. Keidar,* George Washington University, USA

Arc discharges sustained at atmospheric pressure are one type of thermal plasma commonly used in welding, material processing, and more recently, in the synthesis of nanomaterials like graphene, carbon nanotubes, and monolayers of transition metal dichalcogenides. Atmospheric arc plasma fed with periodic power pulses constitutes an excellent way to merge all virtues in one plasma nanosynthesis method, namely competitive deposition rates, lower thermal loads, better utilization of the ablated material, economical use of supplied power, and improved stability of discharges. In contrast with standard glow discharge technologies optimized to obtain nanocomposite materials, anodic arc discharges excited with pulsed power show the unique capability of producing high-purity, stand-alone nanomaterials outside of any supporting host matrices. Here, we review recent efforts to implement pulsed anodic arc discharges for nanosynthesis in four distinct directions: (1) tuning the growth and properties of fullerenes and single- and double-wall carbon nanotubes; (2) localized deposition of nanomaterials on substrates with high spatial resolution; (3) synthesis of heterogeneous nanostructures, especially core-shell nanoparticles, by pulsed plasmas in liquids, and (4) design of pulse waveforms able to generate repetitive and stable arc discharges with minimal production of undesired byproducts, like powder macroparticles. Advanced plasma diagnostics and modeling have been introduced to study the kinetics of nanoparticle growth with spatial-temporal resolution, and the outcome of this research constitutes the forefront of atmospheric arc physics nowadays. Future work requires a deeper understanding of the plasma species transport and its connection with pulse parameters and basic structural information of the grown nanomaterials, such as diameter of nanotubes and thickness of atomic multilayer stacks. A crucial milestone consists of decoding the synthesis-structure-properties sequence involving arc discharges, whose correlations should be developed from a neural network approach. In conclusion, the inherent flexibility of pulsed arc processes by modulating current and voltage waveforms is widely beneficial for the engineering of nanostructured materials with tailored properties attractive for electronic, photonic, and biomedical applications.

FP-ThP-3 Structure, Mechanical Properties, and Thermal Stability of (Gd,Hf,Sc,Ti,Zr)-Nitride Thin Films*, **Alexander Kirnbauer**, M. Derflinger,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In recent years the exploration of so-called high-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) is in the focus of many research groups. Their unique properties, attributed to the high entropy (> 1.5R) on the metal sublattice, make them interesting for many applications. These materials combine high-hardness and toughness with increased thermal stability as, due to sluggish diffusion, softening processes are slowed down. In a previous study on (Hf,Ta,Ti,V,Zr) nitride we could show that thin films based on the high-entropy concept exhibit outstanding thermal stability as the coatings are single-phased and the elements are randomly distributed up to an annealing temperature of 1300 °C [1]. At higher temperatures the coating decomposes due to nitrogen loss. To overcome the problem of nitrogen loss Ta and V which form a Me_2N solid solution are exchanged by Gd and Sc which do not exhibit a Me_2N phase. For the synthesis of (Gd,Hf,Sc,Ti,Zr) nitride thin films reactive magnetron sputtering was used. We investigated the influence of nitrogen partial pressure as well as substrate temperature on the phase formation and mechanical properties. Therefore, X-ray diffraction and nanoindentation measurements were carried out. The results show that with low nitrogen partial pressure the coatings are partly amorphous while with increasing nitrogen flow the coatings crystallise in a single-phase fcc structure. With increasing substrate temperature, the hardness increases from 23 to 32 GPa. Additionally, to a variation of the deposition parameters, differential scanning calorimetry (DSC) measurements were carried out to investigate the thermal stability and evaluate temperature ranges where phase changes occur. Furthermore, the coating which exhibits the highest hardness was vacuum annealed up to 1200 °C to investigate the change of the mechanical properties upon annealing. The results show that the coatings stay single-phased up to 1000 °C, whereas at higher temperatures phase separation occurs. The hardness thereby decreases from ~32 to 22 GPa.

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FP-ThP-4 Demystifying the Entropy Forming Ability – The Role of Atomic Size Effects*, **Andreas Kretschmer**, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The desire for rapid materials discovery calls for efficient procedures to explore unknown compositions. This task is especially daunting in the field of high-entropy materials due to the sheer number of possible element combinations to explore. One such procedure has been proposed by Sarker et al. [1], who formulated the so-called entropy forming ability (EFA), using AFLOW-POCC calculations [2], and demonstrated its use on 10 different high-entropy carbides. The tendency to form a single-phase compound was correctly predicted by the magnitude of the EFA.

However, this abstract descriptor lacks a physical explanation, which we have now uncovered by our own simulations. We quantified the lattice distortion in the same carbides as treated in [1], using 10 individual special quasi-random structure (SQS) cells with 64 atoms per carbide, and then calculated the radial distribution function (developed in [3]) of the first coordination sphere. Hereby, we see a strong correlation between the lattice distortion and low EFA values, signifying multi-phase structures. We confirmed this relationship on solid solution carbides with 2, 3, and 4 metals, by calculating both the POCC-derived EFA and the SQS-derived lattice distortion.

Due to the causal relationship of large atomic size mismatch and large lattice distortion we can conclude that the EFA descriptor effectively screens for compositions with low atomic size mismatch, which is already well-known as the Hume-Rothery rules of solid solutions.

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FP-ThP-5 High-Temperature Oxidation Resistance of CrB_2 Coatings Alloyed by Transition Metal Disilicide Phases*, **Ahmed Bahr**, T. Glechner, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Transition metal diborides (TMB_2) are a promising family of materials to be applied as protective coatings in several high-performance applications owing to their high melting point, chemical inertness and outstanding mechanical properties [1]. Among them, CrB_2 exhibits attractive aggregate of properties as good wear resistance, high thermal conductivity and corrosion resistance. However, it suffers rapid oxidation above 600 °C by forming non-protective scales [2].

In this study, we explored the alloying of CrB_2 with secondary TM-silicide phases (TM = Cr, Mo) and investigated the role of the $TMSi_2$ alloying phases on the phase formation, oxidation behavior and mechanical properties of these coatings. We employed direct current magnetron sputtering (DCMS) technique to synthesize alloyed Cr-(TM)-Si-B coatings from compound targets of $CrB_2/MoSi_2$ and $CrB_2/CrSi_2$ providing different compositions. The oxidation kinetics of these coatings have been investigated up to 1400 °C. The alloyedcoatings were analyzed in terms of phase formation and stability, chemical composition, as well as mechanical properties using diverse high-resoultion characterization techniques.

Keywords: CrB_2; Sputtering; Protective Coatings; Oxidation; Phase Stability; Mechanical Properties;

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FP-ThP-6 The Photodetection of the in-, Sn-, and Te-Doped Bi_2Se_3 Nanoplatelets*, **Chih-Chiang Wang**,* National Chin-Yi University of Technology, Taiwan*; H. Shih,* Chinese Culture University, Taiwan*; F. Shieu,* National Chung Hsing University, Taiwan*; A. Lo,* National Chin-Yi University of Technology, Taiwan

The compound Bi_2Se_3 has a narrow band gap of 0.35eV with a rhombohedral crystal structure and is a unique material with the gapless surface-state and the insulating bulk. It is a potential material in the application of photodetection, FET, quantum computation, etc. Bi_2Se_3 has the layered structure composing of 5-atomic layers of Se^1-Bi-Se^2-Bi-Se^1 known as a quintuple layer (QL) with a thickness of around 1 nm. The main bonding type inside the QL is the covalent bonds, and the van der Waals force dominates the bonding between the QLs.

In this investigation, the pure Bi_2Se_3, and In-, Sn-, and Te-doped Bi_2Se_3 nanoplatelets (NPs) were synthesized by the thermal CVD process using horizontal quartz tube at 600℃ under the pressure of 2×10^{-2} Torr, using sapphire as the substrate. The FESEM images show the hexagonal-like morphologies of the NPs. The results of XRD, HRTEM, Raman, and XPS confirm the typical rhombohedral Bi_2Se_3. The photodetection of the pristine Bi_2Se_3NPs shows that the photocurrent and the ratio of photocurrent/dark-current under UV- and under red-light are of the 4×10^{-11} and 23.8×10^{-14}A and 7.7 and 1, respectively, while the co-dopants of In and Sn enhance the photocurrent as well as the ratio of photocurrent/dark-current of the Bi_2Se_3 NPs under UV- and under red-light up to 52×10^{-11} and 3.5×10^{-11}A and 30.7 and 52.2, respectively. The proposed factors can be summarized as the following: (1) formation of the donor defects (In^{3+}_{V0}) and (Sn^{4+}_{Bi3+}), the acceptor defects (V^0_{Bi3+}) and (Sn^{2+}_{Bi3+}), and the neutral defect (In^{3+}_{Bi3+}), (2) the reduced optical band gap of the doped Bi_2Se_3 NPs, and (3) the similar melting point of the powder precursors.

FP-ThP-7 Metallic Zn and Mg Nanowire Coatings by Conventional Reactive DC Sputter Deposition*, J. Zawadzki,* ***Michał, Adam Borysiewicz****, M. Wzorek,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Metal nanowires owing to their enormous surface-to-volume ratio as well as one-dimensional structure, possess outstanding chemical and physical properties in comparison to bulk materials and are interesting for a broad range of absorbing applications. Magnesium nanowires exhibit a high hydrogen absorption capacity (7.6 wt.%), which determines their potential application in hydrogen storage [1]. Along with zinc nanowires, they are successfully used in energy storage devices such as Mg/air batteries [2] andZn/air batteries [3], respectively. Moreover, zinc nanowires are used as a precursor for obtaining Zn-based semiconductors such as ZnO [4,5], ZnS [5], ZnTe [6], ZnSe [5], which are applied widely in optoelectronics, photonics, and sensing.

Despite of a great effort of scientific groups all over the world, the synthesis of nanowires is still a low-scale process related mostly to solution-based synthesis, or chemical vapor transport processes. The methods of physical vapor deposition (PVD) are an excellent instance of bottom-up techniques not requiring chemical solvents, thereby being eco-friendly and yielding more pure nanostructures. The majority of Zn, Mg nanowire synthesis by PVD methods is based on evaporation techniques [7,8,9,10], while the use of the magnetron sputtering technique [11] remains seldom studied.

On the basis of previous works done by our group on the growth of porous Zn films by reactive magnetron sputtering [12,13], we here demonstrate a catalyst-free method of metallic Zn and Mg nanowire growth using conventional geometries of the reactor chamber (not glancing angle) and cathode. We discuss the synergistic effect of oxygen controlling the morphology of the wires and substrate heating for mass transport for nanowire formation usingbothZn and Mg [see Fig. 1,2]. We discuss the different results for both elements. We comment on the structural and chemical properties of the material and apply high-temperature oxidation to convert them into metal-oxide nanowires. The proposed approach is a big step to achieve a universal method for high-purity, ligand-free metallic nanowires using magnetron sputtering deposition, paving the way for their widespread applications.

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FP-ThP-8 Synthesis and Electrical Properties of Gasb Nanowires*,* ***Tzai-Wei Chen****, C. Wang,* National Taiwan University of Science and Technology, Taiwan

In this work, we used anodic aluminum oxide (AAO) template-assisted vacuum die-casting method to prepare GaSb nanowires. Due to their good stoichiometric controllability, low cost and good stability. We can control chemical composition of nanowires easily by modifying composition of bulk. At first, a mixture of gallium ingot (99.99 % purity) and antimony ingot (99.99 %) with an appropriate amount of atomic ratio was entered into quartz tube. Using single zone furnace to heat up to 950 °C and keep for 2 hr then quench into water. GaSb nanowires were synthesized with AAO (annealing at 550 °C for 1hr and non-annealing) template-assisted by vacuum die-casting method. Dissolving time of annealing (400 °C for 24 hr) and non-annealing GaSb nanowires were discussed, respectively. We used different etching solutions (H_2CrO_7 and NaOH solution) to dissolve single and two flakes AAO templates, respectively. The results show that excessive dissolving time and concentration of etching solution cause the nanowires to be damaged or even disappear. The as-fabricated photodetectors via EBL process with 250 nm of Ni as electrode. At 1.0 V bias, the responsivity, EQE and detectivity were calculated to be 7.085 × 10^3 A/W, 1.352 × 10^6 % and 6.384 × 10^{12} Jones, and 2.292 × 10^3 A/W, 3.42 × 10^5 % and 1.713 × 10^{11} Jones under 650 and 780 nm laser illuminated, respectively.

FP-ThP-9 Spacing-controllable core@shell TiO_2@Ru/RuOx Nanotube Array for Biocompatible Stimulating Electrode Applications*,* ***Jia-Jun Li****,* National Taipei University of Technology, Taiwan

Recently, implantable bio-electronic devices have attracted considerable attention owing to their promising potential in monitoring and regulating malfunctioned neural systems and internal organs. In operation, these devices require a bio-compatible interface to facilitate the electrical signal communication between inorganic Si-based circuits and neurons/cells in an aqueous environment. A critical parameter for a bio-electrode is its “charge storage capacity” (CSC). A larger CSC is desirable for electrode miniaturization and sufficient neurostimulation.

We develop a chemical bath for a conformal Ru/RuOx deposition with a thickness of ~15 nm on TiO_2 nanotubes with a length of ~800 nm. In addition, we develop an anodization process that can control the spacing of the TiO_2 nanotube array. These Ru/RuOx nanotube arrays undergo electrochemical analysis in charge storage capacity (CSC), charge injection capability (CIC), and electrochemical impedance to evaluate their potential as neurostimulation electrodes for bioelectronics. Images from electron microscopes confirm the formation of uniform Ru/RuOx on both nanotubes' internal and external surfaces. An X-ray diffraction pattern indicates a good crystallinity of the Ru/RuOx nanotube array. In addition, the cycling lifetime of Ru/RuOx nanotube arrays is evaluated by performing CV scans for 1,000 cycles with a scan rate of 0.1 V/s. The Ru/RuOx nanotube arrays reveal large CSC values and low electrochemical impedances, which are attributed to hollow tubular nanostructure with Ru/RuOx deposition.Additionally, the Ru/RuOx-coated TiO_2 nanotube array exhibits stability, durability, and good biocompatibility.

FP-ThP-10 Nickel Sulfide on Organic Framework for Efficient Hydrogen Evolution Reaction*,* ***Yu-An Chi****,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan*; T. Chang, C. Kung,* Department of Chemical Engineering, National Cheng Kung University, Taiwan*; C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

Hydrogen is eco-friendly and high-efficient energy. Choosing the electrocatalysts for hydrogen evolution reaction (HER) is an essential challenge to water splitting. And then transition metal chalcogenides (TMCs) are easy to prepare and cheap, so this works chemical vapor deposition (CVD) to sulfurize nickel-based metal-organic framework (MOF). The Scanning Electron Microscope (SEM) results of α-NiS-MOF indicate that the extensions on the branch can increase surface area. Experimentally, the electrochemical measurement results reveal that MOF after sulfidation has enhanced HER electrocatalytic performance in 1 M KOH (overpotential is 76.7 mV and 210 mV at the current density of -10 mA/cm^2 and -100 mA/cm^2), and widely improve electrochemical surface area (electrical double-layer capacitance is 0.8336 F/cm^2) compared to nickel foam after sulfidation. At the same time, X-ray photoelectron spectroscopy (XPS) was used to observe the chemical state changes of the surface elements of the electrocatalyst before and after the hydrogen evolution reaction. As a result, this work demonstrates a facile synthesis to optimize nickel sulfide electrocatalysts to improve their electrocatalytic performance for practical applications in future energy devices.

FP-ThP-11 Research of The Growth Mechanism of Solvothermally Synthesized Sb_2Te_3 Nanosheets*,* ***Yen-Jen Lin****, C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

Sb_2Te_3 is one of the topological insulated (TI) materials. Owing to the strong electron spin-orbital coupling, TI materials have conductive surfaces, and the inside parts are insulated. One of the most critical factors in showing the topological insulating property is the thickness of the materials. In this work, we successfully synthesized Sb_2Te_3 nanosheets by solvothermal method. Inspecting the growth process using scanning electron microscopy showed that we obtained Te nanowire initially. Te nanowire then turned into Sb_2Te_3-Te hierarchical nanostructure with increasing of time and finally into Sb_2Te_3 nanosheets. We can suggest the growth mechanism of Sb_2Te_3 nanosheets from the results. We also found that the absorption range in UV-Vis was different by the difference of experimental products. It has become a convenient method to identify the section of the as-prepared products. Furthermore, we also found that by tuning the concentration of

NaOH or increasing temperature, we can successfully synthesize nanosheets with a radius and thickness of 1.5 µm and 9.8 nm, respectively. Being able to well-control the thickness of Sb_2Te_3 nanosheets is very helpful for the subsequent component fabrication.

FP-ThP-12 Exploring Zn-Sn-O (ZTO) Composition Spreads with Combinatorial Sputtering*, **Siang-Yun Li**, Y. Shen, K. Chang, W. Wu, J. Ting,* National Cheng Kung University, Taiwan

Transparent conducting oxide (TCO) films are extensively applied as electrodes in the fields of solar cells and displays, due to their high transparency and excellent conductivity. Multicomponent oxides such as Zn-Sn-O (ZTO) have attracted much attention resulting from no expensive elements, i.e. indium (In), involved. In addition, thermal stability and mechanical strength of ZTO could be tailored as well by varying its stoichiometry. However, making different ratios of Zn/Sn compounds systematically is not trivial.

Combinatorial methodology has been proven its validity in such an application. This approach allows Zn/Sn continuously changing across the single sample area and a feasible intimate mix of Zn and Sn. Therefore, a single ZTO composition spread sample essentially includes a full spectrum of properties to be investigated. A Zn-Sn-O (ZTO) composition spread, consisting of thickness wedges of SnO and ZnO, was prepared using a state-of-the-art combinatorial sputtering system, equipped with a moving shutter and two RF guns for the targets of Zn and Sn, respectively. The thickness gradient was determined using SEM, α-step and SIMS. It was found a smooth thickness variation across the sample area for both ZnO and SnO with the coefficient of determination (R2) ≅ 0.99, indicating a good control of the ZTO composition spread. Structure evolution was characterized using XRD. We found in-situ 500 ºC annealing resulted in crystallization of the samples, where ZnO, Zn2SnO4, ZnSnO3, and SnO2 phases were observed, depending upon the ZnO/SnO ratios on the ZTO composition spread. The resistivity was characterized using a four-point probe on different substrates, which revealed lower resistivity near ZnO-rich. Morphology and optical characteristics were studied as well using AFM, SEM and UV-Vis spectrometry. A clear variation trend of both properties was observed. A systematic study of physical properties of ZTO has been successfully demonstrated.

FP-ThP-14 High-Precision Feedback Control Measurements of the Aluminum-Oxygen Double Hysteresis Curve in Reactive Magnetron Sputtering*, **Josja Van Bever**, K. Strijckmans, D. Depla,* Ghent University, Belgium

Feedback process control [1] of reactive sputtering can be used to achieve specific thin film properties. Although conceptually simple, it is far from trivial to make it reliable and reproducible.

Depending on the initial state of the process two S-shaped process curves can be obtained under certain conditions [1]. It is shown in our most recent work [2-4] that this phenomenon, which is termed *double hysteresis*, is related to implanted oxygen ions that are eroded from the target surface before having reacted with the target metal. While the two S-shaped curves can be clearly observed using *IV-characteristics* [5], no accurate measurements of the states with *feedback control* have been obtained yet.

Feedback measurements of double hysteresis curves are however of great use. First, such measurements deliver a *direct proof* of the phenomenon. When using IV-characteristics, a much broader data set must be obtained [5]. Therefore, the double hysteresis curves cannot be obtained as a function of erosion time or process parameters that are known to influence double hysteresis [2-4]. *With feedback control, the complete double hysteresis curve can be characterized with one target and within a limited amount of erosion.* Finally, good control of discharge voltage and/or oxygen pressure is required to investigate properties of films deposited within the meta-stable region. This is only feasible with feedback control.

In this poster we present high-precision feedback measurements of double hysteresis curves of the aluminum-oxygen system. We address problems encountered during such measurements, ranging from controlling instabilities and relaxation of the sputtering system to accurately switching between different types of feedback. The sampling of totally new target states is discussed. *A new measurement protocol is introduced and implemented in the software package "RSDmeasure"*. We use the developed protocol to obtain the first direct proof of double hysteresis during reactive magnetron sputtering and the *first complete characterization of double hysteresis curves as a function of process parameters* that are of interest to manipulate the reactive sputtering process.

Additional figures and references are found in the supplementary material.

FP-ThP-16 Synthesis and Characterization of Titanium Thin Films by Magnetron Sputtering and the Effect of the Addition of a Graphite Anode*, D. Jacobo Mora, M. Martinez Fuentes, **Stephen Muhl**,* Universidad Nacional Autónoma de México

Titanium (Ti) thin films were deposited onto glass substrates using two different setups: normal DC magnetron sputtering [MS] and by MS assisted by a secondary graphite anode discharge. The films were analysed as a function of the argon gas pressure, the MS power and voltage applied to the anode. The properties of the films, film thickness, adhesion and hardness were studied as a function of the experimental paraments used for the deposition. Lastly, optical emission spectroscopy (OES) was used analyse the two types of discharge.

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Keywords: Magnetron sputtering; Optical emission spectroscopy; Deposition rate; Adhesion.

FP-ThP-17 Developing Materials for Future Generation Nuclear Reactors*, **Vladimir Vishnyakov**,* Huddersfield University, UK

Nuclear reactors have a very extended list of material requirements. Long-term environmental concerns related to decommissioning add to the list of requirements and limit the score of chemical elements which can be utilised. Stringent safety obligations necessitate treating almost any modification of material properties in service as damage. Self-healing in broad sense materials need to be well understood and crafted to enable safe future nuclear reactor operation. The self-healing relies on repair mechanisms when the material preserves its properties under severe conditions and radiation damage. Atomic level processes such as point defect recombination, defect diffusion, defect sinks and process activation energies need to be well understood. Self-healing processes in materials for nuclear energy generation will be examined on the developed solutions in thin film High Entropy Alloys, High Entropy Ceramics and MAX phases. Empirical suggestions for future development of nuclear reactor alloys will be discussed.

FP-ThP-19 Effect of Surface Treatment on the Bifunctional Performance of Core-Shelled High Entropy Spinel Oxides*, **Yi- Ting Jhuo**,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; J. Ting,* National Cheng Kung University (NCKU), Taiwan

Several high entropy spinel oxides were prepared using microwave hydrothermal method and used as electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). The surface plasma treatment was conducted under different powers, times, gases, and pressures. The resulting samples were first characterized using X-ray diffractometer, scanning electron microscope, transmission electron microscope, energy dispersive spectrometer, X-ray photoelectron spectroscopy. Electrochemical performance was evaluated using electrochemical impedance spectroscopy, linear sweep voltammetry, cyclic voltammetry. The effect of surface treatment using plasma on the bifunctional OER/ORR performance is addressed.

Surface Engineering - Applied Research and Industrial Applications
Room Golden State Ballroom - Session GP-ThP
Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-ThP-1 Enhanced Corrosion Resistance, Wear and Antibacterial Properties of TiO_2-Incorporated Micro-Arc Oxidation on AZ31 Magnesium Alloy*, **Wei-Hao Chen**, Y. Lee, S. Huang, Y. Chu,* National Taiwan University, Taiwan

As one of the green materials, magnesium alloys are known for their high specific strength and good workability, and thus widely used in various industrial fields, especially in automobiles and aircraft. However, magnesium alloys tend to suffer severe corrosion due to their high chemical activity, which calls for proper surface modification. Among varied surface modification processes, micro-arc oxidation (MAO) can form a ceramic oxide layer on magnesium alloys to improve their corrosion resistance and wear resistance. Nonetheless, even with the elevated corrosion resistance, the porous structure of MAO coating still leaves a diffusion path for corrosive species to penetrate through the coating and react with the substrate. Therefore, in order to modify the microstructural defects in the MAO coatings, this study investigates the effect of TiO_2 nanoparticle addition on the MAO process operated in a fluoride-containing silicate electrolyte system, including corrosion resistance, microstructure, chemical composition, and photocatalytic effect of the coatings.

The preliminary experimental results showed that the increase in the concentration of TiO_2 nanoparticles increased the number of Rutile-TiO_2 in the MAO coating, which results in both an elevated hardness and a change in color from white to gray-black. As observed in electrochemical impedance spectroscopy (EIS), the addition of 2.5g/L TiO_2 of nanoparticle exhibits no significant influence on the corrosion resistance and the total impedance is around 107 kΩcm^2.However, the coating formed with a high concentration 7.5g/L of TiO_2 nanoparticles performs better corrosion resistance which elevates the total impedance to over 600 kΩcm^2 and the defects within are effectively reduced. In addition, we also noticed that the different power modes and pause time ratio used in MAO process significantly affect the amount of TiO_2 incorporated, which resulted in tunable corrosion, wear and antibacterial performance of MAO coating.

Keywords: Magnesium alloy, micro-arc oxidation, TiO_2 nanoparticles, EIS

GP-ThP-2 The Influence of the Pause Time on Microstructure and Corrosion Resistance of AZ31 Magnesium Alloy Micro-Arc Oxidation Coating*, **Shih-Yen Huang**, Y. Lee, Y. Chu,* National Taiwan University, Taiwan

Magnesium is the lightest structural metal in the world. As known for high specific strength, formability and recyclability, magnesium alloys have received much attention in various fields. However, poor corrosion resistance of magnesium alloys resulting from the high chemical activity still blocks their way into application. To enhance the corrosion resistance of magnesium alloys, various means of surface engineering optimizing the surface properties bring worldwide notice, and micro-arc oxidation (MAO) process is one that has been studied for decades. With high electric potential generated on the surface, MAO process improves the corrosion resistance of magnesium alloys by fabricating hard ceramic oxide coatings thereon. Nonetheless, both the thickness of MAO coatings and microstructural defects within are affected by many factors in MAO process, among which the electrical parameters are found to be of much importance and directly influence the properties of the coating. In former studies, some of the electrical parameters have been widely discussed, including current density, frequency, and duty ratio, while the waveform of the voltage employed is yet seldom discussed separately.

In this study, the effect of the pause time after anodic and cathodic polarization in MAO process is investigated. The preliminary experimental results showed that in a bipolar MAO process with fixed total input current, the pause time has apparent influence on the corrosion resistance of MAO coating. In addition, we found that the pause time after anodic polarization played a significant role in controlling corrosion resistance of MAO coating under the same duty ratio condition. As revealed by EIS analysis, the total impedance of the MAO coated specimen with anodic pause period only is about 6 times greater than that of the specimen with cathodic pause period only, while the coating thickness is almost the same.

GP-ThP-3 Microstructure and Properties of HVOF Sprayed Coatings Remelted by Laser*, E. Jonda, **Marek Sroka**, W. Pakieła,* Silesian University of Technology, Poland*; T. Jung,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland

High-Velocity Oxy-Fuel is a technology that enables the production of coatingsincluding a broad group of materials (metallic, ceramic, cermet, composite, carbides, and polymers) and is most often used to regenerate worn parts of machines or devices or to protect from effect of high temperature, corrosion, and erosion. The undoubted advantage of this method is the slight heating of the substrate during the coating deposition process, thanks to which microstructural changes and substrate deformation are significantly reduced. A characteristic feature of coatings deposited in this way is also the adhesive method of joining the coating with the substrate, as evidenced by the wavy line of these joints resulting from the mechanical jamming of plasticized powder grains during the spraying process.

Laser surface treatment aims to melt the entire thickness of the coating and create a metallurgical bond with the substrate or to melt the coating only to a certain depth. The advantage of this type of surface treatment is the possibility of precise control of remelting process by appropriately selected parameters.

The paper presents microstructure investigations and selected properties of coatings deposited by thermal spraying HVOF (High-Velocity Oxy-Fuel) with the use of WC-CrC-Ni powder and then laser remelted with different values of the laser beam power (YLS-4000). The coatings were heat sprayed with the supersonic method on a substrate made of AZ31 magnesium alloy.

Microscopic investigations and fracture morphology were carried out by scanning electron microscope (Supra 35, Zeiss, Oberkochen, Germany) with secondary electron and backscattered detectors. In addition, chemical composition was analyzed by EDS (Energy Dispersive X-ray Spectroscopy). The experiment was designed to investigate the effects of laser beam power 2 - 3 kW) on microstructure and properties of the remelted coating. Studies were supported by microstructural analysis of remelted zone (RZ), heat-affected zone (HAZ), undissolved carbide particles, substrate material, and precipitates formed during rapid solidification. The study also investigated mechanical features like hardness and instrumented indentation.

GP-ThP-4 Fabrication Feasibility Study on Cu and Cu Alloy Coating for Spent Fuel Canister of Deep Geological Disposal*, **Young-Ho Lee**, Y. Jung, D. Kim, S. Yoon, H. Kim,* Korea Atomic Energy Research Institute, Republic of Korea

The high-level nuclear waste containers should be designed as a multi-barrier system, which is consists of carbon steel vessel and copper canister including bentonite as the backfill material. Due to the manufacturability and economical concerns of copper canister, the container design is considering the applicability of copper or copper alloy coatings on a carbon steel vessel by using additive manufacturing or traditional welding methods including wire arc additive manufacturing (WAAM), arc plasma spray (APS) and direct energy deposition (DED). This copper coating layer serves as a corrosion barrier and its microstructural characteristics is a key factor for determining corrosion resistance of the high-level nuclear waste container at site-specific geological and groundwater properties. In this study, the microstructural characteristics of copper and copper alloys coatings were examined using SEM and electron backscattering diffraction (EBSD), which fabricated by WAAM, APS and DED methods. The coating layers shows completely different microstructures and porosity distribution, which depends on the applied coating methods. However, no significant difference of uniform corrosion resistance can be found due to fine-grained structures of each coating layer when compared to reference wrought copper

GP-ThP-5 Etching of B-doped Diamond Films Using RF Plasma*, **Ryuhei UEDA**,* Chiba Institute of Technology, Japan

Diamond has not only the highest hardness and but also its excellent wear resistance and shape stability, it has been applied as a tool. However, machining of diamond is difficult due to its high hardness.In this study, the effects of RF power and pressure on surface properties on the etching of BDD (boron-doped diamond)by inward RF plasma were investigated.

BDD films were used as the sample. A mixture of Ar and O_2 was used as the etchant with H_2O in the bubbling tank. Pressure was varied from 50 to 200Pa, and RF power was from 50 to 200W. Mo was used as a mask. Surface of the sample was observed by scanning electron microscope (SEM). The surface profile was evaluated by Confocal Laser Scanning Microscopy, and the etching amount was calculated from the depth profiles. Structural analysis was performed using Raman spectroscopy, and surface electrical resistance was measured using the four-probe method. Plasma diagnosis was performed using an optical emission spectrometer during etching.

Clear crystal habit was observed in all SEM images, but the shape was changed like a sphere after etching. The amount of etching was increased with increasing RF power and pressure. In Raman spectra, a peak due to B-B at 500 cm^{-1} and B-C at 1230 cm^{-1}, and a shift to the low wavenumber due to high boron doping near 1300 cm^{-1} were recognized. The B-B and B-C peak heights relative to the diamond peak height increased in the treated area compared with the untreated area only at RF power of 200 W and pressure of 200 Pa. The surface

electrical resistance of the treated area was same or higher than that of the untreated area. From the emission spectra, Ar (389,696 to 810 nm), O (777 nm), OH (282, 308, 357 nm), Hα (656 nm) were observed under all conditions. CO (283 to 629 nm), CHO (330 nm), and BH (433 nm) emitted from the etching of the sample were observed. The intensity ratio of CHO, BH and BO to Hα were increased with RF power. However, the intensity of CHO to Hα decreased with etching time, and the intensity of OH was increased. This is because of the carbon substance is etched as CHO from the BDD at the start of the treatment, but as time elapsed, boron oxide forms on the surface, inhibiting the progress of the etching.

From the above results, it can be concluded that during etching of BDD, due to irradiation damage caused by physical etching by Ar in the plasma, the crystalline diamond becomes amorphous, and the carbon substance is formed as CO and CHO by O and OH dissociated from H_2O, the boron substance is removed as BH by atomic hydrogen.

GP-ThP-6 Fabrication of Si/C/SiNW Arrays Sandwich Structure at Different Annealing Parameters for Solar Cell Application*, **Ai-Huei Chiou**, J. Wei,* National Formosa University, Taiwan

A Si/C/SiNW arrays ssandwich structure has been fabricated by RF magnetron sputter. The effect of the RTA parameters on the structure, element, hydrophilic-hydrophobic and electrical property of the Si/C/SiNW arrays were studied. The XRD patterns of Si/C/SiNW arrays annealing at different time that clearly show that all structures have an amorphous phase. In this study, a PIN solar cells using titanium dioxide and Si/C/SiNW arrayssandwich structure hybrid. A Si/C/SiNW arrays with un-annealing was relatively hydrophile with a contact angle of 8.42.±4.42°. Heat treatment of the Si/C/SiNW arrays resulted in a substantial and statistically significant increase in surface hydrophobic, which was manifested by a dramatic enhancement of the contact angle to 124.83±2.18°. Raman scattering study of Si/C/SiNW arrays exhibited a development of the relative intensity of the D and G band with increasing of the annealing temperature. The conductivity of Si/C/SiNW arrayssandwich structure t is greatly affected by the annealing time. The present results indicated that the power conversion efficiency (PCE) of the sandwich structure without annealing treatment is superior to that of the annealed solar cells.The PIN solar cells used Si/C/SiNW arrayssandwich structure before annealing, in which the Voc is of 0.046mVand efficiency is of 1.13 × 10^{-3}%.

GP-ThP-7 Barrier Properties Enhancement of Bio-Based Polymers by Means of Multilayer Coatings Applied by Pulsed DC PACVD*, C. Nicoletti, C. Forsich,* University of Applied Sciences Upper Austria*; **Francisco A. Delfin**,* University of Applied Sciences Upper Austria, Austria, National University of Technology, Concepción del Uruguay, Argentina*; S. Augl, S. Danninger,* University of Applied Sciences Upper Austria*; M. Schachinger,* (University of Applied Sciences Upper Austria*; C. Burgstaller, D. Heim, J. Weghuber,* University of Applied Sciences Upper Austria

Biopolymers are very promising materials that find use in several industrial applications, ranging from packaging and food industry to the pharmaceutical and biomedical fields. The main advantages of biopolymers include biocompatibility, biodegradability, non-toxicity and renewability. Despite all their great benefits, biopolymer foils also exhibit a few drawbacks that limit their application, such as poor barrier properties. To overcome these restraints, thin-layer coatings can be applied. One method used for the deposition of coatings is the RF PACVD process, which is difficult and expensive to scale up. In this work, the possibility of coating biopolymer foils using a commercially available bipolar DC pulsed system was studied. This technique turns out to be cheaper and easier to scale up compared to the RF plasma. Polylactic acid and cellulose-based foils were used as substrates. Silicon-based films with a silicon oxide top layer as well as carbon- and silicon-based multilayers were deposited. The coatings were produced according to two-step processes: for the Si/SiOx coatings, the first step consisted of the deposition of the Si-layer followed by a post-oxidation treatment step, while the multilayer coatings comprised two deposition steps, with the first layer being carbon or silicon and the top layer silicon or carbon, respectively. HMDSO and acetylene were used as silicon and carbon precursors. For the Si/SiOx-films, the effect of the coating thickness (up to 15 min deposition time) and the post-oxidation step on the barrier properties of the bio-foils was examined. For the Si- and C-multilayer coatings, a deposition time of 15 min for each layer was used. The generated films were characterized by ATR-FTIR Spectroscopy, WVTR, OTR, SFE and SEM. The ATR-FTIR spectra did not show a clear distinction between coated and uncoated foils, in contrast to the same coatings on PE or PP. The barrier properties were substantially improved for cellulose foils, with a reduction of WVTR up to 66% for the regenerated cellulose-films coated with SiOx and up to 73% for the CA-based foils coated with carbon followed by silicon as top layer. No significant improvements were observed for PLA. SFE was in the range 30-52 mN/m for the Si/SiOx-, 16-25 mN/m for C/Si- and 45-48 mN/m for the Si/C-coatings. SEM observations of the cross-sections permitted to estimate the thickness of the coatings, which was around 100 nm. This study highlights the opportunity to use the bipolar pulsed DC PACVD technique as an alternative for coating polymeric materials, with the appropriate adjustments.

GP-ThP-8 Effect of Fluoride on Adhesion of Electroless Nickel–Phosphorus Coating on MAO-Coated AZ31B Magnesium Alloy*, J. Lee, C. Lee,* National Defense University, Republic of China*; J. Lee,* Lung Hwa University of Science and Technology, Taiwan*; S. Jian,* Ming Chi University of Technology, Taiwan, Republic of China*; **Ming-Der Ger**, A. Cheng,* National Defense University, Republic of China

The MAO of magnesium alloy is nickel-phosphorus (Ni-P) plated. The Ni-P coating can make the MAO coating conductive, which is convenient for subsequent processing and improves its applicability.Most of references about electroless nickel-phosphorus plating of magnesium alloys mentions that fluoride is added to the electroless plating solution. It is also known from previous study that fluoride has a certain protective effect on magnesium alloys and keep the electroless plating solution in a stable state.

In this study, the MAO of magnesium-aluminum alloy was improved its corrosion resistance. The MAO coating of magnesium-aluminum alloy with high corrosion resistance and uniform pore size was coated with Ni-P plating, Focus on different level fluoride (NH4HF2) in the electroplating solution. fluoride-free, 6 g/L ,12 g/L and 18 g/L , observing the bonding force and corrosion resistance of MAO coating with Ni-P coating.Scanning Electron Microscope (SEM) and Elemental Composition Analysis (EDS) Mapping to observe surface morphology and elements,The adhesion of Ni-P coating test by the Posi-test AT-M pull-off adhesion tester, PDP tests by Versa STAT 4 potentiostat/frequency to analyze the corrosion behavior of the MAO/Ni–P composite coatings, and the salt spray test (SST) is used to judge the characteristics of the Ni-P coating with different level fluoride.

The results show that the nickel plating solution without fluoride ions will corrode the high corrosion resistance MAO coating, and the Ni-P coating will be coated and peeled off. , it will also damage the MAO coating. In fluoride-free situation , the broken MAO coating has poor bonding force with Ni-P coating and very easy to peel off, a complete Ni-P coating can be obtained by adding the appropriate amount of fluoride, and the adhesion of Ni-P coating 6 g/L ,12 g/L and 18 g/L respectively 5.62Mpa, 7.61 Mpa and 2.33 Mpa. Ni-P coating 12 g/L has better adhesion and corrosion resistance on the MAO coating of AZ31B magnesium alloy.

GP-ThP-9 Effect of Mechanical Stress on Electrical Characteristics of Low-Dielectric-Constant Dielectric Materials*, **Yi-Lung Cheng**,* National Chi-Nan University, Taiwan

This paper investigated the effects of mechanical stress on the electrical characteristics of SiO_2, dense low-*k*, and porous low-*k* dielectric films. Both tensile and compressive stresses were applied to the metal-insulator-semiconductor (MIS) capacitor by bending the device. Both mechanical stresses increased the capacitance and reduced the breakdown field for SiO_2, dense low-*k*, and porous low-*k* dielectric films while bent. Compressive stress yielded a larger reduction in the breakdown field and the porous low-*k* film had a serious degradation. As the mechanical stress was removed, the electrical properties were recovered. Furthermore, the breakdown fields of low-*k* films were improved by performing the specified mechanical stress.

GP-ThP-10 Monolithic Integration of Lead Selenide Films via Surface Morphology Engineering*, **Sejeong Park**, J. Park,* Opto Diode Corporation, USA

The major challenges in lead chalcogenide-based optoelectronic devices processed with chemical bath deposition (CBD) are uncontrollable electronic properties of thin films. The morphologies and the chemical functions of surfaces strongly influence adhesion at interfaces within the deposited layer and surface-modified supporting substrate as well as the physical properties of the synthesized thin film. Surface treatment modifies these properties at the surface and can improve adhesion. However, the outcome depends upon the specific parameters of the processing.

In this work, we employed the surface modification strategy onto silicon-based substrates to explore how surface treatment parameters will affect the growth of lead selenide thin films in CBD growth and their opto-electrical characteristics, applicable for developing low-cost mid-wavelength IR photodetectors. As a model system, we have chosen CBD-grown PbSe thin films on oxide-free and oxidized Si substrates. To control the interfacial stability between PbSe layers and Si substrates, we utilized a surface plasma treatment of Si substrates and systematically investigated the effects of surface conditions onto the physical properties of as-grown PbSe thin films. To understand the underlying growth process of the integrated PbSe thin films, we characterized the optical and electrical properties using a conventional PL, an IR-PL, and I-V measurements. We also investigated the structural and surface morphology of the PbSe films by means of XRD and SEM/EDS.

GP-ThP-12 Degradation Effect of Multilayer Stacking Super-latticeSi/SiGe/Sichannel on FinFET and GAAFET Device*, Yu-Hsin Chen,* National Tsing Hua University, Taiwan*; D. Ruan,* Fuzhou University, China*; K. Chang-Liao,* National Tsing Hua University, Taiwan

In recent years, silicon-germanium (SiGe) has been widely used as the substrate material for the fin field effect transistor (FinFET) or gate-all-around field effect transistor (GAAFET) to extend Moore's law beyond 3 nm technology node, due to its superior processing compatibility and higher carrier mobility. In order to further shrink the device scale and increase the drive current, multilayer stacking SiGe, especially the super-lattice (SL) Si/SiGe/Si buried channel, was proposed to replace monolayer SiGe without increasing process complexity. However, the sub-threshold slope and device reliability may be sacrificed, due to the Ge out-diffusion and the defects generated from lattice gap over critical SL thickness. In this work, both the FinFET and GAAFET devices with different periods of SL Si/SiGe/Si were fabricated for investigating the degradation effect. Notably, the mobility of device with one period SL Si/SiGe/Si is higher than that of sample with two periods. It means that the carrier mobility might be serious degraded by those defectsunexpectedly, even exceeding the enhanced mobility effect caused by a higher Ge concentration.

GP-ThP-13 Industrialization of Precious Metal-Free Bipolar Plates for Use in Pem Fuel Cells*, Julian Kapp,* *V. Lukassek, V. Mackert,* ZBT GmbH, Germany*; M. Welters,* KCS Europe GmbH, Germany*; H. Hoster,* ZBT GmbH, Germany*; R. Cremer, P. Jaschinski,* KCS Europe GmbH, Germany

Limiting climate change by reducing global CO2 emissions is one of the key challenges of the 21st century. Achieving the climate targets requires a transformation of our energy systems and a complete switch to zero-emission technologies in all energy consumption sectors. Hydrogen and fuel cells will play a central role in this in the future and will become one of the key technologies.

In order to make fuel cells accessible to a wider range of applications, cost reduction is required. An important component of the fuel cell with great cost reduction potential is the bipolar plate. At the same time, the quality of the bipolar plate is of crucial importance for the function of a fuel cell and its lifetime.

Metallic bipolar plates have high thermal and electrical conductivity, good mechanical properties and low permeability to the gases hydrogen and oxygen. Furthermore, metallic BPP can be easily transferred to mass production at low cost. Stamping processes, such as traditional stamping and hydroforming, are established manufacturing processes for mass production of metallic BPP.

Due to the possibility of producing metallic BPP very thin and thus very light, they are of great interest especially for mass production and mobile applications. A disadvantage of metallic BPP is their tendency to corrode and form passive layers in fuel cell environments, which increases the contact resistance to the adjacent GDL. The metallic BPPs therefore require a corrosion-resistant and electrically conductive coating.

One aim of this work is the further improvement of developed protective coatings with excellent electrical conductivity on metallic bipolar plates for PEM fuel cells. The coatings were optimized with respect to their corrosion protection properties. The PVD (physical vapor deposition) arc and sputtering processes are used to apply these coatings. When selecting the material for the bipolar plate, attention is paid to cost-effective steel and aluminum alloys. Precious metals are completely avoided in the coating material for cost reasons. At the same time, the coatings were optimized for a series production process to meet the productivity requirements for the large number of bipolar plates.

GP-ThP-15 Corrosion Resistance in Synthetic Seawater Plus Diluted Sulfuric Acid of DLC/Crc/Cr Multilayers Co-Deposited by HIPIMS and DCMS*, Martin Flores,* *L. Flores Cova,* Universidad de Guadalajara, Mexico

Diamond-like carbon (DLC) and CrC coatings are utilized in a wide range of applications to reduce the sliding friction and improve wear and corrosion resistance of bearings and other components. AISI 4317 steel is used in bearings of crane grabs for the transport of minerals with sulfur content in port facilities. These steels suffer from wear and corrosion promoted by sulfide and chloride ions at the port. The multilayers were deposited by High Power Impulse Magnetron Sputtering (HIPIMS) and DC magnetron sputtering (DCMS), using HIPIMS for Cr target and DCMS for C target. The ion etching cleans the substrate and the metal ion etching promotes a good adhesion to the substrate. In this work the metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target. This work reports the results of the potentiodynamic polarization and Daimler-Benz Rockwell C test methods used to evaluate corrosion and adhesion respectively. Synthetic seawater and seawater plus dilute sulfuric acid (.01M) were used as electrolytes. Raman and XPS techniques were used to study the sp2 and sp3 content of the DLC layer. SEM was used to observe the cross section and corroded surface of coated and uncoated samples of AISI 4317 steel. The structure of the multilayer was studied by XRD. The results show an improvement in the corrosion resistance of the samples coated with the multilayer.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Golden State Ballroom - Session HP-ThP

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-ThP-1 Femtosecond Laser Ablation (FESLA) XPS – A Novel XPS Depth Profiling Technique for Thin Films, Coatings and Multi-Layered Structures*, Mark Baker,* *S. Bacon, S. Sweeney,* University of Surrey, UK*; A. Bushell, T. Nunney, R. White,* ThermoFisher Scientific, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers through the use of argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. A prototype XPS depth profiling instrument has been constructed which employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (10s - 100s microns) and is much faster than sputter XPS sputter depth profiling. FESLA XPS results will be shown for selected bulk, thin films and oxidised surfaces and the outlook for this new technique discussed.

HP-ThP-3 *in Situ* and Real-Time Measurements in Metallic Thin Film Research and Applications: The MISSTIC Experimental Setup*, Ramiro Zapata,* Laboratoire Surface du Verre et Interfaces UMR 125 / Institut des 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

Magnetron sputtering deposition is one of the main PVD deposition techniques, for a wide range of materials ranging from metals to semiconductors and insulators. Current research efforts in thin film growth and characterization are often hindered by extraneous interferences and impurities, stemming from film surface contact with the atmosphere between the film elaboration and *ex situ* characterization steps.

In order to overcome these challenges, the **MISSTIC** (Multilayers and Interfaces Sputtered-deposition on STructured substrates and In-situ Characterization) vacuum experimental setup was developed. This setup (Fig-A) is composed of a deposition chamber and an analysis chamber, connected via a load-lock mechanism through which samples can be transferred under vacuum conditions. This internal sample transfer between chambers avoids contact with the atmosphere, thereby avoiding interfering phenomena such as film ageing and adsorbed species from air. As such, by eliminating the need for capping (protective) layers on top of the deposited metallic films, *in situ* X-Ray Photoemission Spectroscopy (XPS) in the analysis chamber can characterize the deposited film surface chemistry, without any depth profiling necessary. Sample annealing under vacuum, with an electron beam setup located in the same chamber, can even be used for studying elemental diffusion in thin film stacks. Finally, surface characterizationusing *in situ* Low Energy Electron Diffraction (LEED) is used for the study of crystallized surfaces, and for studying thin film epitaxial growth – such as for the case of Ag film sputtering on ZnO underlayers.

Real-time characterization techniques are another kind of measurement, present in the **MISSTIC** deposition chamber. These measurements are carried out during film deposition, and allow for the detection of different stages of film growth: they include Surface Differential Reflectance Spectroscopy (SDRS), film electrical resistance, and a new method for film mechanical stress measurements (PReMC, Refs[1,2]. For the study of Ag film growth on silica substrates during magnetron sputtering deposition, real-time measurements allow for the detection of the nucleation, growth, coalescence, percolation, and continuous film formation threshold thicknesses. Combinations of these techniques are used for studying the effects of different parameters of the sputtering deposition process, on the Ag thin film growth mechanism.

Ref1: Sergey Grachev et al 2022 Nanotechnology 33 185701

Ref2: Quentin Hérault et al. Acta Materialia 221 (2021) 117385

HP-ThP-4 Ultrasonic Contact Impedance Measurements at Nanometer Scale*, **Jurgis Daugela**,* Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

Active ultrasonic microhardness aka Ultrasonic Contact Impedance (UCI) testers have been around since 1970s.While UCI microhardness testers relied on microscale contact elastic deformation, this technique, *at the nanoscale*, has a new application in the area of multi-cycling nanofatigue monitoring [1, 2]. A theoretical contact mechanical impedance model was explored during design stage in order to match impedances of ultrasonic tip/resonator and contacting surface.The contacting surface impedance consists of the contact compliance term since reactive terms are insignificant at the nano scale. The resulting operational mechanical impedance functions were employed in design optimization of the ultrasonic tip.

With the newly developed instrumentation such as the ultrasonic nanoindentation tip integrated into a nanoindentor that localizes nanonometer range displacements, millions of precisely placed loading cycles can be delivered within seconds.Thin film interface breakthrough induced nanoindentation displacement excursion and simultaneously monitored ultrasonic signals indicate fatigue failure and provide the number of failure cycles.

An experimental ultrasonic nanoindentation tip operated at 272kHz is delivering approximately 4.5 million cycles till 80nm thick SiC film interface fracture.It had to be pointed out that ultrasonically induced nanofatigue cycles reasonably agree with Ratcheting and Mason-Coffin fatigue models.

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HP-ThP-5 A Direct Correlation between Structural and Morphological Defects of Tio$_2$ Thin Films on Fto Substrates and Photovoltaic Performance of Planar Perovskite Solar Cells*, **Mario Alejandro Millan Franco**,* IER-UNAM, Mexico

Titanium oxide (TiO2) is often deposited on conductive fluorine doped tin oxide (FTO), followed by a thermal annealing to obtain anatase phase for planar perovskite solar cells (p-PSCs). Although high annealing temperature is desirable to increase the crystallinity of TiO2, morphological changes are induced in both TiO2 and FTO. In this work, structural and morphological changes in thermally annealed (400 - 550°C) FTO, TiO2 and TiO2/FTO system are identified and semi-quantified by X-ray diffraction, scanning electron and atomic force microscopy. 400 °C annealed TiO2 show the lowest crystallinity and the highest dislocation density, resulting in the lowest efficient p-PSCs. Conversely, 550 °C annealed TiO2 exhibits the highest crystallinity and lowest dislocation density, but the FTO film undergo an increase of surface roughness by more than 25%. Additionally, the 550 °C annealed TiO2 coatings on FTO show the highest concentration of surface ruptures and the largest exposed FTO substrate area. Such morphological defect concentration originates a larger direct contact of FTO and the perovskite film. TiO2 thin films annealed at 450 or 500 °C show a compromising between the crystalline structure and defect density, giving a better photovoltaic performance of p-PSCs prepared under ambient conditions with a conversion efficiency of 16.3%.

HP-ThP-6 In-Situ Stress Evolution in Sputtered Metal Alloy Films*, **Vania Jiao**, C. Appleget, C. Panetta, K. Folgner, J. Barrie,* The Aerospace Corporation, USA

Space-based optical glass sensors are sensitive to the harsh radiation of Earth's Van Allen belts, and one approach to protect these sensors is by using thick optical coatings. However, thick films of radiation absorbing materials, such as silver or gold, often exhibit increased surface roughness compared to the thin films used for high reflectivity mirrors. This surface roughness degrades the desired reflectivity and increases the optical scatter as film thickness increases. Alloying Ag with Al is an approach towards improving the surface roughness of these thick optical films, but alloying can lead to high residual stresses. These residual stresses are compositionally dependent and can be detrimental to surface figure and film adhesion. In this work, in-situ stress of sputtered AgAl alloy thick optical films (≈1 µm thickness) was monitored to better understand stress evolution. Films of varying composition were deposited on pre-characterized Si substrates via RF magnetron sputtering to investigate the interplay of alloy content on microstructure, stress, and optical performance. For the AgAl alloys, the focus was on compositions within the intermetallic region, as this has been shown to yield films with greatly improved optical properties. All AgAl thick films showed improved surface roughness and scatter performance compared to their thick undoped Ag counterparts. In-situ stress measurements for all compositions revealed compressive films, developing into a more compressive state with increasing thickness. However, ex-situ stress measurements revealed films with tensile residual stresses. Monitoring the film stress post-deposition and during venting showed that the films underwent a stress reversal as they cooled. Various venting conditions were explored to further investigate this phenomenon.

HP-ThP-7 Characterising Thin Films Using Hard X-Ray Angle Resolved XPS*, **T Swift**,* Kratos Analytical Inc, USA*; J. Counsell, S. Coultas,* Kratos Analytical Ltd, UK*; C. Tupei, Y. Li,* Nanyang Technological University, Singapore

High-energy X-ray photoelectron spectroscopy has been used to determine the structure and chemical nature of HfOx thin-films deposited on Alumina substrates.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased uniformity and control of layer thickness. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS allowed determination of film thicknesses up to 7nm however beyond this it was not possible to accurately quantify the Si 2p peak from the substrate. Ag Lα excitation results in electrons of higher KE for the same photoemission peak. This increases the over-layer effective attenuation length which in real terms means the sampling depth increases by approximately a factor of two.

Here we use high-energy Ag XPS (Ag Lα radiation - 2984eV) in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data is analysed using algorithms linked with physical data parameters based on thermodynamic models, maximising the entropy to find a solution of best fit [1] and generate a reconstructed depth profile over the greater sampling depth provided by the higher energy excitation source.This approach allows the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina and a combination of the two not possible with the conventional Al Kα excitation source. The use of the higher photon energy excitation source mitigates the need for destructive depth profiling using Ar-ion beams to remove material with the risk of ion beam induced chemical changes.

We conclude with calculation of film thickness, the chemistry at the interfaces and the usefulness of Ag Lα excited XPS for such applications.

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HP-ThP-8 The Anisotropic Behavior of Super-Hard TiB_2 Films Studied by Synchrotron Nano-Diffraction, ***Anna Hirle**, C. Fuger, R. Hahn, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, A-1060 Vienna, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; Institute of Materials Science and Technology, TU Wien, A-1060 Wien, Austria

For hexagonal structured materials, anisotropic properties are well known due to their specific lattice distortion with respect to basal and prismatic planes. In the case of magnetron sputtered transition metal diborides direction-dependent hardness was reported for WB_{2-z}, ZrB_2, as well as for TiB_2 [1-3]. In more detail, the anisotropic behaviour of hexagonal AlB_2 structured diborides is explained by a more difficult dislocation movement due to energetically less preferred slip systems. For TiB_{2+z} it was shown that a preferred crystal growth in 0001 direction predominates super-hardness (> 40 GPa) over any stoichiometry variations [3,4]. Furthermore, the growth orientation of TiB_{2+z} is highly dependent on process parameters, especially the pressure, which was suggested by Neidhardt et al. [5] and experimentally confirmed in a recent publication [3].

For state-of-the art protective coatings not only a high hardness is beneficial, but also specifically low residual stress states are preferred. By varying the pressure during the growth of TiB_{2+x} coatings, the mechanical properties have been tailored by structural adaptions throughout the film cross-section. In addition, the incorporation of metallic Ti interlayers is an interesting tool for stress management within these films. To study the progression of the stress sates as well as orientation relations throughout the film cross-section, X-ray nano-diffraction synchrotron experiments (beamline P03 at PETRA III) have been performed. Furthermore, the structure-mechanical properties were described by a broad set of characterization techniques such as SEM, Nanoindentation, or micro-mechanical testing techniques.

Keywords: Transition Metal Diborides, Anisotropy, Residual Stresses, Synchrotron Investigations, PVD

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Topical Symposia
Room Golden State Ballroom - Session TS1P-ThP

Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications - TS1 Poster Session

TS1P-ThP-1 Bacezryybo$_{3-\delta}$ Coatings Deposited by Colloidal Coating Process for Sustainable Energy Application, ***Chien-Ming Lei**, P. Lin, Y. Chen,* Department of Chemical and Materials Engineering, Chinese Culture University, Taiwan

$BaCeZrYYbO_{3-\delta}$ (BCZYYb) is one of the high temperature proton-conductive materials, which widely applied in protonic ceramic fuel cell, alkane and alkene reforming, water-gas shifting, ammonia synthesis, CO_2 reduction, etc. The main purpose of this research is to fabricate the BCZYYb coatings on NiO/yttria stablished zirconia (YSZ) substrate via a colloidal coating process. The BCZYYb powders were prepared by solid-state reaction method. The powders were well-dispersed in de-ionic water to prepare the BCZYYb colloidal suspensions. The suspensions were spin-coated on a pre-sintered NiO/YSZ substrate to obtain BCZYYb coating samples for the sequent sintering processes. Several properties of the as-prepared coating samples were analyzed including the crystal phases by X-ray diffractometer (XRD), microstructures by scanning electron microscopy (SEM), electrical properties by electrochemical impedance spectra (EIS). The results show that the main crystalline phase of BCZYYb powders are a single-phase perovskite structure, when the calcination temperature is higher than 1500°C. According to the observation results of SEM microstructures, the BCZYYb coating sample were formed a dense layer on the substrate when the sintering temperature higher is than 1500 °C. But there are still a few pores found from the surface of the coating layer. The average thickness of the coating layer is around 3.3 µm. After the second coating cycle, the pores on the surface were obviously eliminated, and the average thickness of the coating layer is around 5.7 µm. The results of electrical analysis show that the conductivity of BCZYYb single-coating samples are 0.0134 and 0.11261 S/m tested at 500 °C and 800 °C, respectively, and the activation energies are 0.299 eV and 0.292 eV, respectively. The conductivity of the double-coated samples is similar with that of the single-coating sample.

TS1P-ThP-2 PVD Core-Shell-Catalysts for Use in Electrolyzers, ***Jan-Ole Achenbach**, S. Cremer, R. Cremer,* KCS Europe GmbH, Germany

Up-scaling of electrolyzers is necessary to provide sufficient quantities of hydrogen for fuel cells in the future. Alkaline polymer membrane water electrolysis (APM-WE) in particular offers promising potential for the production of hydrogen. However, a requirement for the widespread use of this technology is the cost-effective production of suitable quantities of catalyst.

KCS Europe is pursuing the approach of replacing the usual expensive catalysts containing precious metals with cheaper core-shell particles within the research project AlFaKat. In this approach, particles of a suitable low-cost material are activated by the deposition of a more expensive catalyst material by means of physical vapor deposition (PVD). To realize this, various PVD technologies were evaluated at the beginning of the project with regard to the aspects of 'basic suitability', 'deposition rate' and 'homogeneity'. In a feasibility study on a commercially available batch coater, it was demonstrated that a homogeneous coating of the core particles is possible by PVD process. Furthermore, an economical production of core-shell particles appears possible. The gained knowledge was transferred to a demonstrator, aiming mass production of core-shell catalyst powders on an industrial scale in the future.

Keywords: PVD, Core-shell, Electrolyser, Hydrogen, Catalyst

TS1P-ThP-3 Repressing Noble Metal Ruthenium Target to Reduce the Cost of Bipolar Plate Manufacture in Fuel Cells, ***Jing Yang,*** SCI Engineered Materials, inc, USA

Bipolar plates, as the key component, contribute up to 60% of cost in a proton exchange membrane fuel cell. The most expensive part in bipolar plates is the noble metal coating for catalyst layers. Although there is research and development work done on non-noble metal catalyst, the noble metal coating on stainless steel, is still one of the most widely used combinations due to its good electrical and phonon conductivity, and corrosion resistance.

Sputtering is a preferred coating technique for bipolar plates catalyst layer due to its uniformity, as well as little chance to introduce impurity. However, due to the high price of the noble metal powder and the low usage of a planar sputtering target (15%-30%), the target is one of the costly factors for the process. At SCI, we have developed a process for adding a small portion of the metal powder on top of a spent target to fill in the sputtered area. SCI's process produces a high-density target with an interface between the original target and additional powder that doesn't interfere with the sputtering process. Depending on the target geometry, a spent target backer can be repressed up to ten times before the noble metal backer would need to be fully reclaimed. The repressing process can have a cost reduction on a noble metal powder costs up to 50%.

TS1P-ThP-4 Corrosion Protection of Bipolar Plates in Electrolysers, *M. Welters,* KCS Europe GmbH, Germany*; N. Kruppe,* Schaeffler Technologies GmbH & Co. KG, Germany*; **Peter Jaschinski**, T. Breuer, S. Yang, R. Cremer,* KCS Europe GmbH, Germany*; M. Öte, N. Bagcivan,* Schaeffler Technologies GmbH & Co. KG, Germany

By 2050, 80% of the total energy supply in Germany is to be converted to renewable energies. Since renewable energy generation fluctuates significantly, possibilities for storage and cross-sectoral use must be developed. The direct conversion of regeneratively generated electricity into a secondary energy medium such as hydrogen represents an elementary solution for the technical implementation of the energy transition.

Bipolar plates (BPP), which are combined into stacks, are an essential component of electrolysers in terms of functionality and service life.

Currently, both untreated and coated steel and titanium BPP are used. Thereby, a coating can extend the operating conditions and increase the service life. Two main approaches are currently being pursued with regard to corrosion protecting coating systems: carbon-based and metal-based coatings. With regard to the technologies utilized for the production of coatings, there has only been little experience in order to be able to specifically assess the advantages and disadvantages of individual process variants. In addition to the functional suitability of the coatings, in this context the economic process efficiency and suitability for large-scale production are essential aspects. Corresponding aspects often correlate with the coating system to be synthesized.

For this reason, KCS Europe carried out fundamental analyses as part of the StacIE joint project, in which physical vapor deposition (PVD) processes, were compared. Both, the layer morphology and the deposition rate of metallic and non-metallic coatings were investigated and compared. The coated samples were provided to Schaeffler and analyzed with regard to the interfacial contact resistivity using through plane voltage (TPV) measurements. The corrosion stability was investigated using electrochemical cell tests in laboratory scale adapting electrolyzer cell conditions. These findings provide the basis for the development of new concepts, which can be used in the environment of industrial coating of bipolar plates by PVD technology.

Keywords: PVD, Electrolyser, Hydrogen, Corrosion, Protection

TS1P-ThP-5 MOF-Derived Molybdenum Carbide-Copper as an Electrocatalyst for The Hydrogen Evolution Reaction*, W. Chen,* ***Yu-Chin Shen****, J. Huang,* National Cheng Kung University (NCKU), Taiwan*; S. Wang,* Southern Taiwan University of Science and Technology, Taiwan*; Y. Shen,* National Cheng Kung University (NCKU), Taiwan

The only side product of water electrolysis for hydrogen production is water, which is a clean and environmentally friendly process. However, the HER efficiency is quite low, and the electrocatalyst is required to improve the reaction efficiency. Molybdenum carbide has good catalytic activity and acid resistance. However, high temperature is generally required to prepare molybdenum carbide and the high temperature process leads to excessive growth of nanoparticles. To solve this problem, one of the solution is to combine it with conductive substrates to avoid excessive growth and agglomeration of nanoparticles, and to improve the conductivity of electrons.

In this study,Mo-Cu-MOF was used to confine the growth of molybdenum carbide nanoparticles, and Cu with high conductivity in Mo-Cu-MOF served as the electron transporter through the change of the gas flow (nitrogen → 20% CH_4/H_2) during the annealing process, MoO_2-Cu transformed to η-MoC-Cu. And then with the increase of temperature(800°C→1000°C), η-MoC phase disappeared and β-Mo_2C phase appeared, leading to the transformation from η-MoC-Cu to β-Mo_2C-Cu. Electrochemical performance results show that the overpotential at -10 mA/cm^2 of η-MoC-Cu carbonized at 800°C is -233 mV and the Tafel slope is 73 mV/dec. Finally, some analysis were taken by XRD, TEM, XPS and BET.

TS1P-ThP-7 rGo-SiOx Nanocomposite as Anode Material in Lithium Ion Battery*,* ***Sheng Hsu****, J. Huang,* National Cheng Kung University (NCKU), Taiwan*; B. Sanjaya,* National Cheng Kung University (NCKU), Taiwan, India

Research to develop negative electrode materials in lithium ion batteries is an emerging topic. Graphite, the most commonly used anode in LIBs, may be useful to operate typical electronic equipment but the theoretically capacity(372mAhg^{-1}) is quite low for applications in advaced devices such as electric hybrid vehicles. Recently, silicon has been leading as a key material of choice owing to its easy availability, low discharge voltage vs. Li/Li+, and outstanding capacity(3580mAhg-1). However, challenges remain due to the significantly high volume change(~400%) which leads electrode degradation and a quick decline in capacity. Recently, SiOx have emerged as one of the promising high capacity anode materials due to lower cost, less volume expansion(~200%), high cyclic stability and rate performance than pure Si making it more suitable material for applications in power batteries. However, SiOx has lower electrical conductivity that requires a high-level conductive agent to fabricate the anode. So far, top-down approach and complicated synthesis procedure at high temperature is usually used to prepare SiOx-C composite. We have expertise in the synthesis of metal oxide and reduced graphene oxide nanocomposite at room temperature that delivered very good reversible capacity, cyclic stability and rate capability when used as anode in LIB. Therefore, we explore a room temperature, low temperature and bottom-up approach for the synthesis SiOx-rGO, Si/SiOx-rGO nanocomposite and apply them as anode material in LIB.

Topical Symposia
Room Golden State Ballroom - Session TS2P-ThP
Sustainable Surface Solutions, Materials, Processes and Applications - TS2 Poster Session

TS2P-ThP-1 The Study of Different Crystalline Moissanite: Nucleation and Growth of Nanoparticle Gold Coatings*,* ***Tsung-Jen Wu****, S. Song, W. Chen,* Institute of Geosciences, National Taiwan University, Taiwan*; W. Lin,* Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taiwan

The localized surface plasmon resonance effect (LSPR) of gold nanoparticles (Au NPs) causes color diversity at the nanoscale, which is often applied to form color of material appearance. Particles below 10 nm of Au NPs show pink-red on coating surface. Results from the analyses of spherical aberration-corrected transmission electron microscopy (AC-TEM) with electron energy loss spectroscopy (EELS) methods, the pattern of nucleation and growth of Au NPs coatings on moissanite (silicon carbide, SiC) with different crystalline are highly variable.

When the Au NPs coating is grown on the amorphous interface layer produced by the CVD method, it is suitable for growth but not nucleation. Under the TEM observations show that the atomic structure is disordered, and only a few inconspicuous lattice fringes form the quasi-granular shapes. On the contrary, the Au NPs coating is directly grown on the moissanite matrix of 4C-SiC or 6C-SiC structures, which is more suitable for nucleation than growth. Therefore, images of TEM with EELS show that the Au-crystal has a pronounced particle shape in the coating surface. The lattice fringes of nanoparticles are prominent and unevenly distributed in coating layers.

Color coating of moissanite needs to be stable and not easy to peel off for different usages. Therefore, the Au NPs coating on the amorphous SiC interface is less prone to exfoliation due to the different surface energy. That is why it is the most suitable way for color coating.

TS2P-ThP-2 Multilayered Structure of PE-Based Polymer Film Composites*,* ***Marcin Bilewicz****,* Silesan University of Technology, Poland

Polymer processing of films becomes widely developed recent years and evolved in different directions to obtain more complex structures includingmono- and multilayer films and films filled with different fillers like micro- and nano-sized particles. Achievements in polymer chemistry and polymer processing through more advanced technologies equipped with precise sensors and computer controlled brings possibility to obtain more advanced structures of polymer composites. Multilayered films are used recently for many applications like packaging, materials with special barrier properties or with resistance for specific liquids or radiation, e.g. UV. The investigation aims to obtain the composite in form of 3-layer polymer film (fig. 1). Structure of the composite contains polymer based layers. To obtain the film was used blow molding technology on 20 meter high machine with advanced, rotating basket, gravimetric dosing and precise sensors. Tensile strength of 3-layer layer films can be even doubled comparing to single layer film. Additionally material composition and arrangement can brings additional improvement of properties.

TS2P-ThP-3 Understanding the Mechanical Behavior of Nanoporous Si by Molecular Dynamics Simulations*, B. Crutchfield,* ***Robert Fleming****,* Arkansas State University, USA

Nanoporous materials are of great interest for developing low-density, high-strength materials for a variety of applications, such as zeolites, light-weight structural elements, and scaffolds for biomaterials. These materials are often created from a ceramic or oxide matrix, with porosity generated by sacrificial polymer inclusions that are burned out during thermal processing. As a result, there is much interest in fine-tuning the structure of nanoporous materials and understanding how the mechanical properties are influenced by the porosity volume fraction. In this project, molecular dynamics (MD) simulations have been performed to better understand how porosity affects the stress-strain behavior of nanoporous crystalline silicon (c-Si) as function of crystalline orientation, as well as amorphous silicon (a-Si). From these simulations, the elastic modulus and strength-to-weight figure of merit were determined as a function of porosity and applied strain rate. These results give insights into the mechanical behavior of porous Si-based materials, and can be used to improve the understanding of structure-property-processing relationships for nanoporous materials.

Topical Symposia
Room Golden State Ballroom - Session TS3P-ThP

Processes of Materials for Printed and Flexible Film Technologies - TS3 Poster Session

TS3P-ThP-1 Organic and Perovskite Solar Cells based on 3D-Printed Transparent Conducting Electrodes*, H. Lee, B. Tyagi,* ***Jae-Wook Kang****,* Jeonbuk National University, Republic of Korea

The photovoltaic performance of organic/perovskite solar cells (OSCs/PSCs) are directly governed by the optoelectronic properties of the transparent conducting electrodes (TCEs) used. However, there exists a classic trade-off the optical transmittance and sheet resistance (R_{sheet}) in most of the TCEs which limited their usage in photovoltaic devices. Moreover, most of the solution-process based TCEs suffer from poor scalability, making them incompatible with large-area device application. To overcome these limitations, we demonstrate the innovative use of three-dimensional direct-ink writing (3D-DIW) techniques for the scalable fabrication of bottom/top transparent conducting electrodes (TCEs) in photovoltaic devices.The 3D-DIW technique allows us to use a wide selection of inks/pastes to form TCEs with various structures. A layer-by-layer printing strategy through 3D-DIW technique can produce TCEs with high aspect ratio and excellent optoelectronic properties unbounded by the transmittance-R_{sheet} trade-off.

TS3P-ThP-2 Development of a Microfluidic System for Oxygen Environment Detection in Cell Culture*,* ***Wen-Cheng Kuo****, L. Wu, J. Wang,* National Kaohsiung University of Science and Technology, Taiwan

The development of bioreactors based on microfluidic chips has been the focus in the field of drug screening in recent years. In this study, a MEMS process was used to integrate a flexible Clark-type dissolved oxygen sensor into a wafer, and graphene materials with high mechanical strength were used to fabricate electrodes, and the surface modification properties of oxygen plasma were studied. Nano-silver particles (AgNPs) are doped, and electrodes are prepared based on the suction filtration method on a biocompatible Parylene substrate, and Nafion is coated on the electrodes as a selective thin film and a solid electrolyte layer. The bottom and outer layers are encapsulated with biocompatible Parylene, which can avoid cell rejection when implanted in the body, and integrate electrodes into the flow channel of PDMS material, which is conducive to monitoring the dissolved oxygen concentration of the cell environment. Electrode performance analysis was performed using an electrochemical analyzer. The measurement results show that at the two groups of flow rates, it can be seen that the linear range of dissolved oxygen concentration is 0.4-2.08 mg/L, the difference of current density is about 0.1 μA/cm^2, and the reliability is above 0.99. Sensitivity increases slightly with an increasing flow rate of approximately 3%. The response times were about 1.5 and 1.6 seconds, respectively, demonstrating the excellent sensor's response and repeatability.

TS3P-ThP-3 Radiation Effect on Trapping States Modification for Nanowire Junction-less Charge Trapping Flash Memory Devices*,* ***Che-Wei Lin,*** National Tsing Hua University, Taiwan*; D. Ruan,* Fuzhou University, China*; K. Chang-Liao,* National Tsing Hua University, Taiwan

Recently, charge trapping (CT) flash memory architecture has become the most mature non-volatile memory in commercial market. Following with the scaling trend, the high-energy extremely ultraviolet would be applied on development of high density memory integration and fabrication. Therefore, radiation effect for charge trapping (CT) flash memory will be one of the most important issues in the coming years. Notably, the radiation damage plays a completely different role for different trapping layer material, which may be strongly related to the original trapping states in trapping layer. It seems that the radiation illumination can provide a promising method to optimize the trapping level without complicated band-gap engineering.

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 García 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. Czerwiec,* 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.

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[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. Wieczorek, 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_2 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 shirk. 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 sits, 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 complimentary 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 deposition regimes are directly relevant to laser target applications, including both sphero-cylindrical 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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Functional Thin Films and Surfaces
Room Pacific F-G - Session C2-2-FrM
Thin Films for Electronic Devices II

Moderators: Dr. Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Dr. Jörg Patscheider**, Evatec AG, Switzerland

8:00am **C2-2-FrM-1 3D Device Integration Technology for AI Computing**, *S. Chang,* Powerchip Semiconductor Manufacturing Corporation, Taiwan; ***Chun-Lin Lu,*** Powerchip Semiconductor Manufacturing Corporation, USA **INVITED**

To cope with the massive computation requirement of semiconductor chips in 5G and AI, 3D device integration incorporating with new system architectures is developed, to mitigate the computational von Neumann memory wall via minimized data movement. Both the 3D Memory-Logic chip stacking and monolithic SoC integration are developed for near-memory and in-memory analog computing, to perform high bandwidth and efficient power performance, leading AI computing toward a green technology era.

3D Memory-Logic Chip Stacking

We focus on wafer-on-wafer Memory-Logic 3D stack technologies, including (1). Oxide bond with paired TSV (Through Silicon Via), (2). Hybrid bond with TSV middle embedded in DRAM, and (3). Multi-DRAMs stack on Logic. The interconnect density is among 1E4-1E6/mm^2 range.

For intensive data-movement computation applications, hybrid bond with 2-3µm Cu bond pitch is developed to provide 1E6/mm^2 high interconnect density and < 0.5Ω low interconnect (Via-pad-bond-pad-Via) resistance. After implementing dispersive DRAM I/O and skipping interface PHY circuit in the system design, 55nm-node Logic chip and 38nm-node customized 6GB DRAM chip are bonded together to demonstrate 3-9X excellence in system performance, better than the products using advanced Logic chip while choosing commercial DRAM with standard I/O interface.

For AI image recognition applications, oxide bond with paired TSV is implemented for Logic-DRAM stacking, which a 10µm/15µm dual TSV with 20µm pitch is used for interconnection, providing < 0.2Ω (pad-TSV-Cu line-TSV-pad) resistance and 1E4/mm^2 interconnect density. The AI inference (# of image recognition/s) performance is expected to improve > 50%, as the I/O bandwidth enlarges 8X to 51.2GB/s. These 3D schemes can minimize energy consumption to <1pJ/bit during data movement.

3D Monolithic SoC for Analog in-Memory Computing (AiMC)

AiMC eliminates data movement during computation, offering low-power multiply-accumulate (MAC) operations in AI computing. To improve the poor power consumption and worse temperature variation reported in some emerging memory AiMC, monolithic 3D Si/CAAC (c-axis-aligned crystalline)-IGZO 3T1C AiMC chips with ultra-low operation cell currents (<1 nA/cell), multiple analog states (8 and 64), and high computing efficiency (143-210 TOPS/W) are demonstrated [1,2]. We further implement Ferroelectric material into the MIM capacitor to keep the MNIST inference accuracy > 90% even at 125^{o}C high temperature operation, while retention time > 50hrs. We believe it is a good candidate for the next-gen AI computing.

Ref. [1,2] IEDM 2021/2022

8:40am **C2-2-FrM-3 Magnetic Nanolaminates Deposited by Magnetron Sputtering for Next Generation Electronic Devices**, ***Claudiu V. Falub****, M. Bless, J. Richter, X. Zhao, H. Rohrmann, M. Tschirky, M. Padrun,* Evatec AG, Switzerland

The emerging Internet-of-Things (IoT) and artificial intelligence (AI) applications, combined with the ongoing miniaturization of mobile devices, has led to an increasing demand for heterogeneous systems that need to be integrated with the silicon complementary metal-oxide-semiconductor (Si-CMOS) platform, such as smart power management units based on integrated voltage regulators (IVR) and ultrahigh density non-volatile memory (NVM) cells. Besides numerous challenging surface engineering processes and corresponding equipment concepts for high volume manufacturing, the realization of these 3D monolithic architectures often requires advanced magnetic thin-film materials with precisely designed magnetic properties and thickness ranging from just a few tenths of nanometers up to several micrometers. In this talk we will illustrate some of these challenges using two examples where nanostructured magnetic thin film systems enable the requested functions for new generation electronic devices: (i) soft magnetic nanolaminates n×[m×(FeCoB/CoTaZr)/Al_2O_3] with tunable in-plane magnetic anisotropy that form the inductor cores for high-frequency RF filters and on-chip IVR; (ii) enhanced permeability dielectrics n×(FeCo/Al_2O_3) for single-layer Magnetoresistive Random Access Memory (MRAM) and programmable logic systems. These novel composite magnetic multilayers can be economically deposited on Si-CMOS wafers up to 300 mm in diameter using the high-throughput, multi-source, dynamic sputter systems in our portfolio, by simultaneously using two or more cathodes, and by carefully adjusting the thickness of individual nanolayers, i.e., by changing the cage rotation speed and sputter power of the individual stations [1]. Thus, due to the continuous rotation of the substrate cage, such that the substrates face different targets alternatively, the obtained thin films exhibited a nanolayered structure with very sharp interfaces in the case of soft magnetic nanolaminates [2], or a discontinuous structure with magnetic nanoparticles smaller than the superparamagnetic (SP) limit embedded in an insulating matrix [3]. We will discuss the interdependence of structure and magnetic properties in these thin films, and we will show how the latter can easily be tuned by choosing the sequence of magnetic and non-magnetic layers, and the thickness ratio of individual nanolayers.

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9:00am **C2-2-FrM-4 Tungsten-Based Thin Film Metallic Glass as Diffusion Barrier between Copper and Silicon**, ***Pei-Yu Chen****, J. You, C. Hsueh,* National Taiwan University, Taiwan

A qualified diffusion barrier layer in integrated circuits (IC) industry is essential to prevent the degradation of devices due to the rapid inter-diffusion of copper (Cu) and silicon (Si) for Cu metallization. In recent years, thin film metallic glass (TFMG) barrier materials are getting considerable attentions due to the advantages over the others by its thermal stability, low resistivity and excellent mechanical properties for some compositions. In this work, the performance of amorphous W–Ni–B TFMG as a diffusion barrier between silicon and copper layers is reported. The Cu (150 nm)/W–Ni–B (10 nm)/Si multilayered structures were fabricated by direct-current (DC) magnetron sputtering and annealing at 700–950 °C for 30 min in vacuum. The nanomechanical properties and thermal characteristics of the W–Ni–B TFMG was evaluated bynanoindentation and differential scanning calorimeter, respectively. The interfaces and microstructures of Cu/W–Ni–B/Si multilayered structures were characterized by a field-emission gun scanning electron microscope, X-ray diffractometer and transmission electron microscope. The findings indicated thatW–Ni–B TFMG showed extremely high hardness of 20 GPa and high reduced modulus of 217 GPa.

In addition, W–Ni–B TFMG effectively blocked the intermixing of Cu and Si atoms at 800 °C. However, the failure ofW–Ni–B TFMG barrier against Cu and Si inter-diffusion was observed after annealing at 950 °C. Based on itsunique combinationof excellent barrier performance and high hardness, W–Ni–B TFMG could be regarded as a robust diffusion barrier for Cu interconnect technology.

9:20am **C2-2-FrM-5 Investigation of Properties and Microstructures of Ag-Cu Alloy Thin Films by Co-sputtering and First-principles Calculations***, **Yu-Chieh Wang**, C. Chen, F. Ouyang, H. Chen,* National Tsing Hua University, Taiwan

As the demands of electronic devices continue to be high performance and small transistor size, the current density in electronic devices will significantly increase and electromigration (EM) is expected to be a critical reliability issue. Thus, developing a high EM-resistant interconnect will be desired in the electronic industry. Ag interconnects have drawn many eyes because they possess extreme thermal and electrical conductivity. In addition, Ag has low stacking fault energy (SFE), which is easy to form a twinned structure that exhibits unique properties, including low electrical resistivity, high EM resistance, high mechanical properties, and high thermal stability. [1] Alloying is a common way to enhance the EM resistance, but it would simultaneously change SFE with the doping elements and concentration, further impacting the formation of nanotwin structure in thin films. In this study, we first investigated how the doping concentration of Cu affects SFE of Ag-Cu alloy thin films by first-principles calculations. Their intrinsic stacking fault energy (γ_{ISF}) and unstable stacking fault energy (γ_{USF}) were calculated. In addition, the wide-angle powder X-ray diffraction was conducted to measure the SFE of pure Cu and Ag-Cu alloys. Then, Ag-Cu alloy thin films with different doped Cu concentrations were fabricated by co-sputtering system and their properties and microstructures were studied. The results show all Ag-Cu alloy thin films exhibited highly (111) orientation. The results show that low Cu concentration in Ag films exhibits a higher density of nanotwin structure with good properties than pure Ag, demonstrating that adding Cu into Ag films can effectively lower stacking fault energy and facilitate the formation of nanotwin structure.

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9:40am **C2-2-FrM-6 Multi-Step Method for the Fabrication of High-Performance Continuous Ultra-Thin Silver Films for Energy Applications***, **Phillip Rumsby**, B. Baloukas, O. Zabeida, L. Martinu,* Polytechnique Montréal, Canada

While Ag films offer significant advantages over other transparent conductors, their high surface energy gives rise to a Volmer-Weber, or island growth mode. In order to achieve films which are both thin enough to be highly transparent and continuous as so to ensure their conductivity, various methods are used to suppress the Volmer-Weber growth mechanism. Typically, one will decrease Ag adatom mobility via doping, lower Ag surface energy using nitrogen as a surfactant, or increase the surface energy of the substrate.

In this work we propose a novel method for producing continuous ultra-thin silver (Ag) films in different architectures and with different microstructural characteristics which exploits rather than avoids the high surface energy of Ag. Specifically, we deposit continuous films at an arbitrary thickness, and we then etch them using RF plasma until a desired thickness and performance are achieved. In this way, the surface energy minimization constraints which drive the agglomeration of adatoms into islands during film growth now help maintain the film morphology, as re-separation would increase the Ag surface area. Thus, continuous films can be produced at thicknesses below the threshold of continuous film formation during deposition.

The formation or breakdown of continuous Ag films can then be resolved using a facile *in-situ* ellipsometryapproach. After depositing a fully continuous Ag film onto a well-characterized substrate, the thickness and optical properties of the continuous Ag film are modeled. Then, using the obtained Ag optical properties and only the thickness of the layer is fitted, for each data acquisition. The mean square error (MSE) obtained on the fit then reflects divergence of the optical properties of the Ag layer from those previously modeled. Thus, as the film goes from continuous to discontinuous, plasmonic effects alter the optical properties and the MSE increases, and conversely for a discontinuous film achieving a continuous morphology during deposition, an example of which is shown in **Figure 1.**

We have validated the methods described above using *in-situ*-- sheet resistance measurements and cross-section transmission electron microscopy. Furthermore, we have demonstrated that this method enables the deposition of transparent, conductive, continuous thin films in atypical conditions, such as on a silica seed layer and at elevated temperatures, and can additionally be used to supplement the performance of Ag films in typical configurations. Finally, we propose additional processing steps between deposition and etching which may further improve coating performance.

10:00am **C2-2-FrM-7 Structural, Electrical, and Thermal Properties of Ge-Rich $Ge_2Sb_2Te_5$ Alloys***, **Matias Kalaswad**, A. Jarzembski, P. Kotula,* Sandia National Laboratories, USA*; T. Beechem,* Purdue University, USA*; M. King, D. Adams,* Sandia National Laboratories, USA

Materials which undergo vast and rapid transformations in optical, electrical, and thermal properties due to a phase change (e.g. amorphous to crystalline) at, or near, room temperature have long been utilized as key components in memory devices. Among these materials, germanium-antimony-telluride alloys, particularly $Ge_2Sb_2Te_5$ (GST), are especially prevalent due to their fast switching and large resistivity difference between the amorphous and crystalline states. Although chalcogenide phase change materials have been implemented in various non-volatile memories, efforts to improve phase stability and data retention in high-temperature (i.e. >100 C) environments (e.g. automotive) are still ongoing. Nearly a decade ago, a “golden composition” of a Ge-rich GST alloy exhibited a crystallization temperature of up to 250 C while still maintaining relatively fast (~80 ns) switching speed. Recent computational ab-initio studies have predicted that increasing Ge content in Ge-rich GST alloys leads to increased crystallization temperature, at the expense of phase stability in the form of segregation into regions of pure Ge and GST.

In this work, we present experimental results of structural, electrical, and thermal properties of three Ge-rich GST alloys: $Ge_2Sb_1Te_2$, $Ge_5Sb_2Te_4$, and $Ge_3Sb_1Te_2$. These are also compared to a benchmark GST film. From in-situ X-ray diffraction experiments, the Ge-rich GST alloys are observed to crystallize into cubic GST at temperatures between 250 C and 260 C, which is consistent with previous reports of similar alloys. Raman measurements generally support the XRD results, with cubic Sb-Te bonds forming around 200 C. Interestingly, Ge-Ge bonds form at 250 C, which is evidence of phase segregation as suggested by previous computational studies. In-situ measurements of the electrical resistivity show a decrease in resistivity beginning around 175 C for GST-212 and 230 C for GST-524 and GST-312, compared to 150 C for GST. The resistivity of all three Ge-rich GST alloys decrease by nearly four orders of magnitude, which is comparable to that of the benchmark GST alloy, albeit not as drastically (i.e. over a greater range of temperatures). Lastly, thermal conductivity measurements show an abrupt transition around 200 C from 0.2 W/mK to 0.7 W/mK for all three Ge-rich GST, which is nearly 50 C more than the transition temperature of GST.

10:20am **C2-2-FrM-8 Preparation and Electrical Properties of Tantalum Silicate Thin Films***, **You-Sheng Lu**, C. Chen, C. Huang, S. Chen, Y. Liu,* Ming Chi University of Technology, Taiwan*; W. Huang,* Chien Hwa Coating Technology Inc., Taiwan*; W. Yang,* General Research Institute for Nonferrous Metals, China

The electric resistivity and temperature coefficient of resistivity (TCR) of a material are important parameters when developing thin-film resistors for advanced electronics and electricity consumption. There are many materials that can be applied to thin film resistors, among which the tantalum silicate (Ta-Si-O) thin film material has attracted much attention, which is due to the excellent thermal stability and adjustable TCR of this material. However, the electrical properties of such thin film materials are highly correlated with the composition control and structure of the material. How to develop an efficient process method to more precisely control the composition and structure so as to obtain the required resistivity and TCR has always been an important issue. In the past, there were very few academic reports on the manufacturing process of these materials, so the related electrical research has been very limited. In this work, we prepared two targets with different target compositions, such as $Ta_{65}(SiO_2)_{35}$ and $Ta_{80}(SiO_2)_{20}$, to study the effects of target composition and sputtering power on the material structure and electrical behavior of the film. Our series of experimental results indicate that a Ta-Si-O film with a high Ta content can be produced by using a target material with a high Ta content, and a film with low resistivity and low TCR can be successfully produced with an appropriate sputtering power. According to material analysis, the excellent electrical properties of the film are highly related to the formation of Ta_5Si_3 as the main structural phase in the film.

10:40am **C2-2-FrM-9 Enhanced Reliability Characteristic Oftri-Gatepoly-Ge Charge Trapping Flash Memory with Ultra-Thin Tunneling Layer Engineering***, **Che-Wei Lin,*** National Tsing Hua University, Taiwan*; D. Ruan,* Fuzhou University, China*; K. Chang-Liao,* National Tsing Hua University, Taiwan

In this report, a high performance FinFET based junction-less charge trapping flash memory with poly-germanium (Poly-Ge) channel was successfully fabricated. Due to the high carrier mobility of Ge material, the operation speed of flash memory device can be improved by using a low temperature Poly-Ge channel. However, the reliability of poly-Ge flash device fabricated under harsh thermal budget limitation may be degradedafter inevitable thermal process. The reason may be Ge out-diffusion phenomenon and narrow energy band gap of Ge material. After stacking tunneling layer and plasma treatment, the memory device with aluminium oxynitride (AlON) tunneling layer may exhibit high programming speed, high erasing speed, long data retention time, and excellent endurance cycle. Firstly, those improvements can be attributed to better thermal stability and interface quality of AlON. Besides, the trap charge level of AlON might be much shallower than that of traditional silicon nitride trapping layer. It means that the operation speed can be further enhanced without scarifying data retention time and endurance cycle.

Functional Thin Films and Surfaces
Room Town & Country B - Session C3-2-FrM
Thin Films and Novel Surfaces for Energy II

Moderators: Dr. Clio Azina, RWTH Aachen University, Germany, **Prof. Carlos Tavares**, University of Minho, Portugal

8:40am **C3-2-FrM-3 Survey for Ferroelectric/Antiferroelectric Films for Energy Storage***, **Mitsuru Itoh,** H. Takashima,* National Institute of Advanced Industrial Science and Technology/Tokyo institute of Technology, Japan **INVITED**

Ferroelectric (FE) materials such as $BaTiO_3$, $KNbO_3$, and $Pb(Zr,Ti)O_3$ have dipole moments aligned to one direction. FEs have been already industrially applied as capacitor, piezoelectric actuator, filters, optical devices, and so on. However, antiferroelectric (AFE), such as $PbZrO_3$, $AgNbO_3$, and $NaNbO_3$, has two sublattices of the dipole moments, and each sublattice have dipole moments with opposite directions. As a whole, AFE does not have a net polarization and is structurally centrosymmetric. Under a smaller external electric field (E), AFE shows a linear response of electric displacement (D) against E like a paraelectric. Applying larger E causes flipping of dipole moments in one sublattice parallel to E. This constrained aligned dipole moments in one direction are comparable to a FE state that has a net polarization. However, once E is decreased, dipole moments in one sublattice flip to the original direction and consequently the structure returns to an original centrosymmetric and non-polar state. Utilizing such a characteristic of AFEs under E, a field-induced FE, they can be applied for the energy storage especially for the power devices, utilizing two step D-E responses of a linear one near the origin followed by a hysteresis loop at larger E.

Design of FE is easier compared to AFE because of the rich accumulated scientific knowledge of FE both in the structure and property during last 100 years. However, chemical design of AFE is still difficult due to the reason that the number of AFEs is limited compared to that of FEs. This study is going to try giving a comprehensive explanation on the phase stability of complex oxide materials including perovskites in the bulk and thin film including metastable state. Candidate compounds of AFE will be discussed for various phases in A_2O_3 and ABO_3.

9:20am **C3-2-FrM-5 First Attempt to Describe the Effect of the Substrate Temperature on the Depth Concentration Profile of Reactively Sputtered $ZnGeN_2$ Thin Films***, A. Virfeu, F. Alnjiman, A. Borroto, S. Migot, J. Ghanbaja, D. Mangin, D. Pilloud, **Jean-Francois Pierson,*** Institut Jean Lamour - Université de Lorraine, France

The reactive sputtering process is widely used at the academic and industrial scales to deposit thin films of various nitrides, oxides, oxynitrides… For some materials, the crystallization of the film can occur even when the deposition temperature is fixed at room temperature (Cu_2O, ZnO, TiN, …). Nevertheless, other materials require to heat the substrates during the deposition to obtain a crystallized film (VO_2, $LaCoO_3$, Si_3N_4, …).

Zinc germanium nitride ($ZnGeN_2$) exhibit optoelectronics properties that makes this abundant material an interesting compound to replace the indium and gallium nitrides for LEDs applications. As previously mentioned by several groups, the deposition of crystalline $ZnGeN_2$ using sputtering processes can only be achieved by heating the substrate during the growth.

A new approach to describe the mechanism of growth induced by the temperature during reactive co-sputtered $ZnGeN_2$ deposition is reported. The complex crystallization of this system requires the deposition of films at high temperature involving difficulties in controlling the stoichiometry of the films due to the evaporation of zinc atoms relative to germanium at these temperatures. The range of temperature considered in this work is between 70°C to 280°C. The study of this material is done at different scales and a model is proposed to bring answers to the observations made. X-ray/electron diffraction, transmission electron microscopy combined with in-depth SIMS analyses reveal the origin of two different zones of composition and crystallization. At a temperature above 130°C, the first step of growth is described by an under-stoichiometry of Zn entailing an amorphous phase. The second zone appears after an increase of the zinc content makes it possible to obtain a stoichiometric crystallized material. Hypotheses are announced, supported by calculations of sputtered zinc atom energy and zinc vaporization temperature in the present conditions of growth. The model provides a good agreement with the observation of the difference of composition for films deposited at temperatures above 130°C in our sputtering process. In this paper, an original work on the phenomena taking place at different stages of the growth of $ZnGeN_2$ thin films is described and gives new elements of understanding to the previous studies in the literature.

9:40am **C3-2-FrM-6 CVD Process Development of Thin Film Triniobium-Tin on Copper SRF Cavities***, **Mohamed A. Cheikh,** S. McNeal, V. Arrieta,* Ultramet, USA

Innovative fabrication technologies for cost-effective high quality factor (high-Q), high-field superconducting radio frequency (SRF) components are needed for the economic viability of future accelerator facilities. The worldwide particle accelerator community continues to investigate alternatives and performance-enhancing modifications to bulk niobium accelerator components via the application of superconducting films. The Department of Energy (DOE) is interested in development of advanced process technologies to deposit superconducting materials such as triniobium-tin (Nb3Sn), which has the potential to exceed the performance capabilities of bulk niobium when formed on the interior surface of existing bulk niobium, or less costly copper, accelerator component structures, enabling substantial fabrication and operating cost reductions for continuous wave and high-gradient accelerators.

In recent research for DOE, Ultramet has developed chemical vapor deposition (CVD) techniques to create well-bonded layers of Nb3Sn on copper, niobium, and molybdenum substrates. Multiple copper single-cell 1.3-GHz SRF test cavities of the International Linear Collider (ILC) design were fabricated using the new CVD Nb3Sn process. The CVD Nb3Sn-on-copper fabrication methodology was scaled up and used to produce testable flanged Nb3Sn-lined copper cavities and copper/Nb3Sn cavities with an interlayer of CVD niobium formed using a thick film CVD process technology developed in concurrent research for DOE. RF performance capabilities and survivability at cryogenic temperatures were characterized by RF testing of the cavities at Cornell University.

Ultramet's thick film niobium and thin film CVD Nb3Sn processes are uniquely well-suited for coating complex SRF accelerator component geometries because the virtually 100% dense coatings are formed on the substrate at the molecular level, and purity levels in excess of 99.99% are achievable. The CVD coating process exhibits the greatest throwing power, or ability to uniformly deposit materials onto/into intricately shaped or textured substrates.

Completion of this research was a necessary step toward the eventual commercial and scientific application of advanced accelerator component-forming technologies. A significant technical milestone was reached by the advances made in developing reliable fabrication techniques for reproducible CVD Nb3Sn- and niobium-lined copper accelerator components that offer high-gradient operation and substantial cost reduction for SRF applications worldwide.

10:00am **C3-2-FrM-7 Engineered Metal-Organic Framework-Based Heterogeneous Membranes with High Ionic Rectification for Ultrahigh Osmotic Power Generation from Organic Solutions***, Amalia Rizki Fauziah, L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Taking inspiration from the electrocytes in the electric eel, consisting of numerous "subnanometer-scale" rectified ion channels allowing unidirectional and amplified ion transport, assorted artificial solid-state ion channel membranes have been developed over these past few years. Nevertheless, the conventional membrane designs were only limited to either one structure homogenous or two structures heterogeneous membranes. Herein, we report a feasible yet versatile strategy to fabricate the breakthrough membrane design that has never been reported before. An engineered metal-organic framework (MOF)-based ionic diode membrane (termed as ZIF-8/PSS@BANM), composed of a continuous zeolitic imidazolate framework-8 (ZIF-8) membrane incorporated with negatively space-charged polystyrene sulfonate (PSS) and branch-type alumina nanochannel membrane (BANM), was successfully developed (Fig. 1). Results obtained confirm that the heterogeneous membrane is with high geometry gradient from sub-micro-scale to sub-nano-scale and high space charge property. We show that the engineered MOF-based heterogeneous sub-nano-channel membrane can vividly rectify ion transport even in LiCl-methanol solution with a ratio as high as ~13 (Fig. 2a), capable of amplifying ionic current uni-directionally at the subnanometer-scale confinement, due to the broken symmetries in channel sizes, charges, and wettabilities (Fig. 2b). We thereby probe the use of this subnanometer-scale MOF-based ionic-diode membrane in harvesting osmotic energy from organic solutions. Captivatingly, a record power output of up to ~9.58 W/m^2 at a 50-fold LiCl gradient in methanol can be harnessed (Fig. 3a), majorly because of its unique geometry gradient channel structure (Fig. 3b), outperforming the bandgap of the commercial benchmark value (5 W/m^2) and the other conventional membranes structures. The continuous MOF-based heterogeneous membrane we developed here is with high novelty in membrane technology and the design strategy provides a promising approach for constructing new multifunctional biomimetic membranes towards advanced high-performance energy conversion devices.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F1-FrM

Nanomaterial-based Coatings and Structures

Moderators: Dr. Ondrej Kylian, Charles University, Prague, Czechia, **Dr. Vladimir Popok**, Aalborg University, Denmark

8:20am **F1-FrM-2 Giant Actuated Van der Waals Metal/Muscovite Heteroepitaxy***, **Jia-Wei Chen**,* National Yang Ming Chiao Tung University, Taiwan*; Y. Chu,* National Tsing Hua University, Taiwan

A large-response bimorph thermal actuator plays a vital role in the research field of actuation. Various architectures were designed using polymer-based materials with significant differences in thermal expansion. However, polymers' undesirable thermal and chemical instabilities severely hinder their applications. This work achieves a giant thermal actuation via van der Waals heteroepitaxy composed of room-temperature deposited metal and layered muscovite. A maximum bending curvature of 264 m^{-1} at 243 ℃ can be obtained in the Ag/muscovite heteroepitaxy through uniform heating. Moreover, the outstanding performance of the designed systems in both retention ($>10^5$ s) and cycling tests ($>10^5$ cycles) was observed through the electromechanical measurements, delivering the robustness and superior interface quality of the heterostructure. In addition, the robust interface and giant thermal actuation were supported by theoretical calculations and electron microscopy. The electrothermal and photothermal methods were conducted to demonstrate the generality of the control of actuators. This work presents the manufacturable actuator with a giant actuation based on metal/muscovite heteroepitaxy, invoking potential applications in robotic technology and intelligent systems.

8:40am **F1-FrM-3 Brain-Like Behaviour in Percolating Films of Nanoparticles***, **Simon Brown**,* The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Physical and Chemical Sciences, University of Canterbury, New Zealand **INVITED**

Recent progress in artificial intelligence and machine learning means that humans are now far inferior to computers at playing games like chess and go. However the brain is still far more efficient than even the largest supercomputers at performing some types of tasks, such as pattern or image recognition.

This has motivated a worldwide effort to build brain-like, or "neuromorphic", computers using a number of different approaches. [Note that the focus of neuromorphic computing is on *hardware*, in contrast to the usual *software* approaches to AI.] I will review some of those approaches, which include the use of traditional silicon transistors to emulate neurons and synapses, and new solid-state devices which have synaptic and neuronal functionality.

I will then talk about how my group has attacked a key remaining challenge, which is to achieve truly brain-like networks using self-assembled nano-components. I will show that we have not only been able to build highly complex brain-like networks but that the dynamical signals within those networks are remarkably similar to those of the brain. Further, I will show that stochastic signals from these networks can be used to engineer high quality true random number generators, which have applications in secure information processing, and that the devices can be used to perform classification and time series prediction tasks within a reservoir computing framework.

9:20am **F1-FrM-5 RBS Study of Silver/Copper Diffusions in the Matrix of Amorphous Carbon Coatings Produced by Magnetron Sputtering***, G. Sanzone,* Teer Coatings Ltd, UK*; M. Sharpe, P. Couture, J. England,* University of Surrey, UK*; S. Field, H. Sun, **Jinlong Yin**,* Teer Coatings Ltd, UK

In previous work, we have developed Ag-, Ag/Cu-, and Ag-cluster doped amorphous carbon coatings using magnetron sputtering techniques, for antimicrobial applications in space stations [1]. Inside a spacecraft, the temperature and humidity, suitable for the human crew onboard, also creates an ideal breeding environment for the proliferation of bacteria and fungi; this can present a hazard to human health, and create issues for the safe running of equipment. Utilising the antimicrobial properties of Ag and copper particles, we embedded these particles in a thin film of amorphous carbon and created an antimicrobial solution. These nanocomposite thin films have shown extremely high antimicrobial activities under both terrestrial gravity and micro-gravity conditions [1]. In addition, these thin films are scratch-resistant and wear-resistant with high hardness, providing a long lifetime which is critical for the applications in a space station. The slow diffusion of Ag towards surface from the carbon matrix body can replenish those Ag particles lost over time due to daily wear and tear.

However, the mechanism of Ag diffusion inside the carbon matrix has not been well understood. If the diffusion rate were too fast, the process of losing Ag would be too quick which would inevitably lead to a much shortened antimicrobial lifetime. On the contrary, too slow a diffusion rate would mean those lost Ag particles could not be replenished in time, which would severely impair the coatings' antimicrobial activity. Therefore, it becomes apparent and critical to identify the key factors that influence the Ag diffusion rate in a carbon matrix, and also to understand how they influence it.

In this presentation, we are going to report the latest results on RBS (Rutherford Backscattering Spectrometry) and TOF-ERD (time of flight elastic recoil detection) study of silver and copper diffusion in amorphous carbon coatings. The samples have been annealed at 100ᵒC, 150ᵒC and 200ᵒC, to investigate the temperature influence on the metal species migration. Preliminary results have shown that higher temperature causes a higher diffusion rate, and the addition of copper has slowed down the diffusion rate of silver.

References

[1] G. Sanzone et al.," Antimicrobial and aging properties of Ag-, Ag/Cu- and Ag cluster-doped amorphous carbon coatings produced by magnetron sputtering for space applications", *ACS Appl. Mater. Interfaces* 14 (2022) 10154−10166 (doi.org/10.1021/acsami.2c00263)

9:40am **F1-FrM-6 C:H:N:O Plasma-polymer with Anchored LSPR Active Ag Nanoparticles for Detection of Borrelia Pathogen**, *S. Kumar,* University of South Bohemia, Czechia*; H. Maskova,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia*; A. Kuzminova,* Charles University, Czechia*; R. Rego,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia*; J. Sterba,* University of South Bohemia, Czechia*; O. Kylian,* Charles University, Czechia*; **Vitezslav Stranak**,* University of South Bohemia, Czechia

The contribution focuses on Ag/C:H:N:O nanocomposite acting as a transducer for Localized Surface Plasmon Resonance (LSPR) detection of borrelia pathogen with high selectivity and sensitivity. The nanocomposite composes of gas-phase synthesized Ag nanoparticles (of about 20 nm in diameter) anchored onto/into C:H:N:O plasma-polymer matrix deposited by magnetron sputtering of nylon 6.6 target. The stability of Ag nanoparticles is achieved by the thermal treatment during the deposition process. The produced nanocomposites with plasmonic Ag nanoparticles may detect changes in the distance of several tens of nanometres observed as an LSPR shift of the absorption spectra. Hence, surface changes, e.g. immobilization of pathogens onto the surface, can be easily monitored.

The immobilization of pathogens is achieved by the C:H:N:O surface functionalization done here in a sequence of (i) thin-film plasma polymer deposition for the introduction of -NH_2 groups that (ii) enable subsequent immobilization of specific antibodies for (iii) binding of the target agents. Borrelia proteins-specific polyclonal antibody, Borrelia lysate, and live Borrelia were employed as testing target agents. Detailed investigation indicates both a high selectivity for the target agents and high sensitivity with a practical detection limit in the range of 50 Borrelias per sample effective area 0.785 cm^2 causing LSPR red-shift Dl_{50}» 2.2 nm. The proposed concept could be used as a platform for the detection of a wide family of species depending on the suitable surface functionalization.

Acknowledgments: This work was supported by the Czech Science Foundation (Grant Number GACR 19-20168S).

10:00am **F1-FrM-7 Aln Nanostructures for Piezoelectric Nanogenerators**, ***Manohar Chirumamilla**, M. Sandager, V. Popok, K. Pedersen,* Aalborg University, Denmark

With recent advancements in bioelectronic devices, self-powered sensors and smart wearables, efficient nanogenerators are required to harvest biomechanical energy. In this respect, aluminium nitride (AlN) is an excellent material choice for nanogenerators due to its piezoelectric nature, high chemical and thermal stability, high thermal conductivity and resistivity, and mechanical strength [1, 2]. Thin films and nanostructures of AlN can be grown using a direct current (DC) reactive magnetron sputtering process.

In this work, c-axis oriented wurtzite AlN nanostructures consisting of a number of laminas grown by sputter deposition on Si substrates are investigated. Ag nanoislands were preliminarily formed acting as a catalyst to initiate the nucleation of individual and separated nitride nanostructures. The quality of the deposited AlN is optimized by utilising ellipsometry, AFM, SEM and XRD, where the nanostructures grown at different conditions, like Ar to N_2 gas ratio, applied bias power, working pressure, substrate temperature, etc., are investigated. By optimizing the AlN growth parameters, well-defined AlN nanostructures with lengths up to 600 nm can be obtained. The piezoelectric behaviour of the structures was investigated using piezoresponse force microscopy (PFM). It was found that piezoelectric coefficients of the grown nanostructures can exceed the values typical for continuous AlN films, thus, forming a good basis for applications towards AlN-based nanogenerators. In this presentation, the AlN structures and their piezoelectric response for various nanofabrication conditions will be discussed.

Acknowledgements

The authors acknowledge the financial support of the Novo Nordisk Foundation under the project “Nanoscale Energy Generators” (grant No. NNF20OC0064735).

References

[1] J. Y. Tsao et al., Adv. Electron. Mater. 4 (2018) 1600501.

[2] L. Algieri et al., ACS Appl. Energy Mater. 1 (2018) 5203.

10:20am **F1-FrM-8 Super-Amphiphobic Nano-Wall Structured Teflon Films Deposited by Microwave Plasma**, ***Ta-Chin Wei**,* Chung Yuan Christian University, Taiwan

Super-hydrophobic and oleophobic surfaces have attracted much interest for both fundamental research and practical applications. In this study, Teflon-like fluorocarbon films with nano-wall structure were deposited on various substrates by microwave-generated C4F8/CF4 plasma. The reactor was a long tubular quartz tube with diameter of 5 cm. The substrates were placed in 22 different locations along the flow direction in upstream region, plasma discharge, and afterglow region. It was found that the surface morphology of the deposited film is very location-dependent. As seen in Figure 1, the results are relatively symmetrical to the center of plasma discharge, which reveals the diffusive behavior of the plasma process. The fluorocarbon film is rough with low F/C atomic ratio when substrate is located in the center discharge region (No. 11~15). Fluorocarbon films with nano-wall structure can be deposited on substrates located in the end of upstream region (No. 8) and in the beginning of the afterglow region (No. 18). The F/C ratio of the nano-wall film is 2.0, namely the Teflon structure. It was also found that water contact angle on the Teflon-like nanowall film was above 160° and the CH2I2 contact angle was above 140°. Actinometric OES showed that Teflon-like nanowall film deposited on locations with high CF2 relative intensity. Combining the location dependency and OES result, it is suggested that Teflon-like nanowall film is deposited by soft ion bombardment and abundant CF2 radicals. Finally, by using the same operating parameters, we successfully deposited transparent super-amphiphobic fluorocarbon nanowall film onto various substrates such as glass, copper, polycarbonate, and etc. Moreover, we found that Teflon-like films with nano-wall structure could also be deposited from other fluorocarbon plasmas. We will discuss more details at the conference.

10:40am **F1-FrM-9 Diamond-Based Nanostructured Interfaces for Electrochemical Applications**, ***Robert Bogdanowicz**,* Gdańsk University of Technology, Poland

The most common material for electrodes in electrochemical systems is gold or other noble metals, as these can be applied through physical vapor deposition. The recently interesting novel, candidate materials for electrochemical studies are i.e.: (i) boron-doped diamond (BDD) or (ii) diamondized carbon nanowalls (B:CNW), and (iii) composite nanodiamond interfaces. The tailored diamond-rich sensing surfaces are grown by microwave plasma-assisted CVD. The effect of boron incorporation not only enhances the electrical or electrochemical properties but also influences the structure of electrodes by changing it from the maze-like to a heterogeneous distribution of nearly straight walls. B:CNW or BDD could be nanostructured to achieve microelectrodes.

The modification of diamondized boron-doped carbon nanowalls (BCNWs) with an electropolymerized polydopamine/polyzwitterion (PDA|PZ) coating revealing tunable mechanical and electrochemical properties. Zwitterions are codeposited with PDA and noncovalently incorporated into a structure. This approach causes a specific separation of the diffusion fields generated by each nanowall during electrochemical reactions, thus increasing the contribution of the steady-state currents in the amperometric response.

Morevoer, we have manifested also the scalable fabrication of flexible laser-induced graphene (LIG)-boron doped diamondized carbon nanowalls (BCNW) hybrid nanostructures for microsupercapacitors. Direct laser writing on polyimide film is tuned by the presence of BCNW powder where an appreciable absorbance of the BCNWs at the CO2 laser wavelength enhances the local film temperature. The thermal shock due to laser irradiation produces graphitized and amorphous carbon at the diamond grain boundaries which increases the thermal and charge transfer capacity between the LIG–diamond interfaces.

Among numerous materials, functionalized nanodiamonds are specific versatile nanocarbon material attracted ample attention thanks to their exceptional chemical, optical and electronic properties beneficial in the decomposition of harmful organic chemicals. Moreover, the stability of the nanodiamonds in the cocktail media was studied, along with various nature-originated compounds influencing their surface termination, polarity, and charge states. Thanks to the stability and biocompatibility of the nanodiamond, it can be applied in monitoring the condition of i.e. foodstuffs, and in the detection of toxins and pathogens in them.

This research work was supported by the "TEAM-NET" project carried out within the POIR.04.04.00-00-1644/18 program of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

11:00am **F1-FrM-10 Engineering Nanostructured Metallic Thin Films by Pulsed Laser Deposition with an Outstanding Combination of Mechanical Properties***, **Francesco Bignoli**, D. Faurie,* CNRS, France*; C. Gammer, A. Lassnig,* Austrian Academy of Sciences, Austria*; S. Lee, C. Aguiar Teixeira,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; A. Li Bassi,* Politecnico di Milano, Italy*; M. Ghidelli,* CNRS, France

In recent years, thin metallic films have become object of intense research due to the activation of mechanical size effects enabling a combination of large yield strength (~3 GPa) and ductility (>10%) [1]. However, the correlation between microstructure and mechanical behavior is still not fully grasped and the research on new nanostructures with improved mechanical properties is ongoing. In this context, among the physical vapor deposition techniques, Pulsed Laser Deposition (PLD) have shown a great potential to widely tune the film morphology by simply changing the deposition pressure affecting the growth mechanisms ranging from atom-by-atom to cluster-assembled growth [2]. Nevertheless, very few studies focus on PLD deposited metallic films [3].

Here, I will show the potential of PLD to synthetize two (2) classes of emerging metallic thin films, namely metallic glasses (MGTFs) and high entropy alloys thin films (HEATFs). Firstly, I will cover the results involving the synthesis and the mechanical behavior of $ZrCuAl_x$ MGTFs with different compositions (x = 0,5,8,13 %at.) and morphologies i.e. compact and nanogranular. HRTEM shows a unique self-assembled nanolayered structure with local chemical enrichments alternating ZrCu and Al-rich nanolayers. This leads to a large and tunable elastic modulus and hardness, respectively up to 145 and 9.3 GPa. Furthermore, *in situ* SEM micropillar compression show that compact films have outstanding combination of yield strength (3.2 GPa) and ductility (5.5%), among the highest values reported in literature, while nanogranular films show a fully homogenous deformation (up to 20%) with the suppression of the shear bands process.

In the second case, I will present new results focusing on $Al_xCoCrCuFeNi$ HEATFs deposited by PLD with different compositions (x = 0,9,16 %at.) and morphologies, i.e. compact and nanogranular. HRTEM reveal a unique nanolayered structure with nanoscale Al segregations resulting in a nanocomposite FCC/amorphous structure. This leads to enhanced mechanical properties with hardness up to 11 GPa and an exceptionally large (> 3.5%) onset of crack formation when deformed on polymer substrate.

Overall, the presented results show the potential of PLD to synthetize a novel class of metallic thin films with large and tunable mechanical properties and potential interest as structural coatings.

References:

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11:20am **F1-FrM-11 Preparation and Properties of Fluoroalkyl End-Capped Oligomer/Cellulose Nanofiber Composites***, **Hideo Sawada**, Y. Endo, Y. Oikawa,* Hirosaki University, Japan

Cellulose reveals the great sensitivity to water and moisture, quite different from the traditional synthetic organic polymers.[1)] Therefore, the transformation of such hydrophilic materials into hydrophobic, especially superhydrophobic derivatives has been hitherto strongly desirable in order to open a new route to the development of novel cellulose-based materials.[2)] Here we report that sol-gel reaction of fluoroalkyl end-capped vinyltrimethoxysilane oligomer[3)] in the presence of cellulose nanofiber (CNF) under non-catalytic conditions can provide the corresponding fluorinated oligomeric silica/CNF composites. The fluorinated composites thus obtained were applied to the surface modification of poly(ethylene terephthalate) [PET] fabric swatch, affording a superoleophilic/superhydrophobic characteristic on the modified fabric surface. Modified PET fabric swatch was applicable to not only the separation membrane to separate the mixture of oil/water but also the perfect adsorption of oil droplets spread on water interface. In addition, we have prepared the fluorinated oligomeric CNF composites films by casting homogeneous aqueous methanol solutions containing the corresponding composites. Pristine CNF film afforded the superoleophilic property on the surface; however, it was demonstrated that the obtained transparent colorless CNF composite films can supply highly oleophobic characteristic on the surface. The mechanical properties such as Young's modulus, tensile strength and elongation at break of the CNF composite films were superior to those of the pristine CNF film.

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11:40am **F1-FrM-12 Synthesis and Electrical Properties of Single Crystalline Cu_3Ge Nanowires***, **Chang Ting- Hsiang**, L. Bo-Yan, W. Chiu-Yen,* National Taiwan University of Science and Technology, Taiwan

This study reports the synthesis of copper-germanide metal nanowires (NWs). First, the molten Cu_3Ge bulk was homogenized at 450 °C for 12 hours and cooled in the single-zone furnace tube to obtain a smooth and uniform bulk. In order to easily control the composition of Cu_3Ge nanowires, anodic aluminum oxide (AAO) template-assisted hydraulic press die-casting approach is used to obtain a large number of Cu_3Ge nanowires with uniform composition and straight. Second, we used the $H_2Cr_2O_7$ solution to etch and remove the AAO template substrate to obtain Cu_3Ge nanowires. According to the SEM images and EDS analysis, we can further realize the interface and the content information. It can be observed the existence of high-density nanowires, which have a length of more than 10~15 µm and a diameter of about 80~100 nm. In addition, the atomic ratio of copper to germanium is about 3/1. Furthermore, Cu_3Ge nanowires are fabricated into single-nanowire devices with Ti/Pt contacts through electron beam lithography (EBL), electron beam evaporation, and lift-off processes. Lastly, the I-V measurement shows Ohmic behavior. Cu_3Ge nanowires had a resistivity of 106.1 µΩ • cm and a relatively large current density of $6.35x10^7$ A/cm^2 which can be attributed to the massive free electron transport.

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