Topical Symposia

Room On Demand - Session TS1

Anti- and De-icing Surface Engineering

TS1-1 Role of the Thin Coating in the Durability of Icephobic Thin-on-Thick Coating Systems*, Stephen Brown (stephen.brown@polymtl.ca),* *J. Lengaigne,* Polytechnique Montreal, Canada*; N. Sharifi, A. Dolatabadi,* Concordia University, Canada*; L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montreal, Canada

In-flight aircraft icing occurs when supercooled water droplets suspended in clouds collide with exposed aircraft surfaces. The buildup of ice increases the weight of the aircraft while also changing its shape, leading to an increase in fuel consumption and a decrease in lift and thrust. In the worst case scenarios, icing can also cause the malfunction of sensors or moving parts, leading to accidents. Of the potential solutions which exist, superhydrophobic surfaces (SHS) are among the most promising, due to their ability to repel water droplets at sub-zero temperatures and reduce the adhesion strength of any formed ice. When fabricating SHS, a common methodology is to create a surface which exhibits hierarchical roughness, and to coat this surface with a thin hydrophobic topcoat. While this method of fabrication is effective, it also means that the durability of the SHS is intrinsically linked to the durability of this topcoat.

In the present study, we develop a thin-on-thick superhydrophobic coating system, focusing on the durability of the thin hydrophobic layer. The thick portion of the coating system is hierarchically rough TiO_2, deposited by suspension plasma spraying, while the thin portion is a coating stack deposited by plasma enhanced chemical vapor deposition and is based on $DLC:SiO_x$—diamond-like carbon networked with silicon oxide. $DLC:SiO_x$ was selected for its improved mechanical properties compared to other hydrophobic coatings, with the deposited films having a contact angle up to 95° and a hardness up to 11 GPa, and the whole thin-on-thick system having a contact angle of 159° and a contact angle hysteresis of 3.8°. Durability of the coatings is first assessed through icing/deicing cycling, and the results are compared to TiO_2 samples coated with commonly-used hydrophobic coatings, including stearic acid and fluoropolymer, as well as a sample coated with Rustoleum NeverWet. Following this, the most interesting coatings were subjected to rain erosion tests and accelerated aging tests. The thin-on-thick coating system is shown to offer improved durability over the others, maintaining water droplet mobility after 170 icing/deicing cycles, resisting prolonged UV and high-temperature exposure, and offering a 300-times improvement over the stearic acid in rain erosion tests.

TS1-2 Improving the Efficiency of Electro-Thermal De-Icing Systems With Icephobic Coatings*, Jack Brierley (emxjpb@nottingham.ac.uk),* *X. Hou, B. Turnbull, W. Sun,* University of Nottingham, UK

Active ice protection systems implemented in aerospace are incredibly power-hungry, but necessary safety feature. Applying icephobic coatings is a potential zero-energy passive solution to this problem. This study explores the viability of icephobic coatings to work alongside a thermal de-icing system to guide this field of research into designing a hybrid energy-saving solution. A coating that reduces ice adhesion strength passively is synergised with an electro-thermal de-icing system to make it more energy-efficient. Studies on the effects of surface roughness,coating thickness (Sylgard 184) and the implementation of thermally conductive fillers (silicon carbide fibres), have been carried out in the present work, to highlight a pathway for this combined solution: a hybrid system of an active heating system that is enhanced, and not limited by, an icephobic coating. The influence of surface treatment using 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (POTS), a self-assembling monolayer to reduce the surface energy of the aluminium was also investigated. The inclusion of silicon carbide fibres in the PDMS coating provided a 5-fold reduction of energy consumption for de-icing was observed compared to pure polymer alone.The control of coating thickness was also a critical issue for both the ice adhesion and the energy consumption in de-icing. The design of an icephobic coating to focus on its specific operational environments is essential.

TS1-3 Icephobic Coatings by Thermal Spraying as Surface Engineering Technique*, Heli Koivuluoto (heli.koivuluoto@tuni.fi),* Tampere University , Finland*; R. Khammas, V. Donadei,* Tampere University, Finland

Icing causes challenges and serious problems in different industrial sectors e.g., in aviation, energy and construction as well as logistics. Increasingly, surface engineering offers various solutions to solve these challenges. However, still more sustainable solutions are needed and for this, thermal spraying as one of the surface engineering techniques opens a novel approach to produce icephobic coatings. These surfaces can act as potential passive anti-icing solutions in arctic environments. Thermal spraying technology makes it possible to produce coatings with a wide range of materials including metals, metal alloys, ceramics, composites, and polymers. Feedstock materials are fed to the thermal spray gun, where these are melted, heated, or accelerated towards a substrate or component surface to form a coating. Additionally, the material selection, coating structure and properties can be tailored with a thermal spray processing method where coating formation is based on either thermal or kinetic energy. Thermally sprayed icephobic coatings are typically polymer or composite based coatings with multifunctional characteristics e.g., wetting performance, slipperiness and protection against different wearing and corrosion conditions. These coating solutions can be divided into three categories such as thermally sprayed solid icephobic coatings (TS-SIC), thermally sprayed slippery liquid infused porous surfaces (TS-SLIPS) and thermally sprayed lubricated icephobic coatings (TS-LIC). These coating designs possess low to medium-low ice adhesion values measured with the centrifugal ice adhesion test (CAT). For the tests, ice was accreted in the icing wind tunnel (IWiT) at Tampere University (TAU) in ICE Laboratory. Generally, it can be noted that the lower ice adhesion leads to the higher icephobicity. Thermally sprayed icephobic coatings have shown their potential to avoid the icing of the components and minimize the adhesion between ice and the coating surfaces.

TS1-4 Limitations of Anti-icing Materials for Aeronautic Applications*, Paloma Garcia (garciagp@inta.es),* National Institute of Aerospace Technology, Spain*; J. Mora,* Isdefe, Spain*; A. Agüero,* National Institute of Aerospace Technology, Spain

Atmospheric icing is a severe issue which affects many different sectors in different ways: energy (Eolic), communications (power lines), or transport (trains, ships, aircrafts). In aeronautic, even a thin layer of ice, accreted in a few seconds, can be a serious problem, due to the possibility losing control which imposes accident risks. Modern aircrafts are equipped with effective systems to avoid ice accretion (anti-icing), or favour its release once it accretes (de-icing mode) over the sensitive surfaces.

These systems require energy, and an objective in this field is the use of more efficient systems to decrease the energy requirements, or alternatively, the development of material systems that do not accrete ice called anti-icing materials and therefore no energy supply is required during flights.

Icing mechanisms are not completely understood, and many different surface modification strategies have been explored without sufficient success in recent decades. Most of them are based on low wetting solutions (super-hydrophobicity and high water droplet mobility), low surface energy materials, or biomimetic strategies.

There are some reported promising results, but still far from the anti-icing level, durability and reliability required for use in aeronautical applications. In addition, there are no standard for the different required testing methodologies, complicating the search for solutions which meet aeronautical regulations.

During the PHOBIC2ICE European project several types of coatings, including metallic, ceramic and polymeric materials as well as composites applied by different coating deposition technologies where tested according to a common protocol designed by the project partners. Testing included ice accretion and adhesion of samples produced in laboratory scale icing tunnels, as well as in a large scale icing tunnel in which the coated specimens were rotated at high RPMs during the test.

The results of the diverse anti-icing strategies, using common testing methodologies, indicated some partial trends, but in all studied cases, the anti-icing behaviour is too low to be considered as an alternative to actual anti-icing aeronautic systems despite the high level of super-hydrophobicity exhibited by many samples.

These results, together with many others found in bibliography, raise questions about whether the development of proposed strategies could deal to useful results, or radical changes are needed to advance in real solutions.

TS1-5 Fluorination of Aluminum Surfaces as a General Strategy to Induce an Effective Anti-Icing Response*, Carmen López Santos* ***(mclopez@icmse.csic.es)****, V. Rico, J. Mora, P. Garcia,* University of Seville, Spain*; A. Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; A. González-Elipe, C. López-Santos,* Instituto de Ciencia de Materiales de Sevilla (CSIC-USE), Spain

Icephobicity and anti-icing response of common materials used in aviation, such as Al6061, depends on different factors, such as surface morphology or chemical state. This work presents a systematic study of the wetting and anti-icing properties of aluminum surfaces that are modified by different procedures. Firstly, it is found that surface roughness modification by nanosecond pulsed IR laser treatments may induce a superhydrophobic behavior that also conveys an effective anti-icing response. An enhanced effect in wetting and anti-icing responses is observed for rough aluminum surfaces covered with porous Al_2O_3 layers providing a dual roughness surface microstructure. Then, we show that the anti-icing behavior can be highly improved by the surface functionalization of these aluminum surfaces with fluorine containing compounds or layers. The applied methodologies encompass the deposition of fluorinated polymeric coatings (CFx) prepared by plasma enhanced chemical vapor deposition, the infusion of a low surface tension slippery liquid (Krytox) or the surface grafting of fluorocarbon molecules (perfluorooctyltriethoxysilane, PFOTES).

A comparative analysis of the wetting, water condensation and anti-icing properties (freezing delay time and ice accretion in a wind tunnel) of these three fluorine modified surfaces have serve to determine the factors contributing to the observed good anti-icing performance and long term stability of metal fluorinated surfaces. This analysis takes into account the influence of roughness parameters, the chemical state of the surface and the mobile character of the fluorocarbon molecules to promote an efficient anti-icing response. A general methodology to develop fluorinated metal surfaces with an effective anti-icing behavior is proposed (1,2).

1.-V. Rico et al., Hydrophobicity, Freezing Delay, and Morphology of Laser-Treated Aluminum Surfaces, Langmuir 35 (2019) 6483–6491

2.- V. Rico et al., Robust anti-icing superhydrophobic aluminum alloy surfaces by grafting fluorocarbon molecular chains, Applied Materials Today 21 (2020) 100815

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Topical Symposia
Room On Demand - Session TS2
New Horizons in Boron-Containing Coatings: Modeling, Synthesis and Applications

TS2-1 The Industrially Deposited W-B-C Coatings from Segmented Target*, Michael Kroker* ***(kroker@physics.muni.cz)****, P. Matej, P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM, Czechia*; P. Vašina,* Masaryk University, Czechia

The coatings composed of transition metal (Me = Mo, W, Ta, Nb, …), boron, and carbon are promising candidates for next-generation hard protective coatings. The experimental studies are reporting a combination of high hardness and increased fracture resistance for Mo-B-C and W-B-C coatings, which are deposited using sputtering techniques at laboratory conditions. Such properties favor the use of Me-B-C coatings in the industry, where the demand for replacing the hard but brittle state-of-the-art ceramic coatings is significantly increasing.

For this study, the W-B-C coatings were sputter-deposited by non-reactive magnetron sputtering using an industrial system provided by the company SHM, Czech Republic. The system utilizes as a sputter source a cylindrical rotating segmented target composed of metal, boron carbide, and graphite segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate the batch coating of the tools. The depositions were carried out in both stationary regime and single-axis rotation regime to understand the differences between laboratory-like and industrial preparation of the coatings.

The properties of the W-B-C coatings were studied over a broad range of their chemical composition. Despite the coatings were mostly amorphous, they still exhibited high hardness (up to 30 GPa) and elastic modulus (up to 450 GPa). The coatings deposited in the rotation regime exhibited multilayered character due to different transport pathways of the light (B,C) and heavy (W) elements. Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic based protective coatings. Low internal stress in the coatings together with good adhesion enabled to deposit sufficiently thick coatings on the test samples and tools used in forming applications. The application relevant testing was performed at the end-customers of SHM in the Czech Republic.

This research is conducted within the FV30262 project, which is funded through TRIO program of the Ministry of Industry and Trade with financial support from the state budget of the Czech Republic.

TS2-2 Thermo-physical Properties of CVD Ti(B,N) Coatings*, Christina Kainz* ***(christina.kainz@unileoben.ac.at)****, N. Schalk, M. Tkadletz, C. Saringer,* Montanuniversität Leoben, Austria*; M. Winkler,* Fraunhofer Institute for Physical Measurement Techniques IPM, Germany*; A. Stark, N. Schell,* Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Germany*; J. Julin,* Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Germany*; C. Czettl,* Ceratizit Austria GmbH, Austria

Hard protective coatings are commonly subjected to temperatures up to 1000 °C, which has a significant influence on their thermo–physical properties and the associated performance in application. Within the present work, temperature dependent physical properties of chemical vapor deposited (CVD) coatings within the Ti(B,N) system were correlated with their chemical composition. High–energy X-ray diffraction experiments in inert atmosphere proved that CVD TiN, TiB_2 and ternary TiB_xN_y coatings with varying B contents are thermally stable up to 1000 °C. With increasing B content, the TiB_2 fraction in the coating increased gradually, whereas the grain size decreased. First order tensile strains of TiN and ternary TiB_xN_y coatings with different compositions decrease during heating. Contrary, TiB_2 exhibits compressive strain enhancement up to the deposition temperature, followed by strain relaxation thereafter up to 1000 °C. Nanocrystalline TiB_2 exhibits more pronounced grain growth during annealing compared to coarse grained columnar TiN. The mean thermal expansion coefficient decreases as the B content increases from 9.18×10^{-6} K^{-1} in TiN to 7.95×10^{-6} K^{-1} in TiB_2. The thermal conductivity decreases from 45 W/mK in TiN to 14 W/mK in TiB_2 and correlates with the grain size of the coatings. Annealing of TiB_2 resulted in an increment of the thermal conductivity (38 W/mK), which is ascribed to the less pronounced phonon scattering with increasing grain size and lower defect density. In summary, the present work provides a comprehensive overview of the thermo-physical properties of CVD coatings in the Ti(B,N) system filling a gap in the existing literature.

TS2-3 Chemical Shift in W-B-C Systems: Experiments and Modeling*, Jaroslav Ženíšek* ***(jzenisek@mail.muni.cz)****,* Masaryk University, Czechia*; P. Ondračka,* RWTH Aachen University, Germany*; P. Souček,* Masaryk University, Czechia*; D. Holec,* Montanuniversität Leoben, Austria*; M. Stupavská,* Masaryk University, Czechia*; J. Schneider,* RWTH Aachen, Germany*; P. Vašina,* Masaryk University, Czechia

This work discusses and reviews the generally accepted assumptions commonly used in the XPS bonding analysis of different materials. These are in the presented case applied to amorphous W-B-C materials with different compositions. We focus ourselves on the chemical shift of 4f electronic states of W atoms. In the W-B-C systems, the formation of binary W–B and W–C bonds leads to a shift in core-level to lower and higher binding energies, respectively, of W 4f core electrons due to the differences in the Pauling electronegativity of W, B and C. For the theoretical verification of this assumption we generated three amorphous W-B-C atomic models of different compositions (W:B:C ratios), calculated the W 4f core electron binding energies from *ab initio* methods and compared them with the measured XPS profiles of deposited W-B-C with the same W:B:C ratios. The atomic models reproduced the behaviour of the deposited systems in terms of XPS profiles. In the next step, we used the models to analyse the relationships between the W 4f electron binding energies and the local atomic environments of W atoms. It was found that the relative W 4f peak positions depend on the B/C ratio in the system, as was expected and as is commonly assumed in the bonding analysis. However, the relative amount of W and its density fluctuations in the volume of the unit cell on the other hand, which is usually omitted in the bonding analysis, also led to a chemical shift of the W 4f peak. Therefore, several series of amorphous W-B-C coating were deposited in a way to obtain amorphous coatings with compositions allowing to separate the effect of B/C ratio and the amount of W on the W 4f peak positions. The experimental positions of the W 4f peaks confirmed the theoretical predictions and have shown that general simplified assumptions based on electronegativity of elements need to be taken with care for precise chemical analysis of the bonding in W-B-C coatings.

TS2-4 Superior High-temperature Behavior of Amorphous Coatings from Quinary Hf-B-Si-C-N System

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Multielement ceramic coatings are appropriate candidates for high-temperature applications due to their excellent behavior at temperatures exceeding 1000°C. When the excellent oxidation resistance is combined with the thermal stability of a high optical transparency, they can be applied for high-temperature passive protection of optical and optoelectronical devices. On the other hand, a combination of the high oxidation resistance and the thermal stability of the electrical conductivity makes them suitable for capacitive pressure, vibration or tip clearance sensors in a severe oxidation environments.

The present work focuses on systematic investigation of high-temperature behavior of two amorphous Hf-B-Si-C-N coatings with different electrical and optical properties. The coatings were prepared by reactive pulsed dc magnetron co-sputtering of a B_4C-15%Hf-20%Si target in two Ar+N_2 mixtures (15% and 20% N_2 fractions). Particular attention is paid to thermogravimetric analysis and differential scanning calorimetry of the coatings in air and Ar, and to the evolution of the film structure, microstructure and elemental composition with increasing annealing temperature from 1100°C to 1700°C.

The coating prepared at the 15% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{22}C_6N_{40}$ and is electrically conductive, while the coating prepared at the 20% N_2 fraction has an elemental composition of $Hf_7B_{23}Si_{17}C_4N_{45}$ and is optically transparent. Both coatings are sufficiently hard ($\approx$ 20 GPa) and exhibit a superior oxidation resistance up to 1600°C due to the formation of a nanocomposite diffusion barrier surface layer consisting of HfO_2 nanocrystallites surrounded by a borosilicate amorphous matrix. A small difference in the composition results, however, in a different thermal stability of the amorphous structure of the coatings above 1400°C. While the $Hf_7B_{23}Si_{17}C_4N_{45}$ coating underneath the oxide layer retains its amorphous structure, the $Hf_7B_{23}Si_{22}C_6N_{40}$ coating crystallizes into different phases (Si_3N_4, B(C)N, HfCN, HfB_2) with a unique self-organized structures [1,2].

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TS2-5 Application of the Heat Balance Integral Method to the Growth Kinetics of Nickel Boride Layers on Inconel 718 Superalloy

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The nickel-based superalloys are designed to meet industrial requirements to withstand higher temperatures during the long-term service. They have wide applications in the aerospace, marine, nuclear, and petrochemical industries due to their excellent oxidation and corrosion resistance. However, because their high nickel content, these alloys are susceptible to abrasive, erosive and adhesive wear damage. Boriding process is considered as an efficient method for improving the tribological properties of nickel-based superalloys. These superalloys were successfully borided by using different methods without impairing corrosion and oxidation resistance. Among the boriding processes, the powder-pack boriding is a highly effective and low-cost method to produce hard nickel borides with outstanding properties.

From a kinetic viewpoint, the growth kinetics modeling is very substantial to select the optimum values of boride layers' thicknesses matching the practical use of nickel-based superalloys in terms of wear conditions.

The Heat Balance Integral Method (HBIM) is an alternative to investigate the boriding growth kinetics of nickel-based superalloys. This approach, originally applied for analyzing thermal problems, is based on numerical resolution of a system formed by differential algebraic equations (DAE) under certain assumptions.

In the present work, new results about the growth kinetics of nickel boride layers on an Inconel 718 superalloy was estimated considering a diffusion model based on the HBIM. The boron diffusion coefficients in nickel boride layers were estimated in the temperature range of 1123 - 1223 K at different exposure times. In addition, the layers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and Berkovich indentation techniques to determine the phases formed on the surface, the microstructure and the chemical composition across the depth of the layer-substrate, and the distribution of the hardness, respectively.

TS2-6 Influence of the Diffusion Annealing Process in the Corrosion Susceptibility of Cobalt Boride Layer Immersed in Hank's Solution

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The corrosion susceptibilities of the borided CoCrMo alloy exposed to the diffusion annealing process (condition I) and the borided CoCrMo alloy (condition II) immersed during 7 days in Hank's solution were evaluated. Firstly, the CoCrMo alloy was exposed to the powder-pack boriding process (PPBP) during 5 h at 1273 K, to obtain a biphasic layer (CoB-Co_2B) with a total thickness around 30 µm. Then, the diffusion annealing process (DAP) was performed in the borided CoCrMo alloy during 2h at 1273 K in an inert argon atmosphere to obtain a 30 µm of monophasic Co_2B layer. The potentiodynamic polarization technique was used to evaluate the corrosion resistance (R_p) using the linear polarization technique (LPR) and the corrosion current density (j_{corr}) from the Tafel extrapolation technique. In addition, the corrosion resistance estimated from conditions I and II were compared with the CoCrMo alloy (reference material). The results showed, in the 7th day of immersion in the Hank's solution, that the condition I (~357 kΩ cm^2) exhibited corrosion values ~24 times higher than those obtained by the condition II (~15 kΩ cm^2) reaching values close to the reference material (~385 kΩ cm^2). The corrosion behavior of the borided CoCrMo alloy exposed to the diffusion annealing process was attributed to: i) the presence of the monophasic Co_2B layer on the surface of the borided CoCrMo alloy, ii) the redistribution of Cr and Mo after the process, which increased the content of these elements at the surface of the borided alloy and iii) the inhibition of the B_2S_3 and $CrPO_4$ species, which has a detrimental effect on the corrosion behavior at the surface of borided CoCrMo alloy. Finally, the effect of the diffusion annealing process (condition I) reduced the corrosion susceptibility of the cobalt boride layer around 7% in comparison to the value of 96 % estimated for the borided CoCrMo alloy (condition II).

TS2-7 Pulsed-DC Powder-Pack Boriding: Growth Kinetics of Boride Layers on AISI 316 L Steel and Inconel 718 Alloy

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The conventional powder-pack boriding process (PPBP) is a surface hardening treatment, which results in the formation of boride layers to enhance the mechanical and chemical properties of the materials. Particularly, in the PPBP, the growth kinetics of the boride layers depends basically on the boriding temperature, the exposure time, and the content of the powder mixture (B_4C, SiC and KBF_4), using temperatures for the process in the range of 1123 to 1223 K with long exposure times (4 to 12 h).

Facing this problem, several studies have developed an alternative process to reduce exposure times in the formation of boride layers at the surface of various steels and alloys, using a direct current field in the powder-pack boriding process (PBDCF). During the process, the current flux between the electrodes follows the direction of the conventional current (from positive to negative), however, the migration of the boron atoms, on the surface exposed to the cathode, is opposite to the normal direction of diffusion, consequently, the growth of the boride layer is slower than that exposed to the anode.

Based on the aforementioned, this study develops a novel treatment called pulsed-DC powder-pack boriding (PDCPB). This treatment employs a DC power supply coupled to an electronic programable control device (EPCD) to generate timed cyclic polarity changes on the flux of ionized boron atoms. The effect of the pulsed DC current field provides a homogeneous boron diffusion during the PDCPB, which promotes the growth of similar boride layer thicknesses on both surfaces (anode and cathode) exposed to the direct current field. The PDCPB treatment was performed on the AISI 316 L steel and Inconel 718 alloy at temperatures of 1123 - 1223 K with different exposure times for each temperature. The powder mixture consisted of B_4C, SiC and KBF_4, supplying a current input of 5 A and polarity inversion cycles of 10 s.

Finally, the growth kinetics of the boride layers, in both materials, was established using a diffusion model that considers two mass balance equations at the growth interfaces, considering that the boride layers obey the parabolic growth law. The boron diffusion coefficients in the boride layers, were expressed as a function of the experimental temperatures using the Arrhenius relationship to estimate the boron activation energies. The results showed that the boron activation energies, estimated for the boride layers, decreased drastically (17% for the borided AISI 316 L steel and 31% for the borided Inconel 718 alloy) compared to those obtained for the conventional powder-pack boriding process.

TS2-8 Stoichiometry, Structure and Mechanical Properties of Co-Sputtered $Ti_{1-x}Ta_xB_{2\pm\Delta}$ Coatings, ***Branislav Grancic (grancic@fmph.uniba.sk)**, K. Viskupova, M. Mikula,* Comenius University in Bratislava, Slovakia*; M. Caplovicova,* Slovak University of Technology in Bratislava, Slovakia*; L. Satrapinskyy, T. Roch, M. Truchly,* Comenius University in Bratislava, Slovakia*; M. Sahul,* Slovak University of Technology in Bratislava, Slovakia*; M. Gregor,* Comenius University in Bratislava, Slovakia*; P. Svec Sr.,* Slovak Academy of Sciences, Slovakia*; M. Zahoran, P. Kus,* Comenius University in Bratislava, Slovakia

Ternary transition metal diborides $M^1_{1-x}M^2_xB_2$ represent a promising class of materials for hard wear-resistant coatings [1]. By using co-deposition from two binary stoichiometric targets, it is possible to prepare a ternary system in a wide x range. However, the varying boron-to-metal ratio often embodies obstacles/difficulties in the evaluation of the effect of x on coating properties. The mechanisms that determine the resulting boron-to-metal ratio are dependent on the target material and may significantly alter the resulting coatings' properties [2].

We use magnetron co-sputtering from TiB_2 and TaB_2 stoichiometric targets to prepare AlB_2-prototype ternary $Ti_{1-x}Ta_xB_{2\pm\Delta}$ solid solution, with x in the range from 0 to 1. Using this technique, the boron-to-metal ratio (B/Me) varies with the actual Ti and Ta content. The boron-to–tantalum ratio can be increased by decreasing the TaB_2 target voltage, which has a considerable effect on the coating structure. Coatings with B/Me > 2 reveal highly textured nanocolumnar structure, while the coatings with B/Me < 2 tend to be nanocrystalline (without any preferred crystallite orientation) or amorphous. All the deposited coatings have a hardness higher than 32 GPa. The under-stoichiometric (B/Me < 2) coatings show material pile-up around the cube-corner indent edges, an indication for plastic flow and increased ductility.

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[2] B. Grančič, et al. Surface & Coatings Technology 367 (2019) 341–348

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TS2-9 Effect of MB_2 (M = Zr, Ta, Nb, Hf, Ti, V, Cr) and W_2B_5 Target Composition on Plasma Properties and Thin-Film Stoichiometry During Magnetron Sputtering, ***Igor Zhirkov (igor.zhirkov@liu.se)**,* Linköping University, Sweden*; F. Klimashin,* Linköping University, Sweden*; G. Greczynski,* Linköping University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; I. Petrov,* University of Illinois, USA, Linköping University, Sweden*; J. Rosen,* Linköping University, Sweden

DC magnetron sputtering (DCMS) is a widely used technique for the deposition of decorative, protective, and wear-resistive coatings. However, high power impulse magnetron sputtering (HiPIMS), due to the pulsed nature and higher peak current/power, is able to provide a much higher degree of sputtered atom ionization. This allows for a better control of the material flux, and a pathway for tuning of thin-film stoichiometry and microstructure. The physical vapor deposition synthesis of metal diborides (MB_2) is an expanding area of research and is primarily carried out by sputtering from a compound target. For both HiPIMS and DCMS, the material flux from the target goes through three primary stages – sputter ejection, plasma transport, and film deposition. The target composition is rarely preserved in the resulting film stoichiometry. In the present work, we have performed a systematic study of HiPIMS and DCMS plasmas generated from circular 5 cm diameter ZrB_2, TaB_2, NbB_2, HfB_2, TiB_2, VB_2, W_2B_5, and CrB_2 targets at Ar pressures of 3 and 20 mTorr. For all depositions, the average power is kept constant at 50 W, with HiPIMS being operated at a repetition rate of 100 Hz and a pulse length of 100 µs. Plasma characterization, including plasma chemistry and time- and charge-resolved ion energy distributions, is performed with a spectrometer-to-target distance of 15 cm. Corresponding films were deposited using the same geometry, for compositional characterization and a comparison to the plasma and target composition. The obtained results are discussed as a function of the material properties of the metal diboride targets, and in view of the differences in mass of the metal component. The study is aimed at developing an understanding of the synthesis of stoichiometric MB_2 using sputtering techniques.

TS2-10 Recent Process Development of Magnetron Sputtering Deposited Boron Carbide Thin Films for Neutron Detection at the European Spallation Source, ***Chung-Chuan Lai (chung-chuan.lai@esss.se)**, C. Höglund, P. Svensson,* Detector Group, European Spallation Source ERIC, Sweden*; L. Robinson,* Detector Group, European Spallation Source ERIC,Sweden*; J. Birch, L. Hultman,* Thin Film Physics Division, IFM, Linköping University, Sweden*; R. Hall-Wilton,* Detector Group, European Spallation Source ERIC, Sweden

The construction of European Spallation Source (ESS) is aimed to build the brightest large neutron spallation source for research in material science. Since the decision made in 2009 to site ESS in Lund, Sweden, the staff in ESS has pushed forward the development in all fields to fulfill the goal of a world leading research facility. In line with increasing needs and costs for helium-3 (^{3}He), design and development of neutron detectors using boron-10 (^{10}B) gain practical value as a promising alternative for large area neutron detectors in ESS. Amorphous boron carbide (a-B_4C) is a common chemical form of choice for the detectors mainly due to its 80 at.% of B stoichiometry, chemical stability, and non-toxicity. In ESS Detector Group, a reliable and reproduceable direct-current magnetron sputtering deposition process for amorphous boron carbide (a-B_4C) coatings has been developed by ESS Detector Coatings Workshop in Linköping, Sweden, in collaboration with Linköping University. The process produces coatings with good adhesion to Al and Ti substrates, low H and O content, ~85 % mass density of bulk B_4C, and good radiation hardness. On top of this, the Coatings Workshop are continuously developing new processes of depositing a-B_4C coatings on a wider range of substrate materials or dimensions for the needs of various detector designs, e.g., PCB materials (G-10 and FR-4), other metals (Cu and Au), glass, Al foils with a thickness down to 18 mm, and removable substrates for stand-alone B_4C films. Characterization of the coatings helps to determine the influence of changing deposition parameters, such as substrate temperature, working pressure, and substrate materials, as well as a possible tradeoff of desired properties, such as low O content. We have also observed changes in the microstructure related to the difference in surface material and smoothness, which can further affect the physical properties or adhesion of the deposition films. Development of the coating processes has allowed the Coatings Workshop to be the go-to facility for institutes to search for a new generation of neutron detectors using $^{10}B_4C$ films, which is the core technology for more than half of the instruments in ESS.

TS2-11 Thermomechanical Properties and Oxidation Resistance of Ternary $W_{1-x}Ta_xB_{2-z}$ Coatings, ***Christoph Fuger (christoph.fuger@tuwien.ac.at)**,* TU Wien, CDL-SEC, Austria*; V. Moraes,* Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* TU Wien, CDL-SEC, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Future tasks in many different fields of academia and industry are directed towards environmental sustainability, asking also for new advance in the field of protective coating materials. Especially, transition metal diboride based thin films exhibit a great potential to be applied in various applications because of their extreme refractory character as well as interesting electrical properties. Latest studies on various diborides emphasized their strong and weak points being on the one hand high hardness and phase stability in a wide range but on the other limited fracture and oxidation resistance. Alloying concepts involving transition metals (TM) such as W, Ta, or Zr forming ternary diborides ($TMI_{1-x}TMII_xB_{2-z}$) suggest to be a proper solution to overcome these restriction [1-3].

Therefore, within this study we provide a detailed insight on the thermomechanical properties and oxidation resistance of ternary $W_{1-x}Ta_xB_{2-z}$ thin films prepared by DC magnetron sputtering utilizing diboride based target materials. Based on theoretical investigations using density functional theory, we classified the two binary systems α-WB_{2-z} and α-TaB_{2-z} as highly ductile materials according to semi-empirical criteria e.g. Pettifor and Pugh. On behalf of structural investigations, we could confirm that single phased structured α-$W_{1-x}Ta_xB_{2-z}$ thin films are formed up to Ta contents of x=0.26. The addition of Ta also clearly enhances the phase stability in inert atmosphere shifting the decomposition of the metastable α- into the thermodynamically more stable ω-structure from 800 to 1400 °C for x=0.26. During oxidation treatments up to 800 °C the high Ta alloyed coatings outperform its counterparts, forming dense and stable oxide scale also after long exposure times (1000 min). In addition, these films were investigated by nanoindentation and in-situ micromechanical bending tests to evaluate the mechanical properties. The fracture toughness only slightly decreases with increasing Ta content from 3.7 to 3.0 $MPam^{1/2}$. In summary, the study highlights the potential of Ta alloyed WB_{2-z} coatings and confirms the strategy to form ternary or multinary diborides to expand the limitations in specific material properties.

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TS2-12 Fracture–Microstructure Relations of W-diboride Thin Films*, Rainer Hahn (rainer.hahn@tuwien.ac.at)*, *C. Fuger,* TU Wien, CDL-SEC, Austria*; G. Habler,* University of Vienna, Austria*; H. Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* TU Wien, CDL-SEC, Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations [1] suggest an attractive combination of high stiffness and appropriate high ductility for α-structured WB_{2-z} (space group 191, AlB_2-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W_2B_5-prototype, $P6_3/mmc$) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) in the PVD process. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Therefore, within this study we deposited various WB_{2-z} coatings using different deposition techniques as well as parameters to modify the crystallite size and grain boundary constitution but also predominating phases. Subsequently, the mechanical properties of these coatings in the as deposited and annealed state have been analyzed by means of nanoindentation, microcantilever bending tests, and micropillar compression testing. Depending on the coating morphology, which varies from nanocrystalline (amorphous) to crystalline fibrous grown structures, the hardness, indentation modulus, and fracture toughness obtains a strong variation. Hardness and indentation modulus can be varied between 31±2 to 42±2 GPa and 440±30 and 560±30 GPa, respectively. The most significant variation though was found in the fracture toughness of these coatings: We calculated values within the framework given by Matoy et al. [2] between 2.5 and 4.7 $MPa\sqrt{m}$. Furthermore, we critically evaluate the comparability of distinct micromechanical testing techniques assessing the fracture behavior also with respect to the residual stress state.

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TS2-13 Configurational and Vibrational Thermodynamics of Metastable Ternary $Ti_{1-x}Al_xB_2$ Alloys with Age-Hardening Potential, and their Constituent Binaries*, Erik Johansson (erik.johansson@liu.se)*, Linköping Univ., IFM, Theoretical Physics Div., Sweden*; N. Nedfors,* Linköping University, IFM, Thin Film Physics Division, Sweden*; F. Eriksson,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; A. Ektarawong,* Linköping Univ., IFM, Theoretical Physics Div., Sweden*; J. Rosen,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; B. Alling,* Linköping Univ., IFM, Theoretical Physics Div., Sweden

$Ti_{1-x}Al_xB_2$ metastable ceramic alloys were predicted in [1] to exhibit a tendency for isostructural decomposition despite the fact that binary TiB_2 and AlB_2 belong to the same hexagonal space group and have very similar lattice parameters. Due to the reported high hardness of TiB_2 and the prospect of age-hardening through isostructural clustering, these alloys could be good candidates for hard protective coatings on industrial cutting tools. In this work, we present theoretical predictions regarding phase stability and temperature dependence of structural parameters, based on first-principles density functional theory. The phase diagram for this ternary system is derived and shows an isostructural miscibility gap that closes only at temperatures beyond the melting temperatures of TiB_2 and AlB_2.

Out of the constituent binaries, TiB_2 is a well-studied line compound that has received more focus than AlB_2. In this work, initial phonon calculations of stoichiometric AlB_2 indicates that the thermal expansion trend does not follow experimental measurements as closely as TiB_2. Furthermore, it is known in the literature that there is an inherent metal deficiency present in AlB_2. Therefore, special attention is put on AlB_2 to further our fundamental understanding of the compound. We investigate configurational thermodynamics of metal vacancies, their origin in the electronic structure and their interplay with lattice vibrations. Through the use of cluster expansion, effective cluster interactions are obtained and used in Monte Carlo simulations in order to study vacancy order-disorder transition temperature and to derive a phase diagram. For a subset of vacancy structures, phonon vibrational contributions in the quasiharmonic approximation are calculated to obtain volume expansion for metal deficient AlB_2, and are compared with experimental measurements performed by our partners.

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TS2-14 Design of Under/Overstoichiometric Superhard $TaB_{2\pm x}$ Films*, Viktor Šroba (viktor.sroba@gmail.com)*, *T. Fiantok, M. Truchlý,* Comenius University in Bratislava, Slovakia*; P. Švec, Jr.,* Slovak Academy of Sciences, Slovakia*; T. Roch, L. Satrapinskyy, M. Zahoran, B. Grančič, P. Kúš, M. Mikula,* Comenius University in Bratislava, Slovakia

Transition metal diborides (TMB_2) are very interesting due to their high temperature chemical stability and excellent mechanical properties. Growth of diboride films by physical vapor deposition (PVD) methods, such as magnetron sputtering from stoichiometric compounds, is accompanied by several interesting aspects. Different angular distribution of sputtered elements plays an important role leading to the formation of under/overstoichiometric nanocomposite films. The best-known superhard overstoichiometric TiB_{2+x} film consists of oriented α-TiB_2 hexagonal filaments embedded in the boron-rich tissue phase. In addition, thermodynamically non-equilibrium PVD processes lead in Nb-, Mo-, WB_2 to the synthesis of metastable structures by incorporating point defects such as vacancies. Understoichiometric $MoB_{1.6}$ and $NbB_{1.7}$ films form despite boron deficiency vacancy-containing α-nanofilaments surrounded by a boron matrix. In the case of slightly understoichiometric α-WB_{2-x} films, boron vacancies promote α-type of the structure exhibiting more ductile behavior in comparison with brittle character of stoichiometric ω-WB_2. Tantalum is probably the most interesting metal of the abovementioned transition metals of VB and VIB group due to its superior oxidation resistance and mechanical properties. Grančič et al. [1] sputtered TaB_{2-x} films from a stoichiometric compound. They drew attention to the significant impact of reflected Ar neutrals from heavy Ta atoms in the target toward the growing film. This led to a large re-sputtering of boron and formation of a significantly understoichiometric amorphous $TaB_{1.2}$ film. Only the maximum decrease in acceleration voltage reduced the energy of Ar neutrals resulting in the nanocrystalline $TaB_{1.7}$ film, but without the typical nanocolumnar character as in the other diborides. Here, we grow under/overstoichiometric $TaB_{2\pm x}$ films using High Target Utilisation Sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon particles accelerated towards the target

(target voltage) while maintaining the same amount (target current). We used SRIM (Stopping and Range of Ions in Matter) simulation of sputtering processes and experiments supported by density functional theory (DFT) calculations to investigate the effect of reflected Ar neutrals on the chemical composition, structure and mechanical properties of tantalum diboride films.

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TS2-15 Vacancies and Related Substoichiometry in Magnetron Sputtered Transition Metal Diboride Thin Films*, Vincent Moraes (vincent.moraes@tuwien.ac.at)*, *H. Riedl, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In the last couple of years, borides or diborides in particular, have drawn great attention in the development of protective coatings with exceptional properties. Their high melting points and excellent hardness are promising attributes to outperform nitride-based materials in various fields of applications.

Transition metal diborides tend to crystallize in two related but slightly different hexagonal structures. Whereas early TMB_2s have their stable configuration in the AlB_2-prototype (α-type, SG-191), late TMB_2s energetically prefer the W_2B_{5-x} prototype (ω-type, SG-194) showing a difference in the crystallographic ordering. Recent investigations on WB_2 have shown that in the case of thin films, the material crystallizes in the α-type, though its energetically preferred structure is the ω-type. Moreover, the thin films show a rather boron deficient chemical composition compared to measurements of bulk materials. On the contrary, HfB_2 clearly crystallizes in the α-type (bulk as well as thin films) with a tendency to an increased boron content.

In this study, we investigate the theoretical and experimental possible influences on stoichiometry, microstructure and the preferred structure type of various transition metal diborides. Therefore, we used Density Functional Theory calculations to study phase stabilities and the impact of point defects in combination with experimental variations on binary and ternary diboride systems such as HfB_2, CrB_2, $V(W)B_2$, or $W(Ta)B_2$.

TS2-16 INVITED TALK: Boron-containing Metallic-glass Coating: Unique Properties and Various Applications*, Jinn P. Chu (jpchu@mail.ntust.edu.tw)*, National Taiwan University of Science and Technology (NTUST), Taiwan **INVITED**

A group of thin film metallic glasses have been reported to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. Boron is one of the widely-used constituents for forming metallic glasses. Amorphous FeB-based alloys are excellent examples for this case, which have been developed for widely use as the energy efficient transformer core material. In this presentation, I will give a review of unique properties of this type of coating, followed by the first-ever metallic glass nanotube (MGNT) arrays on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, with wall thicknesses of ~103 nm. Two examples are presented based on modifications of this scheme. First, the MGNT array is prepared on a heating device on Si wafers and, with an applied electric voltage to the heating device underneath, the array surface is functioned as biomimetic artificial suckers for thermally adhesion response in biological systems. Second, after modification of biotin, the MGNT array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin. The detection limit of the MGNT arrays for streptavidin is estimated to be 25 nM. Thus, the MGNT arrays may be used as a versatile platform for high-sensitive label-free optical biosensing.

TS2-18 XPS Analysis of TiB_x Thin Films*, Niklas Hellgren (nhellgren@messiah.edu)*, Messiah University, USA*; G. Greczynski,* Linköping University, Sweden*; M. Sortica,* Uppsala University, Sweden*; I. Petrov,* University of Illinois at Urbana Champaign, USA*; L. Hultman,* Linköping University, Sweden*; J. Rosen,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

We report on comprehensive analysis of TiB_x thin films by x-ray photoelectron spectroscopy. Films were grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target in Ar discharge. By varyig the deposition parameters, the film composition could be tuned over the wide range $1.34 \leq B/Ti \leq 3.0$, as determined by elastic recoil detection analysis (ERDA) and Rutherford backscattering spectrometry (RBS). By comparing spectra over this wide range of compositions, we can draw new conclusions about how to interpret XPS spectra of TiB_x. By careful spectra deconvolution, the signals from Ti-Ti and B-B bonds can be resolved from those corresponding to stoichiometric TiB_2. The intensities of the off-stoichiometric signals can be directly related to the B/Ti ratio of the films. Furthermore, we demonstrate a way to obtain consistent and quantum-mechanical accurate peak deconvolution of the whole Ti 2p envelop, including plasmons, for both oxidized and sputter-cleaned samples. Due to preferential suttering of Ti over B, the film B/Ti ratio is best determined without sputter etching of the sample surface. This allows compositional determination, assuming extensive levels of oxygen has not penetrated below the sample surface. Fully dense films can be accurately quantified for at least a year after deposition, while under-dense samples do not give reliable data if the O/Ti ratio on the un-sputtered surface is ≥ 3.5. Titanium sub-oxides detected after sputter etching is also indicative of too much oxygen penetrating the sample, and quantification by XPS should not be trusted.

TS2-19 Mechanical Property Evaluation of VNbMoTaWCrB Refractory High-entropy Alloy Thin Films by Micropillar Compression and Nanoindentation*, Yen-Yu Chen (cyy15@ulive.pccu.edu.tw)*, Chinese Culture University, Taiwan*; S. Chang,* National Tsing Hua University, Taiwan*; S. Hung, C. Wang,* National Taiwan University of Science and Technology, Taiwan*; J. Duh,* National Tsing Hua University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan

Refractory high-entropy alloys (HEAs) show outstanding mechanical and thermal properties than traditional alloys. Recently, the application of HEA thin films as functional and protective coatings has been widely investigated. Following our previous studies on VNbMoTaW based refractory HEA thin films, the mechanical properties of the thin films were further investigated by micropillar compression and nanoindentation methods in this study. A series of VNbMoTaWCrB thin films were fabricated by a pulse direct current magnetron sputtering method. The hardness and elastic modulus of thin films were evaluated by nanoindentation. The yield strength of each HEA micropillar under uniaxial compression was analyzed. The elastic and plastic deformation behaviors and the fracture toughness of these HEA thin films were studied. The effect of Cr and B concentrations on the hardness, elastic modulus, and fracture toughness of VNbMoTaWCrB HEA thin films were also discussed in this work.

TS2-20 Effects of Stoichiometry and Individual Layer Thickness Ratio in the Quality of Epitaxial CrB_x/TiB_y Superlattice Thin Films*, Samira Dorri (samira.dorri@liu.se)*, *N. Ghafoor, F. Eriksson, J. Palisaitis, B. Bakhit, L. Hultman, J. Birch,* Linköping University, IFM, Thin Film Physics Division, Sweden

Studies of single crystal artificial superlattices (SL) have been instrumental to understand hardening mechanisms at the nano-scale in transition metal (TM) nitride and carbide multilayers. The lack of such fundamental studies for TM diborides is the motivation for this study of CrB_x/TiB_y (0001) SLs, grown epitaxially onto Al_2O_3 (0001) wafer substrates by direct current magnetron sputtering from compound diboride targets. Growth conditions for obtaining well-defined SLs with good interface quality are found at a sputter gas pressure of 4 mTorr Ar and a substrate temperature of 600 °C. 1-µm-thick SL films deposited with modulation periods Λ between 1 and 10 nm, and $\Lambda = 6$ nm SLs with TiB_y-to-Λ layer thickness ratios Γ ranging from 0.2-0.8 are characterized by means of HRTEM, STEM, EDX, EELS, XRD, ToF-ERDA, RBS, and XPS. It is found that SLs with $\Lambda = 6$ nm and Γ in the range of 0.3-0.4 exhibit the highest structural quality. The effects of Γ and the stoichiometries (B/TM ratio) of the CrB_x and TiB_y layers on the distribution of B in the SL structures are highlighted. We show that by increasing the relative thickness of TiB_y, the crystalline quality of SLs starts to deteriorate due to B segregation in over-stoichiometric TiB_y layers, resulting in narrow epitaxial SL columnar growth with structurally-distorted boron-rich boundaries. An increase in relative thickness of under-stoichiometric CrB_x on the other hand, enhances the SL quality and hinders formation of boron-rich boundaries. Detailed structural analyses, mechanical properties with hardness, and stress as well as possible solutions for further improved SL definition will be presented.

TS2-21 INVITED TALK: Boron-based Thin Film Materials for Future Neutron Technologies at the ESS*, Jens Birch (jens.birch@liu.se),* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

The European Spallation Source (ESS), currently being built in Sweden, will be capable of delivering neutron beams more than an order of magnitude brighter than existing neutron sources, which will enable faster neutron scattering experiments on new materials using new techniques. For best utilization of the brightness, novel thin film based neutron-optical components, such as neutron mirrors and area detectors, are being developed. The Thin Film Physics division at Linköping University aims at developing novel thin film concepts enabling future neutron technologies.

Together with ESS, affordable ^{10}B -based thin film neutron converter coatings have been developed that allows for eliminating the present unsustainable use of the rare isotope ^{3}He in state-of-the-art neutron detectors. The primary material choice is magnetron sputter deposited B_4C, enriched in the neutron absorbing isotope ^{10}B. We have shown that $^{10}B_4C$ thin films can be grown by magnetron sputter deposition with properties that fulfill the requirements of mechanical and chemical stability as well as being radiation hard, while maintaining a high volume density of ^{10}B. For example1µm thick films with residual stress as low as 0.09 GPa can be grown by DC magnetron sputtering and by employing HiPIMS it is possible to lower the substrate temperature to ~100°C which is useful for sensitive substrates. This $^{10}B_4C$ thin film technology is proven superior to ^{3}He-based detectors and is chosen for most of the foreseen detectors for scattering, reflectometry, as well as time-of-flight inelastic spectroscopy at the ESS.

Novel solid-state neutron detector designs, requiring neutron converter filling of narrow high-aspect ratio wells and trenches in semiconductor surfaces, require conformal coverage CVD methods. We have recently shown that conformal coatings of BC_x in wells with aspect ratios as high as 10 000:1 are possible using triethylborane, $B(C_2H_5)_3$ as precursor. This allows for future ^{10}B-based solid state neutron detectors with sensor pixels in the range of 10x10 μm^2 (rather than the present ~cm^2).

Nanometric metallic multilayers act as neutron mirrors and are key to guiding neutrons from source to experiment. By combining incorporation of ^{11}B in the multilayers with temporal ion-assistance modulation during sputter deposition, we obtain a significant reduction of interface width which, in turn, leads to significantly improved neutron reflectivities. For example in Ni/Ti:^{11}B multilayer mirrors reflectivity increased by 43% using this technique, implying up to 10x higher neutron flux throughput and significantly increased spectral range of future neutron guides.

TS2-23 Thermal and Mechanical Properties of $(W,Zr)B_{2-z}$ Coatings Deposited by RF Magnetron Sputtering Method*, Justyna Chrzanowska-Giżyńska (jchrzan@ippt.pan.pl),* *R. Psiuk, P. Denis,* Polish Academy of Sciences, Poland*; Ł. Kurpaska,* National Centre for Nuclear Research, Poland*; T. Mościcki ,* Polish Academy of Sciences, Poland

W-Zr-B films with different stoichiometric ratio Zr/W were deposited by RF magnetron sputtering on silicon and tungsten carbide substrates. The coatings were deposited from plasma spark sintered targets using one-inch sputtering cathode. The impact of zirconium content on the film mechanical and thermal properties were investigated. Nano-indentation test was performed to analyze the hardness, Young modulus and subsequently flexibility of the films. It is shown that α-WB2 magnetron sputtered coatings alloyed with zirconium content 0 ⍰ 24 at% are superhard and in all investigated compositions possess similar hardness. In the same time Young modulus is decreasing about 10% what make deposited films more flexible. Obtained W-Zr-B films represent a new class of coatings which are simultaneously superhard H = 43±3 GPa, exhibit high values of the hardness and effective Young's modulus E* ratio H/E* >0.1, elastic recovery We > 60%. The results of thermal studies i.e. thermal shocking, annealing in vacuum and TGA show that deposited coatings are thermally stable at least to 800 °.

Topical Symposia

Room On Demand - Session TS3

In-Silicio Design of Novel Materials by Quantum Mechanics and Classical Methods (jointly sponsored by ICMCTF and AQS)

TS3-1 INVITED TALK: Computational Modeling of 3D Thin Film Growth Morphology: Influence of Angular and Energy Distribution of Particle Flux*, Grégory Abadias (gregory.abadias@univ-poitiers.fr),* *C. Mastail, C. Furgeaud, F. Nita, R. Mareus, A. Michel,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France **INVITED**

Considerable work has been done in recent years, both experimentally and theoretically, to characterize and predict

the properties of thin films from external conditions, including substrate temperature, deposition rate, angular distribution of atoms, and incident kinetic energy. The interplay between some deposition parameters often renders the task to obtain the desired film morphology challenging. On the other hand, the control of the desired morphology is essential for the applications searched for. Predictions from computational approaches are therefore very helpful in this sense.

We have developed a 3D kinetic Monte Carlo (kMC) atomistic code to help understand the role of the elementary atomistic diffusion mechanisms and impact of deposited energy on the resulting thin film growth morphology. The simulation model aims at mimicking the full sputter-deposition process, from ejection of atoms from the target, their transport in the gas phase, and film formation. First-principle calculations are also implemented to determine the potential energy landscape for preferable adsorption sites, or energy barrier for surface diffusion.

In the work presented here, the code has been applied to simulate the growth of TiN and Cu thin films. Examples will be provided for the growth at either normal or oblique angle incidence. The code is capable of reproducing the development of TiN columnar morphology, with column tilt angle in good agreement with experimental findings. For the case of Cu, the growth proceeds in a 3D mode, with nucleation of isolated islands, percolation and formation of continuous layer. The influence of kinetic energy on film morphology and defect incorporation will be also discussed.

TS3-3 Prediction of Composition, Crystalline Structure and Microstructure of Sputtered Multi-Component Coatings by a Virtual Machine*, David Böhm (david.boehm@tuwien.ac.at),* Vienna University of Technology, Austria*; T. Schrefl,* Danube University Krems, Austria*; A. Eder,* MIBA High Tech Coatings GmbH, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria

To be able to predict the composition and the structural properties of multi-component thin films deposited by magnetron sputtering a so-called Virtual Machine (VM) was designed. The VM is an interactive ray tracing software that simulates film growth by a line-of-sight model, also taking into account the decay of the flux density of the particles due to gas phase scattering.The VM is initiated with a 3D model of a real sputter system which includes the static arrangement of multiple targets and the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. Then the composition, the microstructure and the crystallographic phases with their associated XRD patterns are calculated for the simulated film. On each sampling point a composition is calculated over several time steps associated with an adjustable temperature which can be different for each step enabling the correlation of the real temperature distribution during the coating experiment. Depending on the material and the applied simulation parameters e.g temperature or coating rate models of grain growth and island formation are applied.With this information and a library of binary phase diagrams the corresponding crystallographic phase can be calculated and displayed per time step. The XRD patterns are calculated from the crystallographic phases and summed over all time steps. This procedure allows to construct a diffractogram which can be compared to the diffractogram of an accordingly produced sample. Another way to display the data is to stack the appearing composition and phases over all time steps. Such a phase stack is equivalent to an EDX line scan performed on a metallurgical cross section from the substrate to the surface of the coating. Several phase stacks can be compared with an element mapping of the cross section. Since surfaces and volume diffusion are not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples the above mentioned comparisons are presented.

TS3-4 Atomistic Modelling of Diffusion in Quasi-amorphous Nanocomposite Coatings*, Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at),* *D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V). The microstructure of real coatings has a polycrystalline or nanocomposite nature. Here, the intergranular region consists of quasi-amorphous (amorphous materials interfaced with TiXN, X=Al, V) tissue which serves as a diffusion highway for transporting species from bulk to the coating surface.

While approaches exist for estimating diffusivity in crystalline materials, the situation is much less explored in the case of (quasi-)amorphous materials. In this contribution, we will report on our recent progress in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline as well as amorphous materials and subsequently their relative rates. Molecular dynamics (MD), which traces the motion of each particle contained in the system by numerically solving Newton's equations, coupled to the accuracy of density functional theory (DFT) to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. We will present the DFT-based "5-frequency model" allowing us to calculate the diffusion coefficient in the crystalline fcc material. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN. Next, we show how to approach both crystalline and amorphous materials by employing the Green-Kubo relation together with a detailed analysis of diffusion pathways as provided by MD.

TS3-5 Identifying Fingerprints of Point Defects in X-ray Photoelectron Spectroscopy Measurements of TiN and TiON with *ab initio* Calculations*, Pavel Ondračka (ondracka@mch.rwth-aachen.de),* RWTH Aachen University, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Point defects have great influence on mechanical, electrical, optical and other properties of (not only) nitrides and oxynitrides. Significant point defect concentrations are produced by highly energetic deposition processes such as high power pulsed magnetron sputtering (HPPMS), or, in the case of oxynitrides, are a direct consequence of the O incorporation. As the direct observation of point defects is complicated, the characterization of point defects is usually based on indirect information, such as the lattice parameter and composition measurements. In this work we explore a new combined theoretical and experimental approach for obtaining information about point defects from the X-ray photoelectron spectroscopy (XPS) measurements and *ab initio* calculations of cubic TiN and TiON.

Density functional theory calculations using the all electron Wien2k code with the core-hole approach were used to calculate the N 1s and Ti 2p core electron binding energy shifts in TiN_x and TiO_xN_y. Considered point defects include N and Ti vacancies, different N and Ti interstitials and Frenkel pairs. It was shown that the majority of point defects have a significant influence on the binding energy of its first neighbours. For example, a single Ti vacancy decreases the binding energy of its nearest nitrogen neighbours by 0.6 eV. The aim of the *ab initio* calculations was to create a fingerprint database which could be used when analyzing experimental data.

The *ab initio* calculations were later utilized when analyzing XPS data from TiN and TiON thin films deposited by reactive DC and HPPMS magnetron sputtering. Thereby we were able to identify point defect-introduced features in the XPS spectra and, combined with lattice parameter and composition data, propose a quantification method. This work represents an important step on the road towards a more precise point defect identification and quantification in these materials.

TS3-6 Structural Ordering of Molybdenum Disulfide studied via Reactive Molecular Dynamics Simulations*, Paolo Nicolini (nicolpao@fel.cvut.cz),* Czech Technical University in Prague, Czech Republic*; R. Capozza,* Italian Institute of Technology, UK*; T. Polcar,* Czech Technical University in Prague, Czech Republic

Molybdenum disulfide, the most studied member of the transition metal dichalcogenides family, has been used as solid lubricant for several decades, showing extremely low friction coefficients[1] and stability to high temperature. Its lubricating properties are ascribed to the weak van der Waals interactions between sulfur atoms in the crystalline layered structure. Moreover MoS_2, even when prepared in the amorphous state or made of randomly oriented domains, can undergo shear induced structural transitions to the more ordered layered state affecting its tribological properties[2].

Exploiting a reactive classical force field[3] able to treat explicitly formation and breaking of bonds, we investigated by means of molecular dynamics simulations, the shear-induced structural changes and the possible layer formation in amorphous molybdenum disulfide. The ordering process is studied in details, with particular regard to the estimation of the thermodynamic properties that govern the process itself. A connection with crystallization theories is finally found, conferring a predictive power to the achieved results.

Overall, this study aims at gaining an atomic level understanding of the dynamics of layer formation process in MoS_2, thus controlling and possibly improving its tribological properties.

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TS3-7 Strength, Transformation Toughening and Fracture Dynamics of Rocksalt-structure $Ti_{1-x}Al_xN$ ($0 \le x \le 0.75$) Alloys*, Davide Sangiovanni (davide.sangiovanni@liu.se),* *F. Tasnadi, M. Oden, I. Abrikosov,* Linköping University, Sweden

We employ density-functional molecular dynamics simulations to determine the elastic response, ideal strength and toughness, and ability to plastically deform up to fracture of defect-free rocksalt-structure (B1) TiN and B1 $Ti_{1-x}Al_xN$ (x = 0.25, 0.5, 0.75) solid solutions subject to [001], [110], and [111] tensile deformation at room temperature. Overall, TiN exhibits greater ideal moduli of resilience and tensile strengths than TiAlN alloys. Nevertheless, the binary compound systematically fractures by brittle cleavage at its yield point. The simulations also indicate that 25% Al substitutions in $Ti_{1-x}Al_xN$ have negative effects on mechanical performances; the alloy remains brittle, while both strength and resilience slightly decrease. In sharp contrast, $Ti_{0.5}Al_{0.5}N$ and $Ti_{0.25}Al_{0.75}N$ solid solutions exhibit inherently high resistance to fracture and greater toughness than TiN due to the activation of local B1 → wurtzite-like structural transformations beyond the elastic-response regime. The results of this work illustrate the inadequateness of elasticity-based criteria for the prediction of strength, brittleness, ductility, and toughness in materials able to undergo phase transitions at extreme loading. Furthermore, we discuss rationales for design of hard ceramic solid solutions that are thermodynamically inclined to dissipate extreme mechanical stresses via transformation toughening mechanisms.

Topical Symposia
Room On Demand - Session TS4

Photocatalytic and Superhydrophilic Surfaces

TS4-1 Bixbyite-based Ta-N-O film: A Promising Candidate for Water Splitting?*, Jiri Capek (jcapek@kfy.zcu.cz),* *S. Batkova, S. Haviar, M. Matas, J. Houska,* University of West Bohemia, Czech Republic*; F. Dvorak,* University of Pardubice, Czech Republic

The Ta–O–N materials are an interesting group of materials that may provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). However, it is still a big challenge to prepare highly crystalline Ta–O–N materials in a form of a thin film mainly due to their very high crystallization temperature (800–900 °C).

In our research we utilize the advantages of high-power impulse magnetron sputtering in combination with film post-annealing in a vacuum furnace to prepare single-phase Ta–O–N thin films. Recently, during our work[1] dealing with monoclinic TaON films, fine-tuning of the elemental composition of the films led to a successful preparation of bixbyite-based Ta_2N_2O films. To the best of our knowledge, this material has not been yet reported. In this work, we present the way of preparation of the films and we investigate their properties with respect to the water splitting application. The optical band gap width of this material is 2.0 eV, allowing absorption of visible light up to 620 nm and the band gap is also well aligned with respect to the water splitting redox potentials (based on the ultraviolet photoelectron spectroscopy data). Furthermore, in this work we present and discuss results of carried out ab-initio calculations providing a closer insight into the band structure of this material. Finally, we also present preliminary results of the activity of these films based on electrochemical measurements.

[1] J. Čapek, Š. Batková et al., *Effect of annealing on structure and properties of Ta-O-N films*

prepared by high power impulse magnetron sputtering, Ceram. Int. 45 (2019) 9454.

TS4-2 Double Perovskite $LaFe_{1-x}Ni_xO_3$ Coating Urchin-like Golden Nanoparticles to Enhance Water Splitting Reaction*, Hsiang-Wei Tsai* ***(flylittlewei@gmail.com)****, Y. Su,* National Cheng Kung University (NCKU), Taiwan

$LaFe_{1-x}Ni_xO_3$ (LFNO) has attracted considerable attention. Ni^{3+} is in the low spin state (t^6_{2g}, e^1_g) and the conduction band is formed by the hybridization of Ni^{3+} e_g orbitals and O^{2-}2p orbitals. Since the t_{2g} band is full and e_g electrons form the delocalized σ∗band, it has no localized moments and exhibits Pauli para-magnetism above 50K. In this research, I used the 0.00 mol, 0.01 mole, 0.03 mole, 0.05 mole, and 0.07 mol Ni concentrations to dope into the $LaFeO_3$. As a fundamental understanding, the bonding strength between surface TM (transition-metal) 3d and O 2p states is considered to be the major factor that determines the intrinsic OER activity. The bonding strength between catalyst and adsorbate is predicted by the $E-E_f$ parameter (relative to the E_f), where the larger $E-E_f$ value, the greater the bonding strength because the larger $E-E_f$ indicates a low energy 3d state of TMs and would produce higher hybridization between the TM 3d and O 2p states due to the shortened energy distance. The d-band center close to the E_f can enable strong bonding between adsorbed oxygenated species and surface TMs, which promotes electron transfer and thus boost OER activity.

Furthermore, another my attempt is to improve the localized surface plasmon resonances with sea-urchin-like Au nanoparticles fabricated. Au–Ag alloy Nus (Nano urchin structure) are novel metal nanoparticles that have been employed as a SERS active substrate. Moreover, an individual Au–Ag alloy Nus exhibit a high density of nanotips, which could dramatically increase its surface area and bring more active sites, further enhancing its catalytic properties. The photocatalytic water-splitting into H_2 and O_2 is a direct solar-to-chemical energy conversion technology and has become a research hotspot globally. Photocatalytic H_2 production usually goes through a route that photoexcited electrons reduce the protons in solution to hydrogen atom chemisorbed on the catalyst surface and then desorbed into H_2. Finally, $LaFe_{1-x}Ni_xO_3$ is combined with sea-urchin like Au nanoparticles to be as the hetero-junctional photocathode. Due to LSPR, porous structures, and mixed secondary-phase, the water-splitting process is augmented under visible-light irradiation.

TS4-3 Effect of Tungsten-Substitution on the Structure and Photocatalytic Properties of Anatase TiO_2 Thin Films Deposited on Polymer by PECVD*,* ***William Ravisy (william.ravisy@cnrs-imn.fr)****,* Université de Nantes, France*; B. Dey, S. Bulou, P. Choquet,* Luxembourg Institute of Science and Technology, Luxembourg*; N. Gautier,* Université de Nantes, France , France*; A. Goullet,* Université de Nantes, CNRS, France*; M. Richard-Plouet, A. Granier,* Université de Nantes, France

Whereas most coating techniques require a high-temperature step in order to crystallize TiO_2 as the anatase phase, it has been shown that crystallized TiO_2 could be deposited at T≤130°C with a Plasma-Enhanced Chemical Vapour Deposition (PECVD) process, without further thermal treatment and thus allowing the use of thermally sensitive substrates.[1] These films exhibit a potentially high surface area, due to a columnar morphology, with anatase crystallization, which are two necessary features for efficient photocatalysis. However, photocatalytic activity is still limited by the value of TiO_2 band gap in the UV domain, allowing absorption of only 10% of the solar spectrum and hence restricting its efficiency as photocatalyst.

Among other possibilities to enhance properties of the TiO_2 thin films, substituting Ti with an alliovalent cation such as tungsten is expected to increase oxygen vacancies and shift the band gap energy toward higher wavelengths and ultimately to induce absorption in the visible range.[2][3]

In this work, W-substituted TiO_2 thin films have been deposited on Si and polymer substrates by Low-Pressure Low-Temperature PECVD. Titanium Tetraisopropoxide (TTiP) and Tungsten(V) Ethoxide were injected in a 400W radiofrequency inductively coupled oxygen plasma. W concentration was tuned by varying the flowrate of tungsten ethoxide carrier gas (O_2) or container temperature. All the 250nm-thick films were characterized by Raman and X-Ray Photoelectron Spectroscopy, X-Ray Diffraction, SEM and TEM to investigate their composition and nanostructure. The film growth was monitored by in situ spectroscopic ellipsometry. Photocatalytic activity was studied by measuring methylene blue decomposition in aqueous solution.

W concentrations were measured ranging from 1 to 14 at% and it was found that tungsten precursor was partly oxidized in the plasma phase from oxidation state V to VI. In the thin films, the columnar morphology is retained and anatase is still found although in quantities diminishing with W concentration. Moreover, preferential orientation of anatase growth is also impacted by the substitution with W cations. Finally, it was found that photocatalytic activity was significantly improved by tungsten substitution, especially at low amounts (<10%at).

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TS4-4 Photocatalytic Activity of a ZnO/Bi_2O_3 Thin Film Heterojunction*,* ***Sandra E. Rodil (srodil@unam.mx)****,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico*; A. Hernandez-Gordillo, M. Bizarro,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; J. Medina,* Instituto de Ciencias Aplicadas y Tecnologias, Universidad Nacional Autonoma de Mexico

Zinc oxide (ZnO) has been known as an outstanding photocatalyst in water treatment with an important performance in the degradation and mineralization of several organic pollutants with the use of UV radiation. Unfortunately, UV radiation only represents a small part of the solar light spectrum. A possible method to extend the functionality of ZnO into the visible light is the formation heterostructures with another semiconductor material. An adequate candidate is bismuth oxide (Bi_2O_3) which has appeared recently as a photocatalytic material with the advantage of working in the visible range. In this work, bilayers of ZnO/Bi_2O_3 were produced combining spray pyrolysis and magnetron sputtering techniques aiming to produce a visible-light active photocatalyst for the degradation of organic compounds. Firstly, ZnO thin film was sprayed on glass substrates and subsequently Bi_2O_3 dots were sputtered on this surface. The structural, morphological and optical properties were studied and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy as well as the chemical composition by X-ray photoelectron spectroscopy (XPS). The photocatalytic response was evaluated following the degradation of indigo carmine (IC) under UV and visible light. The results show that the photocatalytic activity under white light irradiation of the ZnO film was improved with the coupling of the Bi_2O_3 dots, attaining a superior mineralization degree compared with ZnO and Bi_2O_3 films separately. It was found that depending on the irradiation source, the production of hydroxyl or superoxide radicals is affected which promotes different degradation mechanisms of the IC molecule.

Topical Symposia
Room On Demand - Session TS5
Thin Films on Polymer Substrates: Flexible Electronics and Beyond

TS5-1 Conversion of Aluminium Oxide Coated Films for Food Packaging Applications – From a Single Layer Material to the Finished Pouch*, C. Struller,* Bobst Manchester Ltd., UK*;* ***Peter Kelly (peter.kelly@mmu.ac.uk)****,* Manchester Metropolitan University, UK*; N. Copeland,* Bobst Manchester Ltd, UK

Transparent barrier films based on vacuum deposited aluminium oxide (AlO_x) layers are continuing to create large interest in the market with regards to their use as food and healthcare packaging materials. Nevertheless, their post-metalliser conversion to the final packaging material still presents challenges to current AlO_x producers and the wider converting industry. In this work, AlO_x coated PET films have been developed and then converted in long duration industrial-scale trials via topcoating, printing, lamination and finally pouch making. Throughout this process, each conversion step has been investigated for its effects on the barrier performance. It was found that the printing processes, especially, induce significant damage to the ceramic barrier layer. However, by the use of a protective topcoat prior to any conversion step, the barrier properties of the AlO_x coated film were preserved, or could even be significantly enhanced, depending on the topcoat material. Furthermore, for a barrier topcoat, remarkable stretch- and flex-durability properties were achieved in the final laminate.

TS5-2 Functionalised Copper Nanoparticle Catalysts for Electroless Copper Plating on Textiles

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The MATUROLIFE project utilises two disciplines of materials science and design to meet the needs of older adults to lead independent lives through design-driven Assistive Technology (AT). Metallised conductive textiles are potentially an enabling technology for AT allowing better and more discreet integration of electronics into clothing, footwear, and furniture.

Electroless copper plating can be regarded as an enabling technology for electronic textiles, due to the uniform deposition with consistent thickness, simplicity, and relatively low cost. This procedure is a useful approach to produce electrically and thermally conductive fabrics that are flexible to be utilised as smart textiles. However, the choice of catalyst is crucial to activate the surface and generate nucleation sites for the copper ions to deposit on. The most widely used catalyst is a palladium/tin colloid, however, the use of palladium makes the process expensive. Therefore, alternative and inexpensive metals such as silver and copper have been recently investigated to catalyse the electroless copper plating reactions.

In this study, different catalysts based on Cu nanoparticles (functionalised by various organic molecules) have been utilised for electroless copper plating of textiles. The catalysts were characterised using Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), and X-ray Photoelectron Spectroscopy (XPS). The efficacy of different catalysts was determined by characterising electroless copper-plated textiles in terms of mass gain (after plating), the coatings coverage, and deposits morphology using Scanning Electron Microscopy (SEM). In addition, the sheet resistance of the plated textiles was measured using a four-point probe.

It was found that the degree of coverage of fibres by copper coatings and the resulted conductivities are strongly dependent on the applied catalyst. The results revealed the important role of functionalising molecules on the performance of Cu nanoparticles as a catalyst. Using the best-performing organic molecule in functionalisation of Cu nanoparticle catalyst resulted in coatings with complete coverage and consequently high electrical conductivity being favourably comparable to the coatings catalysed with a Pd catalyst.

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TS5-3 Low-temperature Plasma Enhanced Atomic Layer Deposition of ZnO and Al_2O_3 Thin Films for Applications in Flexible Electronic Devices

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Thin films of zinc oxide (ZnO) and aluminum oxide (Al_2O_3) were grown by plasma-enhanced atomic layer deposition (PE-ALD) using O_2 and H_2O plasma at 70 °C. An optimization of deposition parameters was performed in order to obtain atomically saturated layers. The films were grown on ITO/Glass, quartz, p-type silicon and polyethylene terephthalate (PET) substrates. X-ray photoelectron spectroscopy (XPS) revealed a high purity of the obtained films. The optical constants and thicknesses of the grown layers were determined by spectroscopic ellipsometry, while the roughness was measured by atomic force microscopy. High transmittance, above ~90%, was measured by UV-Vis spectroscopy. Electrical characterization was carried out using Keythley 4200 Semiconductor Characterization System. ZnO and Al_2O_3 films were used to fabricate transparent thin film transistors (TFT) on ITO/Glass substrates by means of photolithography.The thickness of the ZnO (n-type semiconductor) was 60 nm, while the thickness of the gate oxide (Al_2O_3) was varied (25, 50 and 100 nm). Aluminum with thickness of 200 nm was used as a gate electrode and source and drain contacts.

The films obtained showed excellent optical, structural, compositional, morphological and electrical properties, what make them promising candidate for electronic and optoelectronic applications, which require low temperature processes.

Keywords: PE-ALD, ZnO, Al_2O_3, low temperature, TFTs, thin films, flexible electronic

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TS5-4 Roll-to-Roll Reactive Ion Etching of Nanoscale Features in Si for Next Generation Flexible Electronics

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Roll-to-Roll (R2R) processing has garnered significant research interest from industry in recent years due to its potential ability to simultaneously address throughput and cost requirements for next generation flexible electronics and the Internet of Things (IoT). However, a complete ecosystem of R2R tools including patterning, deposition, and etch is needed in order to facilitate the transition of device fabrication from wafer-scale to the continuous regime. Many prospective applications also require nanoscale control and repeatability for yield management which necessitates thorough characterization of each process step and an in-depth understanding of the underlying physics of these R2R tools compared to their wafer-scale counterparts particularly during pattern transfer i.e. etching. This work demonstrates progress towards process development and control on an exemplary semiconductor device fabrication scheme utilizing Emerson & Renwick’s Genesis R2R platform. Specifically, we successfully demonstrate etching nanoimprinted patterns of nanopillars into Si in a continuous R2R fashion with submicron resolution. Process verification details include quantifying etch uniformity, directionality and material selectivity at varying web speeds. Furthermore, we discuss the systematic characterization of the constituent processes and equipment by intelligent Design of Experiment (DOE) allowing for process parameter tuning to meet desired etch targets.

TS5-5 HiPIMS Metallization of Polymers: Titanium on PEEK

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Metallized polymers are becoming a prevalent part of our world, be it in electronic, medical or transport applications, and the performance requirements for these metal-polymer systems are becoming more demanding. Meeting these requirements means gaining a better understanding of plasma-polymer and metal-polymer interactions, both of which can occur in coating processes. High Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor deposition method characterized by a large fraction of ionized metal species in the coating discharge, which allows for a high level of control over film-forming species. This makes HiPIMS a method of choice to study and tailor the substrate-film interphase region responsible for ‘good’ and long-lived thin film adhesion. However, prior to HiPIMS metallization, the polymer must be ‘activated’ such as to raise its surface energy.

In this work, we evaluate the chemistry of a polymer surface before and after plasma activation using XPS, ToF-SIMS and ATR-FTIR. We then relate this to HiPIMS-metallized surfaces and interfaces using the same techniques. The test metal-polymer system for this study is titanium on Polyetheretherketone (PEEK), a system that has shown exemplary adhesion in a former study.

TS5-6 Fragmentation of ALD-PVD Multilayers on Flexible Substrates in Uniaxial and Biaxial Tension: Insights from in situ SEM and Synchrotron Diffraction Experiments

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Brittle layers are often dominating the deformation behavior of flexible thin film multilayer structures, where the modulation period ($t_{brittle} + t_{ductile}$) as well as the modulation ratio ($t_{brittle}/t_{ductile}$) influence the extent of embrittlement [1].

In this work, a unique combination of atomic layer (ALD) and physical vapor deposition (PVD) is used to fabricate model multilayers of Al and Al2O3 and study fundamental deformation mechanisms in brittle/ductile multilayers on flexible polymer substrates (Polyimide, 50 µm, Upilex-S®). The ability of operating the ALD/PVD process without breaking vacuum opens up a wide range of otherwise unachievable modulation and thickness ratios. For Al2O3 layers thickness control with precision down to 0.1 nm can be achieved. The investigated individual layer thicknesses are 50nm for Al

(PVD) and 0.1 nm – 10 nm for Al2O3 (ALD) layers. Constant oxide thicknesses (50/2/50/2…) and cross-sectional thickness variations (50/1/50/3…) are used to determine crack onset and propagation as a function of oxide layer thickness during *in situ* uni- and biaxial tensile experiments. Uniaxial fragmentation is studied *in situ* with scanning election microscopy (SEM) and focused ion beam cross-sectioning. This *in situ* approach avoids crack closure due to relaxation of the polymer substrate after unloading. Biaxial tensile experiments, performed at the Synchrotron Soleil (Paris, France), reveal the evolution of Al film stresses as a function of applied strain from X-ray diffraction and $\sin^2$psi analysis. Digital image correlation is used to measure true strains on the thin film surfaces. All multilayer structures have good adhesion between individual layers as well as to the polymer substrate. Grain growth of Al is limited by the Al2O3 layers, allowing for easy discrimination of individual Al layers. The Al2O3 layers show increasing stretchability with decreasing film thickness, as a result of being extremely well defined and practically defect free. In biaxial tension, fracture of 8nm Al2O3 at 2.2% strain induces through thickness cracking. Crack onset correlates to a relaxation of the Al film stresses. In contrast, samples with 2nm oxide layers do not exhibit a pronounced crack pattern or stress relaxation within the tested strain regime.

The possibility to manipulate Al grain sizes by ultrathin ALD layers and the observed deformation behavior of the multilayers highlights the potential of the combined deposition technique for designing flexible thin film systems with improved strength and damage tolerance.

[1] K. Wu, J.Y. Zhang, J. Li, Y.Q. Wang, G. Liu, J. Sun, Acta Mater. 100 (2015) 344–358.

TS5-7 Optically Transparent Bacterial Nanocellulose Composites and Fibroin Substrates for Flexible Organic Devices, *Marco Cremona (cremona@fis.puc-rio.br)*, Pontifícia Universidade Católica do Rio de Janeiro, Brazil; *H. Barud,* Universidade de Araraquara, Brazil; *R. Carvalho,* Pontifícia Universidade Católica do Rio de Janeiro, Brazil; *A. Cebrian,* UNESP, Brazil; *A. Barreto,* PUC-Rio, Brazil; *F. Maturi,* UNESP, Brazil; *R. Silva,* Chalmers University Technology, Sweden; *C. Legnani,* Universidade Federal de Juiz de Fora, Brazil; *S. Ribeiro,* UNESP, Brazil

Cellulose is the most abundant organic material on Earth and an important resource for eco sustainable platform for flexible electronics. Bacterial cellulose (BC) is a good biopolymer choice for applications in the medical field and already reported as substrates for organic devices as organic light emitting diodes (OLEDs). BC can be produced by some species of bacteria as *Gluconacetobacter xylinus* and have been demonstrating a quite promising material due to its high degree of polymerization and higher tensile strength (200-300MPa) and Young's modulus (up to 80GPa). BC substrates are in general semitransparent in the visible region due to the presence of air in the interstices between the cellulosic nanofibers. Efforts to solve this disadvantage have been reported in the literature, with the use of several polymers to fill BC interstices. However, such methods are not always economically feasible, scalable, simple, fast and with chemically green synthetic route. In this work, a polymer from recyclable source, Expanded Polystyrene (EPS), dissolved in a green solvent, d-limonene, was used as biocompatible and conformable substrates for highly efficient green OLEDs. Polystyrene is a polymer having a refractive index (h = 1.5916) close to that of the BC and can be used to fill the interstices between the cellulosic nanofibers increasing the optical transmission. Visible light transmission improves to up 88%, instead of 40% previously achieved by pristine BC. BC-PS substrates were produced by airbrush technique deposition of PS on BC pristine films. These multifunctional composite substrates were successively covered with silicon dioxide (SiO_2) and Indium Tin Oxide (ITO) thin films to be used as conductive substrates. Finally, transparent BC-PS was evaluated as conformable substrate for OLED application. The biocompatible and conformable green OLEDs produced presented current efficiency up to 5cd/A and power density around 2.8mW/cm^2, and are promising as light source for light therapy such as PDT and burning wound healing. Additionally, organic field emission transistors (OFETs) using polyurethane as dielectrics, P3HT as organic semiconductor and Au as contacts and Al as gate were fabricated onto transparent fibroin substrate. The devices retained their properties even under high curvature stresses, presenting maximum values for mobility of 1.8x10^{-2}cm^2/Vs, threshold voltages of -7.6V and low leakage current up to 50V.

Topical Symposia
Room On Demand - Session TSP

Topical Symposia (TS) Poster Session

TSP-1 Transparent nc-Z_rB_2/a-BN Films for Protection of Optical Devices, *Philipp Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru)*, *A. Kozlova, K. Kozlova, E. Levashov,* National University of Science and Technology "MISiS", Russia

Protection of optical devices (portholes and solar cells, solar collectors, etc.) from abrasive effects can be provided by the use of wear - and erosion-resistant ion-plasma coatings, including those based on oxygen-free ceramics. The use of hard and optically transparent Zr-B-N films is promising. Ceramic nanocomposite films were deposited by DC and pulsed DC magnetron sputtering of ZrB/2/ target in the $Ar+N_{/2}$/ gas mixtures. The targets were manufactured by means of self-propagating high-temperature synthesis. The structure, chemical and phase composition of films were studied by high resolution transmission and scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Raman and infrared spectroscopy, energy-dispersive analysis, and glow discharge optical emission spectroscopy. The films were characterized using nanoindentation, sliding pin-on-disk, impact ball-on-plate, abrasive calowear, and scratch tests. The refraction index, coefficients of transmittance (Tr) and reflectance were measured by Cary 5000 Agilent + UMA attachment for wavelength range from 200 to 2500 nm. Results obtained show that films deposited at low nitrogen partial pressure predominantly consist of nanocrystallites of hexagonal ZrB2-phase, 1-20 nm in size and amorphous regions. N-rich films exhibit amorphous structure (a-BN) with nanograins of Zr-contained phases. Specific optical properties were observed for these Zr-B-N coatings including Tr=70-100%. The hardness of 15-37 GPa and Young's modulus of 150-470 GPa were determined for films deposited onto alumina substrates. Coatings demonstrated friction coefficient 0.2-0.4. The addition of nitrogen significantly increased wear resistance in sliding and impact conditions. The work was supported by the Russian Foundation for Basic Research (Agreement No. 19-08-00187)

TSP-2 Novel AuAgSI Thin Film Metallic Glasses With Outstanding Electrical and Mechanical Properties, *Lisa-Marie Weniger (lisa-marie.weniger@stud.unileoben.ac.at)*, *O. Glushko, C. Mitterer,* Montanuniversität Leoben, Austria; *J. Eckert,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Gold based thin film metallic glasses (TFMGs) on polymer substrates combine the high elastic strain limit, low electrical conductivity and superior chemical properties of noble metallic glasses with the flexibility of polymers. This work systematically investigates the novel AuAgSi system to gain fundamental knowledge about thin film metallic glasses as well as tune the composition towards optimized electrical and mechanical properties.

$Au_{85-x}Ag_xSi_{15}$ TFMGs were deposited by magnetron sputter deposition on polymer substrates from the respective three elemental targets. Different compositions with x varying between 0 and 85 at% were fabricated and compared to Au and AgSi. Film thicknesses ranging between 12 nm and 1000 nm were deposited to investigate possible size effects within this system. The amorphous state was confirmed by X-ray diffraction; additionally, time-dependent measurements were performed to prove stability of the TFMGs. The three-component films with Ag contents between 20% and 60% were amorphous and stable over the observed period of two months. In contrast, AgSi and AuSi as well as $AuAg_{10}Si_{15}$ and $AuAg_{70}Si_{15}$ were crystalline. Moreover, the binary systems were unstable showing spontaneous phase separation or even film delamination with time.

In case of crystalline metals, the resistivity of a thin film drastically increases for thickness below 10-20 nm. Contrary to this behavior, metallic glasses like AuAgSi exhibit a constant resistivity over a wide range of film thicknesses. The investigated AuAgSi TFMGs have a lower resistivity than crystalline gold with thicknesses below 13 nm. Additionally, a negative coefficient of resistance was found within this system, which could prevent overheating in potential microelectronics applications these TFMGs.

Mechanical properties of AuAgSi TFMGs were systematically characterized by monotonic tensile tests combined with in-situ resistance measurements. The critical strain, at which cracks are generated and propagate homogeneously, is at least 3% for all amorphous compositions and even higher for film thicknesses below 25 nm. Scanning electron microscopy characterization revealed a fracture morphology characteristic for metallic glasses with two distinct types of shear bands. The high elastic strain limit of the investigated TFMGs results in excellent bending fatigue properties. After 50,000 cycles with an effective bending strain of 1.25%, AuAgSi TFMGs did not exhibit any damage, whereas massive fatigue damage was induced in the crystalline Au sample. This outstanding cyclic performance makes AuAgSi TFMGs a promising candidate for flexible microelectronic devices.

TSP-3 Fe-based Thin Film Metallic Glass Coated on Porous Substrates as an Alternative Photocatalysts for Decolorization of Dye in Industrial Wastewater*, Bryan Hubert (bryan_hubert_alim@yahoo.com),*** National Taiwan University of Science and Technology,Taiwan*; J. Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan*; P. Yiu,* National Taiwan University of Science and Technology, Taiwan

Fe-based thin film metallic glasses (TFMGs) with different atomic compositions were fabricated by magnetron sputtering deposition on various porous substrates to act as a catalyst for dye decolorization. This method showed high potential for effectively coated TFMGs with lower heat required and low-cost process, while Fe-based TFMGs coated on various kind of porous substrates i.e. filter paper exhibited higher color removal efficiency and faster dye decolorization performance compared to the bare filter paper. This result was occurred due to Fe-based TFMGs was a zero-valent iron which had an amorphous atomic packing structure to activate sulfate radical as a reactive species to decompose organic material in dye solution become non toxic substance and its surface contact area enhancement.

The synthesized TFMGs were first characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to check its morphology, deposition quality, and chemical composition, followed by X-Ray Diffraction (XRD) to confirm its amorphous structure. Photocatalytic activity of TFMGs that involved peroxymonosulfate (PMS) activation on the degradation of typical industrial dye in wastewater, were investigated under combination of various parameters, such as LED irradiation, dye concentration, PMS concentration, film thickness, and catalyst amount. The reusability of TFMGs as a catalyst were also studied in this experiment by repeating the degradation process for multiple times. The result was further discussed in this study by the related authors.

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