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

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

BP-ThP-1 Superhard Tungsten-tantalum Diboride (W,Ta)B_2 Coatings Prepared by High Power Impulse Magnetron Sputtering HiPIMS*, **Rafał Psiuk**, P. Denis,* Institute of Fundamental Technological Research, Polish Academy of Sciences, Poland*; Ł. Kurpaska,* National Centre for Nuclear Research, Poland*; T. Mościcki,* Institute of Fundamental Technological Research, Polish Academy of Sciences, Poland

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

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

In this work we present deposition and characterization of tungsten-tantalum diboride (W,Ta)B_2 coatings prepared by HiPIMS. We evaluated the influence of pulse duration, substrate temperature and substrate bias on properties of (W,Ta)B_2 films. Crystalline structure was obtained at 250°C. High hardness above 40 GPa measured by nanoindentation was obtained simultaneously with good adhesion to steel substrates evaluated by scratch-test. Changing the pulse duration highly affected the B/(W+Ta) ratio which had influence on properties of coatings. Deposited films was thermally stable up to 1000°C in vacuum, and was able to withstand oxidation in 500°C

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[2]Garbiec D., Wiśniewska M., Psiuk R., Denis P., Levintant-Zayonts N., Leshchynsky V., Rubach R., Mościcki T., Zirconium alloyed tungsten borides synthesized by spark plasma sintering, *ARCHIVES OF CIVIL AND MECHANICAL ENGINEERING*, 2021

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

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

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

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

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

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

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[3]Atsushi Togo, Laurent Chaput, and Isao Tanaka, Phys. Rev. B, **91**, 094306 (2015) ; https://phonopy.github.io/phono3py/

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

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

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

Solid films containing gas-filled nanopores (nanobubbles) have several unique characteristics: they allow a large amount of gas to be trapped in a condensed state with high stability, and provide a route to tailor the overall mechanical, optical and electromagnetic properties of the films [1-3]. In addition to ion implantation procedures, the bottom-up magnetron sputtering (MS) using He as process gas has been proven to be an innovative and versatile methodology to produce He-charged silicon films [1,2,4,5]. Of particular interest is the use of these “solid-gas” nano-composite materials containing ^{4}He and ^{3}He as solid targets for nuclear reaction studies [4,5]. The incorporation of heavier noble gases such as Ne and Ar is also of interest in this field. In this work, we demonstrate a synergistic effect when using He-Ne and He-Ar mixtures during the MS deposition of Si films. Together with the He incorporation, higher amounts of Ne and Ar can be trapped as compared to pure Ne and Ar plasmas. Microstructural and chemical characterizations are reported in this work by Ion Beam Analysis (IBA) and Scanning and Transmission Electron Microscopy (TEM and SEM, including EDS). In addition to gas incorporation, He promotes the formation of larger nanobubbles. Most interestingly, for the case of Ne, a combination ofhigh resolution X-ray photoelectron and absorption spectroscopies (XPS and XAS) reveal that the binding energy of the Ne 1s photoemission peak and the inflection point in the Ne K-edge absorption spectra show a strong dependence on the nanobubbles size. The proposed methodology provides a new way to optimize the fabrication of Ne and Ar solid targets by achieving the required amounts of trapped gas. New perspectives appear to characterize the spectroscopic properties of the noble gases in a condensed state without the need for cryogenics or high-pressure anvil cells.

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[3] J. G. Ovejero *et al*. *Materials and Design* 171 (2019) 107691

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[5] A. Fernández *et al*. Mate*rials & Design* 186 (2020) art.nr. 108337.

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

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

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

The SPUTTER technology from PLATIT is supported by LGD® (Lateral Glow Discharge) to ensure very good coating adhesion to the base material; thus, there are no droplets and no layer defects on the subtrates. Ceramicoin is a TiB2-based hard coating replicates every detail of the surface and is thus a significant advantage for coin appearance and design features.

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

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

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

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

A Si substrate (ф2 inch, t: 3 mm) scratched with diamond powder and ultrasonically cleaned with acetone was used as the substrate. CH_4-H_2 mixture gas was used as the reaction gas, CH_4 flow rate: 2, 20 sccm, H_2 flow rate: 200, 300 sccm, microwave power: 1250, 1750 W, pressure: 10, 13.4 kPa, synthesis time was fixed to 3 h, respectively. Reaction gas was supplied to the substrate from the upper and the side. For the evaluation of the deposit, surface observation by a scanning electron microscope (SEM), surface profile measurement using a microscope, and qualitative evaluation by a Raman spectrometer were performed.

As a result of SEM observation, a deposit with a clear shape was observed.The results of surface profile measurement using a microscope showed a concave profile when CH_4 gas was introduced from the upper direction and a convex profile when CH_4 gas was introduced from the lateral direction.From the Raman spectra of the products measured coaxially from the center of the substrate. A peak at 1333 cm^{-1} attributed to diamond and a peak at 520 cm^{-1} attributed to Si are observed at all measurement points. In addition, there is a tendency that the peak height attributed to diamond decreases from the center to the edge of the substrate. Evaluation of the IDia/IDLC ratio in the Raman spectra from the various distances on the same axis, film quality was decreased comparison with from the center and the edge of the substrate.

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

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

In this study, the influence of heat treatment temperatures on microstructure and mechanical properties of the magnetron co-sputtering (MoHf)N coatings were investigated. The relationships between phase, hardness, modulus, and tribological behavior were analyzed. The (MoHf)N films were fabricatedat a fixed Ar/N_2 inlet ratio of 12/8 sccm/sccm and 350°C with tunning of the Hf target input power. Three (MoHf)N thin films of Hf variation co-deposition at 2.3, 7.4 and 10.2at% were produced and compared. The vacuum annealing was conducted at 500, 650, and 750°C for 1 hr. The as-deposited (MoHf)N binary nitride coatings exhibited polycrystalline microstructure with B1-MoN, γ-Mo_2N, and β-Mo_2N multiple phases. After 750°C vacuum annealing, increase in hardness from 20.1 to 28.4GPa was obtained. Similarly, the H^3/E^2 increased from 0.163 to 0.298, and the H/E ratio also increased from 0.1 to 0.102. The wear rate was reduced from 201.0 to 112.6 μm^3/Nm. The microstructure of (MoHf)N binary nitride coatings did not evolve significantly, however the mechanical behavior become stronger after vacuum annealing, meaning (MoHf)N coatings exhibited a great resistance to elevated temperature environment.

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

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

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

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

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

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

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

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

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

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

In this study, the energy flux of sputtered atoms on a substrate was correlated to the properties of titanium nitride (TiN) films deposited using direct current magnetron sputtering (dcMS) under mixed Ar and N_2 atmospheres. The neutral titanium sputtered atoms velocity distribution functions (AVDFs) were measured by tunable diode-laser induced fluorescence (TD-LIF), and the flux of particles and their energy were derived. Mass spectrometry was used to characterize the energy-resolved flux of the ions. It was found that the neutral sputtered atoms flux and deposition rate were in good agreement, indicating that the flux of the neutral titanium ground state represents the number of deposited atoms. Moreover, TiN films were deposited at different gas pressures and at various Ar/N_2 gas mixtures close to the conditions where stoichiometric TiN was formed, without bias voltage and heating of the substrates. The energy flux of the sputtered neutral Ti into the substrate was calculated from TD-LIF measurements. At a relatively low magnetron discharge pressure of 0.4 Pa, we demonstrated that the energy of sputtered neutral Ti impinging on the substrate is higher than the energy flux of ionized particles corresponding mainly to Ar^+. Thus, the influence of the energy flux of the sputtered atoms on the texture and microstructure of the films is revealed. The (200) texture was obtained at 0.4 Pa when the energy flux of the sputtered atoms was higher than the ion energy flux. At 1.3 Pa where the sputtered atoms energy flux is one order lower compared to 0.4 Pa the (111) texture was obtained. The high-energy flux of the ground state of Ti sputtered atoms seems to allow stress removal in the films.

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

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

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

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

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

BP-ThP-15 e-Poster Presentation: Fabrication of Pt-Nanocluster Decorated Porous Ni/MoS_2 for Hydrogen Evolution Reaction Application*, **Po-Chun Chen**, National Taipei University of Technology, Taiwan*

A facile and state-of-the-art approach to synthesize porous Ni/MoS_2 decorated with the Pt-nanoclusters for a synergistic effect on hydrogen evolution reaction (HER). The breakthrough of the research is to conduct a promising chemical vapor deposition approach to generate the 3D porous structure MoS_2 by completeness reactions between the sublimation and the deposition. Additionally, the Pt-nanoclusters and Ni are straightforwardly introduced by a hierarchical chemical reduction process to enhance the catalytic activity. Therefore, the porous MoS_2 and Pt-decorated porous Ni/MoS_2 were employed as the electrochemical catalyst for HER. The results showed that the CVD process and the decorated Pt-nanoclusters play important roles in determining the HER catalytic activity. The porous MoS_2 largely increased the surface area and active reaction site for the HER performance. In addition, the decoration of Pt-nanoclusters on porous Ni/MoS_2 can demonstrate the synergistic effect of the Pt-decorated porous Ni/MoS_2. So, the overpotential (η10) and the Tafel slope of the Pt-decorated porous Ni/MoS_2 are determined in 43 mV and 56 mV/dec, respectively. The promising approach to synthesizing Pt-decorated porous Ni/MoS_2 for adjustment of different compositions is discussed in this study.

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

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

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

In this research, ozone (O_3) plasma with high oxidation ability has been applied for high quality interfacial layer (IL) formation. However, an undesirable equivalent oxide thickness (EOT) growth seems to be unavoidable, which may degrade the electrical performance for germanium (Ge) n-type metal oxide semiconductor field effect transistor (nMOSFET). Notably, the EOT can be thinned and quality of IL of Ge nMOSFET can be kept with an additional post hydrogen plasma treatment. As a result, Ge nMOSFET with O_3+H_2 plasma treatment exhibits lower subthreshold swing and higher on-off current ratio.

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

A multicomponent nitride with multilayer structure design is one of the most promising methods for improving the comprehensive performance of TiAlN-based hard coatings applied to high temperature applications. In this study, nanostructured AlCrN/TiAlNbN and AlCrBN/TiAlNbSiN multilayer coatings were deposited using multi-target cathodic arc evaporation. This work investigates the structure evolution of the different coatings with oxide scale growth and diffusion processes occurring during oxidation at high temperature of 900 ^oC, and the roles of B and Si addition in their oxidation resistance were examined. Different oxidation mechanisms of the coatings are discussed. The deposited AlCrN/TiAlNbN coating showed a typical columnar structure with nanolayer stacking (average bilayer periodic thickness ~14.8 nm). A titanium-rich oxide layer was formed on the surface, and the inner oxide layer of the oxidized AlCrN/TiAlNbN coating was mixed metal oxides with major Al_2O_3 that retarded further oxidation. The addition of AlCrN into the TiAlNbN acted as an oxidation barrier to inhibit the oxidation of TiAlNbN. The AlCrBN/TiAlNbSiN coatings, which had average bilayer periodic thickness 11.4 nm ~12.2 nm, showed fine-fibrous growth morphologies and refining effects of B and Si in the AlCrBN/TiAlNbSiN coatings, and they possessed better high temperature oxidation resistance thang that of AlCrN/TiAlNbN. Oxidation behaviors of the AlCrBN/TiAlNbSiN with different AlCrBN layer thicknesses were studied. The AlCrBN/TiAlNbSiN with larger layer thickness of AlCrBN possessed the best oxidation resistance among the investigated coatings due to the formation of a protective oxidized layer with a mixture of metal oxides, which reduced inward diffusion of oxygen during oxidation.

BP-ThP-19 Annealing Modulated Microstructural and Electrical Properties of PEALD-derived HfO_2/SiO_2 Nanolaminates on AlGaN/GaN*, B. Wang, Y. Li, M. Chen, **Duo Cao**, F. Liu, W. Shi,* Shanghai Normal University, China

In the current work, HfO_2/SiO_2 nanolaminates and HfO_2 films were grown on AlGaN/GaN substrates via plasma-enhanced atomic layer deposition. A comparative study of how rapid thermal annealing modulates the microstructural and electrical properties of both films has been presented. It is found that the HfO_2/SiO_2 nanolaminate keeps an amorphous structure when thermally treated below 600 °C, whereas crystal grains appear within the 800 °C annealed sample. High-temperature annealing facilitates the transformation from Hf-O and Si-O to Hf-O-Si in the HfO_2/SiO_2 nanolaminates, forming an $HfSiO_4$ composite structure simultaneously. The 800 °C annealed HfO_2/SiO_2 shows a low k value and large leakage current density. While the 600 °C annealed HfO_2/SiO_2 possesses an effective dielectric constant of 18.3, a turn-on potential of 9.0 V, as well as a leakage density of 10^{-2} μA/cm^2 at gate biases of both -10 and 2 V, revealing good potential in fabricating high electron mobility transistors.

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

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

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

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

[1] J. Musil, J. Vlcek, P. Zeman et al.: Jpn. J. Appl. Phys. 41 (2002) 6529.
[2] J. Musil, M. Zítek, K. Fajfrlík, R. Čerstvý: J. Vac. Sci. Technol. A 34 (2016) 021508.

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

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

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

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

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

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