Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B1

PVD Coatings and Technologies

B1-1 On Electron Heating and Ion Recycling in the High Power Impulse Magnetron Sputtering Discharge*, Jon Tomas Gudmundsson (tumi@hi.is),* University of Iceland*; D. Lundin,* Linköping University, Sweden*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; T. Petty, T. Minea,* LPGP, Universite Paris-Sud, France*; N. Brenning,* KTH Royal Institute of Technology, Sweden

In the past it has been assumed that the magnetron sputtering discharge is maintained by the sheath acceleration of secondary electrons emitted from the target, upon ion impact. This is described by the well-known Thornton equation, which in its original form [1] is formulated to give the minimum required voltage to sustain the discharge. However it has been demonstrated recently that Ohmic heating of electrons outside the cathode sheath is roughly of the same order as heating due to acceleration across the sheath in dc magnetron sputtering (dcMS) discharges [2]. Furthermore, for the high power impulse magnetron sputtering (HiPIMS) discharge we find that direct Ohmic heating of the plasma electrons is found to dominate over sheath acceleration by typically an order of magnitude [3]. In HiPIMS discharge a high density plasma is created by applying high power pulses at low frequency and low duty cycle to a magnetron sputtering device. Here we discuss the large discharge currents and the discharge current composition at the target surface in HiPIMS discharges. We discuss the role of self-sputter(SS-) recycling and working gas recycling within the discharge. We find that above a critical current density $J_{crit} \approx 0.2$ A/cm^2, a combination of self-sputter recycling and working gas-recycling is the general case [4]. For high self-sputtering yields, the discharges become dominated by SS-recycling, contain only a few energetic secondary electrons. For low self-sputtering yields, the discharges operated above J_{crit} are dominated by working gas recycling, and secondary electrons play a more important role. We explore a discharge with Al target which develops almost pure self-sputter recycling, a discharge with Ti target that exhibits a mix of self-sputter recycling and working gas-recycling [5] and a reactive Ar/O_2 gas mixture where working gas-recycling is dominating [6].

[1] J A Thornton, J. Vac. Sci. Technol. 15 (1978) 171

[2] N. Brenning et al., Plasma Sources Sci. Technol. 25 (2016) 065024

[3] C Huo et al., Plasma Sources Sci. Technol. 22 (2013) 045005

[4] N. Brenning et al. Plasma Sources Sci. Technol. 26 125003 (2017)

[5] C. Huo et al., J. Phys. D: Appl. Phys. 50 354003 (2017).

[6] J. T. Gudmundsson et al. Plasma Sources Sci. Technol. 25, 065004 (2016).

B1-2 Tailoring the Chemical Composition and Microstructure of Cr_xN Deposited by HiPIMS through Duty-cycle Modifications*, Martha Cedeño-Vente (m.cedeno@posgrado.cidesi.edu.mx),* *G. Mondragón-Rodríguez, N. Camacho, A. Gómez-Ovalle, J. González-Carmona, J. Alvarado-Orozco, D. Espinosa-Arbeláez ,* Centro de Ingeniería y Desarrollo Industrial (CIDESI), Mexico

The main challenge in hard coating manufacturing is developing dense, flawless, and smooth surface morphology coatings, which improve the performance of components exposed to severe service conditions. One of the most promising coating techniques to achieve this goal is the High-Power Impulse Magnetron Sputtering (HiPIMS), which produces highly ionized plasmas, resulting in definite improvements on the film microstructure and properties. The application of pulses (50 - 500 µs) during the deposition process attains a high ionization rate in HiPIMS. The pulse modification (*e.g.,* duty-cycle, also known as τ) affects the current density, modifying the stoichiometry and chemical composition of the coating; this indicates that the pulse appropriate selection is a viable and practical alternative for obtaining graded or multilayer metal nitrides at a fixed gas flow, thus tailoring the coating internal stress distribution, microstructure, and mechanical properties.

In this work, the duty-cycle design to modify the chemistry, microstructure, and residual stresses of Cr_xN coatings is presented and discussed. The average current tends to increase from 2.9 to 12 % with the variation of τ during the HiPIMS process. These process conditions lead to a significant increment of the deposition rate and the chromium content in the Cr_xN coating. Various crystalline phases like α-Cr, α-Cr + h-Cr_2N, h-Cr_2N, and h-Cr_2N + c-CrN were obtained in the film, resulting in graded multilayer systems. Cr-rich samples presented faceted columns with intercolumnar pores and cauliflower-like surface morphology. The growth of the h-Cr_2N phase caused a decrease of the grain sizes, and their morphology changed to pyramidal or stacked pyramids at lower duty-cycles. The transformation of the h-Cr_2N to CrN leads to highly dense columnar microstructures, while the residual stresses of the coating increased with the higher duty-cycle.

Keywords: *HiPIMS, duty-cycle, Cr_xN, graded microstructure.*

B1-3 New Approaches for AlCrN-Based Coatings for High Speed Applications*, Markus Schenkel (markus.schenkel@eifeler-vacotec.com),* voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany*; S. Spor,* voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany, Austria*; N. Gerhards, U. Zimmermann, F. Nahif,* voestalpine Eifeler Vacotec GmbH, Düsseldorf, Germany

The CO2 debate—a global challenge requires the necessity of renewed investments and innovations by manufacturers and suppliers with a strong focus on an increase of sustainability. Especially, the automotive sector (driven by the governmentally regulated CO2 emission limit), in detail the trends for the e-mobility, which has reached higher levels of importance. Consequently, high-performance materials and versatile material combinations with focus on weight reduction and energy-efficient automotive design are replacing conventional materials. The trend to a reduction of the cycle times of the production lines, leads to new challenges in the application of tools, such as higher mechanical and thermal loads exposure during operation.

Thus, the talk will focus on the technical possibilities to overcome these challenges by the appropriate choice of coating design using the example of aluminum-chromium nitride based coatings.

B1-4 Investigation of the Influence of the Thickness of Nanolayers in Wear-resistant Layers of Ti-TiN-(Ti,Cr,Al)N Coating on Destruction in the Cutting and Wear of Carbide Cutting Tools*, Alexey Vereschaka (dr.a.veres@yandex.ru),* *S. Grigoriev,* MSTU Stankin, Russian Federation*; N. Sitnikov,* National Research Nuclear University MEPhI, Russian Federation*; J. Bublikov,* Ikti Ran, Russian Federation

The paper presents the results of the investigation into the formation of the nanolayer structure of the Ti-TiN-(Ti,Cr,Al)N coating and its influence on the thickness of coatings, their resistance to fracture in scratch testing, and the wear resistance of coated tools in turning 1045 steel. The structure of the coatings with the nanolayer thicknesses of 302, 160, 70, 53, 38, 24, 16, and 10 nm was studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution (HR) TEM. It is shown that the grain sizes in the nanolayers decrease to certain values with an increase in the thickness of the nanolayers, and then, with a further decrease in the nanolayer thickness, the grain sizes of the nanolayer grow as the interlayer interfaces cease to produce a restraining effect on the growth of the grains. The study found that the nanolayer thickness influenced the wear of carbide cutting tools and the pattern of fracture for the Ti-TiN-(Ti,Cr,Al)N coatings.

B1-5 INVITED TALK: Industrial Scale ta-C Coating Using Laser Arc Technology*, Wolfgang Fukarek (wolfgang.fukarek@tenneco.com),* *B. Gebhardt,* VTD Vakuumtechnik Dresden GmbH, Germany*; V. Weihnacht, F. Kaulfuss,* Fraunhofer IWS, Germany **INVITED**

First reports about a Laser-initiated vacuum arc date back to 1976 /1/. Laser ignition has many advantages particularly for pulsed high current vacuum arcs when spatial and temporal control at high pulse repetition rates for millions of pulses is required. This holds especially for the carbon arc which deviates markedly from metal arcs with respect to arc movement, charge state and degree of ionization and particle generation. The carbon arc is preferentially operated at pulsed arc currents in the kA range and pulse lengths of some 100 µs. The Carbon Laser-Arc has been investigated and applied to deposition of highly tetrahedral amorphous carbon films (ta-C) since the 1990th/2/. Only in recent years the Carbon Laser-Arc was introduced in mass production for coating of automotive powertrain components as well as for other tribological applications and cutting tools. In this paper we discuss different aspects of upscaling ta-C Laser-Arc coating systems in order to increase the throughput and the total amount of deposited carbon per batch. The importance of process stability for long coating runs is discussed. We also report on deviating film properties that have been observed on films deposited at intermittent high-rate deposition of ta-C.

/1/ J.E. Hirshfield, Laser-initiated vacuum arc for heavy ion sources. IEEE Transact. Nucl. Sci. 23, 1006-1007 (1976)

/2/ H.-J. Scheibe et al, Laser-arc: a new method for preparation of diamond-like carbon films. Surf. Coat. Technol. 47, 455-464 (1991).

B1-7 Key Importance of the Controlled Reactive HiPIMS for Low-temperature Preparation of Tunable Oxynitrides and Thermochromic Oxides*, Jaroslav Vlček (vlcek@kfy.zcu.cz), J. Houška,* University of West Bohemia, Czech Republic

Reactive high-power impulse magnetron sputtering (HiPIMS) with a feedback pulsed reactive gas (oxygen and nitrogen) flow control and to-substrate reactive gas injection into a high-density plasma in front of the sputtered metal target was used for a low-temperature deposition of highly optically transparent Al-O-N films (substrate temperature of 120 °C) and thermochromic VO_2-based films (substrate temperature of 330 °C) onto unbiased substrates.

A modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, was used to produce high-quality Al-O-N films with a gradually changed elemental composition (from Al_2O_3 in AlN), structure and properties. We give the basic principles of this controlled deposition, maximizing the degree of dissociation of both O_2 and N_2 molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O_2 and N_2 molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

We developed a low-temperature scalable deposition technique for high-performance durable thermochromic $ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ coatings. The $V_{0.982}W_{0.018}O_2$ layers were deposited by controlled HiPIMS of V target, combined with a simultaneous pulsed DC magnetron sputtering of W target (doping of VO_2 by W to reduce the transition temperature to 20-21 °C), in an argon-oxygen gas mixture. The effective pulsed oxygen flow control of the reactive HiPIMS deposition makes it possible to utilize the enhanced energies of the ions bombarding the growing $V_{0.982}W_{0.018}O_2$ layers for the support of the crystallization of the thermochromic phase in them at the low substrate surface temperature of 330 °C and without any substrate bias voltage. We present the basic principles of this controlled deposition.

B1-8 Monitoring Tantalum Nitride Thin Films Structure by Reactive HiPIMS Magnetron Sputtering: From Microstructure to Properties*, Angeline Poulon-Quintin (angeline.poulon@icmcb.cnrs.fr), A. Achille,* ICMCB-CNRS, France*; D. Michau,* Univ. Bordeaux, ICMCB, France*; M. Cavarroc,* Safran Tech, France

Tantalum nitride thin films were deposited onto steel substrates using Reactive High-Power Impulse Magnetron Sputtering (HiPIMS) allowing reaching a high ionization degree of the sputtered metallic material thanks to high power density applied to the target during few tens of microseconds pulse. The influence of target power density, N_2 partial pressure, total gas (Ar + N_2) pressure and target-to-substrate distance on film crystalline structure is reported. The structures obtained were investigated by X-ray diffraction and transmission electron microscopy. Cubic metastable phase or hexagonal stable phase can be successfully isolated in single phase continuous layer. The TaN crystalline phase obtained depends strongly on processing parameters especially pulse parameters. It is well known that TaN hexagonal single-phase continuous layer is difficult to isolate using conventional reactive magnetron sputtering. Our previous study, based on RF magnetron sputtering, has shown TaN hexagonal structure formation to be enhanced in growth conditions promoting adatoms mobility on the substrate surface. With HiPIMS, TaN hexagonal phase layer is much more difficult to obtain due to the increase number of process parameters to select, the specific composition and the energy of the plasma created. Comparison of mechanisms involved during the stabilization of each TaN structure depending on the process is presented as well as characterization of microstructure, and properties (mechanical, electrical and optical).

B1-9 INVITED TALK: Multilayer nano-composite Oxidation-resistant Coatings for Accident-tolerant Nuclear Fuel Cladding using Reactive HiPIMS with Positive Kick and Precision Ion Energy Control*, Brian Jurczyk (bjurczyk@starfireindustries.com), R. Stubbers, I. Shchelkanov, T. Houlahan,* Starfire Industries LLC, USA **INVITED**

In the wake of the Fukushima nuclear accident in Japan there is worldwide pressure to improve the accident tolerance of fuels used in light water reactors. A near-term pathway is to deposit a thin protective coating directly on existing Zr-alloy fuel cladding trading coating properties (i.e. chemical resistance, wear resistance, fracture toughness, radiation damage), impact on neutron economy and thermal hydraulics, manufacturing feasibility and implementation readiness, per cladding unit, CapEx and operations costs, regulatory acceptance and quality assurance protocols, and applicability for both pressurized-water and boiling-water conditions. In this study we evaluate a high-throughput fabrication method for nanolayered Cr-based corrosion-resistant and fracture-resistant coatings using a high-power impulse magnetron sputtering innovation—namely the IMPULSE® + Positive Kick™. Ultra-fast IMPULSE® switching achieves high instantaneous plasma densities during HIPIMS discharge pulse for easy control over self-sputtering, ionization fraction and reactive gas management. The adjustable Positive Kick™ quickly reverses the polarity on the sputter target to accelerate metal ions to the substrate—increasing delivered ion fraction and rate for higher efficiency. Precision ion energy control results in fully dense films across a wider range of the Thornton diagram controlling film stress and morphology. Metals and ceramics are precision deposited with excellent adhesion, graded composite nanostructure and conformal layering for radiation hardness, thermal shock- and oxidation-resistance. ~10µm Cr-based coatings were deposited via IMPULSE® + Positive Kick™ on 9.5-mm diameter Zr-alloy cladding with Ar and N_2 gas pressure (0.5-5Pa), cathode power density (0.1-2kW/cm^2), main pulse width (5-100µs), Positive Kick™ voltage (+0-600V), kick delay & width (0-100µs), and repetition rates up to 10kHz. Utility of in-situ surface cleaning via the Positive Kick™ is also demonstrated for adhesion. Samples were characterized pre- and post-testing using mechanical testing, optical and scanning electron microscopy (EDS, EBSD) and x-ray diffraction. Thin-film microstructure was evaluated using SEM, EDS, EBSD and FIB. Corrosion tests were performed in an autoclave using boronated and lithiated water at 360°C at 18.7MPa over sequential time periods for weight gain and spallation/delamination inspection. Manufacturability estimates for volume Zr-alloy coating using a patent-pending inverted cylindrical magnetron configuration optimized for conformal HiPIMS deposition is presented.

B1-12 Multifunctional Coatings with Antifouling Properties*, Jose Castro (jodcastroca@unal.edu.co), I. Carvalho, M. Henriques, S. Carvalho,* University of Minho, Portugal

Additive manufacturing (AM) is a hot topic nowadays, having a first order in importance in research trends, improving existent technologies and carrying them further. AM can be applied to all family types materials: metals, polymers, ceramics and compounds. Among abovementioned, ceramics have a huge importance and application in our current technologies. Their capability to maintain functional properties for long time periods combined with the easiness to process and abundance of raw materials make them a fundamental part of mankind development. Within this type of materials, one of the most commonly used nowadays is stoneware. This material has a wide range of uses, from everyday usage such as kitchenware and pottery to high tech applications such as pipelines, which in some cases are affected by biofouling. Some ceramics are not able to prevent the formation of biofouling formation which can affect their finish and appearance. Trying to solve this issue, TiN and Ag:TiN with oxygen addition coatings in 3D printed stoneware, were presented as multifunctional solution, in order to extend the performance of base material, offering a variety in an aesthetical point of view and adding antibacterial properties. This study performed the aforementioned films by reactive direct current (DC) magnetron sputtering. Films obtained were characterized physical, chemical and morphologically, as well as their color variation, roughness, wettability, antibacterial and antibiofouling resistance. The results revealed that the Ag doped coatings (with or without oxygen addition) had an enhanced multifunctionality compared with control samples (without Ag). The Ag nanoparticles addition created a surface with antibacterial and antibiofouling, in order to resist outdoors and aqueous environments, making these films able to be applied in architectural pieces as sculptures or other decorative parts, maintaining their properties with good aesthetical properties.

B1-13 How to Deposit a Porous Thin Film by Magnetron Sputtering ?*, Diederik Depla (Diederik.Depla@ugent.be), R. De Doncker,* Ghent University, Belgium

Without additional efforts, thin films deposited by magnetron sputtering are dense due to the bombardment by sputtered atoms and reflected neutrals. To overcome this intrinsic feature of magnetron sputtering, several routes have been explored to deposit a porous thin film, and still to benefit from the advantages of magnetron sputtering.

Increasing the deposition pressure and/or tilting the substrate belongs to the most common approaches, but these strategies are plagued by technical issues such as enhanced arcing, a low deposition rate, and limited scalability.

Another strategy is based on the deposition of a mixture of materials, or an alloy which is chemically and/or physically treated to remove one of the constituents. Dealloying by applying a heat treatment and subsequently electrochemical etching is one example that belongs to this group of methods. High temperature and/or (electro)chemical treatments limit the substrate choice, and are often environmentally harmful.

This paper suggests an alternative approach based on the sputter deposition of a powder mixture of a metal with NaCl [1]. The deposited layer is simply treated with water to dissolve the deposited salt, leaving a porous metal layer on the substrate. The thin films are deposited from a powder target composed of NaCl and metal powder. Due to the low thermal conductivity of the target, the target gets hot. As a result, the salt is sublimed while the metal is sputtered from the target. The film composition, and therefore the porosity, is controlled by the applied target power.

This one-source approach without the use of film annealing or aggressive chemicals overcomes the major obstacles of other synthesis routes without compromising the benefits of magnetron sputtering.

[1] Sputter deposition of porous thin films from metal/NaCl powder targets, R. Dedoncker, H. Ryckaert, D. Depla, Appl. Phys. Lett. 115(2019) 041601doi:10.1016/10.1063/1.51128225

B1-14 Evolution of the Microstructure of Sputter Deposited TaAlON Thin Films with Increasing Oxygen Partial Pressure*, **Nina Schalk (nina.schalk@unileoben.ac.at)**, C. Saringer,*
Montanuniversitat Leoben, Austria*; A. Fian,* Joanneum Research Forschungsgesellschaft mbH, Austria*; V. Terziyska, M. Tkadletz,* Montanuniversitat Leoben, Austria

Recently, quaternary oxynitrides of transition metals and aluminum have attracted increasing interest due to their tunable properties. Within the present work, a series of TaAl(O)N films was sputter deposited using constant nitrogen and varying oxygen partial pressures. The films were grown from single element Ta and Al targets. The deposition parameters were adjusted to obtain a Ta/Al atomic ratio of ~50/50 for the oxygen-free film and were held constant for the following depositions, with the exception of the increasing oxygen partial pressure and compensatory decreasing argon partial pressure. Elastic recoil detection analysis revealed oxygen contents of up to ~26 at.%, while the nitrogen content decreased from ~47 at.% in the oxygen-free film to ~35 at.% in the film with the highest oxygen content, resulting in a significant decrease of the metal/non-metal ratio with increasing oxygen partial pressure. The micro- and bonding structures of the films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy and transmission electron microscopy. All films exhibited a dominating face centered cubic TaN-based structure with indications for an additional nanocrystalline phase fraction, which increases with increasing oxygen partial pressure. In addition, the mechanical properties were evaluated by nanoindentation, yielding a decreasing hardness and elastic modulus with increasing oxygen content.

B1-15 Towards Knowledge-based Design of Multi-element Target Materials*, **Mehran Golizadeh (mehran.golizadeh@unileoben.ac.at)**,*
Montanuniversität Leoben, Austria*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), and Felix Bloch Institute, Leipzig University, Germany*; C. Mitterer, R. Franz,* Montanuniversität Leoben, Austria

The increasing demand for multi-element thin films and coatings for multifunctional purposes has pushed the target and cathode material industry to produce multi-element products. Nowadays, alloyed and composite targets are commonly employed in various physical vapor deposition technologies including magnetron sputtering and cathodic arc deposition. The targets, which serve as cathodes in the respective discharges, are exposed to the discharge plasma during the deposition process, which alters their surface properties such as phase and chemical composition. The surface modifications are particularly severe for cathodic arc deposition since the cathode spots impose countless melting-solidification cycles on the target material near the surface, leading to the formation of a network of craters and a several 10 µm thick modified layer. The formation mechanisms and properties of the modified layer, semi-empirically quantified by the cohesive energy of the constituent phases, influence the charge states and kinetic energies of the ions and, hence, the film growth conditions and coating properties.

In a first step, a Mo/Al multilayer cathode was designed to reveal information about the heat-affected zone below the craters as well as the evolution of material intermixing as the sequential cathode spot events take place. The modified layer is formed by micro-sized displacements of the cathode material during crater formation. In addition, the material intermixing predominantly occurs in liquid state while the mechanisms based on solid-state diffusion play an insignificant role due to the sharp temperature gradient (shallow heat-affected zone) below craters and very high cooling rates [1]. As a next step, the microstructure and phase composition of the modified layers of Al-Cr composite cathodes with varying grain sizes were studied. The results from high-resolution analysis techniques revealed that metastable phases, including quasicrystalline phases, are formed during the solidification of arc craters and, hence, are the constituting phases of the modified layers. The average cooling rate in these rapid solidification processes was estimated to be in the order of 10^6 K/s. Accordingly, to optimize the plasma properties for film and coating depositions it is necessary to consider non-equilibrium phases of the alloy system as they might be present on the modified surface. This means that the target's or cathode's microstructure and constituent phases need to be designed to enable the formation of phases with optimized cohesive energy during the rapid solidification of arc craters.

1. Golizadeh, M., et al., J. Appl. Phys., 2020. 127(11).

B1-16 INVITED TALK: Coating Design and Mechanical Properties of Multicomponrnt AlTi(X)N Hard Coatings*, **Yin-Yu Chang (yinyu@nfu.edu.tw)**,*
National Formosa University, Taiwan **INVITED**

Due to economical demands to further increase the efficiency of production processes, it is essential to exploit the full potential of wear resistant hard coatings. TiN and AlTiN-based coatings are widely used as protective material for cutting tools, molds, and mechanical components in mechanical industries. Low chemical reactivity of these hard coatings with workpiece materials protects against sticking and thus reduces the adhesive wear. The most widespread wear resistant coatings are those with the following chemical formula Ti-X-(N,C and B) (X = Al, Cr, C, Si, and B etc.) which have proven to have excellent properties for industrial applications in the cutting, forming and stamping fields.

In this study, the coating design, mechanical property, high temperature oxidation behavior and cutting performance of multicomponent and multilayered AlTi(X)N coatings, which X= Cr, Si and B etc., will be discussed. These high performance coatings can be deposited by using cathodic-arc deposition with arc cathodes or unbalanced magnetron sputtering. Various cathode targets, such as Ti, Cr, TiAl, TiAlSi, CrAlSi, and AlSi, are used for the deposition. The microstructure of the as-deposited and high temperature annealed coatings was characterized by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD) using Bragg-Brentano and glancing angle parallel beam geometries. The mechanical properties including hardness and elastic modulus of the coatings were analyzed by a nanoindenter with Berkovich indenter tip.

Depending on the coating design, the deposited AlTi(X)N coatings showed B1-NaCl crystal structure and have multiple orientations of (111), (200), and (220). The nanohardness, which measured by nanoindentation, of these coatings possessed hardness higher than 30 GPa, depending on the gradient and multilayered structures. The high temperature oxidation test showed the oxidation rate during annealing depends on film composition and microstructure. The oxide layer formed on the AlTiSiN coatings consists of large TiO_2 and AlTiSiN grains at the oxide-coating interface, followed by a layer of protective Al_2O_3 in the near-surface region. Interestingly, after oxidation, the AlTiBN coating contained an oxide layer composed of nanocrystalline Al_2O_3 and TiO_2. No crystallite growth or phase transformation occurred in the unoxidized AlTiBN coating part after oxidation. The gradient, multilayered, and nanocomposite AlTi(X)N show significantly improvement of the lifespan of cutting tools and mechanical parts.

Keywords: Hard coating; Mechanical property; AlTiN; Multicomponent; Multilayer

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B2

CVD Coatings and Technologies

B2-1 *In-situ* Investigation of the Oxidation Behaviour of Chemical Vapour Deposited Zr(C,N) Hard Coatings Using Synchrotron X-ray Diffraction*,* ***Florian Frank (florian.frank@unileoben.ac.at)****, M. Tkadletz, C. Saringer,* Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

ZrN, ZrC and $ZrC_{0.4}N_{0.6}$ coatings were successfully deposited via chemical vapour deposition (CVD) in an industrial scale CVD plant on cemented carbide substrates and steel foils. The microstructure and the mechanical properties of the as-deposited coatings were investigated by scanning electron microscopy, X-ray diffraction (XRD) and nanoindentation tests. To gain insight into the high temperature oxidation behaviour, *in-situ* synchrotron XRD experiments were performed. Powdered samples were annealed in air between 100 °C and 1000 °C, while 2D XRD patterns were recorded. Subsequently, the 2D XRD patterns were azimuthally integrated and the resulting 1D diffractograms were evaluated by sequential and parametric Rietveld refinement. Applying these techniques, the phase evolution during oxidation could be determined. The results were then correlated with differential scanning calorimetry measurements, in order to further illuminate the oxidation mechanism of each coating system. It was shown that all Zr(C,N) samples form tetragonal, cubic and monoclinic ZrO_2 phases, whereas the onset temperature of the individual phases depends on the chemical composition. The investigated ZrCN coating exhibits the highest oxidation resistance, followed by ZrC and ZrN.

B2-3 Ti-Si-B-C-N PECVD Nanocomposite Coatings for Tribological Applications at Elevated Temperatures*,* ***Alexander Nienhaus (alexander.nienhaus@ist-extern.fraunhofer.de)****,* TU Braunschweig, Institute for Surface Technology, Germany

With increased demands for service lifetime of tools in hot forming applications, e.g. extrusion molding and die-casting, surface modifications of hot working steels play an important role to improve its tribological properties under thermal load conditions. The machining of aluminum (Al) and copper (Cu) is especially challenging, considering its tendency to stick at the tools surface, which is increasingly impactful at elevated temperatures. Developing Ti-Si-B-C-N PECVD nanocomposite coatings is a promising approach, because, with an adequate Si-content, thermal stability and oxidation resistance can be increased by forming a thin, amorphous (a-) Si_3N_4 tissue layer between the nanocristalline (nc-) grains, mostly nc-TiN, ncTiC, and nc-TiCN. In this study, the influence of nitrogen on its thermal and mechanical properties is under investigation. The N-content ranged from 0.0..14.6 at.-%. Chemically stable TiB2 phases are formed by adding BCl_3 to the PECVD coating deposition process. These phases are not observed in XRD-diffraction patterns, which indicates a-TiB_2 rather than ncTiB2, e.g. in contrast to Ti-B-N nanocomposite coatings. With C-contents up to 32 at.-%, formation of a-C particles in the a-matrix is likely. High temperature (T = 750-900 °C) in-situ XRD-measurements in air atmosphere provided by synchrotron radiation showed different behavior in oxidation resistance, with dependence of N-content. Furthermore, tempering in air atmosphere at 850 and 900 °C for 30 and 60 min was carried out to gain additional information on the oxidation resistance. In contact with molten or close to molten Al or Cu, Bcontaining nanocomposites are expected to reduce the adhesive wear on the tools surfaces. The multiphase coatings form compositionally complex nanostructures, leading to a universal hardness of up to 39 GPa, close to the so called ‘superhardness’ (> 40 GPa). The starting point of oxidation was determined to be in the range of 850-900 °C, underlining the possible application as protective coating for hot forming tools. Further work will focus on the nanocomposite structure, the mechanical properties, and pin-on-disc tests at T = 750 °C with Al_2O_3 counterparts.

B2-4 INVITED TALK: Atomic Layer Deposition for Complex-Shape and Temperature Sensitive Objects: Towards New Functions and Products*,* ***Frédéric Mercier (frederic.mercier@simap.grenoble-inp.fr)****,* Univ. Grenoble Alpes, CNRS, France **INVITED**

Atomic Layer Deposition (ALD) technique finds many applications today in the fields of microelectronic, batteries and catalysts. Indeed, the intrinsic advantages of ALD like conformality, uniformity and precise control of the thickness at the atomic scale can meet the requirements of the increasing complexity and the variety of objects to be coated. Besides the aforementioned fields, other emerging fields can benefit from the advantages of the ALD technique to provide objects with enhanced functionalities or new products. To illustrate the opportunities and challenges of depositing conformal layers on either complex-shape or temperature sensitive objects or both, the talk will focus on ALD coatings on additive manufactured metallic structures and on biopolymers like cellulose matrices. The talk will include a discussion on their potential applications in energy and packaging industry. Our recent results on enhanced functionalities provided by ALD like surface finishing (color, surface smoothing), high temperature oxidation resistance and gas diffusion barrier among others will be presented. The understanding and improvement of the chemical/thermal compatibility between the object to be coated and the coating will be discussed based on a comprehensive evaluation of the structure and composition.

B2-6 INVITED TALK: Plasma-assisted Deposition using Microdroplets*,* ***Tsuyohito Ito (tsuyohito@k.u-tokyo.ac.jp)****, K. Nitta, K. Terashima,* The University of Tokyo, Japan **INVITED**

With recent development of atmospheric-pressure technologies, various plasma applications with liquid have been extensively studied. In this presentations, we are demonstrating spherical particle deposition as well as pattern drawing via atmospheric-pressure non-equilibrium plasma using microdroplets. By using microdroplets, we can apply more various raw materials hopefully obtaining certain controllability, which are difficult only with gas phase processing.

The first part of the presentation will be demonstration of sub-micrometer spherical particles deposition [1]. Here, we apply microdroplets as semi-closed micro-reactors to control size distribution of synthesized particles. A mist atomizer was used to generate microdroplets with diameter of approximately 5 µm. Such microdroplets were carried by He gas to the plasma reactor. Zinc acetate ($Zn(Ac)_2$) solution was used as a raw material for ZnO particles synthesis and the concentration was regulated at 0.5, 1, and 2 mM (mol/L). The generated particles are deposited on a silicon substrate locating under the plasma generator. The size distributions of the generated particles agree well with the ones expected by the distribution of microdroplets and the concentrations of the raw materials; demonstrating that one particle is generated from one microdroplet in conditions tested here. Thus microdroplets could be used as semi-closed micro-reactors at least for controlling particle sizes.

The later part of the presentation will be about plasma-assisted inkjet printing (PIP), where a microdroplet is injected through plasma by an inkjet system. By using an inkjet system, the controllability of a microdroplet in time and space can be significantly improved, developing a new printing technique, PIP. So far, we have successfully demonstrated silver line drawing [2] as well as the simultaneous polymerization of 3,4-ethylenedioxythiophene (EDOT) monomer stock solution ink and printing of the resulting poly(3,4-ethylenedioxythiophene) (PEDOT) [3]. With silver line fabrications, compared with heat treatment, the line with lower electrical resistivity and a narrower width could be achieved with a much shorter treatment time. As for PEDOT line fabrications, it was demonstrated that plasma-assisted chemical reactions could be combined with inkjet printing method.

Details will be presented at the conference.

[1] M. Tsumaki, Y. Shimizu, T. Ito, Materials Letters **166**, 81 (2016)

[2] M. Tsumaki, K. Nitta, S. Jeon, K. Terashima, T. Ito, J. Phys. D: Appl. Phys. **51**, 30LT01 (2018)

[3] K. Nitta, M. Tsumaki, T. Kawano, K. Terashima, T. Ito, J. Phys. D: Appl. Phys. **52**, 315202 (2019)

B2-8 High Throughput Deposition of Hydrogenated Amorphous Carbon Films using High-Pressure Ar+CH_4 Plasmas*,* ***Kazunori Koga (koga@ed.kyushu-u.ac.jp)****, S. Hwang, K. Kamataki, N. Itagaki, M. Shiratani,* Kyushu University, Japan

Plasma chemical vapor deposition (CVD) method has attracted much attention for fabricating hydrogenated amorphous carbon (a-C:H) films because it can realize to deposit large area films with a good uniformity [1]. In the conventional plasma CVD, the working gas pressure was the range between 0.05 Torr and 1 Torr. The lifetime of carbon-related radicals tends to be shorter for larger gas pressure resulting in a low deposition rate. Here we found a high rate deposition of a-C:H films with high-pressure Ar+CH_4 plasmas.

The experiments were carried out using a capacitively coupled plasma reactor [2, 3]. Ar diluted CH_4 gas was introduced to the chamber. The total gas flow rate and CH_4 concentration were at 98.8 sccm and 3.8 %, respectively. A 1cm x 1cm Si substrate was placed on a substrate holder. 28

MHz voltage of 170 V was applied to the powered electrode. The substrate temperature was room one. To analyze the deposition rate and the mass density, a scanning electron microscopy (JEOL JIB-4600F) and microbalance (Mettler Toledo) were used.

We have examined dependence of substrate position from the powered electrode on deposition rate as a parameter of the gas pressure. For the pressure below 2 Torr, the deposition rate monotonically decreases with increasing the distance *d* between the powered electrode and the substrate from 20 nm/min to 10 nm/min. In contrast, for the pressure above 5 Torr, the deposition rate decreases from around 60 nm/min for *d*= 15 mm to about 30 nm/min for *d*= 30 mm. Photos of the plasmas suggest that the radical generation tends to be localized near the powered electrode and the rate increases with the gas pressure in the region. Therefore, the high deposition rate realizes for *d*= 15 mm for 5 and 7 Torr. The mass density for 7 Torr and *d*=15 mm is 1.41 g/cm^3. To further improve the film characteristics, we studied the effects of dc pulse bias on the substrates. A dc pulse bias voltage Vdc with 1 µs in the pulse duration and 25 kHz in the reputation frequency was applied to the substrates. We found high mass density film of 1.67 g/cm^3 is deposited at 66.7 nm/min for V_{dc}= -202 V. This indicates that the impinging ions can modify the newly deposited films and generate the dangling bonds at the surface, leading to the determination of the mass density and deposition rate [4].

[1] K.J Clay et al, J. Diam. Relat. Mater, 7,1100 (1998).

[2] X. Dong et al, J. Phys: Conf. Ser., 518, 012010 (2014).

[3] K. Koga et al, Jpn. J. Appl. Phys, 55, 01AA11 (2016).

[4] M. Shiratani et al, J. Surf. Coat. Technol, 228, 15 (2013).

B2-9 Influence of Co-enriched Surface Zones in WC-Co Cemented Carbides on the Microstructure and Mechanical Properties of $TiC_{0.6}N_{0.4}$/α-Al_2O_3 Coatings, ***Fabian Konstantiniuk (fabian.konstantiniuk@unileoben.ac.at)**, M. Tkadletz,* Montanuniversität Leoben, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

In metal cutting applications functionally graded near surface zones in WC-Co cemented carbide substrates are applied to optimize their properties, in particular toughness and hardness. Thus, the present work focuses on the influence of Co-enriched substrate surface zones and their thickness on the microstructure and mechanical properties of state-of-the-art $TiC_{0.6}N_{0.4}$/α-Al_2O_3 coatings synthesized using chemical vapor deposition. Complementary cross-sectional energy dispersive X-ray spectroscopy and electron back-scatter diffraction maps provided insight into the grain size, preferred orientation and phase composition of coatings and substrates. While the hardness and Young´s modulus of the coatings were hardly affected by the Co–enriched surface zone and its thickness, nanoindentation maps performed on the cross-sections of the substrates confirmed a lower hardness and Young´s modulus in zones with higher Co content. Since the tensile residual stress in both, the $TiC_{0.6}N_{0.4}$ and α-Al_2O_3 decreased with increasing thickness of the Co–enriched surface zone, as determined by X-Ray diffraction, it is suggested that stress relaxation occurs through plastic deformation of the soft Co-enriched surface zone. Despite the influence on the residual stress, the Co–enriched surface zone and its thickness was found to have no effect on the thermal crack networks of the coatings. However, Rockwell-indentation tests demonstrated a reduction of the coating adhesion with increasing thickness of the Co–enriched surface zone. The results obtained within this work contribute to a better understanding of the influence of a Co-enriched surface zone and its thickness on the performance of $TiC_{0.6}N_{0.4}$/α-Al_2O_3 coated cutting tools.

B2-10 CVD Alumina-based Nanocomposite Coatings, ***Zhenyu Liu (Zhenyu.Liu@kennametal.com)**,* Kennametal Inc., USA

Nanocomposite is a multiphase solid material where one of the phases has the size of less than 100 nanometers (nm) in at least one dimension, or structures having nano-scale repeat distances between the different phases that make up the material. Nanocomposite coating represent a new generation of materials exhibiting completely new properties with respect to the conventional used materials. The superior mechanical properties of nanocomposites originate from their peculiar nanostructures (size effects) and high density of interfaces. The unique structure and exceptional properties make nanocomposite materials a possible alternative to traditional polycrystalline materials, which have met their limits in many recent engineering applications.

Inspired by nanolayer coatings of PVD and multilayer CVD coatings development, we demonstrate a couple of potential Al_2O_3-based nanosomposite systems deposited by CVD process directly using multilayer concepts with well-controlled deposition conditions to maintain the deposited “thin film” at early stage, nucleation regime. As a consequence, the “thin film” would maintain at the island forms or particles/nanoparticles states with the size smaller than 100 nm at least in one dimension, whilst the alumina matrix would keep depositing to form a continuous matrix. Ultimately, a nanocomposite coating can be formed with improved wear resistance and metal-cutting performance. The ability to process nanocomposite by direct nucleation and growth of ceramic materials via CVD technique should provide new technical opportunity on the advanced materials and application development.

Keywords: CVD, Al_2O_3-based nanocomposite, thin films, nucleation, crystal growth

B2-11 Compatibility of a CoCrFeNi Multi-principal Element Alloy Substrate with Halide-based Thermal CVD Processes for TiN Deposition, ***Katalin Böör (katalin.boor@kemi.uu.se)**,* Uppsala University, Sweden*; R. Qiu,* Chalmers University of Technology, Sweden*; A. Forslund,* KTH Royal Institute of Technology, Sweden*; O. Bäcke,* Chalmers University of Technology, Sweden*; H. Larsson,* KTH Royal Institute of Technology, Sweden*; E. Lindahl,* Sandvik Coromant R&D, Sweden*; M. Halvarsson,* Chalmers University of Technology, Sweden*; M. Boman,* Uppsala University, Sweden*; L. von Fieandt,* Sandvik Coromant R&D, Sweden

Multi-principal element alloys (MPEAs) are materials consisting of at least four metallic elements in near–equimolar amounts. These alloys can exhibit new combinations of material properties, either deriving from the new phases formed or from the individual components. Their applications may require a protective coating, it is therefore crucial to investigate their compatibility with conventional coating technologies. Titanum nitride is a widely used corrosion- and wear resistant coating, which is frequently deposited by CVD. This presentation assesses the compatibility of the CoCrFeNi substrate, an important MPEA, with a conventional CVD process for TiN deposition using $TiCl_4/H_2/N_2$ as precursors [1]. Different reactions between the substrate, the coating and the precursors will be discussed. These include substrate etching by Cl-containing species and intermetallic compound or nitride building between the substrate elements and Ti or N, respectively. Substrate etching can result in voids in the substrate and the substrate elements may be redeposited and incorporated in the coating. Intermetallic compounds and nitrides can be formed by diffusion of the substrate elements into the coatings or Ti/N diffusion into the substrate. SEM, XRD and (S)TEM combined with EDS were used to determine which of the mentioned processes take place in the CoCrFeNi-$TiCl_4/H_2/N_2$ system between 850-950 °C. Thermodynamic calculations were carried out using the Thermo-Calc software to determine the stable compounds that can be formed during the process.

The substrate was stable under the process conditions. Only Cr was reactive towards the N_2 precursor and appeared in the coating grain boundaries, shown by EDS in TEM. Thermodynamic calculations predicted that Cr-containing nitride phases could form, explaining the driving force for Cr diffusion in the grain boundaries. XRD results only indicated the presence of a TiN and a CoCrFeNi phase. No intermetallic phases were formed between the substrate elements and titanium and no signs of etching were observed.

The results provide an understanding on the processes involved in the substrate-precursor interaction and the driving forces behind. They explain why CoCrFeNi outperforms elemental Ni, Fe [2] and alloys of its components, giving a basis for determining which multi-component alloys can be compatible with conventional CVD processes.

[1] Böőr, K. *et al.*, *Surf. Coatings Technol.* 393, 125778 (2020)

[2] von Fieandt, L. *et al.*, *Surf. Coat. Technol.*334, 373–383 (2017)

B2-12 Silicon Carbide Coatings for High Temperature Receiver of Concentrated Solar Power Plants, ***Michel Pons (michel.pons@grenoble-inp.fr)**, D. Chen,* University of Grenoble Alpes, France*; J. Colas,* PROMES-CNRS, France*; F. Mercier,* University Grenoble-Alpes, France*; L. Charpentier, M. Balat-Michelin,* PROMES-CNRS, France

There is a growing interest in concentrating solar power plants as electricity generation systems. M irrors concentrate the sun's energy to drive traditional steam turbines or engines that create electricity. The thermal energy concentrated in a CSP plant can be stored and used to produce electricity when it is needed, day or night. One of the challenges is to build the solar receiver which can work at temperatures near or higher than 1000 °C for optimizing the yield. Current candidate materials are metallic alloys such as Inconel, or bulk ceramics like silicon carbide, but their operating temperatures may be limited due to oxidation or mechanical problems. Silicon carbide coatings, deposited by chemical vapor deposition technology at 1100 °C, are selected for their high thermal conductivity, low thermal expansion coefficient, high temperature stability and oxidation resistance. They forms stable and protective silica scales at temperatures higher than 1000°C. Oxide dispersion strengthened (ODS) FeCrAl alloys (Kanthal APMT), are alumina-forming alloys which can resist to high temperature oxidation. They are chosen as model substrates to study the potential of SiC coatings. Accelerated cyclic oxidation and high temperature emissivity measurements are performed in Promes solar furnace facilities (France), confirming the potential of silicon carbide coatings as materials for high temperature central receivers. The SiC based multilayered system exhibits low degradation after 1500 h of oxidation at 1000 °C in air. The modelling and simulation of stresses during thermal cycles taking into account the creep and growth of the oxide layer are used to show the limits of use of these materials.

B2-13 Hot Filament CVD Diamond Coatings for Hard-to-machine Materials*, **Michael Woda (michael.woda@cemecon.de)**, W. Puetz, M. Frank, W. Koelker, C. Schiffers, O. Lemmer,* CemeCon AG, Germany

In the group of carbon-based coatings, polycrystalline CVD diamond thin films reveal some extraordinary material properties. Applying the very high hardness of up to 10000HV onto cutting tools enables economically feasable tool usage when machining very high abrasive materials. CVD diamond thin films are typically coated by either microwave or hot filament CVD techniques. On cutting tools with cemented carbide substrates and complex geometries hot filament CVD is well established on an industrial scale nowadays. The basics of hot filament CVD diamond coating technology are briefly introduced in the scope of this presentation. The films coated by this method can be utilized to address cutting of work piece materials including Carbon fiber reinforced plastics (CFRP), ceramics, graphite, Aluminum-Silicon alloys or even sintered carbide. This work presents results of case studies revealing the benefits of CVD diamond coatings upon cutting operations on these very demanding work piece materials.

B2-14 Ald-Pvd Multilayers: Deposition, Thermal Stability And Mechanical Properties*, **Thomas Edwards (thomas.edwards@empa.ch)**, T. Xie, L. Petho, S. Büchel, X. Maeder, B. Putz, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The extent of the embrittlement in ductile-brittle multilayers often depends on the modulation period ($t_{brittle}$ + $t_{ductile}$) as well as on the modulation ratio ($t_{brittle}/t_{ductile}$) [1]. In this work, ductile-brittle multilayers of Al / Al_2O_3 / Al… and Ti / TiO_2 / Ti… were produced on Si substrates by a unique combination of atomic layer (ALD, Al_2O_3, TiO_2) and physical vapor deposition (PVD, Al, Ti) within a single deposition system. Using this ALD/PVD combination, neighbouring layer thicknesses can easily differ by one order of magnitude or more. In particular, the ability to deposit continuous sub-nm layers with ALD opens up a wide range of otherwise unachievable modulation and thickness ratios. The thicknesses and structures of the ALD layers were verified by HR-TEM imaging of lift-outs. Further depositions on flexible substrates have also been performed with thinner Al layer thicknesses to minimize residual stresses. The Al_2O_3 or TiO_2 layer thickness is varied across the multilayer cross-section (0.1 nm – 10 nm) to study the effect on strength of the film as determined by microcompression, and on crack onset and propagation as a function of oxide layer thickness in tensile tested multilayer films. Single layered films (Al or Al_2O_3, etc.) are used as reference materials. Further the thermal stability of such multilayer films was studied up to 0.9 T/T_m, considering the stability and crystallinity of the ALD interlayers and the texture of the PVD layers. Grain growth of Al is limited by the Al_2O_3 layer, allowing for easy discrimination of individual Al layers necessary for locating onset of cracks, and for cross-sectional fragmentation analysis by focused ion beam (FIB) cross-sectioning under tension which avoids crack closure upon unloading. The multilayer structure has good adhesion between individual layers as well as to the polymer substrate and the oxide layers show increasing stretchability with decreasing film thickness, as a result of being extremely well defined and practically defect free. This study helps improve the understanding of deformation mechanisms in flexible thin film structures and can give useful guidelines for strong and damage tolerant thin film metallic systems.

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

B2-15 Investigation of Diamond Coating Characteristics on Chrome-Plated AISI 4140 Steel by Hot-Filament Chemical Vapour Deposition Process*, R. Vignesh, **S Boominatha Sellarajan (rayarajan2005@gmail.com)**, J. Rajaguru, N. Arunachalam , M. Ramachandra Rao,* Indian Institute of Technology Madras , India

In the modern engineering world, extensive research has led to the development of certain unique grades of steel, mostly suitable for enhanced functions. AISI 4140 steel is one such grade, having major applications in power plants, automobile and aerospace industry. HFCVD process on these steel substrates have attracted significantly to improve the mechanical performances due to the superior properties of diamond films. However, CVD diamond films on steel are a great challenge due to the formation of interfacial graphite layers; intrinsic stresses and high stiffness due to considerable differences in thermal expansion coefficients between substrate and diamond. This may lead to premature failure of diamond films. To overcome these limitations, interlayers such as Cr, Ti, Mo, W, etc., were demonstrated for an improved adhesion by different techniques (sputtering and CVD). In this work, Cr interlayer made by hard-chrome plating technique was utilized. Then, diamond film was deposited over Cr interlayer by HFCVD process. High substrate temperature (~750℃) generated during the diamond deposition can significantly affect the mechanical properties of the steel substrate as the material undergoes phase transformation. This leads to material failure in real-time applications. Despite this, the necessary investigation about the influence of diamond coating deposition temperature on the microstructure and mechanical properties of the steel substrate has not been covered yet. Hence, this work aims at analyzing the substrate properties at varying temperature (450-750℃) by adjusting the hot-filament to substrate distance (d: 20-40 mm) and the filament temperature (1800-2200℃) and deposition time (soaking time: 1-8 hrs). Tensile strength, ductility, XRD and microstructure via SEM were carried out. The results indicate that the mechanical properties and microstructural features of the steel are affected significantly by deposition temperature and time. The strength and hardness of AISI 4140 steel drop as the deposition temperature and time are increased. However, the ductility increased with increasing deposition temperature and holding time. Microstructural observations reveal that the carbide precipitates have a plate-like structure at lower temperatures, but are spheroid-like at high temperatures. Carbide formations at high temperature were also confirmed by the XRD analysis. These results suggest that it is essential to select an optimal depositing temperature and time by considering the material high-temperature behaviour. Further, a case study on diamond film formation as a function of filament-substrate gap is discussed.

B2-16 The Challenge and Strategy of a-Si CVD Coating on Aluminum Alloys*, **Min Yuan (min.yuan@silcotek.com)**,* SilcoTek Corporation, USA

Aluminum alloys in general present a particular challenge in thermal CVD of amorphous silicon coating.

Aluminum is known to catalyze the crystallization of amorphous silicon and induce nanowire growth under thermal CVD conditions. The deposited thin film usually contains a mixture of amorphous and microcrystalline silicon, which not only manifest as undesirable cosmetic defects on finished products, but also compromise other coating properties such as coating adhesion, corrosion resistance and chemical inertness.

Here we present a modified thermal CVD process that is designed to prime the aluminum substrate at the beginning of CVD, so that subsequent a-Si deposition can proceed smoothly. The priming step acts to prevent aluminum from catalyzing the amorphous-to-crystalline transition and stop the undesirable silicon nanowire growth. The coated products from this process deliver more appealing cosmetic finish, as well as superior coating properties that will be discussed in the presentation.

The priming effect is achieved by exposing the aluminum substrate to a mixture gas at the initial stage of the CVD process. The synergistic reaction of the gas mixture deposits a thin barrier layer at the substrate/coating interface, which serves to cut off the negative influence of aluminum on the coating. The barrier layer itself has strong adhesion to both the aluminum substrate and the a-Si coating deposited on top of it, thus improving the overall adhesion properties.

This modification is easily incorporated as part of the CVD process and does not require separate wet chemistry or vacuum break. This makes it straightforward to implement and scale up in a manufacturing setting, as has been demonstrated in the facility at SilcoTek Corporation.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B3

Deposition Technologies and Applications for Diamond-like Coatings

B3-1 'Hydrogenated Amorphous Carbon from Magnetized Hollow Cathode Discharges, ***John Miller (miller290@llnl.gov)***, *A. Ceballos-Sanchexz, S. Elhadj, S. Kucheyev, B. Bayu Aji, S. Falabella,* Lawrence Livermore National Laboratory, USA

Diamond-like carbon is a popular hard coating material whose properties widely depend on deposition process and conditions within the process. Variations between the methods and conditions yield films with varying hydrogen, sp2 carbon, and sp3 carbon content who have densities between 1 and 3 g/cc, spanning the difference between a low-density hydrocarbon polymer and polycrystalline diamond (high density carbon). This material is becoming increasingly interesting as a new ablator material for inertial confinement fusion because it is low Z and has the potential to tune its density between that of glow discharge polymer(~1 g/cc) and diamond (3.5 g/cc), two ICF ablator materials of choice. This work investigates the use of a magnetized hollow cathode discharge for depositing thick, density tunable amorphous carbon films for future inertial confinement fusion experiments.A variety of the properties of the films will be discussed including: composition, density, impurity content, thickness limitation, deposition rate and surface morphology.

IM Release: LLNL-ABS-814679

B3-2 Effect of Mechanical and Thermochemical Tool Steel Substrate Pre-treatment on DLC Coating Durability, ***Daniel Tobola (daniel.tobola@kit.lukasiewicz.gov.pl)***, Łukasiewicz Research Network - Krakow Institute of Technology, Poland; *T. Liskiewicz,* Manchester Metropolitan University, UK; *L. Yang,* Leeds University, UK; *T. Khan,* Manchester Metropolitan University, UK; *Ł. Boron,* Łukasiewicz Research Network - Krakow Institute of Technology, Poland

DLC coatings are becoming well established across many industrial sectors including aerospace, automotive, oil and gas, and cold forming tools. While DLC coatings exhibit good mechanical properties and low coefficient of friction for themselves, DLC coating–substrate systems may suffer from insufficient wear resistance. This paper describes the wear mechanisms and reports characteristics of the DLC coating-steel substrate system behaviour after mechanical and thermochemical steel substrate pre-treatments. We have investigated two tool steel substrates, Sverker 21 (AISI D2) and advanced powder metallurgy alloyed steel Vanadis 8. Initially, the substrates were heat treated in vacuum furnace and gas quenched resulting in hardness of 59±1 and 64±1 HRC respectively. Subsequently the samples were subjected to mechanical turning and burnishing with 130N and 160N forces, using diamond composite tools with ceramic bonding phase. Afterwards, a vacuum nitriding process in a PVD chamber as a pre-treatment for subsequent DLC coating deposition was carried out. Coated samples were subjected to a series of ball-on-disc wear tests against Al2O3 and Si3N4 counterparts. X-ray diffraction (XRD), instrumented indentation and scanning electron microscopy (SEM) were employed to examine the phase composition, nano-hardness, Young's modulus, surface microstructure, elemental distribution and 3D surface topographies of the wear scars. Selected variable factors including the type of steel, the burnishing force, type of counter-body material were subjected to statistical analysis. The effect of sequential processes used as pre-treatment on DLC coating durability was demonstrated and the results are discussed in light of improving the cold forming tools tribological performance.

Keywords: DLC coatings, tool steels, vacuum nitriding, slide burnishing

B3-3 Stress Free ta-C Coatings by means of Up-Scaled Pulsed Laser Deposition for Industrial Applications, ***Hagen Gruettner (hagen.gruettner@hs-mittweida.de)***, *D. Haldan, J. Maus,* Hochschule Mittweida - University of Applied Sciences, Germany; *M. Nieher,* Hochschule Mittweida - University of Applied Sciences , Germany; *S. Weissmantel,* Hochschule Mittweida - University of Applied Sciences, Germany

In many industrial applications highly wear-resistant coatings are required to protect and / or functionalize tools and components. While typical representatives of DLC coatings are already in large-scale industrial use, stress free ta-C coatings produced at the Laser Institute Mittweida (LHM) by means of a patented combination of pulsed laser deposition and pulsed laser stress relaxation are currently well under way due to their outstanding properties and the possibility to up-scale the deposition process. These ta-C coatings are special representatives of the DLC coatings and unsurpassed in terms of their hardness and usability. Moreover, they can be prepared almost free of intrinsic stress. Using optimal deposition parameters, a hardness of up to 70 GPa with Young's moduli of 700 to 800 GPa can be achieved, which leads to an extremely high operational wear resistance. Due to the low average surface roughness (Ra) of a few nanometers and the low friction coefficient these layers are also excellently suitable for tribological applications. By using optimized adhesion layers or layer systems it is possible to achieve high adhesion strengths on a variety of substrate materials. The low temperature required during the deposition process (< 90 °C) makes it also possible to coat temperature-sensitive materials. Due to their chemical resistance, biocompatibility and dopability the ta-C coatings offer a wide range of further applications, such as in medical technology, food industry or sensor technology. By means of the combined pulsed laser deposition and laser pulse annealing process the LHM is able to produce homogeneous layers with a thickness ranging from a few nanometers up to a few 10 µm with an adjustable hardness between 25 and 70 GPa and an adjustable intrinsic stress between 12 GPa and nearly zero GPa by choosing the corresponding deposition parameters. That makes it also possible to prepare material and application specific layer designs like Young's modulus gradients or multilayers. It will be shown that the deposition process can be up-scaled to industrial requirements using new high power excimer lasers, which were introduced in 2019. The LHM is now looking for interested partners and potential customers.

B3-4 DLC Coatings Deposited by Novel Doping Strategies with HiPIMS, ***José Antonio Santiago Varela (joseantonio.santiago@nano4energy.eu)***, *I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain; *M. Monclús, J. Molina-Aldareguia,* IMDEA Materials Institute, Spain; *V. Bellido-Gonzalez,* Gencoa Ltd, UK; *M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain; *J. Sánchez-Lopez, T. Rojas,* CSIC, Spain; *S. Goel,* Cranfield University, UK; *J. Endrino,* IKERBASQUE, Spain

Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp^3-sp^2 structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated a novel deposition technique of hard DLC coatings doped with various elements (e.g. W, Cr, Ti, Si) using HiPIMS by incorporation of positive pulses. Highly ionized plasma discharges were obtained during HiPIMS deposition. The high ion energy bombardment resulted in a higher sp^3 to sp^2 bond ratio. EELS and Raman spectroscopy were used to characterize the sp^3 and sp^2 structures in the deposited films. Nanoindentation tests revealed improved mechanical properties (hardness up to 35 GPa) for doped DLC coatings. Additional high temperature nanoindentation tests performed in the range of 27 ºC to 450 ºC showed that the mechanical properties at high temperature are dependent on the sp^3 content. Pin-on-disk tests were carried out in order to assess the tribological performance of the coatings both at room and high temperature. The increased toughness and reduced compressive stress that doping provides to the carbon matrix together with a high sp^3 bonding structure obtained with HiPIMS deposition improves the stability of DLC coatings for high temperature tribological applications. Finally, micromilling trials were carried out to assess the performance of these doped DLC coatings in micromachining of Ti6Al4V samples and compared to an uncoated tool, an increased tool performance was obtained.

B3-5 Preparation of Hybrid ta-C/MoS_2-Films by using Laser Arc Technology, ***Frank Kaulfuss (frank.kaulfuss@iws.fraunhofer.de)***, *F. Hofmann, Y. Han, F. Schaller,* Fraunhofer IWS, Germany; *T. Kruelle,* Fraunhofer IWS,Germany; *S. Makowski, V. Weihnacht, A. Leson, L. Lorenz, M. Zawischa,* Fraunhofer IWS, Germany

Hydrogen-free ta-C coatings are already used to reduce friction in lubricated environments. The application under minimum quantity lubricated and non-lubricated boundary conditions remains a great challenge. The addition of the dry lubricant MoS_2 is intended to improve the performance characteristics of the ta-C in this case. For the production of ta-C coatings, the Laser Arc process is particularly suitable, with which very hard and low-defect coatings can be produced. MoS_2 targets can be combined and alternately evaporated using the same technique.

By adapting the discharge conditions, ta-C/MoS_2 layers could be produced in different variants. In addition to ta-C with simple MoS_2 top layer, multilayers with alternating deposition were also produced with single layer thicknesses in the nanometer range. The plasma states of the components, which have a large influence on the layer formation, were investigated as well as the cathode spot behaviour at the different materials (graphite, MoS_2). The investigations also concentrated on the mechanical properties of the layers, which were determined by SEM, TEM, X-ray diffraction, nanoindentation and scratch testing. In addition, tribological tests provide information on the influence of the layer structure in different applications.

B3-6 Effects of Target Poisoning Ratios on the Microstructure, Mechanical Properties and Corrosion Resistance of WC_x Coatings Fabricated by Superimposed HiPIMS and MF System, ***Igamcha Moirangthem,*** Ming Chi University of Technology, Taiwan; *S. Chen,* National Taiwan University, Taiwan; *J. Lee (jefflee@mail.mcut.edu.tw),* Ming Chi University of Technology, Taiwan

In this work, we studied the effect of target poisoning ratios of tungsten carbide films using a superimposed HiPIMS and MF system. The flow rate of the acetylene (C_2H_2) was controlled using a plasma emission monitoring (PEM) system to feedback control the target poisoning ratio during deposition. Five coatings, WC10, WC30, WC50, WC70 and WC90, were grown under target poisoning ratios of 10%, 30%, 50%, 70% and 90% respectively, on Si, AISI420 stainless steel (SS) and AISI304 SS substrates. A small hysteresis loop area for the emission intensity of W at 429.6 nm was observed with variation of C_2H_2 gas flow rates. With increasing target poisoning ratios, the phases changed from nanocrystalline β-WC_{1-x} to amorphous. The X-ray photoelectron spectroscopy was used to study the chemical bindings of coating. The highest power normalized deposition rate of 25.20 nm $min^{-1}kW^{-1}$ was observed for WC90. The highest hardness value of 32.3 GPa was measured for WC30. WC50 showed the best adhesion among the coatings with L_{C2} value of 65.1 N. The lowest COF of 0.26 was observed for WC90. In potentiodynamic polarization test using 0.1M H_2SO_4 solution, WC90 showed colourful fringes around the corrosion micro-pits with the highest polarization resistance (R_p) of 4552.51 $k\Omega cm^2$.

Keywords: Superimposed high power impulse magnetron sputtering, middle frequency, WCx coatings, tungsten doped diamond-like carbon coating, target poisoning, nanoindentation, tribometer

B3-7 The Influence of Different Power Supply Systems on the Microstructure, Mechanical and Corrosion Properties of Titanium Carbide Coatings, *H. Yu -Tung,* Ming Chi University of Technology, Taiwan, Republic of China; *C. Li-Chun,* Ming Chi University of Technology, Taiwan; *L. Bih-Show,* Chang Gung University, Taiwan; ***Lee Jyh-Wei (jefflee@mail.mcut.edu.tw),*** Ming Chi University of Technology, Taiwan

Titanium carbide (TiC) coatings have attracted wide attention from researchers and industry due to their high hardness, good wear and corrosion resistance. In this study, the TiC coatings were fabricated by four different power supply systems including superimposed HiPIMS-MF, HiPIMS, MF, and DC in a gas mixture of acetylene and argon. During the deposition process, a plasma emission monitoring (PEM) system was used to control the Ti target poisoning status to 70%. The single crystal silicon wafers and AISI304 stainless steel plates were used as substrates. The chemical compositions of TiC films were analyzed by a field emission electron probe microanalyzer. The microstructure of thin film was examined by a field emission scanning electron microscope. The crystalline structure of thin film was analyzed by an X-ray diffractometry. The hardness, adhesion and tribological properties of TiC films were evaluated by nanoindenter, scratch test and pin-on-disk wear test, respectively. The corrosion resistance of TiC films in 0.1 M H_2SO_4 aqueous solution was examined by an electrochemical workstation. The influence of four different power supplies on the deposition rate, microstructure, hardness, adhesion, wear and corrosion resistance of TiC films were studied in this work. Although the deposition rate of the TiC coating deposited by DC power supply was the highest, the film quality was inferior to other films due to its less dense microstructure. On the other hand, the TiC coating fabricated by superimposed HiPIMS-MF power supply exhibited a dense microstructure, good mechanical property and excellent corrosion resistance.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B4

Properties and Characterization of Hard Coatings and Surfaces

B4-1 Investigating the Influence of Nanocomposite Structure on the Thermal Stability of Ag in VSiCN-Ag Coatings, ***Forest Thompson (forest.thompson@sdsmt.edu),*** South Dakota School of Mines and Technology, USA; *F. Kustas,* NanoCoatings, Inc., USA; *G. Crawford,* South Dakota School of Mines and Technology, USA

Self-lubricating coatings have been studied extensively for elevated temperature tribological applications. For coating designs in which a noble metal solid lubricant phase is continuously supplied to the surface from within a ceramic-based matrix, control of noble metal out-diffusion can be challenging. To investigate the potential of manipulating nanocomposite structure to better control solid lubricant stability and transport, VSiCN and VSiCN-Ag nanocomposite coatings were deposited by plasma-enhanced reactive magnetron sputtering. A nominal Ag content of 4 at.% was maintained while amorphous phase content was varied with the intent of modifying coating density, grain size, and grain morphology. As-deposited coatings were characterized by energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. Hardness and apparent elastic modulus were measured by nanoindentation. The thermal stability of Ag within the coatings was evaluated by inspection of the coating surfaces after vacuum annealing at 550°C. Relationships among coating microstructure and Ag thermal stability are identified and potential influences on coating performance in tribological applications are discussed.

B4-2 Spinodal Decomposition of Reactively Sputtered VAlN Thin Films, ***Marcus Hans (hans@mch.rwth-aachen.de),*** *H. Rueß,* RWTH Aachen University, Germany; *Z. Czigány,* Centre for Energy Research, Hungary; *J. Krause, P. Ondračka, D. Music, S. Evertz, D. Holzapfel,* RWTH Aachen University, Germany; *D. Primetzhofer,* Uppsala University, Sweden; *J. Schneider,* RWTH Aachen University, Germany

We investigate the decomposition mechanisms of metastable cubic (c–)$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films, grown by reactive high power pulsed magnetron sputtering, by combination of structural and compositional characterization at the nanometer scale with density functional theory (DFT) calculations. Based on thermodynamic considerations of $d^2G/dx^2 < 0$, spinodal decomposition is expected for c-$V_{1-x}Al_xN$ with $x \geq 0.35$. While no indications for spinodal decomposition are observable from laboratory and synchroton diffraction data after annealing at 1300°C, the formation of wurtzite (w–)AlN is evident after annealing at 900°C by utilizing high energy synchrotron X-ray diffraction. However, the complementary nature of elemental V and Al maps, obtained by energy dispersive X-ray spectroscopy in scanning transmission electron microscopy mode, imply spinodal decomposition of c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ into V- and Al-rich cubic nitride phases after annealing at 900°C. These chemical modulations are quantified by atom probe tomography and maximum variations of x in $V_{1-x}Al_xN$ are in the range of 0.36 to 0.50. The magnitude of the compositional modulations is enhanced after annealing at 1100°C as x varies on average between 0.30 and 0.61, while the modulation wavelength remains unchanged at approximately 8 nm. Based on DFT data, the local x variation from 0.30 to 0.61 would cause lattice parameter variations from 4.111 to 4.099 Å. This difference corresponds to a shift of the (200) peak from 44.0 to 44.1°. As the maximum decomposition-induced peak separation magnitude of 0.1° is significantly smaller than the measured full width at half maximum of 0.4°, spinodal decomposition cannot be unravelled by diffraction data. However, consistent with DFT predictions, spinodal decomposition in c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ is revealed by chemical composition characterization at the nanometer scale.

B4-3 Effect of Functionally Graded Layers on Tribological Behavior of TiZrN Coatings on AISI D2 Steel, ***Jia-Hong Huang (jhhuang@ess.nthu.edu.tw),*** *B. Tsai,* National Tsing Hua University, Taiwan

The objectives of this study were to investigate the role of TiN transitional layer and Ti interlayer in the tribological behavior of tri-layer TiZrN/TiN/Ti coatings and to explore the mechanism of stress relief in the tri-layer coatings. TiZrN coatings were deposited on AISI D2 steel by DC unbalanced magnetron sputtering. There were three series of samples, including single layer TiZrN (S), bilayer TiZN/Ti (B), and tri-layer TiZrN/TiN/Ti (Tx) in this study. The TiN thickness of Tx-series specimens ranged from 200 to 400 nm. The N/(Ti+Zr) ratios of TiZrN layer ranged from 0.9 to 1.0 and the Zr/(Zr+Ti) ratio of TiZrN coatings was about 0.5. The hardness of the specimens varied from 28.1 to 31.9 GPa which slightly decreased by introducing TiN transitional layer. The residual stress of TiZrN layer decreased from -8.56 to -3.28 GPa with increasing thickness of interlayer and transitional layer. Scratch test was used to evaluate adhesion strength. The results showed high L_{c2} critical loads for all specimens ranging from 63.2 to 88.6 N. The TiN transitional layer could improve the adhesion strength, and the L_{c2} increased as the thickness of transitional layer increased. The wear rate of the tri-layer coatings was lower than that of TiZrN single layer and bilayer coatings. The results indicated that introducing the interlayer and transitional layer could enhance the wear resistance. The wear rate almost linearly increased with increasing elastic stored energy (G_s) that was related to elastic constants, residual stress and coating thickness [1]. The difference between the fracture toughness (G_c) and G_s can be considered as the capability that the coating can absorb externally input energy. The increase of Gs may decrease the capacity in absorbing energy and thereby decreasing the wear resistance. Therefore, G_s could be taken as an index to evaluate the wear resistance of coatings [2].

Reference

[1] An-Ni Wang et al., Surf. Coat. Technol. 239(2014)20.

[2] Yu-Wei Lin et al., Surf. Coat. Technol. 350(2018)745.

B4-4 Thin Film Characterization by Picosecond Ultrasonics on High Curvature Surfaces*, Frederic Faese (ffaese@neta-tech.com), J. Michelon, X. Tridon,* Neta, France

Since the discovery of picosecond ultrasonics by H. J. Maris and his team in 1984, this nondestructive technique continuously expanded and found numerous applications. Where the first application concerned thin film thickness measurement in the semiconductor industries with a complex setup, picosecond ultrasonics technique is now much more efficient, user-friendly and widespread. Indeed, thickness measurement is now easily reachable and this technique also allows the elastic properties measurement of thin films, multilayers and nanostructures, adhesion properties evaluation, etc. Thus, among all the fields that are potentially interested in this new technique are mainly surface engineering, microelectronics and biology.

We will see how the photo-generation and the photo-detection of ultra-high frequency ultrasounds (of the order of THz) can accurately and rapidly measure the thickness of a TiN hard coating on a Ti substrate. This measurement can be performed either locally with a high spatial resolution or by scanning the sample, hence giving a mapping of the thickness measurement on the whole surface. Up to now, the shape of the samples had to be very flat; in this presentation, we will demonstrate that we can also analyze even highly curved samples. Compared to concurrent techniques such as ellipsometry or the Calo tester, picosecond ultrasonics presents the unique advantages to be contactless, nondestructive and able to evaluate the properties of a complex shape sample. To illustrate this last point, results will be presented showing outstanding features such as an advanced 3D mapping of a hard coating thickness on a cylinder or a sphere.

B4-5 Fatigue Behaviour of Thin Coating and the Influences of Plastic Deformation of Harden-case using Irreversible Cohesive Zone Model*, **Jiling Feng (j.feng@mmu.ac.uk)**,* Manchester Metropolitan University, UK*; Y. Qin,* University of Strathclyde, UK*; T. Liskiewicz,* Manchester Metropolitan University, UK*; B. Beake,* Micro Materials Ltd, UK

Cohesive-zone modelling technique has been proved to be an efficient approach to simulate the fracture behaviour of multi-layered coatings under monotonically loading (Feng, 2012). This paper aims to investigate the fatigue failure mechanism of coating system by observing the procedure of initiation and propagation of cracks within the coating under the cyclic loads.

We developed a "three-layer" finite element model, composed of the coating, hardened case and substrate, which was validated via nano-indentation technique with 300 µm radius indenter. Homogenous material properties were assumed for both the TiN/CrN coating and the substrate, with multi-linear hardening behaviour. Prior to coating deposition, the substrate was heat-treated by plasma nitriding to enhance the load-bearing capacity of the coating/substrate system.

An irreversible cohesive constitutive equation, taking into account the energy dissipation resulted from frictional interaction of asperities along the cohesive surfaces and crystallographic slip, was employed to identify the crack initiation and to simulate the crack propagation under the cyclic loads. An in-house User Material (UMAT) subroutine was used to simulate the degradation of coating material upon cyclic loading.

Numerical results demonstrated a clear quantitative relationship between the coating stiffness degradation and its damage accumulation. It was observed from a case study that first crack (0.01 µm in width and 0.05 µm in depth) was initiated at 8^{th} loading cycle, and it propagated through the coating thickness with increasing number of loading cycles reaching 1.4 µm at the 100^{th} cycle. It was also noticed that the plastic deformation of the hardened case developed significantly, which might be a major contribution of the initiation of the crack.

The results observed in this study are in agreement with our recent experimental observations (Beake et al, 2019), which indicated that micro crack/wear damage was occurring at the early stage of nano-indentation loading cycles. The numerical study confirmed, that once crack was initiated, it propagated rapidly through the coating, which can lead to delamination when the crack reaches the hardened substrate interface.

Key words: Fatigue failure; Cohesive Zone Model; Cyclic loading;

Reference

1. Feng, J & Qin, Y (2012), Prediction of the critical load of a metal-rolling system by considering the damage of the coated surface, Steel Research International, Metalforming, Special Edition.
2. Beake, B.D., Isernm L., Endrino, J.L., Fox-Rabinovich, G.S., (2019), Micro-impact testing of AlTiN and TiAlCrN coatings, Wear, 418–419, 102-110.

B4-6 Microstructure and Oxidation Behaviour of Arc Evaporated TiSiN Coatings Investigated by *in-situ* Synchrotron X-ray Diffraction*, **Yvonne Moritz (yvonne.moritz@unileoben.ac.at)**, C. Saringer, M. Tkadletz,* Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M. Pohler,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

TiSiN hard coatings are a suitable candidate as a protective layer for various cutting applications, due to their advantageous mechanical properties and excellent oxidation resistance. Within this work, a detailed characterization of the microstructure of TiSiN is complemented by the investigation of its oxidation mechanism using *in-situ* X-ray diffraction (XRD) at a synchrotron radiation facility. XRD, X-ray photoelectron spectroscopy and transmission electron microscopy investigations of an as-deposited TiSiN coating grown on cemented carbide substrate indicate the presence of a nanocomposite structure, consisting of Ti(Si)N nanocrystallites embedded in an amorphous Si_3N_4 matrix. To illuminate the oxidation stability, a powdered coating was annealed in air between 100 and 1200 °C and the recorded 2D X-ray diffractograms were correlated with the results of differential scanning calorimetry. Sequential Rietveld refinement of the obtained synchrotron data provided temperature-dependent information about the phase composition and thermal expansion of the individual phases. The results revealed an oxidation stability of TiSiN up to a temperature of approximately 830 °C, followed by the formation of both, rutile and anatase TiO_2. It was shown that the quantity of the metastable anatase phase reached its maximum at a temperature of 1020 °C and then continuously transformed into the stable rutile modification at higher temperatures. The present findings provide a detailed insight into the complex microstructure and oxidation mechanism of TiSiN coatings, allowing to further optimize this system for future applications.

Keywords: TiSiN hard coatings, arc evaporated, Sequential Rietveld refinement, oxidation resistance, TEM

B4-7 High Temperature Tribology of Hf Doped c-$Al_{0.67}Ti_{0.33}$N Cathodic Arc PVD Coatings Deposited on M2 Tool Steel*, G. Mondragón Rodríguez, **Alvaro Enrique Gómez Ovalle (a.gomez@posgrado.cidesi.edu.mx)**, J. Alvarado Orozco, J. González Carmona, C. Ortega Portilla, J. Hernández Mendoza,* CIDESI, Mexico

c-$Al_{(1-x)}Ti_xN$ hard coatings are widely applied due to their thermal stability up to 800 °C, high resistance to wear and oxidation. Due to these characteristics they are frequently deposited on cutting tools used for machining processes. Improvements on the mechanical and oxidation properties are derived from the microstructure characterized by a stable solid solution of Al in TiN. In the present research, undoped a) c-$Al_{0.67}Ti_{0.33}N$ and hafnium doped b) c-$Al_{0.67}Ti_{0.33}Hf_xN$, which were deposited using the cathodic arc technique using 500 sccm of high purity N_2, Temperature = 430 °C, Pressure = 8 x 10-2 mbar, deposition time = 400 Ah, cathode current = 150 A and bias voltage = -80 V. The elemental chemical analysis displays hafnium contents ranging from 1.0 to 2.26 wt. %. The scanning electron microscopy analysis of the surface of both coatings showed similar droplets sizes and defects density produced by the cathodic arc deposition. Through the grazing incidence X-ray diffraction (DRX), the characteristic peaks of a cubic $Al_{1-x}Ti_xN$ coating were observed for both the reference coating and the doped nitride. Tribology tests of the c-$Al_{0.67}Ti_{0.33}Hf_xN$ coating in an argon jet for 250, 500, 1000, 2500 & 5000 cycles at a temperature of 900 °C showed the evolution and wear behavior under these conditions. The predominant friction mechanisms observed were related to abrasion, showing that hard particle formation and plowing increased wear with increasing distance. Oxidation prevents from further debris formation, while at room temperature debris are oxidized due to friction. The friction coefficients were maintained after the inclusion of hafnium as a doping material, however high temperature wear was reduced. These observations correlated well with the transition and stable oxide phases being formed at 900 °C during the tribology tests.

Keywords: Hf doped, tribology, high temperature tribology, arc PVD.

B4-8 Cross-sectional X-ray Nanodiffraction Characterization of Radiation Damage, Stresses, and Microstructure in Tungsten Coatings*, Kostiantyn Hlushko (kostiantyn.hlushko@unileoben.ac.at),* Montanuniversität Leoben, Austria*; A. Mackova,* Nuclear Physics Institute of the Czech Academy of Sciences*; J. Todt,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; R. Daniel,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; J. Keckes,* Montanuniversität Leoben, Austria

A better understanding of depth-dependent radiation damage in protective coatings which can be used in fusion/fission reactors and in space is essential pending step for further development of novel coating types and microstructures that are capable of withstanding severe environments over long time periods. Tungsten is a perspective material for plasma-facing components of a fusion reactor due to its high radiation resistivity, high thermal conductivity and high melting point. In this contribution, 8µm thick nanocrystalline tungsten coating on WC substrate with columnar microstructure was irradiated using Si^{2+} ions with an energy of 5MeV with a fluence of $2x10^{16}$ ions/cm^2.In order to investigate depth-dependent changes in residual stresses and microstructure induced by the irradiation, cross-sectional X-ray Nanodiffraction (CSnanoXRD) with a beam size of 100 nm was applied at European Synchrotron Radiation Facility in Grenoble, France, to scan 50µm samples at the film cross-section. The experimental results revealed significant changes in the depth-dependent gradients of residual stresses as well as with the changes in unstressed lattice parameters, which will be presented together with the data from transmission electron microscopy.

B4-9 Combinatorial Approach for the Synthesis of Thermally Stable High Si-containing Nanocomposite AlCrSiN Coatings*, Michal Zítek (michal.zitek@unileoben.ac.at),* *N. Jäger, M. Meindlhumer,* Montanuniversität Leoben, Austria*; F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany*; C. Mitterer, R. Daniel,* Montanuniversität Leoben, Austria

High-performance cutting tools are subjected at high cutting speeds to high loads and temperatures typically exceeding 1000 °C. AlCrN alloyed with Si has been shown to be a perspective coating system for protection of cutting tools operating in such harsh industrial environments as it exhibits promising mechanical properties and thermal stability. Especially low Si-containing AlCrN coatings are known for their enhanced mechanical properties as well as improved thermal stability and oxidation resistance due to their nanocomposite structure.

Unlike Si concentrations far below 10 at.% Si, which are frequently reported in literature, the focus of this work is to systematically study arc-evaporated AlCrSiN coatings with a high Si content of about 15 at.%, varying the Al/Cr ratio from 50/50 to 90/10. Elemental composition was controlled by co-evaporation of $(Al_{50}Cr_{50})_{75}Si_{25}$, $(Al_{70}Cr_{30})_{75}Si_{25}$ and $(Al_{90}Cr_{10})_{75}Si_{25}$ cathodes in an industrial-sized deposition system (alpha400P, voestalpine eifeler Vacotec GmbH). This combinatorial approach allowed for a synthesis of coatings with a wide range of elemental composition from $Al_{19}Cr_{21}Si_{16}N_{44}$ to $Al_{30}Cr_5Si_{16}N_{50}$.

XRD measurements revealed that the AlCrSiN coatings display a nanocomposite structure consisting of a mixture of cub-CrN and hex-AlN phases. The observed gradual increase of the Al/Cr ratio led to an increasing compressive residual stress and fraction of softer hex-AlN phase. These two competing mechanisms resulted in hardness of about 25 GPa irrespective of the coating composition, which was preserved even after annealing at 1000 °C in vacuum. That makes this coating system interesting for various high-temperature applications. The thermal stability and oxidation resistance were furthermore studied in detail by differential scanning calorimetry and thermogravimetric analysis in inert atmosphere and in synthetic air to enlighten the origin of the mechanical and structural stability at elevated temperatures. The results show that especially high Si-containing AlCrSiN coatings with Al/Cr ratios higher than 80/20 exhibit excellent oxidation resistance with negligible mass gain up to 1250 °C.

The combinatorial approaches used within this study are powerful in seeking perspective coatings with specific elemental and phase compositions and can be effectively applied also in industrial-sized deposition systems. Moreover, they enable to understand various mechanisms responsible for high thermal stability and oxidation resistance of coatings while combined with modern characterization methods.

B4-10 In-plane Texturing of Silver Thin Films*, Francesca Corbella (corbella.francesca@gmail.com),* Saint-Gobain Recherche/CNRS, France

Pollution and energy waste are main concerns for today's society. In buildings, part of the waste is due to thermal radiation losses through windows1. To address the problem, low-emissive coatings were introduced in the market. By being reflective in the far IR range and transmissive in the visible light, the low-emissive coatings are designed to reduce the heat losses from inside the building to the outside, while maximizing the solar gain. Such properties are achieved through silver based multilayers, deposited on the glass through a PVD process. The efficiency of the coatings is then related to the maximization of the IR reflectance, which depends on the electrical conduction of the nanometric silver layer.2 The minimization of the Ag resistivity becomes, therefore, a key point for enhancing the optical properties of the coatings. In thin films, the conductivity of a material depends on its structural properties, which are influenced by its seed layer. Till today, ZnO was recognized as the best underlayer for Ag and the most used oxide in the industrial glazing. In particular, it was observed that the deposition of the oxide in its textured hexagonal lattice led to the growth of a Ag (111) out-of-plane textured film, with enhanced electrical properties. Film texturization can play an important role on silver conductivity.4-5 Starting from a model ZnO single crystal based stack, our study showed the impact of in-plane and out-plane texturization on silver resistivity . The system was then optimized with the introduction of a buffer polycrystalline ZnO layer, showing promising results. The ultimate goal is to reproduce the structural and electrical properties, observed on the single crystal stacks, in polycrystalline sputtered coatings through Ion Beam Assisted Deposition, a sputtering technique becoming more and more suitable for an industrial implementation.

[1] « Couches conductrices transparentes. Applications aux vitrages isolants et aux vitrages actifs. » Cours (2011)

[2] E. Hagen and F. Rubens, Annalen der Physik 11, 873 (1903)

[3] M. Philipp, PhD thesis, Universitât Dresden and UPMC (2011)

[4] D Köhl, PhD thesis, RWTH Aachen University (2011)

[5] R. Sittner, Ag workshop Paris, "Impact of diverse growth templates on the growth of Ag thin films" (2015)

B4-12 INVITED TALK: Modern Analytical Methods for Characterizing the Tribological Material Properties of Coatings*, Dietmar Schorr (dietmar.schorr@dhbw-karlsruhe.de),* Cooperate State University in Karlsruhe, Germany **INVITED**

This paper presents photothermal principle as a new method for determining the tribological properties of hard coatings. The coating properties, which determine the friction and wear behaviour of a tribological system, are the coating thickness, the adhesive strength and the hardness. The known classical analysis methods have disadvantages in determining the respective coating properties and are not applicable for many coatings and surfaces. Furthermore, these methods only provide information on the individual coating properties, but not on the overall tribological behaviour of a coating. With the photothermal method, these limits are exceeded and it also works where classical methods fail. Photothermics works non-destructively and can be used to determine the coating properties over a wide area. The photothermal technology works with thick and thin layers, for cohesive and adhesive adhesion testing and is independent of surface roughness.

In photothermal peripheral zone analysis, an intensity-modulated laser spot hits an object surface. The radiation is absorbed on the surface and generates a heat flux that propagates into the interior of the component in the form of thermal waves. The waves have the same frequency as the irradiated laser light. The further propagation of the thermal waves is influenced by the thermal properties of the coating (thermal diffusivity).

These cause the waves to be reflected back and radiated at the surface as heat. The thermal resistance of the material ensures that the thermal waves travel through the material with a time delay and that the phase of the radiated heat is offset from the radiated laser. If the thermal properties of the coating change due to thickness, hardness or adhesion strength, this is measured by the phase shift. This is also almost independent of the surface roughness.

The reflected waves are registered by an infrared detector, which is cooled down to increase sensitivity. The penetration depth of the oscillating thermal waves into the interior of the material is determined by the modulation frequency of the laser and depends on the thermal properties of the material. High frequencies in the kHz range are used for layer analysis and low frequencies in the Hz range for material analysis.

B4-14 INVITED TALK: Metal Oxynitride Thin Films: A Review on Synthesis Developments, Performance, and Applications*, **Sharafat Ali (sharafat.ali@lnu.se)**,* Linnaeus University, Sweden **INVITED**

This talk will provide an overview of the latest research development on metal containing nitrogen rich oxynitride thin films as hard, durable and strong material. I will start giving an overview of silicon oxynitride thin, preparation of these films by different techniques and variation of properties with the N content. I will also talk about the new amorphous thin films in the metal containing -Si-O-N systems containing a high amount of nitrogen and metals. Recently we have deposited novel AE-Si-O-N thin-film materials (AE= alkaline earth e.g. Mg, Ca, and Ba), onto float glass surfaces, by magnetron sputtering. Mechanical and physical properties show hardness values up to 22 GPa, reduced elastic modulus values up to 175 GPa and refractive index values up to 2, which can be compared to the uncoated float glass having hardness of 7 GPa, elastic modulus of 65 GPa and refractive index of 1.50. These thin films can be potentially used as a protective cover for displays and touch screens in tablets, smartphones, watches, etc.

B4-16 Influence of the Period of the Substrate Oscillation on Thin CrN Films Obtained by RF Physical Vapor Dynamic Glancing Angle Deposition Technique*, M. Jimenez, F. Cemin, A. Riul, L. Zagonel,* UNICAMP, Brazil*; C. Figueroa,* Universidade de Caxias do Sul, Brazil*; D. Wisnivesky,* UNICAMP, Brazil*; **Fernando Alvarez (alvarez@ifi.unicamp.br)**,* Instituo de Física-UNICAMP, Brazil

The control of the physical properties of hard metallic nitride coatings is mandatory to obtain good performance in applications such as cutting tools. In this work, nanostructured chromium nitride (CrN) films are obtained by combining radio frequency magnetron sputtering (RFMS) and dynamic glancing angle deposition (DGLAD) using Programmable Logic Controller (PLC). By appropriate choosing the substrate oscillation frequency, the physical properties such as micro and nanostructure, morphology, hardness, texture, and crystallite size are feasible to be tailored. Samples are deposited by moving the substrates forward and backward ($-\phi 0 < \phi(t) < +\phi 0$) by controlling the angular velocity $\omega = d\phi/dt$, inducing the formation of wavy-like periodic columnar nanostructures. Herein, we explore the effects prompted by the substrate oscillations at relatively short periods (1 <T< 10 min) on the CrN structure, as well as its influence on some physical and mechanical properties of the columnar films. It is observed the formation of wavy-like nanostructures, that generate the apparent formation of multilayer films. The dependence of the incident flux of particles with the angular position $\phi(t)$ of the substrate and the scattering of the sputtered particles on the gas phase prompt a complex distribution of precursors on the substrate surface. To take in account these effects, the process was simulated by the SiMTra software. Specific details of the results are reported in the Supplementary Information.

Keywords: Hard coatings, Chromium nitride, Dynamic glancing angle deposition, Numerical simulation

B4-17 Fabrication and Microstructure Evolution of Sputtering Single Element Transition Metal Nitride Multilayers*, K. Liu, Y. Yang, J. Xiang, Z. Lin, **Fan-Bean Wu (fbwu@nuu.edu.tw)**,* National United University, Taiwan

Transition metal nitride, TMN, layers nowadays is frequently applied for the enhancement in surface protection applications. Amongst versatile TMN films, multilayer systems attracted intense attentions due to its structure feature and specific strengthening mechanisms. In this work, TaN and MoN single transition metal nitride multilayer coatings were deposited through vacuum sputtering process. Layered configuration was identified since distinct crystal structures, like columnar crystalline, nanocrystalline, and even amorphous features, were manipulated for building layers. The film growth mechanism was discussed in terms of deposition parameters, including gas mixture and sputtering power density. The distinguishable interfaces in the multilayers could be established by different microstructure of adjacent layers. The higher power and larger N_2 gas inlet during deposition generated amorphous layers and suppressed the continuous growth of columnar crystals in crystalline layers. In addition, the high power impulse method was also employed to modify the interfaces between building layers. The intact and flattened interfaces were beneficial to the discontinuity of the microstructure of the building layers for the single transition metal nitride multilayer coatings.

B4-18 Numerical Evaluation of the Contact Fatigue Resistance of AlCrN, N and AlCrN/N Coatings on AISI 4140 Steel*, **Andre Ballesteros-Arguello (aballesteros_90@hotmail.com)**, F. Ramírez-Reyna, A. Meneses-Amador, G. Rodríguez-Castro, D. Fernández-Valdés, O. Reyes-Carcaño,* National Polytechnic Institute, Mexico

An experimental-numerical study of the contact fatigue resistance of coatings over an AISI 4140 steel was developed. Three experimental conditions were carried out: a coating of aluminum chrome nitrides (AlCrN) by physical vapor deposition process (PVD), a coating of iron nitrides (N) by gas nitriding process and finally a multilayer system of AlCrN/N. Contact fatigue tests were performed on a MTS Acumen electrodynamic test system in charge controlled mode, by cyclic loading of a sphere on a flat surface formed by the layer-substrate system. The contact fatigue test methodology consisted of two main stages. First, critical loads were determined under monotonic loads, for each of the systems, where circumferential cracks were considered as the failure criterion. Second, fatigue conditions were performed in a low cycle using subcritical monotonic loads with a frequency of 5 Hz. A numerical model based on the finite element method was developed to evaluate the stress field generated in the systems by cyclic contact loads. The results exhibit a better resistance to contact fatigue in the AlCrN/N multilayer system, due to the presence of the intermediate layer of iron nitrides.

B4-19 Low Temperature Deposition of TiB-based Hard Coating Films by Pulsed DC Plasma CVD*, **Takeyasu Saito (tsaito@chemeng.osakafu-u.ac.jp)**, H. Matsushima, K. Fuji, D. Kiyokawa, N. Okamoto,* Osaka Prefecture University, Japan

Cemented carbide is often used for molds and cutting tools based on high hardness (1800 Hv for WC, 1200-1500 Hv for WC-Co) and toughness (4-6 Mpa・$m^{1/2}$ for WC, 13-20 Mpa・$m^{1/2}$ for WC-Co), in which Ti-based hard coating films are generally used to improve functions such as hardness, heat resistance, durability, releasability and lubricity. Typical Ti-based hard films are TiC, TiN and TiCN, in which TiCN has advantages of TiC with high hardness (3000-3800 Hv) and low friction coefficient (0.1) and TiN with excellent oxidation resistance (ca. 600ºC). In addition, TiB_2 has excellent heat resistance, oxidation resistance (over 400ºC), and high hardness (20-70 GPa). However, it is difficult to form TiB_2 thin film with high growth rate and good crystallinity at low temperatures. It is important to deposit TiB_2 coating films with good crystallinity to get enough hardness, by controlling the ratio of Boron, Carbon and Nitrogen, to balance the superior characteristics of TiB_2 and TiCN.

Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD) are mainly used for Ti-based hard coating films. PVD has the advantage of simple and low-temperature growth (up to 550ºC), on the other hand, thermal CVD (ca. 1000ºC) has a limitation of the base material because of high temperature treatment, whereas adhesion strength and uniformity are superior . Therefore, a film deposition method having good adhesion strength and uniformity at low temperatures is required.

In this study, we focused on lowering the film deposition temperature to increase applicable base material. Growth rate, crystallographic structure, film composition and hardness were measured by a surface profiler, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and a micro-hardness tester, respectively. We carried out Ti-based or TiB-based hard films synthesis from $TiCl_4$, BBr_3, CH_4, and N_2 using RF plasma CVD, DC plasma CVD, and the pulsed DC plasma CVD. For the case of TiB-based hard coating films by RF plasma CVD, growth rate as 350-800 nm/h was obtained, however, XRD exhibited amorphous or microcrystalline. The hardness was lower than the reported value, possibly due to the amorphous phase and existence of oxygen. For the case of TiC hard coating films by DC plasma CVD, growth rate was up to 800 nm/h, also exhibited amorphous or microcrystalline. Pulsed DC plasma CVD can be expected to crystallize the TiB-based hard film, because by introducing pulse, it is possible to control the electron temperature in the plasma, and to control the dissociation reaction in the plasma and the accumulation of charges on the substrate surface.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B5

Hard and Multifunctional Nanostructured Coatings

B5-1 INVITED TALK: PVD of Hard Nanocomposite Coatings Using Multiphase SHS Cathodes - Evolution and New Horizons*, **Philipp Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru)**, E. Levashov,* National University of Science and Technology "MISiS", Russian Federation **INVITED**

The development of PVD technologies is often related with creation of new multicomponent materials that are used as precursors in deposition process. Particularly relevant is the manufacture of cathodes made of ceramics & composite materials. Since the doping of coatings by structure modifiers, such as B or Si, for example, is a non-trivial task. Among the methods of ceramic cathodes manufacturing can be noted the pressing+sintering & hot pressing technology. Self-propagating high-temperature synthesis (SHS) is the cost effective & convenient method for manufacturing of composite cathodes [1].

The SHS method allows obtaining a wide range of materials & cathodes have a high density & a low content of impurities due to self-cleaning effect in the combustion wave. In present review, the several types of advanced coatings deposited with the SHS-materials were demonstrated.

It was shown that the follow nanocomposite coatings can be produced in various energy regimes, including rigid, due to the use of functionally graded & reinforced SHS-materials (FGM & RM):

a) hard oxidation resistant MoHfSiB, MoZrSiB, & TaZrSiB coatings were obtained by DC magnetron sputtering (MS) & pulsed MS of ($MoSi_2$-HfB_2-MoB)/Mo, ($MoSi_2$-ZrB_2-MoB)/Mo, & (ZrB_2-$TaSi_2$)/Mo FGM disk targets [2] b) hard optically transparent TaSiCN coatings - by MS of $TaSi_2$-TaC-SiC-Si_3N_4 RM disk targets c) hard corrosion resistant CrB_2 & TiAlNiCN coatings - by HIPIMS using CrB_2 & TiC-NiAl disk targets [3]. d) hard wear resistant TiCrBN coatings - by ion implantation (MEVVA) or pulsed cathodic arc evaporation (PCAE) of (TiB-Cr_4Ti_9B-Cr_2Ti)/(Ti+TiB) ring FGM targets [4]. e) hard oxidation & corrosion resistant coatings - by PCAE method using CrB_2 & Cr_3C_2-NiAl rod targets. f) hard TiAlSiCN & TiCrSiCN coatings with high thermal stability/oxidation resistance - by MS of $TiAl_3$-TiC-Ti_5Si_3-AlN & TiC-Cr_3C_2-Ti_5Si_3 disk targets at high currents [5]. g) hard wear resistant soft magnetic FeTiB films - by MS of Fe/TiB_2 segment target [6] h) hard oxidation resistant SiBCN films - by ion sputtering (IS) & MS of SiC-B_4C disk SHS-targets [7].

The research was carried out under the financial support of the Russian Science Foundation in the framework of project No. 19-19-00117.

1. E.A. Levashov et al. Int Mater Rev 62 (2017) 203

2. Ph. Kiryukhantsev-Korneev et al. Corros Sci 123 (2017) 319

3. Ph. Kiryukhantsev-Korneev et al. Ceram Int (2019) doi.org/10.1016/j.ceramint.2019.09.152

4. Ph. Kiryukhantsev-Korneev et al. J. Phys.: Conf. Ser. 1238 (2019) 012003

5. K. Kuptsov et al. Acta Mater 83 (2015) 408

6. E. Sheftel et al. Phys Status Solidi 13 (2016) 965

7. Ph. Kiryukhantsev-Korneev et al. Prot Met Phys Chem 53 (2017) 873

B5-3 On the Structure and Mechanical Properties of X_2BC Coatings Prepared by High Power Impulse Magnetron Sputtering at Different Temperatures*, **Pavel Soucek (soucek@physics.muni.cz)**, M. Polacek, L. Zabransky, M. Stupavska, P. Vasina,* Masaryk University, Brno, Czech Republic

As the demands for the quality and speed of machining increase, the application of protective coatings on cutting or forming tools becomes increasingly important. Currently used protective coatings exhibit sufficient hardness, but this trait is often coupled with distinct brittleness. Recently a material combining seemingly mutually exclusive high hardness and moderate ductility has been theoretically predicted [1]. This material contains atoms of a transition metal (X), boron (B) and carbon (C) in X_2BC stoichiometry ordered in a complex high aspect ratio unit cell. The arrangement of the unit cell provides for high hardness of the material due to strong ionic-covalent bonds together with enhanced ductility owing to planes with only metallic bonds providing for plastic deformation of the cell. The properties of X_2BCs with different transition metals were calculated; however, experimental synthesis of only crystalline Mo_2BC was reported so far [2,3]. Apart from post-deposition annealing [3], HiPIMS was shown to be an effective way to prepare crystalline Mo2BC at industrially relevant deposition temperatures [2]. Other X_2BC such as W_2BC have been predicted to exhibit better mechanical properties compared to Mo_2BC, however, this comes at the cost of near-zero formation enthalpy predicting problems with the crystallization of this phase. On the other hand, systems such as Nb_2BC should exhibit lower hardness and ductility, but they should be significantly easier to be synthesized in the correct crystalline form.

This contribution reports on HiPIMS driven deposition of different X_2BC systems covering systems with low as well as higher negative formation enthalpies. Coatings prepared at ambient temperature as well as those prepared elevated temperatures > 700 °C will be compared. The correlation between the deposition parameters, the structure of the coatings and their mechanical properties will be shown.

This research has been supported by the project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic, project CZ.1.05/2.1.00/03.0086 funded by the European Regional Development Fund and GACR project 15-17875S.

[1] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J.M. Schneider, J. Phys.: Condens. Matter 25 (2013) 045501

[2] H. Bolvardi, J. Emmerlich, S. Mráz, M. Arndt, H. Rudigier, J.M. Schneider, Thin Solid Films 542 (2013) 5-7

[3] L. Zábranský, V. Buršíková, P. Souček, P. Vašina, J. Dugáček, P. Sťahel, J. Buršík, M. Svoboda, V. Peřina, Vacuum 138 (2017) 199-204

B5-4 Ammonium Thiosulfate Precursor for Coating Molybdenum Disulfide onto the Surface of Porous Metal for High Anti-Wearing Application in the Machinery Industry*, **Lung-Hao Hu (lunghhu@g-mail.nsysu.edu.tw)**,* National Sun Yat-Sen University, Taiwan*; P. Chen,* Southern Taiwan University of Science and Technology, Taiwan

High anti-wearing capability of friction coating is extremely important to any low friction and machinary industry, especially for highly automated production era coming, "Industry 4.0". Molybdenum disulfide (MoS_2) belongs to Transition-metal dichalcogenids, TMDs . It is composed of layered structures, providing excellent wear resistance due to layer sliding . In this study, a cheap and massive producible ammonium thiosulfate precursor ($(NH_4)_2MoS_4$) has been developed for coating MoS_2 layer onto the nano-porous anodic aluminum oxide (AAO) layer on the surface of 7003 series aluminum alloy. MoS_2 layer on the aluminum alloy surface is detected by scanning electron microscope (SEM). The ammonium thiosulfate precursor is pyrolyzed at 280, 375, 400 and 550°C, respectively to form the MoS_2 layer. The wearing experiment is tested by using the Surface Hardness Abrasion Tester. After 1440 m wear test, the wear rates (weight loss/original weight) of pure 7003 aluminum alloy, AAO and MoS_2 coated aluminum alloy pyrolyzed at 400°C are 0.339%, 0.017%, 0.0109%, respectively. The thickness of the molybdenum disulfide film sliced and observed by focused ion beam-transmission electron microscope (FIB-TEM) is about 40 nm. The surface hardnesses of AAO and MoS_2 coated aluminum alloy are 3~4 GPa and 5~6 GPa, respectively, measured by nanoindentation. As the result of the test, the coating of MoS_2 layer on the surface of aluminum alloy substantially enhances anti-wear capability and hardness. This coating technique is expected to be used in all kind of metal parts for improving the lifetime of automated equipment .

B5-5 Optimization of TiSiCN Coating Properties Obtained by RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering*, **Joël Matthey (joel.matthey@he-arc.ch)**,* Haute Ecole Arc Ingenierie HES-SO, Switzerland Ecole Arc Ingenierie, Switzerland*; O. Banakh, R. Constantin, F. Bisoffi, M. Erard,* Haute Ecole Arc Ingenierie HES-SO, Switzerland

Recently, remarkable properties of the TiSiCN coatings namely low friction and good wear protection have been reported. Our study aimed at a comparison between different technologies (RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering) used for the coating depositions. Operating in RF mode, a composite target Ti-Si-C was sputtered in Ar + N_2 atmosphere. In HiPIMS mode, the coatings were obtained from alloyed TiSi targets with different Si contents (15 and 25 at.%) in a gas mixture containing Ar + N_2 + C_2H_2. Tailoring the coating properties can be successfully performed with a help of the target ion-induced secondary electron emission (ISEE). Technical aspects of both technologies will be discussed in order to set a relationship between thin film properties and process parameters. Physicochemical analyses (XRD, SEM, XPS and RBS) were carried out to evaluate the coating composition, morphology and crystalline structure. Residual stresses were determined by the curvature method on glass plates. Nanohardness values up to 28 GPa and Young's modulus values up to 216 GPa were obtained while the coefficient of friction exhibited values below 0.35 against steel in an unlubricating pin-on-disk setup. The process parameters have been optimized to maximize the ion bombardment of the substrate surface by a monitoring the bias current signal with a Rogowski coil probe. The coating thickness was set to one micron onto polished steel substrates.

B5-6 Characteristics of Hf(*M*)SiBCN (*M* = Y, Ho, Ta, Mo) Coatings: Role of the *M* Choice, ***Martin Matas (matasma@kfy.zcu.cz)***, *M. Prochazka, J. Vlcek, J. Houska,* University of West Bohemia, Czech Republic

Thin films based on light main group elements are attractive due to a unique combination of properties ranging from high hardness through optical transparency to high–temperature stability and oxidation resistance. The properties, in the first place electrical conductivity, can be further modulated by addition of early transition metals. Properties of amorphous Hf(*M*)SiBCN films are investigated by combining their preparation using pulsed magnetron sputtering of boron–rich composite targets B_4C–Hf–*M*–Si (45–65% B_4C, 15–20% Hf, 5% Y/Hf/Ho/Ta/Mo, 15–30% Si) in 85% Ar + 15% N_2 discharge gas mixture with *ab-initio* calculations. First, we study the effect of the *M* choice and fraction on calculated mechanical properties and formation energy (E_{form}) of binary *M*N and ternary $Hf_xM_{1-x}N$ crystals. We discuss the dependence of E_{form} on the crystal structure and on the distribution of Hf and *M* in the metal sublattice. The calculated mechanical properties of *M*N (rather than $Hf_xM_{1-x}N$) very well correlate with measured mechanical properties of a–Hf*M*SiBCN. The driving force towards N incorporation, monotonically decreasing with increasing periodic-table group number of *M* according to the calculated E_{form} of *M*N, very well correlates with measured electrical conductivity and extinction coefficient of a–Hf*M*SiBCN. Second, we use *ab–initio* molecular dynamics to model the a–Hf*M*SiBCN materials of experimental compositions and densities themselves. The calculated band gap, localisation of states around the Fermi level and bonding preferences of the *M* element (in particular the tendency of the *M* element to bind with N) also correlate with the measured increasing metallicity with respect to the periodic-table group number of *M*, and confirm the possibility of predicting the trends of characteristics of a–Hf*M*SiBCN using those of *M*N. Third, we study the a–Hf*M*SiBCN properties as a function of each other, and we identify an optimum target composition (B_4C covered by 15% Hf, 5% Ta and 15–20% Si) leading to hard (>20 GPa) films with relatively high conductivity at a given extinction coefficient and vice versa. The results are important for the design of hard, conductive and/or transparent high–temperature coatings.

B5-7 Thermal Stability of Nanostructured TiAl(Si,B)N Coatings Deposited by HiPIMS with Positive Pulses, ***Álvaro Méndez Fernández (alvaro.mendez@nano4energy.eu)***, *J. Santiago, I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain; *M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain; *M. Monclús, J. Molina-Aldareguia,* IMDEA Materials Institute, Spain

In recent years, due to the advancement of high-speed machining (HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance, anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured TiAlSiN and TiAlBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The influence of Si and B from 0 to 15% at. content on stabilizing fcc-AlN phase results has also been studied. The formation of nanocrystalline grains (TiAlN) embedded in an amorphous phase (a-Si_3N_4, a-BN) provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splitting were used to evaluate toughness and thermal resistance of the coatings.

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

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

B5-8 Tuning Fracture Characteristics of Superhard Tm Carbide Coatings by Nitrogen Alloying, ***Thomas Glechner (thomas.glechner@tuwien.ac.at)***, *R. Hahn,* TU Wien, CDL-SEC, Austria; *D. Primetzhofer,* Uppsala University, Sweden; *H. Zaid, S. Kodambaka,* University of California Los Angeles, USA; *D. Holec,* Montanuniversität Leoben, Austria; *P. Mayrhofer,* TU Wien, Austria; *S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H. Riedl,* TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) nitrides and carbides are well-established protective coating materials due to their specific combination of remarkable thermo-mechanical properties but also chemical inertness. Nevertheless, their unique bonding nature – in particular combination of strong covalent and metallic bonds – is also the origin for their lack in fracture tolerance compared to metals and metallic alloys.

To overcome these limitations the formation of carbonitrides by substitutional alloying of the non-metallic sublattice exchanging C with N atoms is an interesting approach. The so obtained adjustment of the valence electron concentration has strong consequences on intrinsic material properties, e.g. Young's modulus, melting temperature, phase decomposition as well as fracture toughness. Therefore, within this study the impact of non-metallic alloying – exchanging C with N atoms – has been explored systematically for two model systems, TaC and HfC, respectively. TM-C thin films were deposited via non-reactive magnetron sputtering, while ternary TM-C-N coatings have been deposited in mixed Ar/N2 atmospheres. We combined ab initio calculations (DFT by VASP) with experimental studies to correlate predicted properties such as fracture tolerance enhancement with increasing VEC (due to nitrogen alloying). The mechanical characteristics have been assessed by micro cantilever bending, pillar compression or splitting tests in correlation to well-established nanoindentation to gain a comprehensive view on the mechanical characteristics – also at elevated temperatures. Furthermore, detailed insights on the phase formation during coating synthesis (also considering influence of structural defects such as vacancies), and hence morphology as well as chemical composition has been studied via ERDA and SEM/HR-TEM, respectively.

B5-9 Improved Ti–Al–Ta–N Coatings by Doping with LaB_6 and $CeSi_2$, ***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)***, *S. Kagerer,* TU Wien, Institute of Materials Science and Technology, Austria; *P. Polcik,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The ever-growing need for improved mechanical and thermal resistance of protective coatings ask for their continuous enhancement and optimization. Recently, we showed that $CeSi_2$ or LaB_6 doping (<2 mol%) of well-known and used Ti–Al–N coatings leads to a considerable enhancement of their thermomechanical properties and oxidation resistance. The very positive effects of Ta for Ti–Al–N (with Ta/Ti ratios of ~1/3) are already well documented. Within this study, we further follow the alloying concept by preparing sputtered nitride coatings using $Ti_{0.45}Al_{0.45}Ta_{0.10}$ composite targets alloyed with 2 mol% $CeSi_2$ or 1 mol% $CeSi_2$ plus 1 mol% LaB_6. The thereby developed single-phase face centered cubic LaB_6 and $CeSi_2$ doped Ti–Al–Ta–N coatings outperform the previously studied Ti–Al–Ta–N coatings considerably.

In their as-deposited condition, the LaB_6+$CeSi_2$-doped $Ti_{0.44}Al_{0.42}Ta_{0.13}N$ coatings exhibit a hardness (H) of 37.8±1.5 GPa and an indentation modulus (E) of 498±14 GPa (on polished sapphire substrates). Although the hardness after vacuum-annealing at 1100 °C is with 30.7±1.8 GPa below that of the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$ (39.6±1.3 GPa), the oxidation resistance is simply outstanding. Even after exposure to ambient air at 900 °C for 25 h, the oxide scale thickness is only 800 nm. Thus, easily outperforming the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$, but also the already excellent oxidation resistance of $Ti_{0.44}Al_{0.44}Ta_{0.12}N$ and $Ti_{0.43}Al_{0.42}Ta_{0.14}Ce_{0.01}N$, which showed 2.4 and 1.9 µm thick oxide scales after 25 h exposure at 900 °C in ambient air, respectively.

Based on our results we can conclude that knowledge-based alloying design is a powerful tool to meet the ever-growing demands of highly-sophisticated applications.

B5-10 Dislocation Confinement in Core-Shell Nanostructures: A Molecular Dynamics Study, ***Drew Fleming (rofleming@astate.edu)***, Arkansas State University, USA

Recently, a novel nanostructured surface composed of patterned arrays of Al/a-Si core-shell nanostructures (CSNs) has been shown to have a desirable combination of ultra-low friction (COF ~0.015 against a diamond counter face) and high durability. When subjected to instrumented nanoindentation, the individual CSNs show an unusual mechanical response characterized by almost complete deformation recovery, even beyond the elastic limit. Fundamentally, this mechanical behavior is hypothesized to be a result of a back-stress that develops in the confined Al core during compression loading that causes nucleated dislocations to retrace their paths or otherwise annihilate during unloading. In this study, molecular dynamics simulations are utilized to investigate the role that geometry and material properties play on the unique mechanical behavior of CSNs, with special attention paid to the roles of the core material and core-shell interface structure, along with supporting stress calculations.

B5-11 Tribocorrosion Behaviors in Seawater of TiSiCN Coatings Deposited by High Power Impulse Magnetron Sputtering: In-situ Electrochemical Response*, Yixiang Ou (ouyx16@tsinghua.org.cn),* Beijing Radiation Center, China*; H. Wang,* Beijing Normal University, China*; J. Luo,* Beijing Radiation Center, China*; B. Liao, X. Zhang,* Beijing Normal University, China*; W. Wang,* Beijing Radiation Center, China*; X. Ouyang,* Northwest Nuclear Technology Institute

To meet the requirement and needs of seawater lubrication for mechanical components in marine industry, nanostructured coatings with simultaneously high hardness and toughness are expected to deposit on component surface to enhance working performance and lifetime. Hence, in this work, TiSiCN nanocomposite coatings were deposited on Si (100) and AISI 316L stainless steel wafers by high power impulse magnetron sputtering (HiPIMS) at various peak power of 4-8 kW and negative substrate bias of 0- -200V. Metal Ti and MAX phase Ti_3SiC_2 layers serve as adhesion and transition layers, respectively. Nanocrystalline (*nc*)-(TiN,TiC,TiCN)/amorphous (*a*)-(Si_3N_4, SiC, sp^2-C) nanocomposite structure is obtained in TiSiCN nanocomposite coatings, which exhibits high surface/interface integrity and dense microstructure without distinctly preferred orientation. At 7 kW and -60 V, TiSiCN/ Ti_3SiC_2/Ti coatings with high H, H/E*, H^3/E^{*2} and adhesion exhibit high open circuit potential of -0.07 V, low COF of 0.25 and specific wear rate of $6.1\times10^{-7}mm^3N^{-1}m^{-1}$, resulting from mild abrasive wear without the occurrence of pitting corrosion in 3.5 wt.% NaCl aqueous solution. Moreover, cycling tribocorrosion tests exhibit that passive films possess strong abilities of regeneration and repairation on sliding contact surface thanks to high surface/interface integrity and dense microstructure.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B6

Interplay Between Computational and Experimental Design of Coatings and Processes I

B6-1 Data-driven Assessment of Chemical Vapor Deposition of MoS2: a Meta-Study Based on Published Growth Experiments*, A. Costine,* University of Virginia, USA*; P. Delsa,* Lousiana School for Math, Science, and the Arts, USA*; T. Li,* ***Petra Reinke (pr6e@virginia.edu)****, P. Balachandran,* University of Virginia, USA

Transition metal dichalcogenides (TMD) are highly coveted materials with unique properties. The growth of high quality two-dimensional TMD monolayers is critical for enabling key technological solutions. Proof-of-concept devices can be assembled using micromechanical exfoliation from multilayer material, but this is a prohibitively slow process. Another challenge remains the control and minimize defects including point defects and grain boundaries, which have an outsized impact on electronic properties. It is therefore necessary to understand the complex parameter space of TMD monolayer growth, and then adapt, and extrapolate to conditions suitable for materials integration. For this purpose we asked a deceptively simple question: how much can we learn from the published data on MoS_2 growth with chemical vapor deposition from solid precursors (MoO_3 and S)? Can machine learning predict the processing conditions resulting in single layer MoS_2 ? [1] This work consists of two parts, which are equally important, and combine experimental and computational expertise: firstly, the data mining of the literature, assessment of the experimental descriptions, and isolation of suitable and reliable parameters which can be entered into ML algorithms, and secondly, testing and identification of suitable ML approaches. This is a non-trivial problem because the processing space is vast and lack of *a priori* guidelines impedes rapid progress. Starting from the literature data on MoS_2 thin films a database is manually constructed from 82 publications. Unsupervised and supervised machine learning methods are used to learn from the compiled data by extracting trends that underlie the formation of MoS_2 monolayers. Design rules are uncovered that establish the phase boundaries classifying monolayers from other possible outcomes such as incomplete layers, and multilayer, which offers future guidance of CVD experiments. Ideally the design rules can be connected to fundamental processes of growth, but the data sparsity and missing critical information did not allow us to take this path. The presentation will focus on the challenges of constructing a suitable database, the statistical challenges incurred due to its relatively limited size, and offers a view into the wealth of information which can be accessible from a combination of experiment and ML in advancing complex growth processes. An important conclusions remains a call to experimentalists to report failed experiments, which are an important aspect in building an informative map of the multidimensional growth parameter space. [1] A. Costine, P. Delsa, T. Li, P. Reinke, P.V. Balachandran, J. Appl. Phys. **128** 235303 (2020)

B6-2 Kinetic Monte Carlo Simulations of Residual Stress Evolution*, **Eric Chason (eric_chason@brown.edu)**, A. Bower,* Brown University, USA

Kinetic Monte Carlo (KMC) simulations have been a useful way to model the evolution of surface morphology during thin film growth. However, it has been difficult to include stress in KMC simulations because of the long range nature of stress fields. In this work, we have used an approximation that focuses on the stress development at the grain boundaries that allows us to overcome this problem. The results enable us to investigate how residual stress depends on the growth conditions (growth rate, temperature, particle energy) and microstructure (grain size) during thin film growth. . In particular, the KMC shows how the flux of deposited atoms on the surface leads to a supersaturation that creates compressive stress in the film.

B6-3 Maximum N Content in a-CN_x and other Amorphous Nitrides*, **Jiri Houska (jhouska@kfy.zcu.cz)**,* University of West Bohemia, Czech Republic

Structures of amorphous CN_x materials are predicted by extensive ab-initio molecular-dynamics simulations (more than 800 trajectories) in a wide range of compositions and densities [1]. The predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the formation of N_2 molecules, with the aim to predict and explain the maximum N content in stable CN_x networks. The results show that the maximum N content is of »42 at.%. From the kinetics point of view, higher N contents lead to steeply increasing rate of N_2 formation during materials formation. The preferred structures may contain some unbonded N_2 molecules at N contents above »34%, and that they contain many unbonded N_2 molecules at N contents above »42%. From the thermodynamics point of view, networks with more than »42% of N bonded in them may be temporarily stabilized by N_2 molecules sitting in voids around the network, but a subsequent N_2 diffusion into the atmosphere makes them unstable. Next, the methodology is applied to other amorphous nitrides such as Si-C-N [2]. Increasing Si/C ratio from 0 to 100% leads to increasing maximum achievable content of bonded N: from 34% to 57% in the case of no N_2 formation and from 42% to 57% when the amorphous network forms in parallel to N_2 formation. The evolution of experimentally achieved N contens in Si-C-N films prepared by reactive magnetron sputtering is in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation at a given total N content and in a wide range of Si/C ratios is given only by the packing factor, the lowest-energy packing factor increases with Si/C. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

[1] J. Houska, Acta Mater. 174, 189-194 (2019)

[2] J. Houska, ACS Appl. Mater. Inter. 12, 41666-41673 (2020)

B6-4 Transition Metal Carbonitride based Thin Films: A Critical Review on Thermal and Elastic Properties of Group IV to VI $TMC_{1-x}N_x$*, T. Glechner,* TU Wien, CDL-SEC, Austria*; P. Mayrhofer,* TU Wien, Austria*; S. Kodambaka,* University of California Los Angeles, USA*; R. Hahn,* TU Wien, CDL-SEC, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)****,* TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) carbides and nitrides are well established in various industrial applications especially as thin films due to their refractory character including highest thermal stability, chemical inertness, as well as high hardness. Based on their bonding characteristics – dominated by mixtures of strong ionic, covalent, and metallic bonds between their metal and carbon/nitrogen atoms – these compounds are strongly limited with respect to ductility compared to metals and metallic alloys. Therefore, to overcome these limitations as well as further weak points, e.g. oxidation resistance or electrical properties, the formation of carbonitrides by substitutional alloying of non-metal sites is an interesting approach. Recent studies in the field of TM carbonitrides highlighted promising candidates as well as selection criteria [1,2]. Here the valence electron concentration (VEC) as well as structural defects such as point or Schottky defects play a prominent role.

Within this study, we therefore compared the thermal and elastic properties of selected carbonitride based coating materials of the group IV to VI (e.g. Hf-C-N or Ta-C-N) transition metals utilizing theoretical and experimental methods. Various coating materials, also including the binary base systems, have been deposited by reactive and non-reactive magnetron sputtering techniques and subsequently characterized with respect to structure, morphology, chemical composition, and mechanical characteristics – also including micro mechanical testing. These results have been correlated with ab initio calculations utilizing the Vienna Ab Initio Simulation Package. The obtained results clearly indicated that the synthesis of single phase structured fcc $TMC_{1-x}N_x$ structures gets more challenging from group IV to VI. Nevertheless, the enhancement of the fracture toughness through non-metallic alloying is an appropriate approach – e.g. an increase for K_{IC} from 1.8 to 2.9 $MPam^{1/2}$ for $TaC_{0.81}$ compared to $Ta_{0.47}C_{0.34}N_{0.19}$ [2]. In addition, thermal treatments suggest an enhancement of the hot hardness and oxidation resistance with deductions on the still high phase stability. In summary, $TMC_{1-x}N_x$ coatings depict an interesting alternative to other thin film materials but still require a more detailed scientific exploration.

References

[1] K. Balasubramanian, et al., Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides, Acta Mater. 152 (2018) 175–185.

[2] T. Glechner, et al., Assessment of ductile character in superhard Ta-C-N thin films, Acta Mater. 179 (2019) 17–25.

B6-5 INVITED TALK: Weakest Links in Superlattices: Insights from Ab Initio Modelling*, **David Holec (david.holec@unileoben.ac.at)**,* Montanuniversität Leoben, Austria*; N. Koutná,* TU Wien, Austria*; L. Löfler, L. Hantzenbichler,* Montanuniversität Leoben, Austria*; P. Řehák,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; M. Bartosik,* TU Wien, Austria*; M. Friák,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; M. Černý,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Superlattice design has been shown effective to improve Young's modulus, hardness and toughness of many nitride systems beyond the performance of individual building blocks, especially when the bi-layer period is very small, in nm range. Such developments are crucial in order to reach the ever-increasing demands on the coatings (often based on nitrides, carbides or oxides) protecting various working tools. While a structural heterogeneity---as interfaces---serves as an obstacle for dislocation motion, it could also act as a sink for impurities or other point defects with a possibly detrimental effect on interface strength. And even if one thinks about an ideal interface, chemical inhomogeneity certainly influences local electronic structure and hence bonding, which could lead to weakened bonding.

This contribution deals with a principal question whether interfaces are the weakest link in the superlattices. We will present examples of calculated tensile strength of various cubic nitride systems (TiN/CrN, TiN/AlN, AlN/VN, MoN/TaN...) and discuss the local strength together with details of the local atomic structure. A large set of systems (with different lattice mismatch, stability, magnetic state, etc.) we have treated in the past will serve as a basis for drawing general conclusions (e.g., can strength be locally enhanced by modifying interatomic distances?). In addition, we will compare these trends with those predicted for a purely metallic Ti/Ta superlattices as well as cubic/wurtzite TiN/AlN multilayers.

B6-7 Superlattice Design for Superior Thin Films*, **Nikola Koutná (nikola.koutna@tuwien.ac.at)**[1], R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Sangiovanni,* Linköping University, Sweden*; M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Superlattice architecture—comprising coherently grown nanolayers of two or more materials—provides a vast playground for tuning physical properties of thin films via altering different phases and their mutual orientation, the bilayer period, or the defect content and distribution close to interfaces. Changes in these parameters can induce remarkable effects, such as partial structural transformations, superhardening and/or supertoughening. Nevertheless, identifying the layer materials, optimising the film deposition setup and performing micromechanical testing requires delicate experimental work. This talk illustrates the necessary interplay between modelling and experimental techniques to understand and control bilayer-period-dependent trends coming hand in hand with microstructural changes in superlattices. The model superlattice systems are cubic-based MoN/TaN, TiN/WN, and TiN/TaN. In particular, we highlight the important role of vacancies triggering local changes in the electronic structure, stabilisation of (novel) metastable phases or compositional variations at different layer thicknesses, which directly influence mechanical properties. Furthermore, atomistic processes governing strength, plasticity, and fracture of superlattices subject to tensile and shear deformation are discussed in light of the experimental results as well as ab initio molecular dynamics simulations.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B7

Plasma Surface Interactions, Diagnostics and Growth Processes

B7-1 INVITED TALK: Energy and Momentum Fluxes at Plasma Processing of Materials*, **Holger Kersten (kersten@physik.uni-kiel.de)**, T. Trottenberg, M. Klette, L. Hansen, A. Spethmann, F. Schlichting,* IEAP, U Kiel, Germany **INVITED**

For an optimization of plasma-based processes as thin film deposition or surface modification, respectively, suitable diagnostics are required. In addition to well-established plasma diagnostic methods (e.g. optical emission spectroscopy, mass spectrometry, Langmuir probes, etc.) we perform examples of "non-conventional" low-cost diagnostics, which are applicable in technological plasma processes. Examples are the determination of energy fluxes by calorimetric probes and measurement of momentum transfer due to sputtered particles by force probes. In particular, energy and momentum transfer transport through the plasma sheath combined with the possibility to measure the effect of charge carriers as well as energetic neutrals are of interest and become possible by these diagnostics.

Total energy fluxes from plasma to substrate have been measured by special calorimetric sensors. A typical method is the passive thermal probe (PTP) based on the determination of the temporal slope of the substrate surface temperature (heating, cooling) in the course of the plasma process. By knowing the calibrated heat capacity of the sensor, the difference of the time derivatives yields the integral energy influx to the surface. Simultaneously, the electrical current to the substrate can be obtained and by variation of bias voltage the energetic contributions of charge carriers can be determined. By comparison with model assumptions on the involved plasma-surface mechanisms the different energetic contributions to the total energy influx can be separated.

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

[1] **2020 Student Award Finalist**

measurements are compared with TRIM simulations for different experimental discharge conditions.

B7-3 A Force Probe as a Tool to obtain Directionally Resolved Momentum Characteristics during Sputter Processes*, **Mathis Klette (klette@physik.uni-kiel.de)**, T. Trottenberg, M. Maas, H. Kersten,* Kiel University, Kiel, Germany

Ion beam sputter deposition is a well-established technique for producing high quality thin film coatings. The optimization of the coating process requires an understanding of the physical phenomena. Process parameters like the deposition rate can be determined by quartz crystal microbalances, while charged particles in the sputter plume can be characterized by Faraday cups or retarding field analyzers.

However, the majority of the sputter plume consists of neutral particles. Characterizing these requires much more complex diagnostics, such as optical emission, laser-induced fluorescence [1], or mass spectrometry [2].

In contrast, interferometric force probes offer a more direct measurement of all particles including neutrals by measuring the force the sputter plume exerts onto the probe surface. In previous works, these probes have been used to determine the thrust of electric space propulsion engines, forces exerted by a low-temperature plasma onto a solid boundary [3], or the recoil of reflected and sputtered particles at a sputter target [4].

In this work, a sputter plume is generated by an ion beam directed onto a rotatable copper or silver target, respectively. In order to obtain a directionally resolved momentum profile, a force probe is circling the target at a fixed distance, measuring the current and momentum transferred to the probe surface. The obtained momentum profiles are then compared with numerical simulations using SRIM [5]. Both, measurements and simulations, are carried out for different angles of incidence, ion energies, gases, target materials, and working pressures.

References

[1] A. Goehlich et al., *Nucl. Instrum. Methods,***179**, 351 (2001)

[2] C. Bundesmann et al., *Contrib. Plasma Phys.*, **55**, 737 (2015)

[3] T. Trottenberg und H. Kersten, *Plasma Sources Sci. Technol.*,**26**, 055011 (2017)

[4] A. Spethmann et al., *Phys. Plasmas*, **24**, 093501 (2017)

[5] J. Biersack und L. Haggmark, *Nucl. Instrum. Methods*, **174**, 257 (1980)

B7-4 Erosion and Cathodic Arc Plasma of Nb–Al Cathodes: Composite vs. Intermetallic*, S. Zöhrer, M. Golizadeh,* Montanuniversität Leoben, Austria*; N. Koutná,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; **Robert Franz (robert.franz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

In the case of single-element cathodes, many properties of cathodic arcs show a correlation to the cohesive energy of the cathode material including the burning voltage, the erosion rate, or, to a lesser extent, plasma properties like electron temperatures or average ion energy and charge states. For multi-element cathodes, various phases with different cohesive energies can initially be present in the cathode, or form due to arc exposure, complicating the evaluation of such correlations. To test the influence of morphology and phase composition of multi-element cathodes on cathodic arc properties, we used a Nb–Al cathode model system that includes: pure Nb and Al cathodes; intermetallic Nb_3Al, Nb_2Al and $NbAl_3$ cathodes; and 3 composite Nb–Al cathodes with atomic ratios corresponding to the stoichiometric ratios of the intermetallic phases. Pulsed cathodic arc plasmas from these cathodes were examined using a mass-per-charge and energy-per-charge analyser, showing that charge-state-resolved ion energy distributions of plasmas from the intermetallic and corresponding composite cathodes are nearly identical. An examination of converted layers of eroded cathodes using x-ray diffraction and scanning electron microscopy indicates the formation of a surface layer with similar phase composition for intermetallic and their corresponding composite cathode types. The average arc voltages do not follow the trend of cohesive energies of Nb, Al and intermetallic Nb–Al phases, which have been calculated using density functional theory. Possible reasons for this effect will be discussed based on the current knowledge of multi-element arc cathodes and their arc plasma available in literature.

B7-5 Oxygen Diffusion Barrier On Interfacial Layer Formed With Remote Nh3 Plasma Treatment*, **Fu-Yang Chu (xxmoon666@gmail.com)**, K. Chang-Liao, D. Ruan, H. Yeh, S. Yi, Y. Chien,* National Tsing Hua University, Taiwan

In this work, the effects about an additional post interfacial layer (IL) plasma treatment for germanium (Ge) n-type metal oxide semiconductor field effect transistor (nMOSFET) has been discussed in detail. It is founded that the electrical performance could be further improved by an additional plasma treatment after the traditional germanium dioxide IL formation. The Ge nMOSFET with NH3 plasma treatment exhibits higher on-off current ratio, lower subthreshold swing and higher Gm value, while the equivalent oxide thickness or gate dielectric quality might be kept.

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B8

HiPIMS, Pulsed Plasmas and Energetic Deposition

B8-1 INVITED TALK: Evolution of Ionization Fraction of Sputtered Species in Standard, Multi-pulse and Reactive HiPIMS*, M. Fekete, K. Bernatova, P. Klein, J. Hnilica, **Petr Vasina (vasina@physics.muni.cz)**,* Masaryk University, Brno, Czech Republic **INVITED**

High power impulse magnetron sputtering (HiPIMS) technology attracts the interest of the industry as the coatings deposited by HiPIMS exhibit enhanced properties compared to conventional dc magnetron sputtered (dcMS) coatings. This is because HiPIMS generates very dense plasma, which results in a large fraction of ionized sputtered particles. However, a significant drawback of HiPIMS is a lower deposition rate compared to dcMS, which can be mitigated by operation of HiPIMS in multi-pulse mode (m-HiPIMS). M-HiPIMS further changes the coating structure and resulting properties due to the enhanced ion flux to the substrate because of the interaction of the preceding and the subsequent pulse. The evolution of the sputtered species ionization fraction is studied using a recently developed effective branching fraction method. This non-invasive method utilizes the optical emission signal to quantify the absolute ground state number densities of the sputtered titanium species. Influence of the preceding pulse on the subsequent pulse in the non-reactive m-HiPIMS process is examined as a function of delay between two successive pulses.

The sputtered species ionization fraction plays an important role also in reactive processes. In reactive HiPIMS process, the hysteresis curve is generally reduced in width and shifted towards lower reactive gas supplies compared to reactive dcMS. We report on the evolutions of the sputtered species ionization fraction in reactive HiPIMS discharges in oxygen, nitrogen and acetylene gases for a constant mean power and pulse duration, when varying the repetition frequency. The ionization fraction of the sputtered species increases with the partial pressure of the reactive gas, which was attributed to a combination of different effects taking place in HiPIMS plasma. Further, the hysteresis curve shape changes with the change of the repetition frequency. Larger ionization fraction of the sputtered species leads to larger difference in the hysteresis curve shape. The hysteresis behavior of reactive HiPIMS is modelled utilizing a modified Berg model. The back-attraction of the sputtered species to the target is incorporated into the modified Berg model. The results from simulations prove that the back-attraction of sputtered metal ions is the main effect causing the hysteresis curve reduction and shift in reactive HiPIMS compared to reactive dcMS.

B8-3 Dynamics of the Titanium Ground State Atoms and Ions in HiPIMS Discharge*, **Jaroslav Hnilica (hnilica@mail.muni.cz)**, P. Klein, P. Vasina,* Masaryk University, Brno, Czech Republic*; R. Snyders, N. Britun,* University of Mons, Belgium

High power impulse magnetron sputtering (HiPIMS) is a very attractive physical vapor deposition technique, which has been of great interest over the last two decades. Continuous development of the HiPIMS-based sputtering discharges is tightly related to the more profound understanding of the undergoing physical processes, a crucial factor for the optimization of thin-film growth as well as for further development of sputtering technology in general.

In our study, we combined various optical diagnostic methods for in-situ characterization of HiPIMS discharges. Special attention was dedicated to the visualization of the ground state titanium neutrals and ions in the discharge volume as their direct imaging above the magnetron target is a straightforward way to obtain information about their number density. Two-dimensional time-resolved density mapping of the sputtered particles in a HiPIMS discharge was performed by laser-induced fluorescence (LIF) technique. Atomic absorption spectroscopy (AAS) measurements were utilized in parallel to LIF to follow the number density evolution of sputtered species. Above mentioned methods were used to study effects such as plasma-on time, plasma-off time, gas pressure, pulse energy, or oxygen addition on density evolution of sputtered particles.

As a result of discharge characterization, the number densities, as well as temporal propagation of the neutral and ionized sputtered titanium atoms were determined. The result shows that atoms always remain in the discharge volume, the plasma-off time duration mainly alters the amount of background sputtered atom densities at which the successive pulse starts. At the same time, the plasma pulse duration together with the pulse energy, significantly affect ionization degree of the sputtered titanium above the magnetron cathode, especially shortly after the HiPIMS pulse. On the other hand, the observed titanium atom and ion density dynamics are weakly sensitive to the plasma pulse duration which implies that the initial stages of HiPIMS pulse have a stronger influence on the sputtering process evolution.

The results obtained in this study can be utilized to control the ionization degree, sputtering rate, as well as the other discharge parameters in industrial deposition processes involving HiPIMS discharges.

B8-4 The Single-Shot Spatial-Resolved OES of the Spoke in Non-Reactive HiPIMS*, **Marta Šlapanská (slapanska@physics.muni.cz)**, M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as ionisation zones or spokes, firstly observed in non-reactive high power impulse magnetron sputtering discharges (HiPIMS) are at certain conditions present in direct current magnetron sputtering (dcMS) and radio frequency magnetron sputtering discharges (rfMS) as well. The spokes are investigated due to their high impact on the deposition process and sputtered species' transport. To better understand the spoke phenomena, it is necessary to acquire comprehensive data of the plasma parameters inside the spoke; however, in HiPIMS, preferably by non-invasive diagnostics.

This contribution presents the non-invasive spatial-resolved optical emission spectroscopy (OES) of the plasma inside the spoke conducted in non-reactive HiPIMS discharge. The pulses have a duration of 100 µs with a repetition rate of 5 Hz. The 3-inch titanium target was utilised. The experiment was run at argon pressures of 0.4 Pa, 1.0 Pa, and 1.6 Pa to investigate both triangular and round spokes.

The fast photodiode and the cylindrical probe were used to capture and determine the passing spoke position. The photodiode's signal and the probe signal were synchronised with the optical emission spectrum acquisition by the intensified charge-coupled device (ICCD) detector with a gate time of 100 ns. By processing these three signals and creating the normalised time scale for each spoke, the unified spoke (UNI-spoke) has been created. Consequently, the evolutions of the selected emission lines can be shown within the UNI-spoke.

The spatially resolved emissions of Ar atom and ions and Ti atoms and ions spectral lines were investigated within the UNI-spoke. The spatial resolved OES measurements have shown that the Ar and Ti atoms and ions spectral lines have the characteristic evolution of a specific species' intensity and is the same for all observed spectral lines of this species within the spoke independently of applied pressure. The Boltzmann plot method was utilised to determine the excitation temperatures within the UNI-spoke. The excitation temperatures obtained using the Ar ions and Ti atoms and ions are 13000 K, 8000 K, and 19000 K. The ionisation fraction has been calculated from the selected spectral lines of titanium atom and ion. The ionisation fraction reaches approximately 40%, and its evolution and excitation temperature evolutions remain constant in the margin of standard error within the UNI-spoke for all investigated working pressures.

This research was supported by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA19-00579S funded by the Czech Science Foundation.

B8-5 Understanding and Influencing the Energy Delivered to the Film in Bipolar HiPIMS*, **Tomas Kozak (kozakt@ntis.zcu.cz)**, A. Pajdarova, J. Capek,* University of West Bohemia, Czech Republic*; M. Cada, Z. Hubicka,* Institute of Physics, Academy of Sciences of the Czech Republic*; P. Mares,* HVM Plasma, s.r.o., Czech Republic

Benefiting from high degree of ionization of process gas and, especially, target material atoms, the high-power impulse magnetron sputtering (HiPIMS) technique provides increased energy delivered to the film resulting in hard, dense and defect-free coatings [1]. Asymmetric bipolar pulsed magnetron sputtering is one of the major techniques used for deposition of dielectric films allowing the neutralization of charge on the target during a positive voltage pulse on the magnetron. Moreover, the positive magnetron voltage causes an increase of plasma potential leading to enhanced energies of ions incident on the growing film [2]. Using the positive pulse in a HiPIMS discharge, where the degree of ionization is much higher, can result in substantial increase of energy delivered to the film and improvement of film properties [3]. Additionally, this technique might be more suitable for the industry than using separate substrate bias source.

This paper presents a systematic study of ion energy spectra in a bipolar HiPIMS discharge employing a rectangular positive voltage pulse (with controllable amplitude, delay after the main negative pulse and pulse length). The time-averaged spectra of ions measured at the substrate position exhibit a prominent high-energy peak corresponding to the ions accelerated by the increased plasma potential during the positive pulse. The position of the peak can be varied by positive pulse amplitude, its size scales with the pulse length and its width can be slightly influenced by the delay of the positive pulse. Moreover, time-resolved mass spectroscopy has been used to analyze the time of arrival of ions at various energies. Features of the energy spectra related to the magnetron voltage transients were identified. They indicate changes of the plasma potential in front of the substrate. To fully understand the ion energy spectra, the mass spectroscopy results are supported by Langmuir probe measurements of plasma and floating potential, and also electron density and temperature, at several positions in the discharge.

References

[1] Sarakinos K, Alami J and Konstantinidis S, *Surf. Coat. Technol.***204** (2010) 1661

[2] Bradley J W and Welzel T *J. Phys. D: Appl. Phys.***42** (2009) 093001

[3] Santiago J A, Fernández-Martínez I, Kozák T, Capek J, Wennberg A, Molina-Aldareguia J M, Bellido-González V, González-Arrabal R and Monclús M A *Surf. Coat. Technol.* (2019) **358** 43

B8-6 The Use of HiPIMS with Positive Pulses to Tailor Film Ion Assistance and the Resulting Microstructural Properties*, **Ivan Fernandez (ivan.fernandez@nano4energy.eu)**, J. Santiago, A. Wennberg, A. Mendez,* Nano4Energy SL, Spain*; F. Papa,* GP Plasma, USA

Recently, it has been demonstrated that the addition of a positive voltage pulse adjacent to the negative HIPIMS sputtering pulse allows the increase of film ion assistance and thus, the improvement of coating properties on both biased and insulating substrates. Also, the energy of the incoming ions is proportional to the amplitude of the positive voltage. Some examples of experiments carried out in industrial coating machines will be presented in this study, such as the improvement on film density, mechanical properties and deposition rate in an industrial batch coater for metal nitrides, or the increased barrier performance of films deposited on PET in an industrial scale (330 mm wide web) web coater.

L. Velicu et al., Surface & Coatings Technology 359 (2019) 97.

J. Keraudy et al., Surface & Coatings Technology 359 (2019) 433.

N. Britun et al., Appl. Phys. Lett. 112 (2018) 234103.

F. Avino et al., Plasma Sources Sci. Technol. 28 (2019) 01LT03.

J.A.Santiago, I Fernandez-Martinez et al., Surface & Coatings Technology 358 (2019) 43.

B.Wu et al., Vacuum 150 (2018) 216.

G. Eichenhofer, I Fernandez-Martinez et al., UJPA 11(3), (2017) 73

B8-7 Measurements and Modeling of Residual Stress in Sputtered Nitride Films: Dependence on Growth Rate and Gas Pressure*, **Zhaoxia Rao (zhaoxia_rao@brown.edu)**, E. Chason,* Brown University, USA

Transition metal nitride films (e.g. TiN, ZrN and TaN) are often used as coatings because of their exceptional physical and mechanical properties. However, the residual stress induced during deposition can significantly alter their performance and reliability, leading to failure by cracking or buckling. Therefore, it is of critical importance to understand and control the stress evolution during deposition in nitride films. In this work, we investigate the stress evolution in nitride coatings deposited by physical vapor deposition. We report on the dependence of stress on the growth rate and gas pressure coupled with microstructure characterization. The experimental data is interpreted in terms of a kinetic model which includes the effects of film growth kinetics and energetic processes. The ultimate goal is the development of a model for predicting and optimizing stress in sputtered nitride films.

B8-9 Wafer-scale Metallic Nanotube Arrays (MeNTAs): Fabrication and Application*, Alfreda Krisna Altama (d10904819@mail.ntust.edu.tw),* *J. Chu,* National Taiwan University of Science and Technology, Taiwan*; A. Purniawan, S. Wicaksono,* Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

Sputter deposition has been widely used in the manufacturing of high-performance on-chip interconnect. The metal connecting lines at each layer can be formed by filling trenches and vias in the interlayer dielectrics (ILD). High-power impulse magnetron sputtering (HiPIMS) techniques as a novel ionized physical vapor deposition (IPVD) technology has been developed in view years for metallization in integrated circuits and nanostructures manufacturing with high aspect ratio (AR). HiPIMS is an IPVD technique based on pulsed power technology where the peak power exceeds the time-averaged power by roughly two orders of magnitude so. HiPIMS deposition offers a route for depositing uniform coatings onto complex-shaped substrates and structures. In this research, we formed high AR trenches using photoresist lithography on silica wafers. The deposition process was performed using a 6 inch diameter metallic alloy target using HiPIMS and DCMS. The plasma properties were measured using a Langmuir probe at a distance of 70 mm from the target face and below the racetrack. The measurement results show that the plasma produced by HiPIMS has a higher ion and electron density value compared to DC plasma. We consider the experimental condition of high density plasma as the favorable process condition for the trench deposition. In this condition, the film was deposited at different power and working pressure. The cross-sectional pictures performed by scanning electron microscopy (SEM) shows that the film had good trench step coverage and amorphous structure. Furthermore, the results of this study can be used as a reference for trench filling and the manufacture of nanostructures with high aspect ratio using HiPIMS.

B8-10 Plasma Chemistry, Crystal Growth and Mechanical Properties of CrAlYN / CrN Nanoscale Multilayer Coatings Deposited by High Power Impulse Magnetron Sputtering*, Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk), A. Sugumaran, P. Hovsepian,* Sheffield Hallam University, UK

Nanoscale multilayer coatings based on CrAlYN / CrN find applications in manufacturing, automotive components, power generation turbines and petrochemical industry. To perform well in these different environments, the coating microstructure must be tailored via the deposition process. In High Power Impulse Magnetron Sputtering (HIPIMS), which provides a high degree of ionisation of the metal flux and activation of the reactive gas, the relation between process parameters, microstructure and coating properties is not well understood.

We report on the effect of unbalancing magnetic field on species-dependent transport of metal and gas species to the substrate and its influence on film growth, texture formation and mechanical performance of nanoscale multilayer CrAlYN/CrN films. Experiments were carried out in an industrial-sized coater with four cathodes arranged in a closed magnetic field configuration, two of which were operated in HIPIMS mode and two in conventional sputtering.

In a balanced configuration, the magnetic null height was h_m = 12 cm and the volume of plasma near the target was the greatest and resulting in a high metal-to-gas ion ratio (J_{Me}+ / J_G+) observed by optical emission spectroscopy. The transport to the substrate, as measured by the ion saturation current (J_i), was the lowest due to the absence of magnetic field lines connecting to the substrate. The 4-micrometre-thick films exhibited competitive growth and a strong [111] texture evidenced by XRD due to the relatively low flux of dissociated nitrogen to the surface. SEM observations showed that the [111] texture resulted in dome-shaped column tops and clearly defined column boundaries where vacuum impurities were segregated.

As the magnetic field grew more unbalanced, the confinement volume decreased whilst transport to the substrate was enhanced, resulting in both J_{Me}+ / J_G+ and J_i reaching their maximum values. Weakly unbalanced fields with h_m = 10 cm provided sufficient flux of activated species to cause the grains to switch to [220] and then to [200] texture and allowing them to absorb impurities interstitially. This resulted in the elimination of dome-shaped morphology, drastic reduction in roughness, parallel column boundaries and increase in grain size.

Highly unbalanced fields (h_m = 4 cm) constricted the height of the confinement volume, reducing the ionisation of metal and dissociation of nitrogen as evidenced by the significant reduction in J_{Me}+ / J_G+. The loss of dissociation switched the texture back to a strong [111]. Grain sizes were significantly larger than for the balanced configuration due to a higher J_i.

The hardness and dry sliding wear rates are discussed.

B8-12 On the Influence of the Micropulse on Nb Thin Films Deposited by MPPMS and DOMS: A Comparative Study*, Y.G. Li (ygli@dlut.edu.cn), Z. Jiang, H. Yuan, N. Pan, M. Lei,* Dalian University of Technology, China

Nb thin films deposited by modulated pulsed power magnetron sputtering (MPPMS) and deep oscillation magnetron sputtering (DOMS) were comparatively studied under similar average power by controlling the micropulse duty cycle. It was found that DOMS discharge showed both higher discharge peak current and peak voltage, time delay between the current and voltage was much shorter with respect to a MPPMS discharge. All Nb thin films were observed with Nb(110) preferred orientation and compact columnar structure with DOMS Nb thin films hardness with higher hardness and elastic modulus. The increase of micropulse duty led to the gradually movement of Nb(110) to the high scattering angle direction, meanwhile the DOMS Nb(100) diffraction peaks were all on the left of MPPMS Nb(110). An anomalous increase could be observed for compressive residual stress s of Nb thin films for both techniques. The anomalous increase in s also led to the deterioration of scratch adhesion. Despite, the grain sizes of DOMS Nb thin films were all smaller than MPPMS Nb thin films, s in DOMS Nb thin films generated by the adatom diffusion and ion irradiation still overwhelmed the tensile stress generated by the volume shrinkage of the growing grains. The special afterglow of DOMS in microsecond time scale gave a new dimension controlling the grown thin films.

B8-13 The Effect of Metal Transition Dopents on Mechanical Properties TiBCN Based Coatings Deposited by CFUBMS-HiPIMS*, Ihsan Efeoglu (iefeoglu@atauni.edu.tr),* Ataturk University, Turkey*; N. Aksakalli,* Atatürk University, Turkey*; B. Gumus, E. Tan,* Aselsan Inc., Turkey

Ternary and quaternary hard coatings based on carbonitrides of transition metals with amorphous matrix have many advantages; these have high hardness, adhesion, abrasion, oxidation, and corrosion resistance. Functional properties can be gained by adding definite amounts of different transition elements to carbonitride-based coatings**.** In this study, mechanical and tribological properties were investigated by adding Nb and Zr transition elements to TiBCN based coatings. The coatings were deposited on 4140 tool steel and the silicon wafer. TiBCN-based coatings with high adhesion and dense microstructure were synthesized with CFUBMS (Pulsed-dc+HiPIMS) using Cr, Ti, TiB_2, Nb, Zr targets and Ar, N_2, C_2H_2 gases. Microstructural properties of the coatings were obtained from the coatings on the silicon wafer and 4140 steel using SEM, XRD, and XPS. The mechanical properties of coatings synthesized on 4140 steel base materials have been characterized by Microhardness and Scratch tests. The hardness and adhesions of TiBCN-based coatings, which were grown by adding Nb and Zr, respectively on Cr:CrN graded structure (~200nm) as the transition layer, were optimized depending on the process parameters. Scratch test results showed that the adhesion strength varied as a function of the Nb and Zr target negative bias voltages. The highest adhesion strength was obtained as Lc:80N at -800V with adding Zr. In the case of the Nb adding, the highest adhesion strength was obtained as Lc:57N. Adhesion and microhardness test results showed that the utilization of bias-voltage with HiPIMS to the targets and pulsed-dc to the base material was the most effective coating parameter in the critical load and the hardness properties. Friction coefficients were observed as the lowest value, μ≈0.163 in TiBCN-Nb coatings, while it was observed as μ≈0.337 in TiBCN-Zr coatings.

Keywords: TiBCN:Zr/Nb, Adhesion, Microhardness, CFUBMS-HiPIMS,

Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session BP

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

BP-1 Investigation of Ionized Density Fraction in Reactive Hipims*, Katarína Bernátová (kbernatova@mail.muni.cz),* Masaryk University, Czechia

In High Power Impulse Magnetron Sputtering (HiPIMS), high plasma density is achieved by focusing the applied power into the short pulses with a duty cycle of around 2%. Discharge properties, such as a density of sputtered species, are strongly nonlinearly dependent on the reactive gas supply influencing properties as well as the stoichiometry of the deposited layers.

In our study, the effect of nitrogen gas admixture on the temporal evolution of discharge current, voltage, pressure, and ionized density fraction of sputtered species in the HiPIMS process is analyzed. The ionized density fraction is estimated from the sputtered titanium atom and ion absolute ground state number densities both near the target surface and near the substrate region. For the determination of sputtered species density, a well-established spectroscopic method based on effective branching fractions was utilized.

Three regimes within the hysteresis curve were investigated and compared: metal, transition, and compound regime. In both, target and substrate regions, after the pulse ignition, the nonzero value of titanium atom density is always detected, indicating the presence of residual particles originating from the preceding pulse. Near the target, in the metal regime, the Ti atom density increases through the pulse, causing enhanced argon rarefaction near the target. From the quarter of the pulse, the concentration of Ti ions is always higher than Ti atoms and the ionized density fraction is most pronounced around middle of a pulse. With the nitrogen gas addition, the ionized density fraction increases, despite the overall Ti atom and ion densities decrease. In the substrate region, the evolution of Ti atom and ion densities changes, as the distance from the target is increased, therefore the transport time of particles to the measured area is higher. Furthermore, when operating in the transition and compound regime the pressure increases, resulting in even stronger delay of particle transport. Due to argon rarefaction near the target in the metal regime, Ti atoms travel towards the substrate where they are accumulating over the second half of the pulse. In contrast, in the transition and compound regime, the sputtering is not effective, and the transport is strongly delayed, therefore the Ti atom and ion densities are decreasing through the pulse. Here, the ionized density fraction is again enhanced with nitrogen gas admixture.

BP-2 Increasing Oxidation Resistance of Reactive Magnetron Sputtered ($Al_vCr_wNb_xTa_yTi_z$)N Thin Films by Si-alloying*, Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; K. Yalamanchili, H. Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance of these materials.

($Al_vCr_wNb_xTa_yTi_z$)N coatings were formed in a cubic (c) solid solution in thin film form by reactive magnetron sputtering in N_2-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm^3 each) of Si on the cathode racetrack during deposition.

We measured the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30, and 100 h. After these durations we extracted the samples from the hot zone and analysed them with X-ray diffraction, Energy-Dispersive-X-Ray-Analysis, and Transmission Electron Microscopy (TEM). After 100 h the oxide scales on coatings without and with Si were 2800 and 300 nm thick, respectively. Plotting the oxide scale thickness against the oxidation time reveals a parabolic oxide growth behaviour without Si, which changes to logarithmic growth with Si in the solid solution. This different behaviour can be explained with the oxide morphology, visible in TEM. Without Si, the oxide is porous, whereas with Si the oxide is separated into a dense inner region and a porous outer region.

Therefore, we can conclude that Si-alloying improves the oxidation resistance tremendously and may be applicable to increase the performance of other high-entropy nitride coatings in oxidative environments.

BP-3 Properties of Boron Carbide Thin Films Deposited by Pulsed Laser Deposition*, Falko Jahn (falko.jahn@hs-mittweida.de), S. Weissmantel,* Laserinstitut Hochschule Mittweida, Germany

Boron carbide is the third hardest known material behind diamond or ta-C and cubic boron nitride (c-BN). Intensive contact of diamond or ta-C with ferrous materials lead to carbide formation and thus a chemical wear of the layer. Because of this, films of diamondlike carbon are not suited for applications e.g. as wear protective layers in steel processing. For cubic boron nitride on the other hand there is yet no successful deposition method that meets industrial requirements.

Boron carbide could be a promising compromise for these applications. Indeed, it doesn't reach the hardness values of ta-C or c-BN, but due to its better thermal and chemical stability it is suitable for ferrous materials.

Using Pulsed Laser Deposition (PLD) super hard coatings of boron carbide have been produced with a resulting indentation hardness up to 47 GPa which almost reaches the highest values reported so far. The substrate temperature during deposition has been varied between room temperature and more than 500°C. That temperature has been found to have the most impact on the mechanical properties of the coatings. The influence of the ablation fluence on the mechanical properties is shown although it is less significant. The produced layers show good film adherence properties but a very bad surface quality at layer thicknesses sufficient for practical applications and which is characterized by too many particulates and droplets.

Following, research results of applying an alternative boron carbide target are presented. This target is produced by depositing a several ten microns thick boron carbide layer on a steel substrate using PLD. The as deposited film is subsequently used as the new target for the deposition process and results in boron carbide thin films with a significantly better surface quality. Comparing these B_4C films to the first deposited ones resulting from commonly used targets it can be shown that both number and size of the droplets decrease.

BP-4 In-situ Analysis of B-doped Diamond Synthesis using Hot Filament CVD*, Ryo Tanaka (s16a3083gp@s.chibakoudai.jp), M. Takuya,* Chiba Institute of Technology Graduate School, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

B-doped diamond (BDD) has excellent electrochemical properties, and its application for electrochemical electrodes is progressing. BDD is prepared in substrates such as Si by hot-filament chemical vapor deposition (HFCVD), microwave plasma CVD, etc. BDD synthesis using HFCVD apparatus, source gases are decomposed by filaments heated to 2273≦[K] in pressure of between molecular flow and viscous flow. Therefore, complicated convection occurs between filament-substrate, it's difficult to control the B source flow between filaments and the substrate. In addition to control the flow of gases supplied into the chamber, it is necessary to feedback control based on measurements of reaction gas states.

In this study, reaction gas states were measured with quadrupole mass spectrometer (QMS) during BDD synthesis, it was explored relationship of electrical resistance to peak intensity of fragments.

BDD films were synthesized on Si substrates using HFCVD apparatus. CH_4-H_2-$B(OCH_{3})_3$ gas mixture was used, with CH_4/H_2 flow rate: 1/50 [SCCM], $B(OCH_3)_3$ flow rate: 0.025 to 0.150 [SCyCM]. Pressure was 4.0 [kPa]. Filament temperature was 2273≦ [K]. Synthesis time was 1 [h]. Reaction gas states were measured with QMS. Deposits were evaluated by Raman Spectroscopy. Electrical resistances were measured by four-probe method.

As a result of measuring reaction gas states with QMS, it was confirmed that $B(OCH_{3})_3$ fragments of $(OCH_3)^+$, $BH(OCH_3)^+$ and $B(OCH_3)_2^+$. These peak intensities decreased during synthesis, so, it was recognized that can be measured the $B(OCH_3)_3$ with QMS. There was correlation between decreased electrical resistance and increased peak intensity of $(OCH_3)^+$ up to $B(OCH_3)_3$ flow rate 0.100 [SCCM]. In the case of $B(OCH_3)_3$ flow rate exceeded 0.100 [SCCM], electrical resistance indicated constant value. Supersaturated of B and O occurred on the surface of the substrate and electrical resistance of CVD diamond became constant value.

In conclusion, it was confirmed that controlling electrical resistance of BDD was suggested by in-situ analysis of reaction gas states with QMS.

BP-5 Behavior of Partially Oxidized Metal Targets, ***Jiri Houska (jhouska@kfy.zcu.cz)**, T. Kozak,* University of West Bohemia, Czech Republic

We investigate the oxidation of a wide range of metal surfaces by ab-initio calculations. The metals of interest span from transition metals (Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) through noble and post-transition metals (Cu, Ag, Au, Zn, Cd) to the main group (Al) [1,2]. We go through a wide range (up to 329 per metal) of distributions of O atoms on a partially oxidized metal surface. First, we focus on the qualitative information whether the preferred distribution of O atoms is heterogeneous (stoichiometric oxide + metal; e.g. Al or La), homogeneous (substoichiometric oxide; e.g. Ti or Zr), homogeneous at low surface oxygen coverage and heterogeneous at high surface oxygen coverage (e.g. Sc or Y), etc. This is of crucial importance for the quantities such as secondary electron emission coefficient, which correspond to a weighted average of those of stoichiometric oxide and metal only in the case of heterogeneous oxygen atom distribution. Second, we correlate these qualitative results with the known formation enthalpies of oxides of various compositions. Third, we provide the quantitative values of adsorption energies corresponding to the energetically preferred O atom distribution for various partial coverages of various metals by O. We find that the dependence of adsorption energy on the surface oxygen coverage can be decreasing (e.g. Al or La), increasing (e.g. Ti or Zr), concave (e.g. Sc or Y), etc. These data also include the information about the maximum stable surface oxygen coverage (nonzero but lower than 100% for Cu, Ag, Zn, Cd). Fourth, we demonstrate one use of these results by presenting Monte Carlo simulations of sputtering. Fifth, we utilize the theoretical results in order to explain the experimental results, such as the time dependence of the magnetron voltage during sputter cleaning of oxidized metal targets (monotonic e.g. for Al but non-monotonic e.g. for Ti).

[1] J. Houska and T. Kozak, J. Appl. Phys. 121, 225303 (2017)

[2] J. Houska and T. Kozak, Surf. Coat. Technol. 392, 125685 (2020)

BP-6 Phase Formation, Thermal Stability and Mechanical Properties of Nb-B-C Thin Films Prepared by Magnetron Sputtering Using a Combinatorial Approach, ***Stanislava Debnarova (408573@mail.muni.cz)**, P. Soucek, V. Bursikova,* Masaryk University, Czechia*; S. Mraz, M. Hans, J. Schneider, D. Holzapfel,* RWTH Aachen University, Germany*; P. Vasina,* Masaryk University, Czechia

The performance and lifetime of a tool can be significantly improved by the use of an appropriate protective coating. The most commonly used materials for these applications are ceramic-based coatings, favoured due to their high hardness. However, these coatings are inherently brittle which enables the spreading of cracks and coating failure. Therefore, new materials are being explored, which would combine the hardness of ceramics with a degree of ductility.

Ab-initio calculations have predicted that such a combination of properties could be present in a crystalline X_2BC material where X is a transition metal such as Mo, Ti, V, Zr, Nb, Hf, Ta or W [1]. Out of this group, only crystalline Mo_2BC has been successfully prepared and studied so far. There have been attempts to prepare a W2BC phase but these remain unsuccessful due to the near-zeroenthalpy of formation of this material. However, these studies have shown that the X-B-C system exhibits interesting mechanical properties even in an amorphous state [2, 3].

This study focuses on the Nb-B-C system as Nb_2BC is predicted to have a lower enthalpy of formation. The coatings have been prepared by magnetron sputtering from 3 targets using a combinatorial approach. A wide range of compositions has been studied and evaluated in regard to their structure and mechanical properties. As thermal and oxidation stability is a vital requirement for protective coatings, the studied coatings have been annealed up to 900°C in argon and up to 1000°C in an Ar/O_2 gas mixture. The study examines the effect of annealing on the structure and mechanical properties of the coatings.

References

[1] H. Bolvardi, J. Emmerlich, M. To Baben, D. Music, J. Von Appen, R. Dronskowski, J.M. Schneider, Systematic study on the electronic structure and mechanical properties of X2BC (X = Mo, Ti, V, Zr, Nb, Hf, ta and W), J. Phys. Condens. Matter 25 (4) (2013) 045501

[2] S. Debnárová, P. Souček, P. Vašina, L. Zábranský, V. Buršíková, S. Mirzaei, Y. Pei, The tribological properties of short range ordered W-B-C protective coatings prepared by pulsed magnetron sputtering, Surface and Coatings Technology (2019) 357 364-371

[3] S. Debnárová, L. Zábranský, P. Souček, V. Buršíková, P. Vašina, Study of W-B-C thin films prepared by magnetron sputtering using a combinatorial approach, International Journal of Refractory Metals and Hard Materials (2019) 85

BP-7 Mechanical and Tribological Performance of V-C-N Coatings Deposited by RF Magnetron Sputtering, ***Akram Alhussein (akram.alhussein@utt.fr)**,* Universite de Technologie de Troyes (UTT), France*; L. Aissani,* Khenchela University, Larbi Ben M'Hidi University, Algeria*; C. Nouveau,* CER Arts et Metiers Paris Tech, France

Vanadium nitrides are known as hard and wear resistant materials widely used for cutting tools and other components. Vanadium carbides present excellent properties at high temperature, such as good wear resistance and high hardness. This work aims to evaluate the influence of the following deposition parameters on the structure, mechanical and tribological properties of V-C-N thin films deposited by RF magnetron sputtering: nitrogen partial pressure, $Ar-N_2$ deposition atmosphere and film thickness. VN, V–C-N coatings were deposited on silicon wafers and steel substrates and characterized with X-ray diffraction, XPS, EDS, SEM, nanoindentation and tribological tests.

Controlling the gas pressure in the deposition chamber is important to elaborate the desirable coatings (good adhesion and performance). It has been found that compared to the VN system, the VC-N films showed a smooth surface and the films deposited at 0.06 Pa presented the best mechanical and tribological properties: highest hardness of 26.1 GPa and lowest friction coefficient of 0.42 [1].

The Variation of nitrogen percentage in the deposition camber (10 - 20%) and the film thickness (0.26 – 2.5 µm) influenced significantly the film structure, hardness and wear resistance. Multiple phases of V2N and VN were formed and the thick films containing more nitrogen were slightly dense compared to the thinner ones [2].

Keywords: *Vanadium carbonitride thin films, PVD, microstructure, mechanical properties, tribological performance.*

References:

[1] Linda Aissani, Akram Alhussein, Corinne Nouveau, Lamia Radjehi, Issam Lakdhar, Elia Zghei, Evolution of microstructure, mechanical and tribological properties of vanadium carbonitride coatings sputtered at different nitrogen partial pressures, Surf. Coat. Tech. 374 (2019) pp. 531-540.

[2] Linda Aissani, Akram Alhussein, Corinne Nouveau, Laala Ghelani, Mourad Zaabat, Influence of film thickness and $Ar-N_2$ plasma gas on the structure and performance of sputtered vanadium nitride coatings, Surf. Coat. Tech. 378 (2019) 124948.

BP-8 Radiation Stability of nc- ZrN/a-ZrCu Multilayered Films after He Implantation, ***Grégory Abadias (gregory.abadias@univ-poitiers.fr)**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; V. Uglov, S. Zlotski, I. Saladukhin,* Belarusian State University, Belarus

The development of a new generation of nuclear reactors requires the use of materials and coatings with high radiation resistance. It's necessary to create materials with a large number of sinks for point defects, such as dislocations, grain boundaries, and interphase boundaries to achieve this goal [1-2]. One of the most promising materials with the large number of grain boundaries are nanocrystalline coatings, for example nc-ZrN, formed by vacuum arc deposition [3]. Nanocrystalline coatings with crystalline/amorphous interfaces (such as nanocomposite and multilayered nc-MeN/a-Si_3N_4 systems) exhibit a high radiation tolerance along with crystalline/crystalline systems, due to amorphous nanolayers associated with excellent defects absorption capability [4-5]. In this paper, the idea of replacing amorphous a-Si_3N_4 layers with amorphous a-ZrCu metal layers is proposed.

The work is devoted to the study of the elemental and phase composition, surface morphology and microstructure of the nc-ZrN/a-ZrCu multilayer systems and their evolution after He implantation. Nanoscale nc-ZrN/a-ZrCu multilayers with elementary layer thickness of 5 nm/5 nm and 5 nm/10 nm with different Cu concentration in a-ZrCu layer were grown by reactive magnetron sputter-deposition from Zr and Cu targets at substrate temperature of 300°C. XRD, EDX, SEM and AFM investigation of as-deposited and after He ion irradiation (40 keV and doses up to 1E17 cm^{-2}) of nc-ZrN/a-ZrCu multilayer systems were conducted.

XRD analysis confirms that multilayered films consist of nanocrystalline ZrN and amorphous ZrCu. It was found formation amorphous ZrCu in a wide range of Cu concentrations (up to 80 at.%).

The influence of the Cu composition (in the range of 20-80 at.%) in the ZrCu layers and thickness of individual layers (5 nm/5 nm and 5 nm/10 nm) of nc-ZrN/a-ZrCu multilayer on radiation stability of elemental and phase composition, surface morphology (blistering) and microstructure of films after He ion irradiation is discussed.

[1]. R.W. Grimes et al. Nature Materials 7 (2008) 683.

[2]. Xinghang Zhang et al. Prog.Mat. Sc. 96 (2018) 217.

[3]. A.J. Van Vuuren, V.V. Uglov et al. Phys. Status Solidi C 13 (2016) 886.

[4]. V.V. Uglov, G. Abadias et al. Sur. Coat. Technol. 344 (2018) 170.

[5]. V.V. Uglov, G. Abadias et al. Nucl. Instr. Meth. Phys. Res. 435 (2018), p. 228.

BP-9 Physical and Mechanical Properties of Cr-Al-N and Cr-v-N Ternary Systems*, **Ahlam Belgroune (ahlam.belgroune@utt.fr)**,* University of Technology of Troyes, France*; L. Aissani,* University of Abbes Laghrour, Algeria*; A. Alhussein,* University of Technology of Troyes, France

In the present work, ternary systems (Cr-Al-N and Cr-V-N) thin films were deposited on steel substrates by magnetron sputtering process. The effect of Al and V additions on the properties of the binary Cr–N system was evaluated. The morphology and surface topography of the coatings were investigated. The hardness and elastic modulus were measured by nanoindentation and the friction coefficient was determined by pin-on-disc tribometer.

We found that Al addition improved the mechanical properties of the Cr–N system (H= 27 GPa, E= 304 GPa) presenting a dense structure. Contrary, the V addition deteriorated the mechanical properties of films presenting rough surfaces (H= 10 GPa, E= 280 GPa). The friction coefficient of the CrAlN films slightly increased with rising Al percentage and varied between 0.42 and 0.61. For the Cr-V-N coatings, the friction coefficient was lower than those obtained for Cr-Al-N and Cr-N films. The wear resistance of Cr-Al-N and Cr-V-N coated steel substrates decreased with increasing Al and V contents.

Keyword: *Magnetron sputtering; Cr-Al-N; Cr-V-N; Cr-N; Hardness; Wear.*

BP-10 Understanding Residual Stress in Thin Films: Analyzing the Stress Evolution Using a Kinetic Model for Ag, Cu, Ni, Fe, Ti, and Cr*, **Zhaoxia Rao (Zhaoxia_Rao@brown.edu)**,* *S. Berman,* Brown University, USA*; D. Depla ,* Ghent University, Belgium*; E. Chason ,* Brown University, USA

An analytical model for the evolution of residual stress in polycrystalline thin films is used to analyze numerous previously-reported wafer curvature measurements obtained for a variety of processing conditions and materials (Ag, Cu, Ni, Fe, Ti Cr). The model includes the effects of film growth kinetics by considering stress-generating mechanisms at the grain boundary that forms between adjacent grains as well as subsurface grain growth.Non-linear least-squares fitting is used to obtain a set of parameters for each material.Some of the parameters are material-dependent and are made to be the same for all the data for each material independent of the processing conditions; others are allowed to change with the processing conditions.The dependence of the fitting parameters on the material and processing conditions is compared with the behavior expected from the physical mechanisms in the model.

BP-11 Effect of Target Poisoning Ratios on the Fabrication of TiO_X Coatings Using Superimposed HiPIMS and MF System*, W. Chen,* Ming Chi University of Technology, Taiwan*; B. Lou,* Chang Gung University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

Titanium oxide film is characterized by its clean surface, sterilization, good abrasion resistance and good corrosion resistance, which make it become a functional coating with a wide range of applications.The superimposed high power impulse magnetron sputtering (HiPIMS) and mid-frequency (MF) system (superimposed HiPIMS-MF) is a relatively new deposition system, which adds MF pulses to the off-time of the HiPIMS for higher deposition rate.In this study, a superimposed HiPIMS-MF system was used to fabricate the titanium oxide films. During the deposition process, a plasma emission monitoring (PEM) system was used to feedback control the target poisoning ratio of Ti target. Titanium oxide (TiOx) films grown at five different target poisoning ratios were deposited on single crystal silicon wafer, glass slide and AISI304 stainless steel plate substrates. The microstructure of thin film was examined by a field emission scanning electron microscope. The crystalline structure of thin film was analyzed by an X-ray diffractometry. The optical transmittance measurement of thin films was performed with a UV–vis spectrophotometer. The hardness, adhesion and tribological properties of TiOx films were evaluated by nanoindenter, scratch test and pin-on-disk wear test, respectively. The corrosion resistance of TiOx films in 0.1 M H_2SO_4 aqueous solution was examined by an electrochemical workstation. The influence of target poisoning ratios on the deposition rate, microstructure, transmittance, hardness, adhesion, wear and corrosion resistance of TiOx films were studied in this work.

BP-12 The Role of Oxygen Flow Rate on the Structure and Stoichiometry of Cobalt Oxide Films Deposited by DC Reactive Sputtering*, **Nilton Francelosi Azevedo Neto (nilton.azevedo@unesp.br)**,* *L. Affonco,* São Paulo State University, Brazil*; C. Stegemann, D. Marcel Gonçalves Leite ,* Aeronautics Institute of Technology, Brazil*; J. Humberto Dias da Silva ,* São Paulo State University, Brazil

The cobalt oxide films were grown on amorphous silica (a-SiO_2) in order to investigate the influence of the oxygen gas supply on the stoichiometry, structure and orientation texture of polycrystalline cobalt oxide films. The films were grown by direct current (DC) reactive magnetron sputtering using a metallic Co target and different oxygen partial pressures by controlling the inlet flow rate (0.5 to 5.0 sccm) over a dominant argon atmosphere (40 sccm) keeping constant the deposition power (80 W) and the total working pressure (0.67 Pa). X-ray diffraction results evidence a strong influence of the oxygen flow over the film's stoichiometry and structure, where low oxygen flows (< 2.0 sccm) favor the formation of the rocksalt CoO phase, while higher oxygen flows (>2.5 sccm) favor the spinel Co_3O_4 phase formation. The coexistence of monoxide and tetraoxide phases is observed only for 2.5 sccm oxygen flow condition. Strain and orientation texture effects related to the oxygen partial pressure are also observed and discussed. Computer simulations indicate that low oxygen flow (<2.0 sccm) occur in the metallic regime, while higher oxygen flow favor the poisoned regime. Consistent with the simulations, cobalt emission (Co^I = 340.5 nm) from the plasma show a significant decrease while the oxygen emission (O^I = 777.3 nm) is significantly increased when the oxygen flow is increased.

BP-13 e-Poster Presentation: Bipolar HiPIMS for Tailoring Ion Energies in Thin Film Deposition*, **Daniel Lundin (daniel.lundin@liu.se)**,* *R. Viloan,* Linköping University, Sweden*; M. Zanáška,* Linköping University*; H. Du,* Guizhou University, China*; R. Boyd,* Linköping University, Sweden*; T. Shimizu,* Tokyo Metropolitan University, Japan*; U. Helmersson,* Linköping University, Sweden

Bipolar HiPIMS, where a reversed positive pulse is applied to the target following the negative pulse, has promised great potential to solve challenges in growth of insulating thin films or when insulating substrates are used. In this mode of operation, a significant fraction of the ion energy distribution functions (IEDFs) can be shifted with an energy proportional to the magnitude of the applied reversed potential, U_{rev}. This is a consequence of the fact that a limited region of the plasma, near the cathode, experiences an increased plasma potential with a value close to U_{rev}. However, the ion energy gain and the distribution of energy in the accelerated populations can be affected by the magnetic field arrangement, the anode position and shape as well as the HiPIMS pulse configuration. These aspects are of great interest in the present contribution, where time- and energy-resolved ion mass spectrometry was performed in different discharge configurations to further understand the physics in bipolar HiPIMS discharges. Based on the features of the recorded IEDFs, optimized bipolar HiPIMS deposition processes for relevant material systems, such as aluminum oxide, were investigated to observe the effect of ion acceleration on the tailoring of the phase constitution during film growth.

BP-14 Nb-C Thin Films Prepared by DC-MS and HiPIMS: Synthesis, Structure and Tribo-mechanical Properties*, **Neus Sala (neus.sala@iqs.url.edu)**,* *M. Abad,* Institut Químic de Sarrià, Universitat Ramon Llull, Spain*; J. Sánchez-López,* Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Spain*; J. Caro,* Eurecat, Centre Tecnològic de Catalunya, Spain*; C. Colominas,* Institut Químic de Sarrià, Universitat Ramon Llull, Flubetech S.L. , Spain

Nanostructured Nb-C thin films were prepared by direct current magnetron sputtering (DC-MS) and via high power impulse magnetron sputtering (HiPIMS). The films have been characterized in depth by XRD, GIXRD, SEM, AFM, EPMA and Raman spectroscopy. The mechanical properties have been measured by means of nanoindentation and the tribological properties by pin-on-disk test in ambient air.The wear tracks and the ball scars were analyzed by Raman spectroscopy in order to elucidate the tribochemical reactions appearing at the contact and to determine the wear mechanism present in each specimen type. The obtained DC samples were very dense with tunable mechanical and tribological properties depending on the amorphous carbon (a-C:H) content incorporated in the coatings. The crystal and phase composition changed from pure nanocrystalline (formed by Nb_2C and NbC phases) to nanocomposite structure (NbC/a-C:H). The samples prepared by HiPIMS developed a marked columnar morphology with a NbC/a-C:H nanocomposite structure. Hardness values range from 11 to 20 GPa depending on the deposition technique and the amount of a-C:H soft phase present in the samples. The tribological properties of all the coatings were remarkably good when the carbon content was around 50 at. %. The formation of alubricant sp^2-rich C tribofilm between the ball and the coating during the pin on disk tests was observed by Raman spectroscopy, preferentially in the samples prepared by HiPIMS technique with higher C content.

BP-15 Impact of Stacking Sequence with InWZnOx/InWZnOy Bilayer Conductive Bridge Random Access Memory*, **Chih-Chieh Hsu (cchsu.06g@g2.nctu.edu.tw)**, P. Liu, K. Gan, D. Ruan, Y. Chiu,* National Chiao Tung University, Taiwan*; S. Sze,* Naitonal Chiao Tung University, Taiwan

This work investigates the hybrid oxide devices with different stacking sequence of Cu/TiW/IWZOx/IWZOy/Pt memristor. Typical bipolar resistive switching can be observed in all CBRAM devices. The hybrid oxide device shows good non-volatile memory characteristics, such as endurance cycle, low operation voltage, data retention time and stable on/off ratio. The oxide stacking sequence can improve the endurance cycles to 104, retention time to 104s and more resistance state uniformity. These results have given a prospect for simple and fast method to optimize the oxide-based memory device.

Author Index

Bold page numbers indicate presenter

Author Index