Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

10:00am **B1-1-1 Tunable Low Energy Ion Bombardment and its Influence on AlN Thin Films Deposited in Confocal DC Magnetron Sputtering***,* ***Mathis Trant****, M Fischer, K Thorwarth, J Patscheider, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Many thin film properties are strongly influenced by ion bombardment during the deposition. Control of the ion flux and the understanding of its influence on the growth mechanism are crucial for tailoring thin film characteristics such as residual stress and growth morphology. In this work the effect of the magnetic configuration on plasma parameters are studied along with the impact on aluminum nitride thin film growth.

An electromagnetic coil is used to generate an additional tunable magnetic field in order to alter the plasma confinement. Electrical and calorimetric probes are used to measure the plasma parameters in the vicinity of the substrate. The setup allows varying the ion-to-neutral ratio by more than one order of magnitude. This holds for the closed field as well as the open field configurations. Because of its symmetric geometry the latter provides roughly double the ion current density when averaged over the entire sample holder.

The effect of varied ion bombardment and substrate temperature are compared for aluminum nitride thin films, taking into account plasma heating. The residual stress was found to depend only on the ion flux density and could be varied from tensile (+0.9GPa) to compressive (- 4 GPa) by increasing this parameter. This goes along with a change from columnar structure towards more dense films. The films showed a preferential (002) orientation for the entire range of parameters covered in this work.

10:20am **B1-1-2 Unprecedented Al Supersaturation in Single-phase Rock Salt Structure VAlN Films by Al$^+$ Subplantation***,* ***Grzegorz Greczynski,*** Linköping University, (IFM), Sweden*; S Mraz, M Hans,* Aachen University, Germany*; D Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; J Lu, L Hultman,* Linköping University, (IFM), Sweden*; J Schneider,* Aachen University, Germany

Conventional design approaches for transition metal nitride coatings with improved thermal and chemical stability are based on alloying with Al. The solubility of Al in NaCl-structure transition metal nitrides is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (w-AlN), detrimental to mechanical properties.

Here, we use VAlN as a model system to demonstrate a new concept for the synthesis of a metastable single-phase NaCl-structure thin films with Al content far beyond solubility limits obtained with conventional plasma processes. This is achieved by separating the film-forming species in time and energy domains through synchronization of the pulsed substrate bias with intense periodic fluxes of energetic Al$^+$ metal ions during reactive hybrid high power impulse magnetron sputtering (HIPIMS) of Al target and direct current magnetron sputtering of V target in Ar/N$_2$ gas mixture. 70-µs-long bias pulses with an amplitude of -300 V are applied synchronously with the Al$^+$-rich portion of HIPIMS discharge, to increase implantation depth of ionized Al. At all other times the substrate is floating at -10 V, which suppresses ion mixing due to gas ion bombardment and leads to VN-rich surface even for the case where time-averaged Al flux significantly exceeds that of V. Thus, single-phase cubic VN crystallites dominate the surface and provide a template for subplanted Al$^+$ metal ions to crystallize in the metastable NaCl structure rather than to nucleate second phase w-AlN. We show that Al subplantation enables an unprecedented 42% increase in metastable Al solubility limit in V$_{1-x}$Al$_x$N, from x = 0.52 obtained with conventional method to 0.75. High Al-content cubic VAlN films grown by the Al$^+$-subplantation technique exhibit fully-dense nanostructure and excellent mechanical properties with hardness in the range of 28-30 GPa for Al fractions on the cation lattice as high as 84%. The elastic modulus is with 325±5 GPa in excellent agreement with density functional theory calculations, and approximately 50% larger than for VAlN films grown with dc magnetron sputtering. This substantial improvement with respect to the conventional techniques opens the way for synthesis of supersaturated single-phase alloy thin films combining excellent mechanical properties with high oxidation resistance. Extensions of the presented method to other materials systems are expected to be straightforward.

10:40am **B1-1-3 Ion Beam Designed Thin-film Metasurfaces***,* ***Carsten Ronning,*** Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Germany **INVITED**

Metamaterials and metasurfaces enable unprecedented flexibility in manipulating electro-magnetic waves. The optical response of most metamaterials is static, modified only by adjusting the geometric parameters of the constituent building blocks. Many functionalities of metamaterials and metasurfaces may be greatly enhanced by hybridizing these materials with functional matter, like phase-change materials, where the dielectric properties can be controlled in real-time by an external stimulus such as an applied electric field, light, mechanical stress or temperature.

We demonstrate a new type of temperature-tunable metasurfaces based on ultra-thin films of phase change materials [1]. One of the most widely studied phase change materials is vanadium dioxide (VO$_2$), which exhibits a reversible insulator to metal transition (IMT) as the temperature is increased above a critical temperature TC ~ 68°C. At high temperatures, VO$_2$ is in a metallic rutile phase, while the low-temperature insulating state is monoclinic. The transition temperature is very sensitive to structural defects and strain. In thin epitaxial VO$_2$ films the IMT occurs gradually because of the strain distribution imposed from lattice mismatch with the substrate. Therefore, in the vicinity of the IMT, nanoscale islands of the metallic phase start to nucleate surrounded by insulating VO$_2$, which then grow and connect in a percolation process. Because of this naturally occurring coexistence of sub-wavelength domains of metallic and insulating phase, VO$_2$ can already be thought of as a natural disordered metamaterial during its phase transition.

In this contribution, I will demonstrate that phase coexistence can also be artificially introduced in VO$_2$ by patterned local ion beam irradiation with spatial resolution much smaller than the wavelength of light. The presence of a small amount of structural defects caused by ion irradiation significantly decreases the transition temperature – even below room temperature – of the irradiated regions. Thus, the metal and insulating phase of VO$_2$ coexist in a regular pattern in the temperature range between the IMT of irradiated and intrinsic VO$_2$. This results in a metasurface with effective optical properties that can be predicted applying an appropriate effective medium theory. These thin film structures are promising for dynamic polarization control, reconfigurable absorbers and emitters, and the tuning of plasmonic and dielectric resonant nanostructures for adaptive optics applications.

[1] J. Rensberg, et al. “Active Optical Metasurfaces Based on Defect-Engineered Phase-Transition Materials” *Nano Letters* 16, 1050 (2016).

11:20am **B1-1-5 Mechanical and Thermal Behavior of Magnetron Sputtered Zr–Cu and Zr–Hf–Cu Metallic Glasses***,* ***Michal Zitek****, P Zeman, S Zuzjakova, R Čerstvý, S Haviar, M Kotrlova,* University of West Bohemia, Czech Republic

Metallic alloys are commonly fabricated as crystalline materials by a relatively slow-cooling casting of a melt. Magnetron sputter deposition as a non-equilibrium process with high cooling rates (higher than 10^6 K/s) allows us to prepare metallic alloys also as thin-film materials in an amorphous glassy state. A short-range atomic order, based mainly on icosahedral clusters, in these metastable materials gives rise to their exceptional physical and functional properties compared to their crystalline counterparts.

Recently, we have showed that Zr–Cu thin-film alloys can be prepared as metallic glasses in a very wide composition range (30–65 at.% Cu) by non-reactive magnetron co-sputtering. In the present study, we focus on characterization of their mechanical and thermal behavior in more detail. In addition, we investigate the effect of an incorporation of Hf into the Zr–Cu thin-film metallic glasses on a potential improvement of their behavior. The films were deposited using three unbalanced magnetrons equipped with Zr, Hf and Cu targets in pure argon. The magnetron with the Zr and Hf targets were operated in a dc regime while the Cu magnetron in a high-power impulse regime. The Zr, Hf and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The films were deposited without an external heating onto rotating substrates. The films were analyzed by X-ray diffraction, energy dispersive X-ray spectroscopy, differential scanning calorimetry, micro- and nanoindentation, scanning electron microscopy and atomic force microscopy.

Mechanical properties of the Zr–Cu thin-film metallic glasses are strongly dependent on the elemental composition. A gradual growth of hardness with increasing Cu content up to 70 at.% correlates well with an evolution of the glass transition temperature and the crystallization temperature. This behavior can be explained by an increasing concentration of icosahedral clusters having the highest atomic packing density. The Zr–Cu films prepared with the Cu content higher than 50 at.% or at a moderate substrate bias exhibit a tendency to be more resistant to the formation of shear bands during indentation. An incorporation of Hf into the Zr–Cu thin-film metallic glasses improves the mechanical properties of the films and the thermal stability of their glassy state. Further experiments are still in progress and will be presented as well.

11:40am **B1-1-6 The Development of Ultrathin Zr-Cu-Ni-Al-N Thin Film Metallic Glass as a Diffusion Barrier for Cu-Si Interconnect**, ***Joseph Lee,*** National Tsing Hua University, Taiwan*; Y Chen,* Metal Industries R&D Centre (MIRDC), Taiwan*; J Duh,* National Tsing Hua University, Taiwan

In this study, a Zr-Cu-Ni-Al-N thin film metallic glass (TFMG) has been developed and applied for the diffusion barrier between copper and silicon. The Si/TFMG/Cu stacked structures with various TFMG thickness have been fabricated. Rapid thermal annealing was conducted at 500, 600, 700 and 800 ºC. The X-ray diffraction analysis was applied to identify the formation of Cu_3Si intermetallic compound. The ESCA depth profile was executed to quantitatively evaluate the degree of Cu-Si inter-diffusion. With the aid of HR-TEM, the microstructure of the TFMG and the whole stack could be observed. Finally, the correlation between microstructure, thermal properties, thickness and barrier performance of the TFMG will be revealed and discussed.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

10:00am **B5-1-1 Synthesis and Characterization of HfNbTiVZr High Entropy Alloy Thin Films**, ***Stefan Fritze****, D Karlsson, P Berastegui, D Rehnlund, L Nyholm, M Sahlberg, E Lewin, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

High entropy alloys (HEAs) are multicomponent alloys with at least five elements in approximately equimolar concentrations. Due to the high entropy of mixing, solid solutions of e.g. a simple bcc or ccp phase are formed. Many HEAs exhibit unique properties such as extremely high strength, ductility, high thermal stability and corrosion resistance. Recently, we have also demonstrated that a HfNbTiVZr alloy with a bcc structure has exceptional hydrogen storage capability [1].

In this study we report the first successful deposition of highly textured HfNbTiVZr thin films by non-reactive unbalanced magnetron sputtering using five metal targets. The films were characterized with SEM, XPS, XRD and nanoindentation. Bragg-Brentano XRD analyses of these coatings show that the HfNbTiVZr films crystallize in a simple bcc structure with a strong (110) orientation. No additional phases were observed in the as-deposited films ensuring that the sample is a single phase HEA. The SEM cross-sections exhibit a dense microstructure and EDS mapping shows a random distribution of all five elements with no noticeable segregation.

The as-deposited films exhibited a hardness of 5.4 GPa. This is more two times higher than expected from rule of mixture. The high hardness can be explained by a significant lattice strain due to large differences in atomic radii. Upon annealing, XRD shows the formation of a second alloy phase which is unexpected for a true HEA. The precipitation of a second phase leads to a further hardness increase with at least 100%. The phase stability and the precipitation of secondary phases in the HfNbTiVZr films will be discussed based on lattice strain effects in the alloy. Finally, the electrochemical properties of the HfNbTiVZr films have been investigated. The films exhibited, compared to steel alloys, a very high corrosion resistance in chlorine-containing solutions.

[1] M. Sahlberg, D. Karlsson, C. Zlotea and U. Jansson, submitted

10:20am **B5-1-2 Structural Stability of ZrN/SiN_x Multilayered Coatings under Harsh Environments**, ***Gregory Abadias,*** Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; I Saladukhin, V Uglov, S Zlotski, V Shymasnki,* Belarusian State University, Belarus

Synthesis of nitride-based multilayered structures is prospective for enhancement of mechanical properties and wear resistance as well as for their resistance to harsh environments exposure, in particular, to high temperature oxidation and ion irradiation. Multilayered ZrN/SiN_x films (with bilayer thickness ranging from 6 to 40 nm) with a total thickness of about 300 nm were deposited at 300°C by reactive magnetron sputtering by sequentially alternating ZrN and SiN_x layers [1]. Annealing under air atmosphere was carried out for temperature intervals ranging from 400 to 950°C using *in situ* temperature XRD. Ion irradiation by Xe ions (180 keV, doses $5x10^{16}$ cm^{-2} $1x10^{17}$ cm^{-2}) was performed at room and high (800°C) temperatures.

According to TEM and XRD analysis the multilayered films consist of nanocrystalline ZrN and X-ray amorphous SiN_x layers. While pure ZrN films are characterized by [111] preferred orientation, the presence of SiN_x layers results in its change to [200]. Multilayered ZrN/SiN_x films show the improved oxidation resistance compared to ZrN reference layer. For pure ZrN film, the oxidation starts at 550°C. Higher oxidation resistance is observed for ZrN/SiN_x films and it strongly depends on ZrN fraction and number of layers. So, for ZrN/SiN_x (5 nm/10 nm) film the onset of oxide phase formation is delayed up to 950°C and nitride ZrN phase still remains. The presence of SiN_x layer favors the formation of tetragonal ZrO_2 phase during annealing.

There is no evident change of ZrN/SiN_x film structural state after Xe ion irradiation as it was proved by XRD investigations. However, the lattice parameter increase occurs that is connected with Xe incorporation. It was revealed by RBS analysis that the maximum concentration of Xe in the film bulk is about 4 at.% after irradiation at room temperature and about 5 at.% after high temperature irradiation. The shape of Xe concentration profile also changes. TEM studying indicates amorphization of ZrN layers and Xe bubbles formation in the film. There is a tendency of Xe depth penetration decrease with the SiN_x layer thickness increase. Thus multilayered ZrN/SiN_x films are considered to be promising for oxidation and irradiation resistance enhancement.

1. G. Abadias, V.V. Uglov, I.A. Saladukhin et al., Surf. Coat. Technol., under press

10:40am **B5-1-3 Magnetron Sputtered High-Temperature Hf–B–Si–C–N Films with Controlled Electrical Conductivity and Optical Transparency**, ***Veronika Simova****, J Vlcek, S Zuzjakova, R Čerstvý, J Houška,* University of West Bohemia, Czech Republic

The present work focuses on the effect of nitrogen addition into hard and electrically conductive Hf–B–Si–C films [1] in order to significantly improve their thermal stability in air at very high temperatures (above 1200°C). Our motivation has been to develop new hard thin-film materials with a very low electrical and thermal conductivity, and high optical transparency or with a sufficiently high electrical conductivity for high-temperature protective coatings of electronic and optical elements, and for harsh-environment sensors.

Hf–B–Si–C–N films were deposited onto Si(100) and SiC substrates using pulsed magnetron co-sputtering of a single B_4C–Hf–Si target (at a fixed 15% Hf fraction and a 20% Si fraction in the target erosion area) in Ar + N_2 gas mixtures at the N_2 fraction ranging from 0% to 50%. A planar unbalanced magnetron (127×254 mm^2 target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with an average target power of 500 W in a period and voltage pulse durations of 50 µs and 85 µs (duty cycles of 50% and 85%). The substrates were held at a floating potential and a temperature of 450 °C.

An increasing N content (from 0 to 52 at.%) in the films was compensated by decreasing contents of B (from 39 to 24 at.%), Si (from 24 to 15 at.%), Hf (from 25 to 4 at.%) and C (from 7 to 3 at.%). The structure of the Hf–B–Si–C film prepared in pure argon was nanocomposite, while the Hf–B–Si–C–N films were amorphous. An increase in the N_2 fraction in the gas mixture, resulting in an increasing N content in the films, led to a rapid rise in the optical transparency and the electrical resistivity of the films. All films exhibited a high hardness in the range of 17–21 GPa.

The as-deposited, optically non-transparent $Hf_7B_{23}Si_{22}C_6N_{40}$ film with 2 at.% of Ar possessing a hardness of 20 GPa and electrical resistivity of 4 Ωm, which was prepared with the 15% N_2 fraction in the gas mixture at the voltage pulse duration of 50 µs, and the as-deposited, highly optically transparent and electrically insulating $Hf_6B_{21}Si_{19}C_4N_{47}$ film with 3 at.% of Ar possessing a hardness of 20 GPa, which was prepared with the 25% N_2 fraction in the gas mixture and at the same voltage pulse duration, exhibited a very high oxidation resistance in air even up to 1600°C.

[1] J. Kohout, J. Vlcek, J. Houska, P. Mares, R. Cerstvy, P. Zeman, M. Zhang, J. Jiang, E.I. Meletis, S. Zuzjakova, Hard multifunctional Hf–B–Si–C films prepared by pulsed magnetron sputtering, Surf. Coat. Technol. 257 (2014) 301–307.

11:00am **B5-1-4 Reactively Sputtered Multicomponent (TiZrHfVNb)N Thin Films***, **Kristina Johansson**, E Lewin,* Uppsala University, Angstrom Laboratory, Sweden

(TiZrHfVNb)N thin films, synthesised by reactive DC magnetron sputtering, demonstrate a large homogeneity range for a solid solution phase with the NaCl-type structure. The films have been deposited using elemental targets of the respective element and a gas mixture consisting of Ar and N_2 (15 % of total gas flow). In earlier studies, (TiZrHfVNb)N films have been synthesised by cathodic arc vapour deposition using a high entropy alloy of Ti-Zr-Hf-V-Nb as cathode material. These films have showed very interesting mechanical properties, such as high hardness and high wear resistance.[1] However, there are no previous studies on sputter deposited (TiZrHfVNb)N films. By using this deposition technique it could allow for more design possibilities, which is explored in this study by varying composition of the material. The films were characterised by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

Large variations in metallic ratio were obtained for the (TiZrHfVNb)N coatings, about 10-50 % for Ti, 20-35 % for Zr,10-50 % for Hf,10-30 % for V and 5-15 % for Nb. XPS spectra for each transition metal showed that the films are fully nitrided. The coatings were found to be of single NaCl type phase for all studied compositions. The lattice parameter varied from 4.32 Å for Ti rich coatings to 4.44 Å for Hf rich coatings, which is within the range of the corresponding binary nitrides (4.13 Å for VN and up to 4.58 for ZrN) and thus indicating a solid solution phase of all constituent elements. Cross sections of the coatings studied by SEM showed a columnar growth which varied in density depending on deposition conditions such as substrate temperature and bias.

Reference:

[1] A.D. Pogrebnjak *et al*., *Mater. Chem. Phys.,* 147 (2014) 1079

11:20am **B5-1-5 Deposition of Fluor-doped WS_2-C Coatings on Nanostructured Anodized Aluminum Alloy Substrates for Wettability Control***, S Rodrigues,* SEG-CEMUC, Portugal*; **Sandra Carvalho,*** University of Minho and University of Porto, Portugal*; A Cavaleiro,* SEG-CEMUC, Portugal

Currently, lubrication procedures of mechanical components in automotive industry, such as ignition systems, are often stopped for tool cleaning or replacement due to high friction phenomena faced because of lubricant accumulation. Then, the development of a functional surface; addressing either longer lifetime due to an improvement of the wear resistance, or energy savings, by the decrease of the friction, is now welcome particularly when they can also avoid or reduce the excessive use of liquid lubricants which are harmful for the environment and the human health.

This work intends to create a new surface acting as solid lubricant, gathering the outstanding self-cleaning and *nearzero* friction properties of fluor-doped WS_2-C coatings. These coatings can be deposited onto different porous anodized aluminum alloy surfaces in order to be able to control the water and oil wettability.

W-S-C-F coatings were produced by magnetron sputtering in reactive mode using an Ar/CF_4 gas mixture. The fluorine insertion in the produced coatings was controlled by varying the CF_4 gas flow aperture (0-20%).

Top view and cross-sectional morphologies, chemical composition/bonding, structure and wettability characterization of the coatings were respectively performed through FIB/SEM-EDS, XRD techniques and water/oil contact angle measurements. Mechanical properties such as hardness, elastic modulus and adhesion were also conducted under nanoindentation procedures and *scratch* testing.

The results revealed that the fluorine insertion on the W-S-C coatings did not change significantly the structure and morphology in relation to pure W-S-C coatings. However, a decrease on the mechanical properties was observed. Furthermore, the changes in the contact angles values show a potential for the control of the wettability behaviour in relation to water and oils.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-2

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

1:30pm **B1-2-1 Air-based Deposition of Oxynitride Thin Films**, ***Fu-Hsing Lu,*** National Chung Hsing University, Taiwan **INVITED**

Many oxynitride thin films exhibit superior mechanical, optical, and electrical properties. Conventionally, pure oxygen and nitrogen with different ratios are employed as reactive gases during sputtering to make oxynitride thin films. Here, air instead of O_2/N_2 mixing gases was used as the reactive to make the films. Hence, high vacuum is not required for the deposition, which could save a large amount of processing time and cost. Titanium oxynitride (TiN_xO_y) has been selected as a model system. Increasing the air/Ar ratios, the color would change and the films transformed from crystalline to amorphous phases. A large range of O/N contents for the oxynitride films could be tailored by simply varying the air/Ar ratios. Kinetically controlled formation of the films would be discussed. Hardness of the films was determined by nanoindentation. The films could also exhibit a wide range of electrical resistivities, from conductive, semiconductive, to insulating behavior. The carrier concentration and mobilities of the oxynitride films were also investigated by Hall-measurements. This much simpler technique could achieve similar quality of the films as reported from the literature. The air-based sputtering technique can also be applied to many other oxynitride film systems, which may bring in much more technical applications.

2:10pm **B1-2-3 Effect of Oxygen Contamination on PVD AlN Growth**, ***Katherine Knisely,*** *B Griffin, R Timon, M Olewine, T Young, M Monochie, H Dallo,* Sandia National Laboratories, USA

Sputtered aluminum nitride (AlN) is a widely used piezoelectric material used in sensor and resonator designs because it is CMOS compatible, supports high acoustic velocity waves, and has relatively low levels of electrical loss. The piezoelectric coupling of PVD AlN, a polycrystalline thin film, is highly dependent on the quality and uniformity of the grains. Here we report the effects of substrate surface preparation on AlN grain structure. Oxygen contamination is found to degrade grain structure for AlN grown on Si and metallic surfaces, causing large triangular grain growths in the film that initiate on the substrate surface.

2:30pm **B1-2-4 Optical and Mechanical Properties of Al-doped Zinc Oxide Thin Film Fabricated by a High Power Impulse Magnetron Sputtering**, ***YuCi Hong,*** *J Lee,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

Transparent conducting zinc oxide (ZnO) films have been extensively studied recently due to its unique electrical conductivity, transmittance properties and lower cost. The higher conductivity of ZnO film can be obtained by doping with Al to form AZO film. High power impulse magnetron sputtering (HIPIMS) is the latest coating technology, which can make the film denser and improve its mechanical properties. In this study, aluminum doped zinc oxide thin films were deposited without intentional heating by high power impulse magnetron sputtering under different duty cycles. Effects of duty cycle of HIPIMS power on the optical and mechanical properties of AZO coatings were discussed. The films were characterized using X-ray diffractometer, Field-emission scanning electron microscopy, Atomic force microscope, Nanoindentation, Scratch tester, Tribometer and UV-visible spectrometer. According to the experimental results, it was found that the average transmittance in the visible range was generally above 82% for all the films. For mechanical properties evaluation, all AZO films showed good adhesion and high hardness.

2:50pm **B1-2-5 Non-reactive and Reactive dc Magnetron Sputter Deposition of Molybdenum Oxide Thin Films**, *J Pachlhofer,* ***Robert Franz,*** Montanuniversität Leoben, Austria*; E Franzke,* Plansee SE, Austria*; A Tarazaga Martín-Luengo,* Johannes Kepler University, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; A Bonanni,* Johannes Kepler University, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Due to their unique optical, electrical and chemical properties oxide-based thin film materials are widely used in industrial applications ranging from hard coatings, diffusion barriers to thin films in optical and electronic applications. Molybdenum oxide thin films synthesised by dc magnetron sputter deposition from a Mo target in an industrial-scale system revealed a change in structure and properties as a function of their oxygen content which was controlled by adjusting the O_2 partial pressure during deposition. At medium O_2 partial pressures, MoO_2-structured films were obtained with electrical conductivities similar to metallic Mo and high optical absorbance of up to 70%. Exceeding a critical O_2 partial pressure results in the formation of highly transparent, but insulating MoO_3-structured films. However, such reactive deposition processes are typically disadvantageous for the large-scale synthesis of oxide thin films due to process instabilities that originate from target poisoning effects at elevated O_2 partial pressures. As an alternative, the synthesis of molybdenum oxide films via non-reactive dc magnetron sputter deposition using ceramic MoO_x targets was explored within this work. The films deposited in non-reactive mode exhibited a MoO_2 dominated structure with properties similar to the ones from the reactive process. Adding O_2 to the process gas caused the same transition in structure and properties of the films observed in the reactive mode but at a significantly lower O_2 partial pressure. In general, the use of oxide targets in dc magnetron sputter deposition of molybdenum oxide thin films offers an efficient and reliable alternative to the use of metal targets and, hence, enables the usage of such films for a wide range of optical and electrical applications.

3:10pm **B1-2-6 Piezoelectric Coefficient Enhancement in Low Mg Content Wurtzite $Mg_xZn_{1-x}O$ Films**, ***YiJu Chen,*** *S Brahma, C Liu, J Huang,* National Cheng Kung University, Taiwan

Environmentally friendly piezoelectric nanogenerators are the subject of the intense research in recent years, where waste mechanical energy is converted into electricity through piezoelectric materials. Wurtzite structure materials such as ZnO exhibits piezoelectric and semiconducting properties with piezoelectric coefficient as a dominant physical characteristic. In this paper, we investigated the dependence of piezoelectric coefficient on Mg content in MgZnO thin films onto Si (111), prepared by using radio frequency magnetron sputtering with ZnO and MgO as two independent targets. The Mg content was varied by varying applied power to MgO target, while maintaining a constant power of 50W to ZnO target. The deposition temperature is fixed at 250℃ and all the films were deposited to reach the same thickness around 380 nm. X-ray diffraction analysis confirms that all MgZnO films show high crystallization with strong preferential orientation along [0001] growth direction. Besides, whereas most MgZnO films are Wurtzite phase, the $Mg_xZn_{1-x}O$ films deposited at higher MgO power present a mixed phase of hexagonal Wurtzite phase and tetragonal cubic phase. Moreover, the diffraction peaks shift toward higher angles confirm to the smaller ionic radius of magnesium substituting for larger zinc. The morphology and composition of films are examined by scanning electron microscopy and energy dispersive X-ray spectroscopy. Finally, the piezoelectric coefficient of MgZnO films were measured by piezoelectric force microscopy, exhibiting the maximum occurring at an intermediate Mg concentration, which is largely improved by compared to ZnO. The MgZnO films hold great promise to be applied in piezoelectric nanogenerators.

3:30pm **B1-2-7 Ternary and Quaternary Hard Transparent Thin Films Made from Al, Si, O and N**, ***Maria Fischer,*** *M Trant, K Thorwarth, H Hug, J Patscheider,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Al-O-N and Al-Si-N are two ternary material systems providing attractive properties for transparent hard coatings. Thin films of these materials were deposited by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). Metallic Al targets and the two reactive gases O_2 and N_2 are required for Al-O-N, while Al-Si-N films are made by co-sputtering from an Al and a Si target and N_2 gas only.

O_2 addition induces a gradual transformation of crystalline wurtzite AlN via Al-O-N nanocomposite towards amorphous Al_2O_3. Incorporation of O into wurtzite is feasible up to a solubility limit of 8 at% and induces a replacement of N, which acts as electron acceptor in Al-N bonds. By contrast, Si integration causes substitution of Al, the electron donor. Despite the different nature of these exchanges, the Al-Si-N system transforms equivalently to Al-O-N. For example, the unit cell dimensions and the residual stress states evolve the same way in both ternary systems. The reason for this analogy is an excess of electrons that both O and Si bring along in comparison to N and Al they replace. In each of the two systems, these additional electrons are compensated by the generation of Al vacancies, which exert a major influence on the material system evolution in either case. Ab initio calculations are in good agreement with the experimentally determined lattice spacing changes and result in energy optimization for vacancy generation, confirming the hypothesis.

Combining Al-O-N and Al-Si-N in a quasi-binary way leads to Al-Si-O-N. Thin films of this quaternary material were also deposited by R-UCFDCMS and characterized analogously to the two ternary systems. Understanding the material evolution in Al-Si-O-N allows for the fabrication of transparent coatings with a wide range of finely adjustable properties.

3:50pm **B1-2-8 Characteristics of TiAlSiN Having a Hexagonal Structure***, **Shingo Inagaki**, A Kawana,* Japan Coating Center Co., Ltd., Japan

TiAlN has been developed as for a cutting tool because of its excellent oxidation resistance. The oxidation resistance is proportional to the amount of aluminum, therefore, TiAlN including high concentrated aluminum has been studied. However, when the Aluminum content is more than 60at%, it can be seen that the film hardness decreases drastically, and it has cause a decrease in tool life. That's because hexagonal AlN phase which has low hardness is precipitated in the film. Cubic structure is necessary for film using for a cutting tool to keep that wear resistance and mechanical strength.

The purpose of this study is to improve the cutting performance of TiAlN including Aluminum as high content without losing its excellent oxidation resistance. We have examined a multi-layered TiAlN with the addition of Silicon which has a hexagonal structure and keeps excellent oxidation resistance. We report a new features that cause of improvement of cutting performance by this film. We have prepared some of the target of changing the Aluminum concentration. In this study, these film were deposited by cathodic arc in PVD. It was formed using bias voltage as a parameter.

TiAlSiN whose Aluminum concentration is more than 70at% is confirmed with the hexagonal structure by X-ray diffraction (XRD). When changing the bias voltage in the same composition ratio, whose samples were also confirmed hexagonal structure. However, the crystalline orientation of the hexagonal phase was changed with increase of bias voltage. The hexagonal structure wasn't confirmed in Aluminum concentration 64at% TiAlN by XRD as it is known that Aluminum concentration 60at% TiAlN has cubic structure.

However hexagonal structure was confirmed in films which included 8at% of silicon to the Aluminum concentration 61at%. In general, stable phase for AlN is hexagonal structure. However, when the amount of Titanium increases, AlN takes cubic structure the same as TiN. Since TiAlN is replaced to Al from Titanium in the crystal structure, film hardness is increased by change in the lattice constant. TiAlSiN whose Aluminum concentration is less than 53at% was exhibit a strong peak of cubic structure.

Cutting performance was evaluated about composite film using TiAlSiN. TiAlSiN having a high Aluminum concentrations above 60at%. As a result, cutting performance was improved using TiAlSiN. The tool temperature during cutting was measured by thermography. The tool temperature of TiAlSiN was lower than the tool temperature of TiAlN. They had a difference of 150 degree C.

4:10pm **B1-2-9 A study of Preferred Orientation of VN Thin Film on Si Substrate Deposited by Unbalanced Magnetron Sputtering***, **Cheng-Han Lin**, J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the texture evolution of VN thin film on Si (100) substrate by unbalanced magnetron sputtering (UBMS) method. Based on previous studies of TiN and ZrN thin films, the preferred orientations of the transition metal nitride thin films can be controlled as (111), random and (200) by adjusting nitrogen flow rates or introducing minor oxygen gas. The mechanism of formation (200) texture in TiN and ZrN is mainly by using ion or oxygen to retard the adatom migration on the (200) plane. However, in our previous study of VN film, the (111) preferred orientation of VN thin film become prominent by introducing higher nitrogen flow rate. The result was inconsistent with the studies of TiN and ZrN thin films. However, there was little information on the mechanism of changing preferred orientation in VN thin films. In this study, different nitrogen flow rates and different DC gun powers were adopted to study the evolution of preferred orientation of VN thin film and the accompanying effects on the film properties. After deposition, the composition of specimen was determined by X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) was used to characterize the structure and preferred orientation, and field emission gun scanning electron microscopy (FEG-SEM) was used to measure the thickness and observe the microstructure. The hardness and electrical resistivity were measured by nanoindentation and four-point probe, respectively. Based on the experimental results, a reasonable mechanism of the texture evolution of VN can be proposed.

4:30pm **B1-2-10 Structure and Mechanical Property of AIP Deposited (AlxCr100-x)N Coatings with X > 70at%, *Kenji Yamamoto*,** *H Nii, M Abe,* Kobe Steel Ltd., Japan*; S Takada, Y Iwai,* University of Fukui, Japan

AlCrN has been used for various metal working tools including cutting tools and molds / dies for increasing wear resistance. AlCrN is a solid solution of metastable cubic AlN into CrN NaCl type unit cell. Makino et al. calculated maximum solubility of metastable cubic AlN in NaCl type transition metal nitride by band-parameter method and reported it is 65.3 at% for Al-Ti-N system and 77. 2 at% for Al-Cr-N system [1]. Mechanical as well a chemical property of AlCrN is influenced by the Al composition and crystal structure as well as deposition parameters. In this study, AlCrN coatings with different Al compositions, particularity Al composition is close to the maximum solubility, were synthesized by cathodic arc under different deposition conditions and mechanical and structural property of the resulting coating was investigated.

AlCr targets with 65, 70, 75 and 80 at% Al were used. AlCrN coatings were deposited by laboratory type AIP equipment from Kobe Steel Ltd. (AIP-S20). Coatings were deposited under N2 atmosphere at 4 Pa with arc current of 150A. Substrate bias during the deposition was varied from 40 up to 200V. Chemical composition was determined by EDX and crystal structure was analyzed by XRD. Mechanical property of the coating was investigated by nano-indentation for hardness and Young's modulus. Wear resistance was evaluated by Micro-Slurry Jet Erosion Method [2].

All AlCrN coatings deposited with Al 65 and 70 at % targets were all in cubic single phase independent of substrate bias. Although, the hardness and Young's modulus was monotonously increased as the substrate bias was increased. In case of 75 at% Al sample, hexagonal was observed at 40V and became cubic single phase 70 V and more. In case of Al 80 at %, trace of hexagonal phase was observed up to 100V, but became cubic dominant structure at 125V. The hardness showed increasing trend as the substrate bias became higher which is corresponding to transition from hexagonal to cubic structure. Wear resistance of the coating with different Al composition deposited under fixed substrate bias of 70 V was evaluated by MSE. Erosion rate became small as the Al composition increased up to 75 at% at where showed a minimum value. Further increase in Al composition to 80 at% resulted in a slight increase of the erosion rate.

Micro-structure as investigated by TEM and discussion relationship between erosion rate and hardness or Young's modulus will be presented.

[1] Y. Makino: ISIJ International, 38 (1998) 925

[2] Y. Iwai et al. Wear 251 (2001) 861

4:50pm **B1-2-11 Control of Elastic-Plastic Deformability and Hardness in Nitride Hard Coatings on Cubic Boron Nitride Sintered Compact Cutting Tool***, **Masakuni Takahashi**, S Sato, T Maekawa,* Mitsubishi Materials Corporation, Japan

Recently, with more expansion of automotive production, characteristic to be required to cubic boron nitride sintered compact (CBN) cutting tools for hardened steel parts have changed into not only high efficiency but also a more stable performance and extension of life. One of the keys for stable cutting performance is to make the coating do normal wear without fracture of the coating in intermittent cutting.

On the other hand, generally in case of using high hardness coating for high wear resistance the coatings lose its deformability to external force and break itself, and in case of using high deformability coating to external force for better fracture resistance the coatings lose its hardness and wear resistance. For pursuit of both fracture resistance and wear resistance concerning the cutting performance in turning processing of high hardness steel by using CBN cutting tools, with changing the composition and the composition ratio of the hard coatings which were deposited by arc type physical vapor deposition method on CBN cutting tool we investigated the relationship between the deformability to external force, the hardness and the cutting performance of the tool.

The deformability to external force and the hardness were evaluated by using nanoindentation method. We used elastic-plastic deformation work rate in the indentation tests as a barometer of the deformability. With respect to $Al_xTi_{1-x}N$ and $Al_xCr_{1-x}N$, the elastic deformation work rate and the hardness increase monotonically in the range of x≤0.6. In this range the increase ratio of the elastic deformation work rate and the hardness of $Al_xCr_{1-x}N$ are larger than $Al_xTi_{1-x}N$, and it shows $Al_xCr_{1-x}N$ has controllable potential for both elastic deformation work rate and the hardness.

In addition, by introduction of the 3rd element such as Si in $Al_{0.3}Cr_{0.7-x}Si_xN$, the rate of change of the elastic deformation work rate and the hardness change with the content rate of the Si. Evaluating the cutting performance of the CBN cutting tools which were coated with the coatings of several compositions and composition ratios described above, the hard coatings were able to show the wear resistance and also the fracture resistance to external force. This result shows the importance of coating design optimizing materials properties, especially elastic-plastic deformability and hardness, in order to bring out cutting performance of coated CBN cutting tools.

5:10pm **B1-2-12 Effect of Preferred Orientation on the Fracture Toughness of VN Hard Coatings***, **Liang-Ru Wei**, J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to measure the fracture toughness of VN hard coatings using internal energy induced cracking (IEIC) method, and find out the effect of pure (200) and mixed (200) with (111) textures on the fracture toughness of VN coatings. VN coatings were deposited on Si (100) substrates by unbalanced magnetron sputtering (UBMs) with different nitrogen flow rates. By changing the nitrogen flow rates, we could control the ratio of (111) and (200) texture coefficient in VN coatings. The fracture toughness of one set of strong (200) textured VN and two sets of mixed (111), (200) textured VN coatings were compared with the mechanism of TiN and ZrN. So far there were relatively few studies about VN coatings, especially on the fracture toughness. On the basis of Griffith's criterion and the modified delamination model proposed by Freund and Suresh [1,2], the total stored elastic energy (G_s) existing in the film can be given by,

$G_s=[(1-\nu_f^2)/2E_f]\sigma_m^2h_f$

where ν_f and E_f are the Poisson's ratio and Young's modulus of the thin film, respectively, h_f is the thickness of the thin film, and σ_m is the residual stress. As the film thickness increases, G_s will reach a critical value G_c that leads to the occurring of fracture in the film. Therefore, G_c can be considered as the fracture toughness of VN. For the measurement of G_c, the Young's modulus was determined by nanoindentation (E_{NI}), film thickness was measured from the cross-sectional image of scanning electron microscopy (FEG-SEM), and residual stress was obtained from two methods: the laser curvature method (LCM) and the average X-ray strain (AXS). The LCM method was utilized to obtain the overall residual stress in the film. The average X-ray strain (AXS) [3,4] was measured by $\cos^2\alpha\sin^2\psi$ XRD method at several rotational angles. By using AXS plus E_{NI} technique the accuracy of the stress measurement can be increased and comparable to LCM.

[1] A.A. Griffith, Philos. Trans. R. Soc. S-A, 221 (1921) 163.

[2] L.B. Freund, S. Suresh, Thin film materials: stress, defect formation and surface evolution, Cambridge University Press, 2004.

[3] J.-H. Huang, Y.-H. Chen, A.-N. Wang, G.-P. Yu, H. Chen, Surf. Coat. Techol., 258 (2014) 211.

[4] A.-N. Wang, C.-P. Chuang, G.-P. Yu, J.-H. Huang, Surf. Coat. Techol., 262 (2015) 40.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-2

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

1:30pm **B5-2-1 B_4C and Mo Coatings Characterization regarding Stamping Dies Application***, F Silva, **Liliana Fernandes**, M Andrade,* ISEP - School of Engineering, Polytechnic of Porto, Portugal*; R Alexandre,* TeandM - Technology, Engineering and Materials, S.A., Portugal*; A Baptista,* INEGI - – Instituto de Ciência e Inovação em Eng. Mecânica e Eng. Industrial, Portugal*; C Rodrigues,* Colep Portugal, S.A., Portugal

Prestigious brands of cookies usually use metallic tins as package to distribute and sell their products, trying to impress the customer through the look and avoiding cookies' break and/or damage during logistics operations. These packages are made commonly in tin coated (2.8 g/m^2) thin steel sheet (electrolytic Tin plate), which originates severe wear problems on both die and punch tool components during the stamping process. The border of the package represents a non-considerable deformation, despite their almost perpendicular orientation to the top surface, but this top is usually patterned, also implying the flow of the sheet between the top and bottom die surfaces. Due to the softness of the Tin coating, it easily adheres to the die generating premature wear and several concerns in maintaining the required final shape of the tin lid. Lubrication would be an easy way to solve the problems above referred but lubrication operations should be avoided regarding that these kind of packages are for food purposes.

This study has been developed in order to find the best coatings which avoid Tin adhesion and wear on the stamping surfaces when deforming Tin coated steel plate. Two advanced PVD coatings (B_4C and Mo) were characterized and tested leading to improve the wear behavior of the punch and die under these work conditions. The transfer of Tin material from the metallic sheet to the punch and die was also studied, as well as the friction coefficient of this sheet against some selected coatings, also trying to minimize the Tin adherence to the tool surfaces. Tribological tests under medium loads were carried out in order to realize what kind of coating presents better wear behavior in those work conditions. Worn surfaces were studied by Scanning Electron Microscopy (SEM) and material transfer was analyzed by Energy Dispersive Spectroscopy (EDS).

Results obtained with some of the tested coatings allow to confirm that it is possible to minimize the Tin transfer from the covered steel sheet to the die and punch, ensuring a longer life of these parts, decreasing the tool maintenance operations and improving the Overall Equipment Efficiency (OEE) of that stamping process.

1:50pm **B5-2-2 Effect of Energy on Structure, Microstructure and Enhanced Resistance to Cracking of Hard Sputter Deposited Ti(Ni)N_x and Ti(Al,V)N_x Films***, **Martin Jaroš**, J Musil, R Čerstvý, S Haviar,* University of West Bohemia, Czech Republic

The paper reports on the preferred orientation, structure and mechanical properties of magnetron sputtered Ti(Ni)N_x and Ti(Al,V)N_x films and their resistance to cracking in bending. The films were reactively sputtered on Si(111) plate and Mo strips in a mixture of Ar+N_2 gases using a DC magnetron equipped with a TiAlV alloy target (6 at.% Al, 4 at. % V), or a TiNi alloy target (5 at. % Ni) respectively. The preferred orientation, structure, macrostress, mechanical properties (the hardness H, effective Young's modulus E^*, elastic recovery W_e), of Ti(Ni)N_x and Ti(Al,V)N_x films and theirs resistance to cracking in bending were characterized by (i) the X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) the bending of Si(111) plate using the Stoney`s formula, (iv) the diamond indentation test and (v) the bending of coated Mo strip around a fixed cylinder of small radius (down to 5 mm), respectively. It was found that: (1) the preferred orientation of sputtered Ti(Ni)N_x and Ti(Al,V)N_x nitride films depends on energy $E_{bi} \approx U_s \times i_s/a_D$ delivered to the film during its growth, here is U_s the substrate bias, i_s the substrate current density and a_D the deposition rate. The texture continuously changes from (i) TiN(220) -> TiN(111)+TiN(200) -> TiN(220) for Ti(Ni)N_x films and (ii) TiN(200) -> TiN(220) -> TiN(111)+TiN(220) for Ti(Al,V)N_x nitride films with increasing E_{bi}. (2) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with low resistance to cracking are prepared at lower value of E_{bi} < 1.5 MJ/cm^3 exhibit (i) low ratio $H/E^* \leq 0.1$, low elastic recovery $W_e \leq 65$ %, compressive macrostress ($\sigma < 0$ GPa) and (ii) are composed of grains contain TiN(200) and show a columnar structure. (3) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with enhanced resistance to cracking are prepared at higher value of E_{bi} > 3.7 MJ/cm^3 exhibit (i) high ratio $H/E^* > 0.1$, high elastic recovery W_e > 65 %, compressive macrostress ($\sigma < 0$ GPa) and (ii) are composed of grains witch do not contain TiN(200) and show a dense structure.

2:10pm **B5-2-3 Ultra-thick, Superhard Nanocomposite Coatings Deposited using Plasma Enhanced Magnetron Sputtering (PEMS) and their Practical Applications***, **Ronghua Wei**,* Southwest Research Institute, USA **INVITED**

In this presentation, the research on thick TiSiCN-based nanocomposite coatings (up to 560 µm) conducted at Southwest Research Institute (SwRI$^®$) will be reviewed. These coatings have been developed using a plasma enhanced magnetron sputtering (PEMS) process via sputtering of Ti from all targets in a gas mixture of Ar, N_2 and TMS (trimethylsilane). In the PEMS process, in addition to the magnetron plasma, a global plasma is generated by W filament thermionic emission for the enhanced ion bombardment. The coatings thus produced have a dense structure, good adhesion to the substrate, low internal stress and superior mechanical properties compared to those obtained with the conventional magnetron sputtering. The coatings formed have a microstructure composed of nanocrystalline TiC_xN_{1-x} (x=0, 0.3 or 0.7) with the grain size of 4-10 nm in a matrix of amorphous SiC_yN_z, or nc-TiC_xN_{1-x}/a-SiC_yN_z. The microstructure of the coatings results in the super-hardness (up to 4600HV). However, the internal stress was found to be less than 1 GPa, thereby allowing the deposition of ultra-thick coatings of over 500 µm. The coatings also have high toughness characterized by high values of H^3/E^{*2} and H/E^*. The nanocomposite coatings have been developed specifically for severe environments including sand erosion, sand abrasion, water droplet erosion, and heavy load sliding wear on various alloy substrates including Ti-6Al-4V, Inconel 718, Al alloys, synthetic diamond inserts, WC-Co and various steels. These coatings have a few specific industrial applications including compressor blades or vanes for aero engines; piston rings, cylinder liners and stamping dies for automotive; and ball valves, valve stems, valve seats and plungers the for oil and gas industry. In this paper we review the method for preparing these coatings, discuss their microstructural, mechanical and tribological properties, and present examples for practical applications.

2:50pm **B5-2-5 Role of Interfaces in Determining the Fracture Resistance of Nanocomposite/Metal Nitride Multilayers***, **Naureen Ghafoor**,* Linköping University, IFM, Thin Film Physics Division, Sweden

Role of interfaces in determining the fracture resistance of nanocomposite/metal nitride multilayers

Naureen Ghafoor[a], Jeni Barrirero[b], Claire Davis[c], F. Mücklich[b], W.J. Clegg[c],

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We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN-and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces.

The degree of plastic deformation and work hardening is found to be dependent on the bilayer periodicity as well as on the nature of internal interfaces inside ZrAlN nano-composite layers. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. Nanoindentation measurements of the multilayers display a systematic variation of hardness with a value between 34 ± 1 to 22 ± 0.8 GPa as a function of layer thickness and interface structure. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

1: K. Yalamanchili,….N. Ghafoor, et al., Acta Materialia 89 (0) -2015, K. Yalamanchili,….N. Ghafoor, et al., Acta Materialia, [http://dx.doi.org/10.1016/j.actamat.2016.07.006]

2: S. Korte, W.J. Clegg, Scr. Mater. 60 (2009) 807–810.

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3:10pm **B5-2-6 Novel CrVN/TIN Nanoscale Multilayer Coatings Deposited by DC Magnetron Sputtering***, **Elbert Contreras**, Y Galindez, G Bejarano, M Rodas, M Gómez,* Universidad de Antioquia, Colombia

The constant search by development coatings with higher properties opened the doors to the research and development of nanoscale multilayer coatings, hardness higher than 40 GPa, friction coefficients lower 0.3, improved adhesion and increased heat and corrosion resistance are some of the most interesting properties of these multilayer coatings compared to monolayers. In this research novel CrVN/TiN nanoscale multilayer coatings were deposited onto H13 steel substrates by DC unbalanced magnetron sputtering. Prior to the coatings deposition an ionic cleaning was carried out to clean the surface of the substrates with a 40 sccm flow of Ar and a pressure of $2\text{-}3\text{x}10^{-2}$ mbar during 30 minutes. The deposition of multilayer coatings was using two targets opposite each other, Cr-V (70-30 %wt) and Ti, with a power density of 2.4 W/cm^2 at both, a nitrogen gas flow of 20% in the gas mixture ($N_2/(Ar+N_2)$) obtaining a working pressure of $6\text{-}7\text{x}10^{-3}$ mbar, deposition temperature was 250°C and a BIAS voltage of -70V. In order to varying the bilayer period a microcontroller was used to control the rotation and residence time of the substrates against each target in 15, 30 and 40 seconds, looking for some different bilayer periods, CrVN and TiN monolayer coatings were also deposited. Microstructural analysis by X-ray diffraction (XRD) showed a FCC crystal structure to the monolayer coatings CrVN and TiN with preferential orientation (111); multilayer coatings showed a preferred orientation (200); the roughness and grain size was characterized using an AFM technique, CrVN monolayer coating showed less roughness and the multilayer coatings showed a decrease of the grain size while decreasing the bilayer period. SEM images revealed columnar structure for CrVN and globular structure for TiN, similar structure was found in the multilayer coatings. Tribological properties of the coatings were investigated using Pin-on-disk, all the multilayer coatings showed lower friction coefficients and wear rates compared with the monolayer coatings.

3:30pm **B5-2-7 Carbon Supersaturated Fe-Cr-Ni-C Thin Films with a Unique Nanocolumnar Structure - a Tough, Low Friction and Corrosion Resistant Coating***, **Tomasz Suszko**, W Gulbinski, E Dobruchowska,* Koszalin University of Technology, Poland*; J Morgiel,* Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Poland

Carbon supersaturated, amorphous FeCrNi:C coatings showing a unique nano-columnar structure have been deposited by pulsed magnetron sputtering of the 316L steel target in argon/acetylene atmosphere. HRTEM, EELS and XPS studies have shown that metallic cores of nano-columns oriented along the film growth direction are surrounded by amorphous carbon shells. The mechanism of growth of such a self-organized structure is discussed in terms of thermodynamically beneficial release of carbon from metastable metal carbides and from ternary phases formed during sputter deposition. The coatings are tough, have very good tribological behaviour in dry friction vs alumina and demonstrated excellent resistance to the formation and growth of pits in the corrosion environment containing chloride ions.

3:50pm **B5-2-8 Study of Wear Mechanism of Carbide and Ceramic Cutting Tools with Nano-structured Multi-layered Composite Functional Coatings***, **Alexey Vereschaka**, A Vereschaka,* MSTU Stankin, Russian Federation*; A Batako,* Liverpool John Moores University, UK*; N Sitnikov,* Federal State Unitary Enterprise "Keldysh Research Center", Russian Federation

The purpose of this study was to research wear mechanisms of carbide cutting tools with nano-structured multi-layered composite functional coatings under stationary cutting conditions. The study presents the results of extensive research of wear and failure mechanisms of carbide cutting tools with developed coatings on the basis of multi-component systems (for example, on the basis of systems Ti-TiN-(TiCrAl)N, Zr-ZrN-(ZrNbCrAl)N, and Ti-TiN-(NbZrTiAl)N) in longitudinal turning of steel of various compositions. The particular attention was paid to research of the kinetics and wear mechanisms of wear centres on contact areas of rake and flank faces of the tool with the use of a SEM equipped with microprobe analysis system. Chemical and phase compositions of developed coatings were studied by X-ray diffraction analysis. The objects of comparative analysis were represented by samples of carbides with wear-resistant coatings of traditional types (TiN, (TiAl)N). The particular attention was paid to the study of specifics of cracking mechanisms in coatings, as well as to interdiffusion processes taking place in the areas of contact between tool material and material being machined.

The following results were obtained:

- Tools with developed coatings provided the increase in tool life by 2-3.5 times as compared with uncoated tool and by 1.5-2 times - as compared with tool with tradition coatings .

- In the developed coatings deposited to carbide substrates, the mechanism of cracking is substantially different from the mechanism of cracking in the coatings of traditional type. In particular, the multi-layered architecture of developed coatings and the presence of sublayers of nano-meter thickness contribute to inhibition of initiation and development of cracks; nano-structured multi-layered composite coatings can be subjected to formation of rare longitudinal cracks less hazardous in context of failure of the coating in general with virtually no hazardous cross cracks, which are the major cause of premature complete failure of the coatings.

- The tests have detected active formation of oxides in areas adjacent to cracks and in the area of coating failure. Oxides of such metals as titanium and zirconium are formed very actively.

- Application of developed nano-structured multi-layered composite coatings contributes to the transformation of wear mechanisms of cutting tool. In particular, it almost completely excludes formation of cracks, microchipping and chipping of tool substrate (which is especially important for ceramic tools) and reduces the intensity of adhesion-fatigue wear; abrasive wear is mainly observed, and that results in increased tool life.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-3

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

8:00am **B1-3-1 Synthesis and Applications of High-precision Thin Film Multilayers***, **Andreas Leson**, S Braun, P Gawlitza, C Gruhne, A Kubec, M Menzel,* Fraunhofer Institute for Material and Beam Technology, Germany **INVITED**

Nowadays thin film coating technologies like magnetron or ion beam sputter deposition are successfully used for the fabrication of extremely precise and smooth nanometer thin films, which are needed for optical coatings especially in the short wavelength range. In most of the applications coatings with thickness gradients on curved substrates are needed. Using optimized coating parameters thickness deviations of only a few picometers from the target profile can be obtained. Another important parameter for the performance of the coatings is roughness. Recent improvements of the deposition process resulted in HSFR values of < 0.1 nm rms (HSRF = high spatial frequency roughness, usually measured with atomic force microscopy).

One of the current main drivers for the development of nanometer multilayers is extreme ultraviolet lithography. For this application Mo/Si multilayers are needed that have to have highest possible reflectances, precise thickness distributions, low film stress as well as high long-term and thermal stability. With dedicated improvements of our coating processes and by applying diffusion barrier layers we have succeeded to increase the EUV reflectance to world record values of > 70.5 % (photon wavelength l = 13.5 nm, incidence angle a = 5 degree). Additionally, the amount of diffuse scattered EUV light could be reduced by decreasing the roughness of the coatings down to Rq < 0.1 nm rms. In addition to Mo/Si multilayers numerous other material combinations of absorber (Ni, Cr, Mo, La, W) and spacer (B4C, C, Si, Sc) layers have been developed during the last years and applied for mirrors and monochromators.

Nanometer multilayers are not only used as reflectors for X-rays. It is also possible to use depth-graded multilayers as diffractive elements. In this case multilayer lamellas have to be fabricated and the individual layer thicknesses have to be chosen according to the zone plate law of Fresnel zone plates. Such kind of diffractive optics is called multilayer Laue lens (MLL). MLLs are promising complementary optics to zone plates particularly in the hard X-ray range where the small aspect ratios of zone plates limit the efficiency. One of the main challenges with the coating of MLL is that several thousand of nanometer layers are necessary in order to obtain lenses with apertures in the range of 20…100 µm. Only if all these layers have the right thickness, the diffraction at the artificial grating results in efficient X-ray focusing. With the latest developments MLLs with apertures of 50 µm x 50 µm have been developed that show X-ray spot sizes in the range of 30 nm x 30 nm at a photon energy of E = 10.5 keV.

8:40am **B1-3-3 Influences of Frequency and Duty Cycle on the Mechanical Properties of TiCrBN Thin Films Grown by a Hybrid Superimposed High Power Impulse Magnetron Sputtering and Radio Frequency sputtering technique***, **ChiYu Lu**, J Lee, W Diyatmika,* Ming Chi University of Technology, Taiwan

The high power impulse magnetron sputtering (HIPIMS) technique has been studied intensively due to its extremely high peak power density to grow thin films with dense microstructure and excellent mechanical properties. Lots of efforts have been made to improve the low deposition rate of HIPIMS technique. In this study, a hybrid coating system consisting of a radio frequency power supply and a superimposed HIPIMS system was used to deposit the TiCrBN coatings with higher deposition rate. The phase of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. It can be found that the deposition rate increased greatly due to the superimposed module and also the addition of RF sputtering. Influences of the frequency and the duty cycle of HIPIMS on the microstructure, chemical composition and mechanical properties were studied in this work.

9:00am **B1-3-4 Controllably Manipulating Adatom Mobility during PVD Deposition through Surface Acoustic Waves***, **Piyush Shah**, A Reed, A Waite, B Howe, M McConney,* Air Force Research Laboratory, USA

In this work we explore the ability to controllably manipulate adatom mobility in a spatially defined anisotropic way using standard physical vapor deposition (PVD) technique. Here we investigate the nucleation, growth, and microstructural evolution of PVD-based thin film growth under the influence of electrically induced surface acoustic waves (E-SAWs). Thin films made from classical and next generation resilient plasmonic materials are deposited on SAW grade lithium niobate substrate with inter-digitated electrode pattern to generate SAWs. Increase in adatom mobility and surface diffusion is primarily attributed to SAW-adatom coupling during the early stage nucleation process. As a result, we demonstrate improved crystallinity in thin films deposited under the influence of E-SAWs. Films are characterized using XRD, SEM and AFM techniques. We believe this technique of growing films is complementary to elevating the substrate temperature during deposition in a conventional PVD deposition system. These results are very promising for future work in the area of thin films deposition onto substrates coupled with SAWs.

9:20am **B1-3-5 Effects of Processing Parameters on the Fabrication of TiCrSiN Thin Films Deposited by a Hybrid HiPIMS and RF Sputtering System***, **Yi-Xiang Qiu**, Y Yang,* National Taipei University of Technology, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

High power impulse magnetron sputtering (HiPIMS) is a relatively new physical vapor deposition technology, which is characterized for its ultra-high peak current, peak power density and high-density plasma to achieve unique thin film mechanical properties, such as high hardness, good adhesion and good wear resistance. In this work, a radio frequency (RF) and HiPIMS hybrid coating system was used to deposit TiCrSiN coatings with higher deposition rate. The TiCr and Si targets were connected to the HiPIMS and RF power supplies, respectively. The phase of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. The pin-on-disk wear test was employed to study the tribological property of coating. Effects of processing parameters, including duty cycle and pulse frequency of HiPIMS power on the microstructure, mechanical and tribological properties of TiCrSiN coatings were further discussed in this work.

9:40am **B1-3-6 Exploring the High-temperature Hardness of Nanocrystalline W-Ti Coatings***, **Yip-Wah Chung**, C Gross, X He,* Northwestern University, USA

Nanocrystalline coatings are harder than their bulk or microcrystalline counterparts because of the Hall-Petch effect. Their hardness tends to degrade with increasing temperature due to grain coarsening. Previous studies by Weissmüller, Kirchheim, and Schuh suggest that introduction of proper alloying elements can provide thermodynamic stabilization of the grain size, even at elevated temperatures. In this work, we have synthesized a series of W-Ti coatings by magnetron co-sputter-deposition of W and Ti. The coatings range in thickness from 450 to 525 nm and in composition from 85W-15Ti to 67W-33Ti. These coatings show high hardness at room temperature, with peak hardness values near 28 GPa. The hardness values are almost unchanged after 1h exposure at 600°C, remaining near 27 GPa. These results suggest the validity of a general strategy for designing thermally stable hard coatings that can maintain high hardness even after extended exposure to elevated temperatures.

10:00am **B1-3-7 Growth Mechanism of Sputter Deposited Self-assembled Alternating Layered Metal Containing Hydrogenated Amorphous Carbon Film***, J Ting,* National Cheng Kung University, Taiwan*; **Wan-Yu Wu**,* Da-Yeh University, Taiwan

The growth and characteristics of metal containing amorphous hydrogenated carbon thin films (a-C:H/Me) were studied in this research. a-C:H/Me thin films were synthesized using one single target, a rotating but not revolving substrate, and constant feed gas compositions in a conventional reactive sputter deposition chamber. The metals used include Al, Si, Cu, Pt, Fe and Ni. Various mixtures of methane and argon having fixed total flow rates were used as the feeds tocks. A number of growth parameters, including methane concentration, working pressure, electrode distance, dc power, substrate bias, and substrate temperature were used. Among the three distinct structures formed, self-assembled, alternating nano-layered structure is of particular interest. In order to understand the formation of these three distinct structures, correlations were first made among the deposition rate, the composition, the crystallinity, the surface chemistry, and the microstructure of a-C:H/Me thin films. It was found that the self-assembled, alternating nano-layered structures can be obtained under controlled growth parameters for selected metals. A growth mechanism based on the considerations of clustering of carbon and metal, segregation of carbon, catalytic effects of metal, formation of carbide, energy of adatoms, and surface diffusion of metal and carbon, has been developed. Further data analysis was also performed to verify the validity of the mechanism.

10:20am **B1-3-8 Phase Formation in Sputter Deposited Tantalum Coatings***, **Glen West**, M Ratova, P Kelly,* Manchester Metropolitan University, UK

Tantalum is a refractory metal with many applications. In bulk form, Ta generally has a bcc crystal structure, referred to as the α -phase. However, in thin film form, the metastable β -phase commonly forms. The β -phase is harder, but also more brittle than the α -phase and has other less desirable physical properties.

Control of phase formation in Ta films has been the subject of a number of recent studies. Several process/operating parameters have been put forward as influencing the final structure of the films, including choice of substrate material, use of a metallic interlayer between the substrate and film, substrate bias voltage, operating pressure, substrate temperature, mass of bombarding species and type of power delivery mode. These parameters can essentially be divided into those which influence the nucleation and growth of the film (e.g. substrate parameters) and those which control the energy delivered to the growing film (e.g. pressure, power delivery mode, temperature, etc.).

Of the thin film deposition processes available, magnetron sputtering is the process of choice for many commercial applications. It is a highly versatile, scalable technique capable of depositing high quality coatings of a very wide range of materials. The design of the magnetron(s) and the choice of power delivery mode allow a very wide process window to be readily explored to enable the determination of optimised deposition conditions for specific film/substrate combinations. A range of deposition parameters, magnetic field designs, power delivery modes, and biasing regimes, combined with a suite of surface analysis techniques has been utilized in a detailed study of the phase formation in tantalum films. This has enabled the conditions necessary for the deposition of α-tantalum to be identified.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-1-1 Thermal Stability and Mechanical Properties of Sub-stoichiometric TiAlN Thin Films***, **Katherine Calamba**,* Linköping University, Sweden*; I Schramm,* Saarland University, Sweden*; M Johansson-Jõesaar,* SECO Tools, Sweden*; J Pierson,* University of Lorraine, France*; M Odén,* Linköping University, Sweden

Aspects on thermal stability of (Ti$_{1-x}$Al$_x$)N$_y$ alloys (y<1) were investigated because recent findings show that small amounts of nitrogen vacancies cause significant stability improvement by suppressing detrimental phase transformations, i.e. phase transformation of *c*-AlN to *w*-AlN is delayed to higher temperatures compared to stoichiometric films. The substoichiometric TiAlN alloys were deposited via cathodic arc evaporation technique and the degree of ionization of the arc plasmas was tuned by varying the bias voltage from -30V to -80V. The microstructural evolution and thermal stability of the coatings were examined using transmission electron microscopy, x-ray diffractometry, differential scanning calorimetry, and atom probe tomography. In the as-deposited state, the highly biased films show higher hardness, i.e. the enhanced ion bombardment caused beneficial changes in morphology, microstructure, compressive stresses, and densification. However, at elevated temperature low biased films retain their hardness to higher temperatures compared to high biased films. This behavior is discussed in terms of an enhanced driving force for phase separation in the high biased films caused by self-interstitials, generated by the ion-bombardment during growth, diffusing into the excess vacancies to relive the stress. Such annihilation of defects causes the enthalpy of the system to increase, which promotes phase separation. On the other hand, low biased films with less self-interstitials show the highest phase stability and the age hardening effect was retained to the highest reported temperature to date for the Ti-Al-N material system. Our study shows that varying the nitrogen vacancy concentration of transition metal nitride thin films offers a mean to tune of thermal stability and mechanical properties for hard coating applications.

8:20am **B4-1-2 Microstructure and Hardness of Ti-B-N-C Nanocomposites Deposited from Ti and B$_4$C Targets***, **Christina Wüstefeld**,* Institute of Materials Science, TU Bergakademie, Germany*; M Motylenko,* Institute of Materials Science, TU Bergakademie Freiberg, Germany*; M Síma, M Jílek,* SHM Ltd., Czech Republic*; D Rafaja,* Institute of Materials Science, TU Bergakademie Freiberg, Germany

The addition of boron to titanium nitride during the deposition of the Ti-B-N based coatings is known to facilitate the formation of nanocomposites with excellent thermal stability and very high hardness that are required for special machining applications. The Ti-B-N-based nanocomposites investigated in this study were deposited by using a combination of cathodic arc evaporation (operating with a Ti cathode) and magnetron sputtering (operating with a B$_4$C cathode). The amount of boron in the coatings was controlled by the magnetron power and the [B]/[N] ratio by the nitrogen flow in the working atmosphere. An additional parameter of the deposition process was the bias voltage, which influences mainly the kinetic energy of titanium ions.

The indentation experiments have shown that all deposition parameters, i.e., the magnetron power, the nitrogen flow and the bias voltage, strongly influence the hardness of the Ti-B-N-C nanocomposites. In order to be able to explain the observed correlation between the deposition parameters and the hardness of the coatings, the phase composition, the distribution and morphology of individual phases, the size and preferred orientation of crystallites and the residual stress were investigated by using a combination of glancing-angle X-ray diffraction (GAXRD), transmission electron microscopy with high resolution (HRTEM) and electron energy loss spectroscopy (EELS). The correlations between individual microstructure parameters like distribution of individual phases, morphology of crystallites or grains, preferred orientation of crystallites and residual stresses are discussed. The residual stress was measured via sample bending and by modified sin^{2}y method (GAXRD). The residual stresses obtained from the complementary methods will be compared.

8:40am **B4-1-3 Strategies for Fracture Toughness Enhancement of Nanostructured Films by Microstructural and Grain-boundary Design: The Role of Microstructure, Stress and Property Heterogeneity***, **Rostislav Daniel**, C Mitterer, J Keckes,* Montanuniversität Leoben, Austria **INVITED**

In nature, extraordinary material properties are achieved by combining hard and soft or stiff and elastic constituents, which form very tough, hard and damage resistant architectures. The key for these outstanding properties is the variation in material microstructure and mechanical property distributions over large scales. In this paper, the inherent advantages of these principles will be demonstrated for nanostructured brittle thin films with the aim to establish a universal concept for improvement of fracture behavior of materials where a lack of plasticity compromises their application for surface protection despite their high strength and thermal stability. Besides strategies to enhance fracture toughness by transformation toughening, coherency strain or intrinsic compressive stress, the main focus will be on microstructural design of thin films to control crack formation and propagation. The microstructure- and property-dependent mechanisms controlling crack propagation (e.g. deflection by weak interfaces or crack path tortuosity) with subsequent toughness enhancement will be discussed in detail for various material combinations. Microstructurally and mechanically heterogeneous films including representative hard/soft crystalline/amorphous and crystalline/crystalline materials such as CrN/Cr, TiN/SiO$_x$ and AlCrN, characterized with respect to their stiffness, fracture stress and toughness by micromechanical testing of microcantilever beams, will be some of the examples. In addition,special attention will be paid to a new strategy for fracture toughness enhancement by grain-boundary orientation and interface engineering, where crack propagation is inhibited by deflection of cracks at interfaces of columnar grains designed with chevron-like architecture and combined with elastic interlayers. In this way, even common nanocrystalline brittle materials may exhibit considerably enhanced plasticity.

9:20am **B4-1-5 Epitaxial Growth of HfN Films using Synchronized Pulsed Substrate Bias during HiPIMS Discharge**, *M Villamayor,* Linköping University, (IFM), Sweden*; T Shimizu,* Tokyo Metropolitan Univeristy, Japan*;* ***Julien Keraudy****, R Boyd,* Linköping University, (IFM), Sweden*; D Lundin,* LPGP, France*; U Helmersson,* Linköping University, (IFM), Sweden

Low-temperature epitaxial growth of high quality transition metal nitride materials is considered so far as one of the great challenges in advanced thin film technology. In this study, we demonstrate that low-energy-ion irradiation at the growth surface during high power impulse magnetron sputtering discharge (HiPIMS) is one of the most promising and widely applicable concepts to deposit stoichiometric, single-crystal HfN films on MgO(001) in the absence of applied substrate heating. The key point of this process is the appropriate selection of the chemical nature of the incident ions, *i.e*, inert gas vs. metal. To control the nature of the ion irradiation, two approaches have been chosen and have consisted to change the nature of the sputtering gas, Ar and Kr, and the time domain to apply substrate bias either continuously (DC) or synchronous in the last moment of the HiPIMS pulse (60 µs after the initiation of the pulse). The substrate bias was set at -60 or -100 V with a pulse width of 100 µs. *In situ* mass spectrometer measurements reveal that, by changing the gas atmosphere from Ar/N_2 to Kr/N_2, the last moment of the HiPIMS pulse evolved from a N^+-dominated phase to Hf^+-dominated phase. High-resolution x-ray diffraction, ω-2θ, azimuthal ϕ scans and reciprocal lattice maps combined with high-resolution cross-sectional transmission electron microscopy analysis established that switching from N^+ to Hf^+ bombardment, as well as switching from DC to pulse synchronized bias, help to promote the growth of fully-relaxed epitaxial HfN layers with an enhancement of the crystallinity by reducing the density of residual point defect.

9:40am **B4-1-6 HiPIMS and Ni Doping Induced Structure Reinforcement and Phase Change in nc-TiC/a-C:H Coatings***,* ***Pavel Soucek****, J Daniel, J Hnilica, K Bernatova, L Zabransky,* Masaryk University, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic*; M Stupavska, P Vašina,* Masaryk University, Czech Republic

Nanocomposite coatings consisting of nanocrystallites embedded in an amorphous matrix such as nc-TiC/a-C:H can be tailored to exhibit an unusual combination of properties such as high hardness and modulus combined with low friction and wear. These coatings are usually deposited utilizing direct current magnetron sputtering (DCMS) leading to low ionization of the sputtered titanium. High Power Impulse Magnetron Sputtering (HiPIMS) depositions usually lead to much higher ionization of the sputtered titanium which can alter the deposition process and in turn the properties of the deposited nc-TiC/a-C:H coatings. Using HiPIMS it was possible to make arc-free deposition of coatings with much higher carbon content (> 90 at.%) which was impossible for DCMS. When DCMS was employed black carbon layers were created on the target including the racetrack, whereas HiPIMS employment led to a much cleaner target. This was due to significant ionization of sputtered titanium and its back attraction to the target in HiPIMS. This proved to be highly advantageous for deposition of coatings with high carbon content with regards to arc occurrence and moreover the deposition rate of carbon rich coatings was higher for HIPIMS compared to DCMS. Lower fraction of the a-C matrix phase was found to be created in HiPIMS deposited nanocomposite coatings with < 55 at.% of carbon as compared to DCMS deposited coatings. HiPIMS deposited coatings also exhibited better stoichiometry of the TiC grains. This shows that HiPIMS ensured carbon incorporation into TiC grains rather than forming of a-C matrix. Lower amount of a-C matrix corresponded with smaller mean grain separation distance of the TiC grains by the a-C matrix. This enhanced the nanocomposite grain boundary strengthening leading to overall higher hardness of HiPIMS deposited coatings compared to those deposited by DCMS. HiPIMS deposited coatings also exhibited lower lattice parameter. The crucial parameters for obtaining hardest coatings were found out to be the TiC grain stoichiometry and small mean grain separation by the a-C matrix corresponding to only a few monolayers of the matrix between the grains. HiPIMS utilization favored this structure enhancement making it a promising method of nc-TiC/a-C:H coating preparation. Ni doping led to Ni incorporation into the grains. The grain size as well as the mean grain separation was smaller and the surface features were refined. Thus doping by weak carbide forming Ni can also be used as tool for fine tuning of structure of nc-TiC/a-C:H coatings.

This research has been supported by project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of the Czech Republic.

10:00am **B4-1-7 Correlation of Plasma Parameters and Thin Film Properties of HiPIMS Al-Cr-N films using a Combinatorial Approach***,* ***Lars Banko****, D Grochla, S Ries, P Awakowicz, A Ludwig,* Ruhr-Universität Bochum, Germany

HiPIMS power supplies provide a variety of settings to tune the plasma in PVD processes. In this work, the direct influence of plasma properties like ion energy, ion flux and electron density on coating features like microstructure and mechanical properties was investigated.

Single phase fcc - Al-Cr-N films were deposited at 500°C by reactive co-deposition of Al und Cr in N_2/Ar – plasma. Continuous composition materials libraries ((Al_{100-x} -Cr_x)-N (0.4 < x < 0.9)) were synthesized by confocal alignment of two 4 inch cathodes. Both cathodes were powered by HiPIMS with an average power of 200 W. The pulse length was kept constant at 40 µs. Three depositions with frequencies of 100, 200 and 400 Hz were carried out resulting in a variation of peak power (0.3 – 2.5 kW/cm^2) and peak current density (0.5 – 3.8 A/cm^2).

Time- and space-resolved plasma diagnostics were applied to characterize ion energy, ion flux and electron density at five positions corresponding to different compositions. The electron density was investigated using Langmuir probe and the ion energy distribution function was determined by retarding field energy analyzer. Without additional bias, maximum ion energies of 70 eV were measured. The mean ion energy was found to vary between 4.5 and 9 eV, depending on the applied frequency.

The materials libraries were characterized regarding microstructure, morphology, composition, hardness, Young's modulus and residual stress. The residual stress was measured on 120 µm thick micro-cantilever stress sensors. By thermal cycling of the sensors after the deposition, intrinsic and extrinsic stress components could be determined separately.

The results of this investigation clearly show the influence of ion energy and ion flux on composition, microstructure and morphology and thereby on mechanical properties like residual stress and hardness. The effect of ion flux and ion energy on the materials properties are amplified by increasing Al-concentration.

Acknowledgment: SFB-TR 87

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-4

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Jyh-Ming Ting, National Cheng Kung University

1:50pm **B1-4-2 Combinatorial Exploration of the High Entropy Alloy System Fe-Mn-Ni-Co-Cr***, **Alexander Kauffmann,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; M Stüber, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; S Schlabach, D Szabó,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK)*; B Gorr,* University of Siegen, Germany*; H Chen,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany*; H Seifert,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; M Heilmaier,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Germany

The concept of high entropy alloys (HEA) differs from conventional alloy design strategies by increasing the number of base elements as well as their concentrations. Rather than being composed of a single principal element and minor additions for obtaining desired microstructures and materials properties, HEAs are chemically complex composed of multiple principal elements in almost equiatomic ratios. Here, the basic intention is to maximize the configurational part of entropy and stabilizing disordered, single-phase materials with simple crystal structures. Nevertheless, configurational entropy is not the sole decisive factor for the thermodynamic stability of particular phases. Accordingly, efficient theoretical as well as experimental methods have to be conducted in order to screen the vicinity of the center of five or more component systems.

The FeMnNiCoCr HEA crystallizes face-centered cubic and is one of the few examples of HEAs which can be tailored by means of classical metallurgical processes. Thus, FeMnNiCoCr has attracted most interest by the scientific community among the class of HEAs so far. Its outstanding mechanical properties are resulting from a complex interplay of the impact of lattice distortion and an interplay of deformation twinning and dislocation slip. In order to experimentally separate fundamental parameters like stacking fault energy which are strongly depending of Fe, Mn and Ni content and lattice distortion which are influenced by Cr and Mn content, deviations from the almost equimolar composition are necessary.

For exploring the phase field of the solid solution within the Fe-Mn-Ni-Co-Cr system, we use a combinatorial thin film method in the present contribution. The films are prepared by magnetron sputtering from a Fe-Mn-Ni-Co-Cr multi-element target with circular sectors onto Si substrates. The compositions of the prepared films with a thickness of about 5 µm were obtained by EDX. In the as-deposited state, the disordered solid solution is found in the near equimolar region of the films. The lattice parameter of bulk material obtained from conventional metallurgy could be verified. The microstructure of the obtained thin film in the center of the quinary system is examined by using TEM (FIB lift out) and 3D-APT. In addition, the results on the center of the phase diagram are complemented by analyses towards the binary border systems which are in our case Mn-Fe, Fe-Co, Co-Ni, Ni-Cr as well as Cr-Mn. Here, disordered solid solutions with fcc, bcc, hcp and alpha-Mn structure type crystal structure were found. The appearance of all phases is discussed based on CALPHAD calculations.

2:10pm **B1-4-3 The Effect of Mo-Cu Cathode Composition on Thin Film Synthesis and DC Vacuum Arc Characteristics***, **Igor Zhirkov,*** Linköping University, IFM, Sweden*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Rosen,* Linköping University, IFM, Sweden

Mo-Cu alloys demonstrate high electrical and thermal conductivity, low coefficient of thermal expansion, and good high-temperature performance. The material properties are dependent on how well Mo and Cu can be mixed. Classical methods such as powder metallurgy and/or infiltration are limited due to the Mo/Cu grain size. An alternative synthesis method is vacuum arc, which allows generation of metallic flux even from refractory materials, and which also provide an increased Mo-Cu intermixing. In this work, we have studied the influence of $Mo_{1-x}Cu_x$ cathode composition (x = 0, 0.05, 0.1, 0.15, 0.3, 0.63, 0.95, 1 (wt%)) on plasma generation and materials synthesis in a DC vacuum arc discharge. It is found that the stability of the arc process is strongly correlated to the cathode composition. Highest stability, together with the lowest cathode potential (~ 19 V), is detected for the $Mo_{0.37}Cu_{0.63}$ (wt%) cathode, while the $Mo_{0.95}Cu_{0.05}$ (wt%) cathode shows the most unstable arc process with the highest cathode potential (~ 28 V). Moreover, plasma properties such as total intensity of ion flux, ion kinetic energy and ion charge state are all found to be strongly dependent on the relative Mo/Cu ratio. The intensity of macroparticle generation as well as the size of the droplets also correlate with the relative fraction of Cu within the cathode. However, there is an inverse correlation between the visually observed intensity of the macroparticle flux and the number of droplets on the resulting films. In particular, for the cathodes with low Cu content, there is an increased abundance of visually observed macroparticles while the films are (close to) free of droplets. The thickness and elemental composition of the deposited films also demonstrate a dependence on the elemental composition of the cathode. The obtained results are discussed in the light of a very limited solubility between Mo and Cu, surface and material properties of new and used Mo-Cu cathodes, and features resulting from high temperatures of the cathode surface during the arc process.

2:30pm **B1-4-4 Towards High-Rate Magnetron Sputter Deposition: Influence of Discharge Power on Deposition Process and Coating Properties***, **Christian Saringer**, R Franz,* Montanuniversität Leoben, Austria*; K Zorn,* MIBA High Tech Coatings, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Magnetron sputtering offers the possibility of depositing a vast variety of functional coatings and is nowadays widely established in research and industry. Its main advantage is the great versatility, which is owing to the possibility of freely adjusting the conditions during film growth, like the degree of thermalization, the substrate temperature and the ion bombardment. Thus, the mechanical, optical and structural properties of the coatings can be tailored on laboratory and industrial scale. However, the applicability is often limited due to the large amount of energy that is inherently dissipated into heat, resulting in a low deposition rate. Therefore, the increase of deposition rate is of great interest in order to improve productivity and cost-efficiency. Raising the overall power introduced to the process can be perceived as an approach for elevating the deposition rate which is, however, also affecting the properties of the resulting coatings. Within this work, we therefore studied the influence of the target power on the sputter deposition process and resulting coating properties during reactive and non-reactive sputtering. Chromium, titanium, TiN, TiO_2 and carbon coatings were deposited at different average power densities of up to 34 W/cm² in DC and pulsed DC mode. The coatings were examined by X-ray diffraction, scanning electron microscopy and nanoindentation experiments, which revealed that their mechanical and structural properties are significantly affected by the power density. It was also found that by controlling the discharge power it is possible to effectively influence the transition between metallic and poisoned mode during the reactive sputtering of titanium in N_2 as well as O_2 containing atmospheres. Additionally, conducted plasma investigations employing Langmuir probe analysis and optical emission spectroscopy revealed further details about the relations between discharge and coating properties contributing to establish a comprehensive understanding of high-rate magnetron sputter deposition.

2:50pm **B1-4-5 High Temperature Solid PVD Lubricants Based on Vanadium***, **Vjaceslav Sochora**, M Jilek, Jr., O Zindulka,* SHM, s.r.o., Czech Republic

The increase of the production in the industry demands higher cutting speeds of the tools. A higher speed means higher forces which increase the working temperature and decrease the tool life. One of the solutions is to use PVD coatings with a very good thermal stability or we can use a film with a low friction coefficient in high temperatures. In our work, we focus on the high temperature lubricant PVD coatings based on vanadium that are very promising for cutting and forming applications.

The studied systems were CrVN, VAlN, AlCrVN and VAlSiN prepared by the low voltage arc. The disadvantage of these systems is a narrow functional temperature interval that determines the specific application for the film.

We investigated the dependence of the hardness on the amount of vanadium in the film and then annealed the deposited coatings in the air at the temperatures of 500 – 700 °C and researched the change in hardness and oxidation rate. We also examined the structure by using SEM.

In the next step, we used face-turning test to simulate the real conditions to assess the friction properties of the coatings. The parameters of the cutting tests were set to achieve the thermal load from 550 °C to 700 °C.

The presence of vanadium in the system has a significant influence on the friction and enables to optimize the process application like hobbing or aluminum die casting.

3:10pm **B1-4-6 Grain Size-Dependent Metastable Phase Formation***,* ***Marcus Hans****, D Music,* RWTH Aachen University, Germany*; D Kurapov, J Ramm, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland, Liechtenstein*; J Schneider,* RWTH Aachen University, Germany

Physical vapor deposited (PVD) TiAlN is the benchmark hard coating system utilized in metal cutting and forming applications today. However, phase formation prediction efforts by density functional theory (DFT) calculations for TiAlN are often inconsistent with experimental data. It is well known that the phase stability is affected by chemical composition, temperature as well as pressure. Recently, the impact of point defects on the phase stability [1] and the consequences of processing conditions in an industrial deposition system for the phase stability [2] were evaluated.

Here we consider for the first time the impact of grain size on the stability of metastable TiAlN coatings by relating calculated surface and volume energy contributions to the total energy. Typical grain sizes determined for PVD TiAlN are < 50 nm and, hence, these coatings contain domains with large surface-to-volume ratios. Our starting hypothesis is that the energetic "penalty" associated with the formation of these grain surfaces (= interfaces) will affect the experimentally determined stability. Therefore, we investigated the grain size-dependent phase stability of cubic and wurtzite $Ti_{1-x}Al_xN$ theoretically by considering a surface energy term in addition to the volume energy term. With this approach critical grain sizes for metastable phase formation are identified as a function of the Al concentration x.

$Ti_{1-x}Al_xN$ coatings were synthesized combinatorially by cathodic arc deposition and the here proposed, grain size dependent phase stability calculation is found to be consistent with experimental phase formation data. The results provide evidence that the extent of phase stability regions of TiAlN critically depends on the grain size. While these thoughts have been overlooked in the past we will demonstrate that the grain size-dependent phase formation is equally relevant for other material systems with large surface-to-volume ratios.

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3:30pm **B1-4-7 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs***,* ***Billur Deniz Polat Karahan****, B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

3:50pm **B1-4-8 Thin Film Metallic Glass: Novel Coating Providing High Toughness and Low Friction***,* ***Chia-Chi Yu****, J Chu,* National Taiwan University of Science and Technology, Taiwan*; Y Shen,* University of New Mexico, USA

The amorphous nature of thin film metallic glasses (TFMGs) provides outstanding mechanical properties, including high strength, large elastic limits, and excellent corrosion and wear resistance. The grain boundary-free structure of TFMGs produces an exceptionally smooth surface and low surface free energy, resulting in high hydrophobicity and a low coefficient of friction.

In this study, magnetron sputtering was used in the deposition of Zr-based TFMG coatings with the aim of enhancing the bending and fatigue properties of bulk metallic glasses (BMGs). A TFMG coating was shown to increase the plastic strain of BMG by 9.2%, without sacrificing its extraordinary strength. This was also shown to increase the fatigue endurance-limit of BMG by ~33%, from 300 MPa for bare BMG to 400 MPa for TFMG-coated BMG. The results of transmission electron microscopy and nanoindentation testing revealed that TFMGs are able to withstand enormous shear strain without fracturing. Used as a coating on syringe needles, the low coefficient of friction of TFMG (∼0.05) reduced the insertion forces by ∼66% and retraction forces by ∼72%, when tested on polyurethane rubber blocks.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-1

CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

4:10pm **B2-1-9 Combined Effects of Supersaturation and Stress for the Control of AlN Film Quality***,* ***Raphael Boichot****, D Chen,* Grenoble-INP, France*; F Mercier,* CNRS, France*; M Chubarov,* Grenoble-INP, France*; G Giusti,* Sil'Tronix, France*; M Pons,* CNRS, France **INVITED**

The aim of this talk is to show the degrees of freedom offered to CVD experimenter to tune the properties of crystal during hetero-epitaxial growth. We will develop here the example of the AlN epitaxial growth by HT-CVD with $AlCl_3$ and NH_3 as precursors in H_2 as carrier gas.

We showed in previous studies that the epitaxial growth of AlN on various substrates can be obtained by carefully aiming a particular temperature-supersaturation-growth rate process parameters window, but we also found that the AlN crystal quality, into this "epitaxial window", does not depend so strongly on the growth parameters other than growth rate. N/Al ratio surprisingly does not play a crucial role in obtaining epitaxial growth or desirable crystal quality.

Clearly to increase further the crystal quality once epitaxial growth is reached, we must cover a wider range of growth parameters to achieve a good control of crystal properties. In one hand, we will explain how mechanical characteristics of layers at room temperature can give valuable information on the first steps of growth that are critical for crystal quality and properties. In the other hand, we will show how certain growth parameters, even considered as secondary or counter intuitive, could be key to explain crystal quality and properties due to their influence on the early steps of growth.

Due to the high variability in experimental results in CVD and the need to exhaustively cover growth parameters, we will present the interest of using DOE (design of experiments) method to fasten the research in crystal growth rather that the classical one-variable-at-a-time (OVAT) studies.

Our conclusions, summarized from a huge collection of statistically robust experimental results, are that the crystal quality is the harder parameter to control compared to other properties of the grown AlN layer. In particular, the final stress state and roughness is relatively easy to tune with process parameters. We found that good crystal quality are related to high tensile stresses in the grown layers but also to certain parameters not embedded into our previous studies. We propose some explanations to the process parameters/layer properties relationship that can be generalized to other materials grown by CVD.

4:50pm **B2-1-11 Fabrication of Boron-doped Diamond Films on Cemented Tungsten Carbide*, Kunio Saito,*** Japan Coating Center Co., Ltd.,Chiba Institute of Technology, Japan*; A Kawana,* Japan Coating Center Co., Ltd., Japan*; A Suzuki, Y Sakamoto,* Chiba Institute of Technology, Japan

To deposit diamond coating on cemented tungsten carbide is quite difficult. Generally, to reduce reactivity of cobalt which is the binder of cemented tungsten carbide that pretreatment using the acid is carried out. On the other hand, study to improve the adhesion of nanostructured diamond coating is reported, which is to formed borides by plasma enhanced chemical vapor deposition using diborane for reducing reactivity of cobalt. Diborane (B_2H_6) and trimethyl boron {B (CH_3) $_3$} is often used as a boron source. However, it is necessary to control with special equipment because of having poisonous, flammability and explosiveness of these sources.

This study is an attempt to deposit boron-doped diamond directly on cemented tungsten carbide substrates by microwave chemical vapor deposition using trimethyl borate {$B(OCH_3)_3$} as a boron source. Trimethyl borate is liquid which dissolved boric acid(H_3BO_3) in methanol(CH_3OH), and introduce to vacuum chamber as a boron source with bubbling using hydrogen(H_2) as a carrier gas. Cemented tungsten carbide substrate was scratched with diamond powders and cleaned with ultrasonic cleaner before loaded into the vacuum chamber.

Boride was formed on the substrate surface to reduce reactivity of cobalt which is the binder of cemented tungsten carbide with introducing boron source into the vacuum chamber. At this stage, confirming a combination state of the surface product by X-ray photoelectron spectroscopy(XPS), existence of boride was confirmed. Diamond was formed continuously with using reactive gases of methan and hydrogen, after forming borides on the substrate surface. In the Raman spectrum, the peak of diamond due to SP_3 was observed and the presence of diamond was confirmed. As a result of observation the surface with scanning electron microscope(SEM), it was confirmed that diamond which grew up onto substrate surface. And, boron-doped diamond with low electrical resistance approximately 10^{-2}[Ω] was obtained.

It is possible to deposit boron-doped diamond with good adhesion by introducing the bonds with boron and cobalt without pretreatment.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm **B4-2-3 Measurement of Residual Stress on Transition Metal Nitride Hard Coatings by Combining Average X-ray Strain Method and Nanoindentation*, Jia-Hong Huang,*** *A Wang, G Yu,* National Tsing Hua University, Taiwan **INVITED**

Among the nondestructive techniques for measuring residual stress in thin films, X-ray diffraction (XRD) is one of the well-established techniques, by which the strain tensors and crystal structure can be simultaneously determined. However, using conventional XRD $\sin^2\psi$ and the like methods to measure residual stresses in textured thin films are usually problematic. We previously developed an XRD technique named $\cos^2\alpha\sin^2\psi$ method to solve the problem by using grazing incidence asymmetrical diffraction configuration that effectively increased the irradiation volume from a thin-film specimen, thereby generating higher intensity for high-angle Bragg peaks compared with the conventional Bragg-Brentano geometry. The $\cos^2\alpha\sin^2\psi$ method has been successfully applied on single layer thin films, thin film with interlayer and multiphase oxynitride thin films. Nevertheless, the X-ray residual stress (XRS) is usually deviated from the stress measured by optical curvature method, even up to 30%, which is normally attributed to the use of incorrect elastic constants determined by mechanical methods such as nanoindentation. On the other hand, if X-ray elastic constants (XECs) are adopted, the uncertainty of the measured stress can be within 10%; however, the XECs are not readily available for most hard coatings. In this study, we proposed a method where the average X-ray strain (AXS) was determined using $\cos^2\alpha\sin^2\psi$ XRD technique at several rotational (f) angles, combining with elastic constant measured by nanoindentation (E_{NI}), to improve the accuracy of the measurement of XRS. The major concept was to increase sampling volume by measuring X-ray strain at multiple rotational angles. TiN hard coating on Si (100) substrate was selected as the model system, where the residual stress was determined by laser curvature technique and the accompanying AXS was measured by $\cos^2\alpha\sin^2\psi$ method at several rotational angles. By using AXS and elastic constant measured by nanoindentation (E_{NI}) to calculate X-ray stress, the stress deviation from that by laser curvature method could be substantially reduced even down to 3 % with sufficient sampling points. The results also indicated that AXS could be accurately measured down to a thickness of 350 nm by using lab X-ray source; however, the resolution of AXS was not sufficient to differentiate the strain for a specimen with a thickness less than 160 nm, which was mainly due to insufficient sampling volume. Therefore, AXS may serve as a convenient parameter, when combining with E_{NI},in X-ray stress measurement, by which residual stress of hard coatings comparable to that by laser curvature method can be obtained without using XECs.

2:50pm **B4-2-5 Investigation of the Tribocatalysis Mechanisms involved in the Extraction of Amorphous Carbon Boundary Films from Base Oils*, Giovanni Ramirez,*** *O Eryilmaz, B Narayanan, Y Liao, G Kamath, S Sankaranarayanan, A Erdemir,* Argonne National Laboratory, USA

Aimed at solving some of the durability and efficiency problems existing in current mechanical systems, we have been studying the interactions between lubricants and solid surfaces and how one can possibly mitigate friction and wear in components with the use of novel environment friendly technologies. As an innovative approach, here we present the mechanisms involved in the extraction of carbon-based tribofilms directly from the hydrocarbon molecules of the base oils with the use of catalytically active nanocomposite coatings, and without the need of antiwear additives [1].

In this work, we present the tribocatalysis phenomena that allow the extraction of carbon-based tribofilms when surfaces are made of nanocomposite thin films/coatings that include a metal catalyst and called catalytically active nanocomposite coatings. Such metal catalysts (i.e., Cu, Ni, Co, etc.) seems to be responsible for lowering the activation energy that is required for first dehydrogenation and then cracking of the hydrocarbon molecules into dimers and trimers that in the end recombine under pressure to form a carbon-based deposit resembling a hydrogenated diamond like carbon film. To study these processes and show the presence of protective carbon tribofilms, not only several tribometers, but also advance surface characterization techniques such like Raman microscopy, TOF-SIMS and transmission electron microscopy were employed to elucidate the fundamental mechanisms involved. Further, detailed MD simulations were performed using classical and ab-initio molecular dynamics to explain the specific steps in the creation of a protective tribofilm that outperforms the more traditional boundary films resulting from ZDDP and other types antiwear additives. We will discuss the effects of having less catalyst on the coating on the formation of the carbon-based tribofilms.

Work supported by the US Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Vehicle Technologies and Advanced Manufacturing Offices under contract DE-AC02-6CH11357. Use of the Center for Nanoscale Materials was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

[1] Ali Erdemir, Giovanni Ramirez, Osman L. Eryilmaz, Yifeng Liao, Badri Narayanan, Subramanian Sankaranarayanan. Carbon-based Tribofilms from Lubricating Oils. Nature (536) 67-71 (2016).

3:10pm **B4-2-6 Phase Stability and Strain Evolution in TiZrAlN Coatings During Annealing*, Lina Rogström,*** *R Pilemalm, N Ghafoor,* Nanostructured Materials, IFM, Linköping University, Sweden*; L Johnson,* Sandvik Coromant, Sweden*; N Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M Odén,* Nanostructured Materials, IFM, Linköping University, Sweden

TiAlN-based coatings are widely studied, and quaternary alloys within this system can further improve the mechanical properties as well as the thermal stability of hard and wear resistant coatings. TiZrAlN is still a relatively unexplored material system, while there are studies showing that addition of Zr to TiAlN can delay the formation of wurtzite AlN in the coating [1]. Theoretical results show that the decomposition route in TiZrAlN coatings is expected to vary depending on chemical composition [2] while the effect of chemical composition on the thermal stability of TiZrAlN coatings remains to be clarified.

Here, we study the phase stability and the strain evolution in TiZrAlN coatings during annealing. TiZrAlN coatings with Zr-contents on the metal sublattice between 24 and 69 at.% were grown by cathodic arc evaporation on polished WC-Co substrates. The coatings have a columnar structure and consist of a solid solution cubic (c) NaCl structure TiZrAlN phase which grows with a strong preferred 200 orientation. In situ wide angle scattering during annealing reveal that the thermal stability of the c-TiZrAlN phase depends on chemical composition. The coating containing 69 at.% Zr on the metal sublattice displays high stability. After 3 h at 1100 °C there is only a very small change in the lattice parameter of the c-TiZrAlN phase indicating that a small change in composition takes place, corresponding to formation of small amounts of other phases, or that point defects are annihilated. The strain in this coating relaxes during annealing above 800 °C. For the coatings containing less Zr, domains enriched in ZrN and TiAlN form during annealing above 600 °C. In the low Zr-content sample the microstructure is anisotropic with Al-rich domains elongated in the in-plane direction while the domains are more equiaxed in the case of higher Zr-content. The decomposition is associated with a large increase in compressive in-plane strain of the c-TiZrAlN phase. For a Zr-content of 48 at.%, the strain relaxes above 950 °C while for the lowest Zr-content the strain remains high throughout the 3 h anneal. The strain in the formed ZrN-rich domains depends on the composition of the coating and is largest for the low Zr-content (24 at.%) sample. The strain evolution is discussed in terms of microstructure and elastic properties.

[1] L. Chen et al., Thin Solid Films 519 (2011) 5503.

[2] H. Lind et al., AIP Advances 4 (12) (2014) 127147.

3:30pm **B4-2-7 Gas Inlet and Input Power Modulated Sputtering Molybdenum Nitride Thin Films*, JianYing Xiang,*** National United University, Taiwan

The molybdenum nitride films were produced by RF magnetron sputtering with various structural features by the input power and gas flow ratio control. With Ar/N gas flow ratio s from 10/10 to 18/2 and RF input powers from 150 to 300W, the molybdenum nitride films evolved from significant columnar to amorphous structure. The coating deposited at an Ar/N_2 ratio of 16/4 and an input power of 300W showed an intensified Mo_2N microstructure with preferred (111) orientation. In comparison, the crystalline phase of the coating fabricated at an Ar/N_2 ratio of 10/10 and an input power of 150W was suppressed. The thickness, deposition rate and crystallinity of the molybdenum nitride increased with Ar/N_2 ratio and power input. To enhance the protective behavior of the molybdenum nitride coating, the crystalline and amorphous nitride layers were alternately stacked to form a nanolayered film. Hardness, Young's modulus, and tribological characteristics of the molybdenum nitride multilayer films were investigated. The correlation between structural evolution and mechanical behavior was discussed.

3:50pm **B4-2-8 Transition Metal Nitrides Deposition by HiPIMS in DOMS Mode*, João Oliveira,*** *F Ferreira, R Serra, F Fernandes, A Cavaleiro,* University of Coimbra, Portugal

Transition metal nitrides (TMD) coatings are well known for their unique combination of outstanding mechanical properties (hardness and Young's modulus), high thermal and chemical stability and excellent resistance to wear and corrosion. TMD are commonly used in industry to improve the performance and enhance lifetime of tools and components in a wide range of applications, including automotive, energy, electronic, and machining applications. During the past decade huge investments have been made aiming at further improving their properties and thus reduce the costs due to wear and corrosion. High-power Impulse Magnetron Sputtering (HiPIMS) is a recently developed deposition process that already demonstrated a huge potential for coatings properties improvement. HiPIMS relies on the application of very high target power densities to ionize the sputtered material and thus allows a more effective control of the bombarding species during film growth than in D.C. Magnetron Sputtering (DCMS). In this work the properties of TMD thin films deposited by Deep Oscillations Magnetron Sputtering (DOMS), a variant of HiPIMS, are summarized and compared to their DC MS counterparts. Results obtained in four different coatings systems (CrN, TiN, TaN and TiSiN) are presented and discussed in light of the Ion Energy Distributions of metal and gaseous species impinging on the growing films.

The TMD coatings were deposited using a wide range of deposition conditions leading to very different bombardments regimes. The effect of the peak target power on the films properties was systematically studied. The structure, morphology, surface topography and mechanical properties of the films were characterized and related to the bombarding conditions.

It was concluded that HIPIMS-DOMS allows using different sets of energy and incidence angle of the bombarding species as compared to DCMS and, therefore, enables the deposition of thin films with improved properties.

4:10pm **B4-2-9 Advanced HIPIMS Solution for R&D and Process Development*, Jason Hrebik,*** Kurt J. Lesker Company, USA*; R Bandorf,* Fraunhofer IST, Germany

When HIPIMS was first introduced to the thin film coating industry, it was considered an advanced technique for production applications, which would provide optimal film properties and wear resistance. The HIPIMS supply options were very large scale directly suited to the production industry. However, it was found to have significant limitations in rate, which minimized its acceptance in production applications.

Recently, the introduction of smaller scale supplies triggered an emergence of the technology into the R&D community. This enabled a high rate of enhancements and helped innovate a more efficient capability and process optimization that could be utilized by HIPIMS supplies. This ultimately re-energized the interest and potential of HIPIMS in the thin film coating industry.

One of the solutions to emerge from the crowd was the IMPULSE supply, which brings a unique range of features to the HIPIMS community. The IMPULSE is a 2kW supply that is offered in a single and dual configuration. It features touch panel controllability, the fastest pulse frequency, 200A peak current, and the most competitive pricing in the industry. The supply is slave capable and can be scaled from its 2kW standard configuration by adding additional units. This makes it an excellent option for process development.

Test results will be shared that show its unique performance capabilities and compatibility with higher scale power requirements.

4:30pm **B4-2-10 Determining of the Critical Loads of Transition Metal Nitrides on Steels*, Aysenur Keles,*** Ataturk University Faculty of Engineering, Turkey*; H Cicek,* Erzurum Technical University, Turkey*; O Baran,* Erzincan University, Turkey*; Y Totik, I Efeoglu,* Ataturk University, Turkey

Transition metal nitride coatings are very attractive materials due to their hardness and toughness. On the other hand, adhesion properties of these coatings are generally low because of their brittleness. To overcome this disadvantage, this type of coatings are produced with different coating techniques. In this work, V and Nb doped ternary TiN-based coatings were deposited on M2 and H13 substrates with pulsed-dc closed field unbalanced magnetron sputtering (CFUBMS) system. The films microstructure were examined by SEM. The thicknesses of the films changed from 400 nm to 360 nm. The maximum nano hardnesses were meausred 35 GPa and 26 GPa for M2 and H13 steels, respectively. The critical load values of the coatings were pointed out using scratch tester. For M2 steel; the highest Lc value was obtained 63 N and for H13; the highest Lc value was obtained 47 N. It was cleary seen that pulsed-dc created very dense microstructure and utilized to improve the adhesion of transition metal nitride coatings on the steels.

4:50pm **B4-2-11 Tribocorrosion Behaviour of Nanocomposite TiSiCN Coatings Tested in PBS Solution*, Andre Hatem,*** Pontifícia Universidade Católica do Paraná, Brazil*; J Lin, R Wei,* Southwest Research Institute, USA*; R Torres, C Laurindo, P Soares,* Pontifícia Universidade Católica do Paraná, Brazil

Recent articles have investigated the tribological performance of nanocomposite TiSiCN coatings mainly because of their high hardness, low friction coefficient and good adhesion to many substrates, especially, when compared to other ternary system coatings (TiSiN, TiCN). These properties are mainly attributed to the microstructure of the nanocomposite TiSiCN coatings which generally consists of TiC_xN_y nanocrystals embedded in an amorphous Si_3N_4 matrix. The proportional between these phases is much related to the silicon content presented in the coating. Higher silicon contents increase the amorphous matrix and hence decrease the nanocrystals size, which to some extent, provide nanocomposite TiSiCN coatings with higher hardness. Despite the nanocomposite TiSiCN coating appears as interesting candidate for severe wear applications, there are few wear studies under corrosive environments. Therefore, the main purpose of this study is evaluate the tribocorrosion performance under phosphate-buffered saline (PBS) solution of nanocomposite TiSiCN coatings with different silicon contents applied on Ti-6Al-4V samples. Plasma enhanced magnetron sputtering (PEMS) of Ti in a gas mixture of Ar, N_2 and silicon precursors, trimethylsilyl (TMS) and hexamethyldisilazane (HMDSN), were utilized to obtain the nanocomposite TiSiCN coatings in this study.

The coatings silicon content could be varied by controlling the inlet flow of silicon precursors in the deposition chamber. Reciprocal sliding tribocorrosion tests were conducted under PBS solution on the nanocomposite TiSiCN coatings and compared to a Ti-6Al-4V bare alloy sample. Moreover, microstructure and composition of the coatings were evaluated using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectroscopy while mechanical properties were studied by scratch and nanoindentation tests. The results of tribocorrosion tests revealed that exists an optimal silicon content range where occur much lower wear rates. The same behaviour was observed to the mechanical properties of the samples in this same silicon content range. In conclusion, the TiSiCN nanocomposite deposited by PEMS emerge as a new generation of quaternary system coatings that promise high wear performance in corrosive environment since their deposition parameters are optimized for a desirable proportion between the nanocrystalline and amorphous phases.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-2

CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

8:00am **B2-2-1 Investigation of Ti-based Hard CVD Coatings on Various Metals Suited as Alternate Binder Phase for WC-Co Cutting Tools***, **Linus von Fieandt**,* Uppsala University, Angstrom Laboratory, Sweden*; E Lindahl,* Sandvik Coromant R&D Materials and Processes, Sweden*; T Larsson,* SECO Tools, Sweden*; M Boman,* Uppsala University, Angstrom Laboratory, Sweden

Titanium based CVD coatings such as TiN, TiC and Ti(C,N) have been successfully applied as wear resistant coatings on WC-Co cutting tools for almost six decades. Recent research activities for WC based tools aims towards replacement of the Co binder phase, being a suspected carcinogenic. Other metals e.g. Ni and Fe are therefore suggested as possible candidates to replace Co as binder phase.

It is expected that CVD Ti based coatings grown on WC tools with e.g. Fe or Ni as the binder phase will show different nucleation and texture development compared to a conventional WC/Co substrate. The difference in nucleation and initial growth is believed to be attributed to the catalytic properties and reactivity of the binder phase. As such, it is fair to assume that the growth process of the coating needs to be altered in order to facilitate a growth of a controlled morphology and orientation.

Another aspect to be addressed is the coating adhesion. Adhesion is promoted by a low chemical reactivity and a limited diffusion between the binder phase and the coating. Salt like reaction products and brittle intermediate phases are examples of reaction products that can cause poor adhesion.

In this study Ti – based coatings were deposited on various metallic substrates such as; Fe, Ni, Co and Cr using a hot wall CVD equipment. Nucleation, orientation evolution and composition of the deposited layers were investigated. It was found that deposition on pure Ni resulted in a sponge like porous morphology. Deposition on Cr yielded a bimodal morphology with standing platelet crystallites. The coated Fe substrate showed presence of Fe in the deposited coating, which is believed to be caused by substrate corrosion. The conclusions from the experimental results have been supported by thermodynamic calculations.

8:20am **B2-2-2 Hot Filament CVD Diamond Coatings on Cutting Tools for Hard to Machine Materials***, **Michael Woda**, W Puetz, M Frank, B Mesic, W Koelker, C Schiffers, O Lemmer,* CemeCon AG, Germany

Low-pressure thin film CVD diamond synthesis using either microwave or hot filament excitation is a well suited deposition technique for pure sp3 bonded polycrystalline diamond coatings with a large number of various applications on an industrial scale. Most prominent, hot filament CVD diamond coated tools with complex geometries are typically applied at cutting of a certain class of hard to machine materials. Various case studies addressing deposition technology, coating properties and tool performance on some of these materials including graphite, glass-epoxy substances for printed circuit boards (PCB), silicon containing aluminum alloys (with Si larger ≈ 9%), carbon fiber reinforced plastics (CFRP), sintered ceramics or cemented carbides are presented in the scope of this presentation.

8:40am **B2-2-3 Nanocluster Assisted Mesoplasma Epitaxial Bridging***, R Yamada,* The University of Tokyo, Japan*; S Wu,* Chinese Academy of Sciences, China*; **Makoto Kambara**,* The University of Tokyo, Japan

Silicon epitaxial films can be deposited by mesoplasma CVD at rates faster by one order of magnitude than the conventional thermal CVD. In this process, Si source gas is first decomposed completely in the mesoplasma and Si nanoclusters form during rapid condensation as actual deposition precursors just before arriving on the film growth surface [1,2]. Owing to the nanoclusters' unique loosely-bound structure, Si nanoclusters are plausibly deposited on a film with high sticking probability to lead to high deposition rate, while maintaining epitaxial film formation as a result of spontaneous and instantaneous rearrangement of constituent Si atoms upon impingement on substrate. Fast rate epitaxy is also observed covering the SiO_2 mask on Si wafer, suggesting that nanoclusters can also be the growth precursors for lateral epitaxial overgrowth (LEO), i.e. the lateral extension of the epitaxial film. This allow us to anticipate that Si substrate with concave grooves with certain appropriate width could be covered by the epitaxial film that overgrows epitaxially from the adjacent Si region. In this work, we have first employed molecular dynamic (MD) simulation to evaluate the feasibility of the epitaxial film coverage over the nano-sized trench by the cluster assisted mesoplasma CVD for the potential epitaxial bridging. Secondly, Si epitaxial film depositions were also attempted on the Si wafers with porous surface under the typical epitaxial condition.

In brief, in the MD simulation, Si cluster that forms during rapid condensation of high temperature Si vapors is injected from the top at random position and impinges on the nanosized trench with a 100% sticking. It is seen that the Si clusters form the projecting edge from each trench wall and eventually these edges meet and create continuous film, leaving an open space underneath, as expected generally from the coverage phenomena of the trench with high-sticking species. It is however interesting that the film atomic structure preserves the epitaxial relationship from the side single crystal trench wall, indicating the possibility of epitaxial bridging and thus the feasibility of epitaxy over nothing (EON). In addition, smooth epitaxial films are actually deposited on the Si substrate having porous structure that is created by anodic etching, which could be an experimental evidence of feasibility of nanoclusters assisted fast rate epitaxial bridging.

9:00am **B2-2-4 Low Pressure Chemical Vapor Deposition of hex-BN: Relationship between Gas Phase Chemistry and Coating Microstructure***, P Carminati,* LCTS-CNRS, France*; T Buffeteau, N Daugey,* ISM-CNRS, France*; G Chollon,* LCTS-CNRS, France*; F Rebillat,* LCTS-University of Bordeaux, France*; **Sylvain Jacques**,* LCTS-CNRS, France

In the last few years, BN has become the most promising alternative to pyrocarbon as an interphase material in non-oxide ceramic matrix composites (CMCs) for the next generation of aircraft engine parts. Indeed, the use of BN interphases should improve the mechanical properties and lifetime of SiC-based CMCs under oxidative environment at high temperature. Such BN coatings are often deposited by low pressure chemical vapor deposition (LPCVD) from BCl_3–NH_3 gas system. But in this case, an insufficient degree of crystallization can make the obtained boron nitride too unstable to environment. Furthermore, little is known about the deposition mechanisms and their impact on the BN microstructure.

In the present work, the effects of deposition temperature and total flow rate on the microstructure of BN coatings deposited from BCl_3–NH_3–H_2 gas mixtures at low pressure have been studied. From X-ray diffraction measurements and transmission electron microscopy observations, the coatings appear heterogeneous, i.e. made of a mixture of poorly and highly crystallized domains on a very local scale. The structural homogeneity, as well as the degree of crystallization depends on the deposition chemistry (diluent gas, depletion of gaseous species...). For two given sets of deposition parameters, a comparison with BCl_3–NH_3–Ar system was made and the examined coatings exhibit a higher degree of crystallization and a better structural homogeneity than those deposited with H_2 as the diluent gas.

Ex-situ Fourier transform infrared (FTIR) measurements have been carried out on the residual gas mixture at the outlet of the LPCVD reactor in order to detect the species leading to poorly or highly organized BN. The measurements were coupled with ab initio vibrational mode calculations and they allowed the detection and identification of an effective gaseous precursor for highly crystallized BN ex-BCl_3 deposition. The concentration evolutions of the species into the residual gas mixture were also studied as a function of the deposition temperature and total gas flow rate. The NH_3-free system with hydrogen has also been studied by FTIR and results have shown the formation of $BHCl_2$, even at temperatures lower than BN deposition temperatures. This species seems to be an intermediate molecule that reacts further with NH_3 to also form BN. It is thus suspected of being be the source of poorly crystallized domains into BN coatings deposited from BCl_3–NH_3–H_2 gas mixtures. Finally, assumptions have been put forward to identify the main reaction paths leading to BN.

9:20am **B2-2-5 High-speed Structural Control for Functionalization of Various Oxide Films***, **Akihiko Ito**,* Yokohama National University, Japan **INVITED**

We have demonstrated that an intense laser field enhances chemical vapor deposition (CVD) process and the developed process achieves not only a **high-speed deposition** but also a **significant orientation growth** in various kinds of ceramic coatings. In addition, the developed coating technology produces **unique nanostructures**, which exhibit outstanding properties. For example, Al_2O_3, TiO_2 and ZrO_2 are traditional engineering ceramics, but they are still highly valued as practical materials. Functionalization of their films with the control of orientation and microstructure is of great interest in both of academic and industrial aspects.

This talk will introduce you to recent topics on high-speed structural control for functionalization of various oxide films with CVD technology, including orientation control of α-Al_2O_3 films, feather-like structures in β-Al_2TiO_5 films, nanodendrite formation in Al_2O_3–ZrO_2 nanocomposite films, superstructure in Ba β-alumina films, high-speed epitaxial growth of transparent CeO_2 thick films, H_2 generation in $NaTaO_3$ photocatalytic films, and development of Yb–Si–O environmental barrier coatings for SiC/SiC composite in a gas turbine engine.

This work was supported in part by KAKENHI, Japan Society for the Promotion of Science, and Cross-ministerial Strategic Innovation Promotion Program (SIP), "Structural Materials for Innovation, SM^{4}I (Funding agency: JST)".

10:00am **B2-2-7 Protective Coatings Enabled by Atomic Layer Deposition Processing**, ***Christopher Oldham**, J Daubert, G Parsons,* NC State University, USA

Thin film materials for corrosion mitigation is an ongoing area of research and development. Recently several groups have explored using atomic layer deposition (ALD) as a process to form highly conformal protective coatings for metal surfaces. ALD offers unique advantages for depositing uniform coatings in high aspect ratio designs. For corrosion protection applications ALD has been used to protect metal surfaces using common metal oxides materials such as alumina and titania. However, for protection in aqueous environments some ALD coatings etch or dissolve. Other issues with poor nucleation on metal surfaces leads to coatings with high porosity that can compromise the underlying metal surface in corrosive environments. In this presentation we will discuss results on protecting copper and other metals with metal oxide and multi-layer structures deposited by ALD. Results from the surface morphology and electrochemical performance will be presented along with a discussion of using ALD coatings to protect metallic surfaces with challenging coating geometries.

10:20am **B2-2-8 Chromium Carbide Growth at Low Temperature by a High Efficient DLI-MOCVD Process in Effluent Recycling Mode**, *A Michau, **Francis Maury**,* CIRIMAT, France*; F Schuster,* CEA Saclay, France*; R Boichot, M Pons,* SIMaP, University of Grenoble Alpes, CNRS, France*; E Monsifrot,* DEPHIS, France

For a better control of production cost of manufactured objects that comprise CVD coatings, the improvement of the economic productivity of deposition processes is a challenge. The increasing use of metalorganic precursors is a way to improve the economy of the process because this greatly lowers the deposition temperatures leading to substantial energy savings. When expensive molecular precursors as for precious metals are used the by-products are collected at the exit of the CVD reactor then the leading recyclers and traders develop in parallel complex effluent treatments to refine and reused the collected precursors after removing trace contaminants. This approach is also applied in high volume CVD production facilities. For instance a hydrogen recycle system was proposed for CVD of poly-Si. Also in the growth of Si for solar cells the exhaust gases (H_2, HCl, chlorosilanes) were collected, separated and recycled. Generally these strategies reduce the production cost but they did not act directly on the CVD process.

To develop large-scale CVD processes using expensive reactants direct recycling of precursor become necessary to achieve a high conversion yield. However direct recycling of effluent using metalorganic precursors was not reported because the quality of the layers strongly depends on the metal source and these compounds undergo complex decomposition mechanisms producing many unstable metal-containing by-products.

The bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V, Nb, Ta) are an important family of CVD precursors for low temperature deposition of carbides, nitrides and even the metal. A greater knowledge of the growth mechanism, a modeling approach and the use of direct liquid injection (DLI) to feed the MOCVD reactor has led us to study the effect of direct recycling of effluents on the quality of chromium carbide coatings using bis(ethylbenzene)chromium(0). The results are compared with those obtained using a fresh solution of precursor. Interestingly, both coatings are amorphous in the temperature range 400-550°C; they exhibit a smooth surface morphology, a dense structure, the same chemical composition (close to Cr_7C_3) and a high hardness (23-29 GPa). The main criteria for the selection of MOCVD precursors enabling a successful direct recycling are discussed. It was demonstrated that direct recycling of effluents for instance in a recycle loop is an efficient route to improve the economy of DLI-MOCVD which makes this process very competitive for the deposition of this important class of carbide protective materials.

10:40am **B2-2-9 Growth and Characterization of SiO_x Thin Film Deposited by Plasma Enhanced CVD on a Magnesium Alloy**, ***Hyunju Jeong**, J Cho,* POSCO (Pohang Iron and Steel Company), Republic of Korea

Magnesium alloys have good properties such as low density and high thermal conductivity, but their applications are still limited due to their poor surface quality and corrosion resistance. Even though many studies have been suggested to characterize their surface properties and protect the surface using a variety of techniques, it is necessary to furthermore undertake investigations in order to apply them into various industrial applications, resulting in the improvement of surface properties.

In some industrial application, it is required to employ coating techniques which fabricate transparent coating layers which also act as barrier coating layer against gas and vapor permeation. Chemical vapor deposition (CVD) is known as one of promising coating techniques to form good quality thin films such as passivation films in various industrial areas. Most of all, low temperature processes have advantages of cost reduction, productivity and substrate stability. It is well known that plasma enhanced chemical vapor deposition (PECVD) is less dependent on substrate temperature than conventional CVD, leading to good quality films at relatively low temperature below 300°C.

In the present work, SiO*x* films as transparent and passivation layers were fabricated on the surface of a magnesium alloy using a PECVD technique. Particularly, magnesium and magnesium alloys have material properties such as high surface activity and high thermal conductivity. Such characteristics possibly have an influence on growth of films as well as interface of the films and substrates during PECVD. Therefore, we undertook an investigation to characterize growth and characterize the interface of SiO*x* films and a magnesium alloy. FETEM results displayed thin films grown at the interface of a SiO*x* film and magnesium alloy at substrate temperature of 50 and 300 °C where the thin films tended to be grown as deposition time. XPS analysis revealed that an outer layer close to SiO*x* films was mainly composed of SiO2 and $Mg(OH)_2$ whereas an inner layer close to magnesium substrates consisted of $Mg(OH)_2$ and MgO.

The structures on the surface were evaluated using field emission scanning electron microscopy (FESEM). The cross sectional compositions and structures were examined by field emission transmission electron microscopy (FETEM), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS). The detail compositions at the interface of films and AZ31 magnesium alloy were discussed using X-ray photoelectron spectroscopy (XPS) measurements.

Keywords: thin films; SiO_x; PECVD ; Magnesium alloys

11:00am **B2-2-10 Electrochemical Behavior of Graphene Coatings Deposited on Copper Metal by Electrophoretic Deposition and Chemical Vapor Deposition**, ***Mohsin Ali Raza**, A Ali, F Ali Ghuari, A Aslam, K Yaqoob, A Wasay,* University of the Punjab, Pakistan*; M Raffi,* National Institute of Lasers and Optronics, Pakistan

Graphene gains utmost importance for electronics, composites, sensors and biological applications due to its remarkable properties. The attributes such as two dimensional morphology, chemical inertness, high specific surface area and aspect ratio make graphene a promising candidate for anticorrosive coatings. Graphene has ability to retard electrochemical reactions occurring at metal-electrolyte interfaces by acting as a barrier to aggressive ions. This work aims to compare electrochemical performance of graphene coatings deposited on copper metal (Cu) by electrophoretic deposition (EPD) and chemical vapor deposition (CVD) technique. In the CVD process, graphene coatings were deposited on Cu by passing vapors of sodium ethoxide and argon gas (carrier gas) through a quartz tube at a temperature of 900 °C. In the EPD process, graphene was deposited on Cu, made as anode, from a suspension of graphene oxide and water. The EPD deposition process partially reduced graphene oxide and further reduction was achieved by heating coated samples at 200 °C or by treating coatings with hydrazine solution. The coatings were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and Raman spectroscopy. FTIR analysis revealed that graphene coatings produced by EPD had more oxygen bearing functional groups compared to coatings deposited by CVD. CVD-based graphene coatings had higher adhesion to the substrate than that of EPD-based coatings. AFM images showed that thickness of coatings increased as a function of deposition time. The electrochemical behavior of coatings was studied using tafel analysis and electrochemical impedance spectroscopy techniques in 3.5% NaCl solution. The CVD-based graphene coatings performed better than that of EPD coatings and reduced corrosion rate of Cu. The CVD coatings remained intact even after aggressive corrosion testings, while EPD based coatings showed some damage. The comparative study of the electrochemical behavior of graphene coatings clearly demonstrates that graphene coatings deposited by CVD process using sodium ethoxide as percursor are superior to coatings deposited by EPD process using graphite oxide as precursor.

11:20am **B2-2-11 Characterization of Coated Silane Compounds on Aisi 304 Stainless Steel Using Plasma-Oxide Vapour as Adhesion***, **Damilare Baruwa**,* University of Johannesburg, South Africa*; P Oladijo,* Bostwana International University of Science and Technology, Botswana*; J Chinn,* Integrated Surface Technologies, Inc., USA*; N Maledi,* University of the Witwatersrand, South Africa*; E Akinlabi,* University of Johannesburg, South Africa

Quest for safe, low cost and reliable coating has led to the alternative development of various chemical compounds of silane in order to mitigate corrosion process and reduce the risk of carcinogenic compounds that have been previously employed in hexavalent chromium-based coating materials. Silane is a hydrophobic and hydrophilic chemical compound, but with contact angle above 110° is hydrophobic. The present study was conducted to determine the influence of silane coating on AISI 304 stainless steel. In this study, three different saline-based coatings of composition [Tris(Trimethylsiloxy)silyethyl]dimethylchlorosilane (Alkyl); Tridecafloro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) and Henicosyl-1,1,2,2-tetrahydrododecyltricholrosilane (FDDTS) were deposited on 304 stainless steel. The surface of the substrate was grit-blasted by plasma oxide (vapour) adhesion by using nano-composite structures with a hybrid Atomic Layer Deposition (ALD) and Chemical Vapour Deposition (CVD) process. This investigation present results on microstructure (Optical microscopy, SEM/EDX), mechanical test (EMCO Hardness Tester, ultimate tensile strength, yield strength), chemical phase content (XRD), porosity and the electrochemical corrosion behavior of different silanes coating on AISI 304 stainless steel. The results showed that the coating characterization and their corrosion behavior were different to that of AISI 304 stainless steel which was addressed in the study.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-3-1 Aspects of Thermal Stability of TiAlN and ZrAlN***, **Magnus Odén**,* Linköping University, (IFM), Sweden **INVITED**

Today TiAlN material system is the industrial standard for arc deposited protective coatings of metal cutting inserts. A striking feature of this system is that is possible to produce kinetically stabilized while thermodynamically unstable solid solutions inside its miscibility gap by for example arc deposition. A beneficial segregation at elevated temperatures results in improved mechanical properties while a too high temperature causes a detrimental phase transformation to w-AlN. ZrAlN is a related material system with a larger miscibility gap and consequently a stronger driving force for segregation.

In this presentation I will review our efforts to extend the working envelope to higher temperatures. In particular I will discuss the influence of external parameters such as temperature [1] and pressure [2] on the rate of decomposition, and also means to affect the decomposition rate and route. The latter includes aspects of internal interfaces [3], additional alloying elements [4], and nitrogen vacancies [5].

[1] N. Shulumba et al. Phys Rev. Lett. (2016) & A. Knutsson et al. J. Appl. Phys. (2013).

[2] N. Norrby et al. J. Appl. Phys. (2013) & N. Shulumba et al. Phys Rev B. (2016).

[3] K. Yalamanchili et al. Acta Mater. (2016) & F. Wang et al. Phys. Rev. B. (2016).

[4] H. Lind et al. Appl. Phys. Lett. (2011).

[5] I.C. Schramm et al. Acta Mater. (2016).

8:40am **B4-3-3 Effects of Treatment Temperature and Gas Blow Velocity of IH Nitriding on Microstructure of Titanium Alloy***, **Shogo Takesue**,* Keio University, Japan*; S Kikuchi,* Kobe University, Japan*; H Akebono,* Hiroshima University, Japan*; K Fukazawa,* Netsuren Co., Ltd., Japan*; J Komotori,* Keio University, Japan

We have recently developed a gas-blow induction heating (IH) nitriding system, which is a combination of IH and blowing nitrogen gas onto a specimen in a nitrogen atmosphere. This system is capable of nitriding titanium alloys within a few minites, a process that normally requires tens of hours. We previously reported that the nitriding process caused an increase in the surface hardness and wear resistance, but a degradation of the fatigue properties of the alloys. The latter was attributed to grain coarsening and a phase transformation due to an elevated treatment temperature of 900°C. The aim of the present study was to examine the possibility of suppressing these effects by varying the nitriding temperature. The surface properties were analyzed using an X-ray diffractometer, an optical microscope and a scanning electron microscope. In order to characterize the surface modified layers, the surface roughness and micro-Vickers hardness of the specimens were measured. The results showed that grain coarsening and phase transformations were suppressed when the nitriding process was carried out at a lower treatment temperature of 700°C. A high hardness nitrided layer was formed on the surface of the specimen when the gas blow velocity was increased through the use of a smaller diameter gas blow nozzle. The wear resistance of the nitrided specimen at a low temperature and a high gas blow velocity was better than that of the untreated specimen.

9:00am **B4-3-4 Oblique Angle Deposition of Nanostructured ZrC Thin Film by Reactive Magnetron Sputtering and its Effect on Structure and Mechanical Property***, **SathishKumar Shanmugam**, A Sharma, M Gowravaram, S Suwas,* Indian Institute of Science, India

Zirconium carbide films were grown from a Zr target in a mixture gas of Ar/CH_4 on Si (100) substrate by oblique angle reactive magnetron sputtering technique. The influence of glancing angle ($\alpha = 0^\circ$ to 75°) induced anisotropic growth rate of crystallographic planes and the mechanism involving the morphological development of oblique angle deposited zirconium carbide films have been investigated. The crystalline structure and the composition were determined by XRD and XPS, respectively. The changes in morphology, surface roughness in oblique incidence have been further investigated by HRSEM and AFM, respectively. The relative intensity of (111), (200) and (311) X-ray Diffraction peaks of fcc crystal structure vary significantly with deposition angle. The mean crystallite size of the obliquely sputter deposited films was found to be larger than that of the films sputter deposited conventionally. Anisotropic growth rate of crystallographic planes during oblique incidence lead to the evolution of faceted growth in the film with subsequent increase in RMS surface roughness. The hardness and Young's modulus decreased with increase in deposition angle, due to highly porous microstructure. Correlation was drawn between the film's hardness and reduced Young's modulus obtained by nanoindentation with changes in the microstructure.

9:20am **B4-3-5 The Influence of Al Content on Characteristics of CVD-Aluminum Titanium Nitride Films***, **Kenichi Sato**, S Tatsuoka, K Yanagisawa, T Ishigaki, K Yamaguchi, S Nishida,* Mitsubishi Materials Corporation, Japan

Recently, Aluminum Titanium Nitride ($Al_xTi_{1-x}N$) films deposited by thermal CVD method using ammonia gas has been paid much attention to because some papers have reported their good results in milling of alloy steels and cast irons. One of the biggest characteristics of these films is the amount of Al. It is higher than that of AlTiN films deposited by PVD method. It is well-known that conventional AlTiN films deposited by PVD method have cubic structure in the range of Al content lower than about x=0.7, while they obtain hexagonal structure in the range of Al content higher than x=0.7. However, CVD-AlTiN films keep cubic structure in Al content higher than 0.7, which prevents their cutting properties from getting worse. The amount of Al is one of the most important factors which determine cutting properties, because it affects mechanical properties such as hardness, adhesion and so on. We have focused on the influence of Al content of AlTiN films deposited by thermal CVD method using ammonia gas on their characteristics such as hardness and microstructure.

In this research, CVD-AlTiN films whose Al content were different from each other were deposited and evaluated. It was clarified that each CVD-AlTiN film deposited in this research had nano-size particles and showed high (100) orientation from observation by Scanning Electron Microscopy and X-ray Diffraction. Also, they have lamellar structure due to change of Al content. From the nano-indentation test, it was found that the hardness increased as the amount of Al increased although AlN film showed low hardness because it has hexagonal structure softer than cubic structure. In addition, the result of micro scratch tests showed there was no detachment of each CVD-AlTiN film loaded up to 30N and this result implied that CVD-AlTiN films have good adhesion to substrate of WC-Co alloys. Finally, some cutting tests of these films and conventional CVD and PVD films were performed and CVD-$Al_{0.8}Ti_{0.2}N$ film showed the best result.

9:40am **B4-3-6 Wear Resistance Capabilities of B-C-W Coatings***, **Heidrun Klostermann**, M Friedemann,* Fraunhofer FEP, Germany*; M Ottersbach, D Schraknepper,* Fraunhofer IPT, Germany*; J Poetschke, M Mayer,* Fraunhofer IKTS, Germany*; F Fietzke, O Zywitzki,* Fraunhofer FEP, Germany

The present study deals with the evaluation of B-C-W coatings as potential candidates for wear resistance in the cutting of cemented carbides. Comprising different hard materials like boron carbide B_4C, tungsten carbide WC, tungsten boride WB as well as a certain solubility of tungsten in B_4C, deposition of coatings from this material system seems promising for wear resistant applications. Especially, these coatings can combine high hardness, high resistance to crack formation and crack propagation, good thermal stability and low friction. In search for wear resistant layers that are suitable for the cutting of difficult to cut materials like high temperature alloys or cemented carbides,coatings in the system B-C-W have been synthesized by pulsed magnetron co-sputtering of boron carbide (B_4C) and tungsten (W), where the tungsten content can be varied by adjusting the duration of sputtering pulses. Whereas coatings with low tungsten content of up to 25 at-% exhibit high hardness but are prone to oxidation, increasing tungsten content to 30…65 at-% results in stable coatings. Such coatings have been deposited on special analogy tools as well as on polished reference samples made of ultrafine cemented carbides both.

With the coated tools, analogy machining experiments are conducted on a specially developed orthogonal cutting test bench for tool analysis with an integrated force measurement unit and a high speed video camera. With this setup it is possible to gain relevant process data about the potentials of the newly developed coating systems for cutting of a coarse grain WC-25Co cemented carbide by evaluating the chip formation mechanisms of the workpiece, the cutting forces and the wear behavior of the tools. Conclusions are drawn regarding the relation between coating composition, coating structure and the performance in cutting processes.

10:00am **B4-3-7 Micromechanical Properties and Wear Resistance of Quaternary TiAl(X)N Alloys (X=Nb, Cr or V)***, **Yu-Hsiang Chen**, L Rogström,* Nanostructured Materials, IFM, Linköping University, Sweden*; J Roa,* Universitat Politècnica de Catalunya, Spain*; M Johansson-Jõesaar,* SECO Tools, Sweden*; M Anglada,* Universitat Politècnica de Catalunya, Spain*; M Odén,* Nanostructured Materials, IFM, Linköping University, Sweden

Hard coatings consisting of alloys such as TiAlN have been extensively studied and are widely used for high-speed cutting applications due to their superior high temperature properties. The thermal stability can be further improved by designing multi-component alloys via adding a forth element into the TiAlN coating [1]. The mechanical behavior of the coating is essential for improving the tool life in its cutting applications. However, the influence of the forth element on the coating's mechanical and tribological properties has not been fully studied.

In this study, $Ti_{0.33}Al_{0.50}(X)_{0.17}N$ coatings (X=Nb, Cr or V) were deposited by cathodic arc deposition to a thickness of 2-3 µm and analyzed with respect to their mechanical properties at different length scales in order to induce different stress levels to the coating system. All coatings exhibit a solid solution NaCl cubic structure with a columnar microstructure. Nanoindentation results show that TiAl(Nb)N presents the highest hardness among the quaternary alloys. Moreover, micro-scratch tests show similar critical load (~ 60 N) for the first appearance of decohesive coating damage (i.e. spallation of the coating system). However, there is a change in failure mechanism between the coatings, where the Cr and V alloyed coatings fails by recovery spallation, indicating relatively brittle coatings. While TiAl(Nb)N exhibits the most ductile behavior resulting in less damage on the coating surface. With increased scratch load (100 N), the TiAl(Nb)N coating also shows less cracks at the edges of the track. In addition, linearly reciprocating ball-on-flat sliding wear tests were done to investigate the wear resistance of coatings. The quaternary coatings show similar wear rates (~ 1.5×10^{-6} mm^3/Nm), while the reference alloy $Ti_{0.5}Al_{0.5}N$ presents a higher wear rate (4×10^{-6} mm^3/Nm). In summary, the TiAl(Nb)N coatings shows a combination of high hardness and a low wear rate in comparison to the other quaternary and the reference TiAlN coating. The results are discussed in terms of elastic properties, fracture toughness and wear behavior [2] of the coatings to determine the most promising quaternary coating system for cutting applications.

[1] Holec et al. / J. Appl. Phys. 113, 113510 (2013)

[2] A. Leyland et al. / Wear 246, 1–11 (2000)

10:20am **B4-3-8 High Resolution Lateral Force-displacement Measurements as a Tool for the Determination of Lateral Contact Stiffness and Poisson's Ratio***, **Thomas Chudoba**,* ASMEC GmbH, Germany

High resolution normal force-displacement measurements are used since more than 30 years for nanoindentation experiments to investigate indentation hardness and modulus perpendicular to the surface. However conditions in an application are often more complex and the understanding of surface or coating failures also requires the consideration of lateral forces. Further the Poisson's ratio, internal stresses or lateral inhomogeneity cannot be extracted from normal measurements alone. The Poisson's ratio of coatings is mostly not known and only an assumption is used to convert the reduced modulus (that is measured by nanoindentation) to the indentation modulus.

Since few years a lateral force unit can be used in combination with nanoindentation technique to measure lateral force-displacement curves also with nanometer resolution. This unit is not only a tool for friction force measurements. An internal actor like in a nanoindentation head allows the application of lateral forces without any requirement of lateral movement between indenter and sample beside a small elastic deformation. The transition between full sticking, the reduction of the contact area due to increasing shear stresses and the begin of sliding can be fully resolved. This transition range between sticking and sliding friction, which is typically connected with a lateral elastic deformation below 100nm, can be used to measure the lateral contact stiffness. The ratio of lateral and normal contact stiffness was used by Lukas et al. in a publication from 2004 [1] to derive the Poisson's ratio for several materials, but the results could not be confirmed by another group.

It will be shown that it is also possible to derive the Poisson's ratio for hard and smooth materials from a fit of the lateral curves in the reversal points when friction coefficient and contact area are accurately known. Finally some prospects will be given for further test options that result from the combination of high resolution normal and lateral force-displacement measurements.

[1] B.N.Lucas, J.C. Hay, W.C. Oliver, Using multidimensional contact mechanics experiments to measure Poisson's ratio, J. Mat. Res. 19 (2004) 58-65

10:40am **B4-3-9 Influence of a-Si:H Interlayer on the Adherence of a-C:H Coatings Deposited on Different Metallic Surfaces***, G Capote,* National University of Colombia, Colombia*; D Lugo,* Institute for Space Research, Brazil*; J Gutiérrez,* National University of Colombia, Colombia*; **VladimirJesus Trava-Airoldi**,* Institute for Space Research, Brazil

Amorphous hydrogenated carbon (a-C:H) films have been used as protective coatings in many applications due to their attractive properties. These hard coatings have relatively low adherence to metallic surfaces, caused by their high total compressive stress. In order to overcome this low adhesion, a thin amorphous hydrogenated silicon (a-Si:H) interlayer was used as an interface.

The influence of a-Si:H interlayer on the adherence of a-C:H coatings deposited on different metallic surfaces is presented in this investigation. Six metallic materials widely used in industry were used as substrates: (1) AISI M2 molybdenum high-speed tool steel; (2) AISI **D2 tool steel; (3)** AISI 304 stainless steel; (4) Nickel-based alloy INCONEL 718; (5) Nitinol alloy; and (6) Titanium alloy Ti6Al4V. The interlayers and the coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD system with an active screen. This active screen functioned as an additional cathode and allowed depositing the films at very low pressure in an almost collision-less regime with high plasma density. Silane gas was used as a precursor for interlayer depositions, while the acetylene gas was employed as a precursor for a-C:H film depositions. The interlayers were synthetized varying the applied negative pulse amplitude from -0.8 kV to -10 kV, keeping their thickness constant at 250 nm.

The adhesion of the a-C:H coatings was evaluated using the critical load of failure determined by a classical scratch test. Raman spectroscopy was used to analyze the films' atomic arrangements and for the hydrogen content calculation. The total compressive stress was determined through the measurement of the substrate curvature before and after the film deposition with a stylus profilometer, while nanoindentation experiments allowed determining the films' hardness and elastic modulus. The friction coefficients and the wear rates were measured using a tribometer in unlubricated sliding friction experiments, while the corrosion resistance was evaluated via electrochemical potentiodynamic polarization techniques.

The results showed high values of critical loads, suggesting a high degree of adherence of the a-C:H coatings to all metallic surfaces. The highest critical load values (≥ 25 N) resulted when the a-Si:H interlayers were deposited using the highest negative voltage (from -6 kV to -10 kV). The best adhesion was obtained for the Nitinol alloy surfaces. A combination of a modified pulsed-DC PECVD system with an active screen and a-Si:H interlayer allowed depositing hard, adherent, low-stress, high wear, and corrosion-resistant a-C:H coatings on different metallic surfaces.

11:00am **B4-3-10 Reactive Magnetron Sputtering of Transition Metal Nitrides for Electronic and Opto-Electronic Applications***, **Amber Reed,*** Air Force Research Laboratory, USA*; H Smith,* University of Dayton and Air Force Research Laboratory, USA*; M McConney, D Look, D Abeysinghe, V Vasilyev, J Cetnar, B Howe,* Air Force Research Laboratory, USA

With their inherent high temperature stability, hardness, abrasion resistance, and potential complimentary metal-oxides semiconductor process compatibility, transition metal nitrides are a promising material system for next generation electronic and opto-electronic devices. Two materials of specific interest are titanium nitride (TiN) and scandium nitride (ScN). Due to its higher thermo-mechanical robustness and lower losses compared to gold, titanium nitride (TiN) is an ideal material for plasmonic applications, while ScN has integration potential into gallium nitride - based devices due to its close lattice matching with GaN (< 1% lattice mismatch), high carrier concentrations (up to 10^{21} cm^{-3}) and low resistivity (<10^{-4} Ω cm^{-2}). The crystalline quality of these materials greatly affects their performance with low defect single crystals having higher figures of merit for both applications.

In this work, we demonstrate the synthesis of high quality epitaxial TiN and ScN films deposited on (001)-oriented magnesium oxide (MgO) and (0001)-oriented sapphire single crystal substrates using a newly built up controllably unbalanced reactive magnetron sputter epitaxy tool at AFRL. We investigate the role of deposition power, nitrogen gas fraction and ion flux impingement on crystallinity (i.e. degree of orientation, lattice constant and strain) and subsequently the films' optical and electronic transport properties. Films are characterized using x-ray diffraction (XRD), atomic force microscopy, transmission electron microscopy (TEM), Hall measurements and ellipsometry. Films are remarkably smooth (~100pm RMS roughness) and indicate step flow growth with little or no domain boundaries. XRD and TEM further demonstrate the exceptional film quality of epitaxial films on both MgO and sapphire substrates. Hall measurements of the TiN reveal mobilities (μ_H) > 20 cm^2/(V*s), carrier concentrations (N) >10^{23} cm^{-3}, resistivities (ρ) < 14 Ω-cm and metallic behavior. The crystallinity of the ScN films is strongly dependent on sputtering power; the highest quality films are obtained at 50 W. The electrical transport properties of the ScN are strongly affected by crystalline quality and film orientation. Films with a (001)-orientation have μ up to 85 cm^2/(V*s) while for the (111)-oriented ScN μ< 10 cm^2/(V*s).

11:20am **B4-3-11 Comparative Investigation of Zr-B-(N), Zr-Si-B-(N), and Zr-Al-Si-B-(N) Hard Coatings***, **Philipp Kiryukhantsev-Korneev,** M Lemesheva, I Yatsyuk, D Shtansky, E Levashov,* National University of Science and Technology "MISiS", Russian Federation

ZrB$_2$-based coatings demonstrate relatively high hardness and wear resistance, low friction coefficient but have low working temperature limited by 700-800^{0}C. It's well known that oxidation resistance of the boride coatings can be enhanced by Si and Al alloying. The goal of this work is a complex investigation of the Zr-B-(N), Zr-Si-B-(N), and Zr-Al-Si-B-(N) coatings, including estimation of high-temperature tribological characteristics, thermal stability, oxidation resistance, and diffusion barrier properties.

The ZrB$_2$, ZrSiB, and ZrAlSiB cathodes produced by self-propagation high-temperature synthesis technology were subjected to magnetron sputtering either in a pure Ar and N$_2$ atmosphere, or in a gaseous mixture of Ar+15%N2. Molybdenum, quartz, alumina, NiCrAlW and WC-Co alloys were used as substrate materials. To evaluate the high-temperature oxidation resistance the coatings were annealed in air atmosphere at various temperatures range from 500 till 1500^{0}C. The structure of as-deposited and heat-treated coatings was studied by means of X-ray diffraction, scanning and transmission electron microscopy, glow discharge optical emission spectroscopy, Raman and FTIR spectroscopy. The mechanical properties of the coatings were measured by nanoindentation and scratch-testing. The tribological properties were evaluated using impact-tester and high-temperature ball-on-disc tribometer. Optical and electrical properties of coatings were also examined.

Results obtained show that Zr-Si-B-(N) and Zr-Al-Si-B-(N) coatings deposited at low nitrogen partial pressure consist of nanocrystallites of hexagonal ZrB$_2$-phase, 1-3 nm in size (3-5 times smaller compared to undoped coating) and amorphous regions. N-rich coatings exhibit fully amorphous structure. The maximum hardness 26 GPa, Young's modulus 260 GPa, and elastic recovery 60% were determined for Zr-Si-B-(N) coatings deposited in Ar-15%N2. The addition of nitrogen significantly increased wear resistance in sliding and impact conditions. Maximal oxidation resistance (Tox>1400°C) was achieved for low-nitrogen Zr-Si-B-(N) coatings. High protective properties of Zr-Si-B-(N) coatings are due to formation of dense SiO$_2$ top-layer reinforced with ZrO$_2$ nanoparticles which impedes penetration of oxygen into the depth of coating. The mechanical properties and oxidation resistance of Zr-B-(N) and Zr-Al-Si-B-(N) coatings were markedly lower compared to Zr-Si-B-(N) deposited at the same nitrogen partial pressure. Combination of relatively high hardness, good tribological properties, and high oxidation resistance makes Zr-Si-B-(N) coatings promising candidates for protective purposes to be used in high-temperature applications.

11:40am **B4-3-12 Multiphysics Modelling and Experimental Investigation on the Characteristics of Laser Deposited Al-Sn-Si Coatings on Ti6Al4V Alloy***, **Olawale Fatoba,*** University of Johannesburg, South Africa*; A Popoola,* Tshwane University of Technology, South Africa*; E Akinlabi,* University of Johannesburg, South Africa

Corrosion and wear phenomenon has been responsible for the gradual deterioration of components in industrial plants. This deterioration of components results in loss of plant efficiency, total shutdown and aggressive damage in a number of industries. Hence, surface modification and coating technique with enhanced surface properties is desirable. The investigation of Al-Sn-Si coatings by laser deposition technique is aimed at enhancing the properties of Al-Sn-Si coatings on Ti6Al4V alloy. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the alloying process was utilized for the fabrication of the coatings at optimum laser parameters. The fabricated coatings were investigated for its hardness, corrosion and tribological properties. The corrosion behaviour was investigated in 1M H$_2$SO$_4$ and 3.65wt.% NaCl solutions at 28^{o}C via Eletrcochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization techniques. The optical microscope (OM), field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The improved hardness and wear resistance performance were attributed to hard intermetallic compounds like Ti$_3$Al, Ti$_6$Sn$_5$ and Sn$_3$Ti$_5$. The coatings were free of cracks and pores with homogeneous and refined microstructures. The enhanced anti-corrosion performance was also attributed to monolithic Ti$_5$Si$_3$ phases formed. The experimental results correspond with COMSOL multphyics model used in this research.

Keywords: Corrosion rate; wear; Hardness; Al-Sn-Si coatings; multi-physics modeling, temperature fields.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-1

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa Ltd., USA, Klaus Böbel, Bosch GmbH

2:10pm **B3-1-3 New Pathways for Improving Adhesion of DLC on Steel in Low Temperatures***, L Leidens,* UCS and CAPES, Brazil*; Â Crespi,* UCS, Brazil*; F Alvarez,* IFGW-UNICAMP, Brazil*;* ***Carlos Figueroa,*** UCS, Brazil

Diamond-like carbon thin films (DLC) are state-of-art coatings that can have properties which are object of interest such as ultra-low friction coefficient, chemical inertness and low wear rates. Despite of its strident properties, the use of DLC is not yet fully widespread due to the poor adhesion of the film in some substrates, for example, plain and low-alloy steels. In order to improve DLC adhesion on steel, different interlayers have been proposed. On one hand, hybrid technologies containing a step of PVD deposition of a metal/metal nitride interlayer are industrially used, although its costs are high for several applications. On the other hand, PECVD technologies can produce silicon-containing interlayers, although the deposition temperatures that prompt adhesion as high as 300^{o}C. Previous works have pointed out that oxygen atoms act as terminator species in silicon-containing interlayers that diminish DLC adhesion on steel.

The aim of this work is to investigate new pathways of reaching high DLC adhesion by using silicon-containing interlayers in low deposition temperatures. In order to explore alternatives, a hydrogen plasma etching effect was analyzed in two different set of samples. [3] The first set look at analyzing the physicochemical processes due to hydrogen plasma interaction in the silicon-containing interlayer and, consequently, the interlayers were deposited with HMDSO at a constant temperature and time of 300°C and 10 min, respectively, varying the hydrogen etching time (0 to 10 min) at 85°C on AISI 4140 low-alloy steel. The second set look at analyzing the adhesion in low deposition temperatures and, consequently, the interlayers were obtained at different deposition temperatures (80 to 180°C) and the hydrogen plasma etching was performed at a constant temperature and time of 85°C and 6 min, respectively.

The samples were characterized by SEM, GDOES, adhesion tests, and profilometry. One can see that the interlayer thickness decreases with the increasing of the hydrogen plasma etching processing time. The etching mechanism suddenly changes at a processing time of 4 minutes. Whereas shorter etching times than 4 min remove roughly constant contents of carbon, silicon and oxygen, longer etching times than 4 min remove more silicon and oxygen than carbon. Moreover, the hydrogen etching process prompts to good adhesion of the DLC on low-alloy steel as low temperature as 85^{o}C. We propose a mechanism where the outermost interface (DLC/interlayer) is constituted by more carbon than silicon and oxygen atoms after the hydrogen etching process enabling more carbon-carbon chemical bonds than before, which increase the adhesion.

2:30pm **B3-1-4 Stress Evolution of Diamond-like Carbon Films via Controlled Metal Doping*****, Aiying Wang,*** *X Li, L Sun, P Guo,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

>It is well known that, being one family member of carbon-based solid materials, diamond-like carbon (DLC) films own more comprehensive advantages over diamond, carbon nanotube, even as well as very recently the blooming graphene, due to their superior physiochemical properties, facile synthesis with low cost over large uniformity, and amorphous smooth surface etc. In particular, DLC films enable the possibility to apply the eco-friendly surface engineering to satisfy the strong demands of energy saving and emission reduction to update. In this talk, we will introduce our study on the stress controlling of DLC films via metal doping, where the feature and concentration of doped metal were controlled. Specifically, the mechanism to understand the stress reduction originated from the various doped metals will be addressed in view point of combined experimental and theoretical studies. Further synergistic effect of co-doped metals on the microstructure and properties of Me-DLC films will be discussed, which provide a new concept to fabricate the DLC films with comprehensively high performance for wide range of industrial applications.

2:50pm **B3-1-5 Influence of Alloying Metals on Tribological Properties of Diamond-like Carbon Films Synthesized by Metal Plasma Activated Deposition Process***, D Wang,* ***Wei-Yu Ho****, M Shih, W Chen,* MingDao University, Taiwan*; J Wang, J Hung,* Aurora Scientiftic Corp, Canada

The metal plasma activated diamond-like carbon (mpa-DLC) film has been commercially adopted by manufacturing industries for its superior tribological and functional properties to prolong tools and components service life. The multi-layered and gradient mpa-DLC coating consists of a metallic interface layer, a metal nitride/carbide transition layer and the outmost DLC film, which was synthesized by breaking down of acetylene feed gas. The whole process can be categorized as an integrated and PVD-activated CVD synthesis of DLC coatings. TiN and CrN are among the common starting and supporting materials between the substrate and the top DLC layer. This research looked into the strengthening mechanism of the interface bonding and the intrinsic tribological property of the mpa-DLC coating by adding second and/or third metal elements such as Al, Cr, or Si to the TiN and CrN base lattice. The electron states of carbon and the chemical bonding configuration will be studied by using ESCA-SIMS. The tribological properties will be investigated by using ball-on-disk tribo-meter, nano-indentation, and scratch tester. The thermal property will be examined by using TG/DT. Results of this research will provide a mechanism to further improve the mpa-DLC coatings.

Keywords: metal plasma, DLC, tribology, PVD coating

3:10pm **B3-1-6 Thick Diamond Like Carbon Coatings Deposited by Deep Oscillation Magnetron Sputtering for Automotive Applications*****, Jianliang Lin,*** *P Lee, R Wei, K Coulter,* Southwest Research Institute, USA

Hydrogenated diamond like carbon (DLC) coatings with thicknesses up to 20 µm have been deposited by sputtering a graphite target in Ar and acetylene (C_2H_2) mixture using a two-step process including plasma enhanced magnetron sputtering (PEMS) and deep oscillation magnetron sputtering (DOMS). The PEMS technique was used for substrate ion cleaning and sputter deposition of the Ti/TiN bond layer, while the DOMS technique was used to sputter graphite in an Ar+C_2H_2 environment to form the top DLC layer. The effects of the C_2H_2 flow rate (f_{C2H2}) on the deposition rate, adhesion, surface roughness, mechanical and tribological properties of the coatings were studied by means of scanning electron microscopy, Raman spectroscopy, HRC indentation, nanoindentation, dry ball-on-disk test, and block-on-ring test in SAE 10W-30 engine lubricant. Appropriately introducing C_2H_2 (e.g.10 sccm, 4% of the total gas flow) increased the deposition rate, the sp^3/sp^2 ratio, and hardness and wear resistance of the DLC coatings. In contrast, higher C_2H_2 flows (>30 sccm, 12% of total gas flow) showed detrimental effects on the adhesion as well as the mechanical properties of the coatings. These thick hydrogenated DLC coatings exhibited low dry sliding COF in the range of 0.07 to 0.12 in the ambient air, and low friction in SAE 10W-30 engine lubricant in the range of 0.08 to 0.090.

3:30pm **B3-1-7 Deposition of ta-C by Filtered and Unfiltered Laser-arc Technique – Actual Status*****, Volker Weihnacht,*** *G Englberger, A Leson,* Fraunhofer IWS, Germany **INVITED**

Due to their unique combination of superhardness and low friction properties tetrahedral amorphous carbon films (ta-C) are very attractive as tribological coatings e.g. on automotive sliding components like piston pins, piston rings, and valve-train parts. In contrast to conventional DLC films (a-C:H), ta-C cannot be deposited by PECVD or magnetron sputtering techniques. The only effective technique for mass production of ta-C coatings is arc evaporation of graphite. As the arc spot movement on graphite is very difficult to control, a laser triggered pulsed arc evaporation technique was developed at Fraunhofer IWS.

This contribution will show how the laser-arc technique has developed from an idea and first prototypes to an industrially upscaled technology used for mass production of ta-C coatings. Special emphasis will be put on the issue of deposition rate versus ta-C coating properties and possibilities how to modify the coating architecture to deposit well-adhering ta-C coatings with thickness of even more than 10 µm.

Furthermore, the issue of arc-induced particle emission and defects in the ta-C coatings will be addressed. It will be shown how plasma filtering specifically developed for the laser-arc technique will suppress the particle transmission from the cathode to the substrate and hence reduce the defect density and roughness of deposited coatings.

4:10pm **B3-1-9 Wear Behavior of CoCrMo Alloy Coated with Highly Adhesive N-Doped DLC by ICP-CVD***, **Jesus Corona Gomez**, Q Yang,* University of Saskatchewan, Canada

Coating the joint surfaces with diamond like carbon (DLC) is a promising way to increase the service lifetime of hip joints made of CoCrMo alloy. However, the weak adhesion of DLC on the alloy presents problems for this application. This work aims to improve the adhesion of DLC on CoCrMo alloy with Nitrogen doping and nanodiamond incorporation. Nanodiamond particles with different densities was synthesized on CoCrMo alloy sheets by microwave plasma enhanced chemical vapor deposition and nitrogen doped DLC thin films were then deposited on them by Inductively Coupled Plasma assisted Chemical Vapor Deposition (ICP-CVD). The effect of nitrogen doping and nanodiamond incorporation on the film adhesion was investigated by scratch testing and wear behavior of the samples were studied using ball-on-disc testing. Results showed that Nitrogen doping and nanodiamond incorporation could improve the film adhesion significantly and thus the wear performance. The excellent tribological performance of the coated samples is attributed to the graphitization of the top layer of the DLC according to the Raman spectrum analysis. The wear resistance of the DLC coated CoCrMo alloy was superior to the bare CoCrMo alloy due to the high adhesion of DLC on the alloy. The results have demonstrated that the modified DLC films are promising for total hip joint replacement application.

4:30pm **B3-1-10 Carbon-Based Coatings on Nanofabric by Using HIPIMS for Possible EAOPs Applications***, **Pi-Wei Wang**, C Tsen, C Liu, J He,* Feng Chia University, Taiwan

Nanofibers, capable of providing extra functions in contrast to regular-size fibers due to vary high specific surface area. This has brought a large opportunity for the nanofibers to utilize in form of nanofibrous membranes as air and water filtration materials. In combination with advanced coating technique such as high power impulse magnetron sputtering (HIPIMS), it would be able to develop new form of filtration materials for better purifying performance. In this study, carbon-based coatings were deposited on nanofibrous membranes by using HIPIMS (where high density plasma favorites sp3-containing carbon film growth at low-temperature) to achieve additional functions for use as membrane electrode of an electrochemical advanced oxidation processes (EAOPs). Experimental results show that mixed sp2/sp3 carbon film can be obtained, through the result of Raman spectroscopy analysis. The deposited nanofibrous membrane can be electrical conductive for EAOPs purpose. Degradation efficacy for specific organic substance can vary depending on the deposition parameters and were discussed.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-4

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm **B4-4-3 Coatings Selection Criteria for WC/Co Cutting Tools***, **Aharon Inspektor**, P Salvador,* Carnegie Mellon University, USA **INVITED**

Internet of Things (IoT), where all objects have unique identifiers and incessant internet connectivity, will fundamentally change the world we live in and the manufacturing industry. In this paper we will examine the impact of the forthcoming 4th Industrial Revolution on machining industry, the anticipated changes in metal cutting procedures and the emerging new generation of cutting tools.

The use of embedded sensors, fast connectivity and intelligent feedback in metal cutting has the potential to increase material removal rates at significantly tougher thermal and mechanical conditions at the cutting edge. Successful implementation of the new technologies will require similar progress in cutting tools. We will first review and analyze current trends and machining strategies in leading workshops. Then, we will discuss key criteria for the design of new cutting tools, and guidelines for the development of new functional coatings. The coating selection criteria will be based on the current and on the anticipated machining wear-maps that chart the optimum machining conditions for various workpiece materials. The paper will include examples from machining High Temperature Alloys, Stainless Steel and Carbon Composites.

2:50pm **B4-4-5 Investigation of the Plasma Electrolytic Oxidation Mechanism of Titanium***, **Golsa Mortazavi**, E Meletis,* University of Texas at Arlington, USA

Plasma electrolytic oxidation (PEO) is an environmentally friendly technology capable of forming coatings with excellent adhesion strength. Total applied current to the oxide, in this process, is composed of electronic current caused by sparking and ionic current caused by diffusion of electrolyte ions into the oxide. Correlation between the ionic/electronic current contribution rate at different current densities and the oxide layer characteristics is utilized to understand the coating growth mechanism during the PEO stages. In this study, titania films were produced via PEO on commercially pure titanium in an alkaline phosphate electrolyte at various current densities i.e. 30, 40, 50, 60, 80, 100, and 110 mA/cm^2. Voltage-time (V-t) behavior has been investigated to elucidate the contribution of ionic and electronic current and different stages of PEO process. The V-t response showed that at low current densities, voltage attained relatively constant values, due to the dominance of the electronic current that is mainly due to sparking and as such is independent of the film resistance. High density of plasma discharge at this condition, forms large number of discharge channels and increases the porosity and surface roughness of the coating. Also, these plasma discharges provide enough energy to raise temperature facilitating formation of both rutile and anatase. At high current densities though, the ionic current dominates enhancing ionic diffusion through the oxide resulting in a dense, thick anatase film. The present results show that the V-t response can be utilized to elucidate the oxide growth mechanism during PEO process.

3:10pm **B4-4-6 Lessons Learned from Sputtering Icosahedrally Bonded Borides***, O Hunold, P Keuter, P Bliem, D Music, F Wittmers, A Ravensburg,* RWTH Aachen University, Germany*; D Primetzhofer,* Uppsala University, Sweden*; **Jochen Schneider**,* RWTH Aachen University, Germany

We have systematically studied the effect of transition metal valence electron concentration (VEC) of amorphous $T_{0.75}Y_{0.75}B_{14}$ (a–$T_{0.75}Y_{0.75}B_{14}$, T= Sc, Ti, V, Y, Zr, Nb) on the elastic properties, bonding, density and electronic structure using *ab initio* molecular dynamics. As the transition metal VEC is increased in both periods, the bulk modulus increases linearly with molar- and mass density. This trend can be understood by a concomitant decrease in cohesive energy. T' = Ti and Zr were selected to validate the predicted data experimentally. A–$Ti_{0.74}Y_{0.80}B_{14}$ and a–$Zr_{0.75}Y_{0.75}B_{14}$ thin films were synthesized by high power pulsed magnetron sputtering. Chemical composition analysis revealed the presence of up to 5 at.% impurities, with O being the largest fraction. The measured Young's modulus values for a–$Ti_{0.74}Y_{0.80}B_{14}$ (301±8 GPa) and a–$Zr_{0.75}Y_{0.75}B_{14}$ (306±9 GPa) are more than 20% smaller than the predicted ones. The influence of O incorporation on the elastic properties for these selected systems was theoretically studied, exemplarily in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Based on *ab initio* data, we suggest that a–$Ti_{0.75}Y_{0.75}B_{14}$ exhibits a very dense B network, which is partly severed in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Upon O incorporation, the average coordination number of B and the molar density decrease by 9% and 8%, respectively. Based on these data the more than 20% reduced Young's modulus obtained experimentally for films containing impurities compared to the calculated Young's modulus for a–$Ti_{0.75}Y_{0.75}B_{14}$ (without incorporated oxygen) can be rationalized. The presence of oxygen impurities disrupts the strong B network causing a concomitant decrease in molar density and Young's modulus. Very good agreement between the measured and calculated Young's modulus values is obtained if the presence of impurities is considered in the calculations. The implications of these findings are that prediction efforts regarding the elastic properties of amorphous borides containing oxygen impurities on the at.% level are flawed without taking the presence of impurities into account.

3:30pm **B4-4-7 Ductile Behavior of Hard MoBC and WBC Nanolaminates***, **Petr Vašina**, P Soucek, S Mirzaei, L Zabransky,* Masaryk University, Czech Republic*; J Bursik,* IPM, Academy of Science, Czech Republic*; V Perina,* NPI, Academy of Science, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic

State-of-art ceramic materials nowadays used as protective coatings such as TiN, TiAlN, c-BN etc. generally exhibit high hardness and high stiffness. These positive features are often accompanied by negative brittle deformation behaviour. To overcome this limitation a new generation of materials with high hardness and moderate ductility is desired. Recently, there has been an increased interest in boron and carbon based nanolaminates such as Mo_2BC [1] which exhibit a very similar structure to the MAX phases. According to the ab-initio models, these materials were predicted to exhibit unusual combination of high stiffness and moderate ductility [1]. The coatings were deposited either by DCMS at extremely high substrate temperature of 900°C [1] or at moderate temperature of 380°C employing HiPIMS [2]. In our research, co-sputtering of Mo (W), C and B_4C targets to finely tune the coating composition of Mo_2BC and W_2BC was used. Mid-frequency pulsed DC plasma excitation was employed to enhance the ion flux on the substrate by factor of 3 compared to DCMS case which promoted the crystallization of Mo_2BC. Coatings with the same XRD patterns as those deposited by HiPIMS at the same substrate temperature were prepared. The moderate deposition conditions resulted in grown of partially crystalline Mo_2BC coatings with nanocomposite structure where small Mo_2BC crystallites of approx. 10 nm size were embedded in an amorphous matrix. These coatings showed high hardness of 31.6 ± 0.8 GPa and extremely high fracture toughness – it was even impossible to form a crack in these coatings at extremely high indentation load with cube corner indenter where both the coatings and the underlying hard-metal substrate were severely plastically deformed. Only a shear/slip plane defects typical for ductile materials were detected. This required ductile behavior of hard coating observe for partially crystallite Mo_2BC with nanocomposite structure is hard to be met with other commercial coatings tested by similar manner.

1. J. Emmerlich, D. Music, M. Braun, P. Fayek, F. Munnik, J.M. Schneider, J. Phys. D: Appl. Phys, 2009 42 185406 (6pp).

3:50pm **B4-4-8 Coating Characterization with Surface Acoustic Waves**, ***Martin Zawischa***, *D Schneider, M Leonhardt, S Makowski, V Weihnacht,* Fraunhofer IWS, Germany

Measuring film properties is essential for understanding and designing coating systems and for controlling quality in coating manufacturing.

For more than ten years now, the laser-induced surface acoustic wave technique has been proven as a fast and non-destructive way to characterize coating and surface properties. Several parameters influence the velocity of the waves like Young's modulus, coating thickness, porosity, subsurface damage or hardening zone. Due to the fact, that the penetration depth of propagated waves depends on wave frequency, a bundle of information about the above mentioned parameters can be obtained from the measured dispersion curve of the detected waves. Once the dispersion curve has been measured, a physical model of the coating system is fitted to the measured data to derive the information of interest.

Fields of applications in both research and industrial environments are PVD and CVD coatings, thermal-sprayed coatings, semiconductors, low-k films and bulk materials.

Up to now, the physical model was limited to a single layer or to multilayers with two alternating materials. In this work, an implementation of a more advanced model is presented, which accounts for up to five individual layers with full data set. By means of examples, fitting of some multi-layer systems is demonstrated. In one example several variants of a DLC coating system with a chromium interlayer deposited on a silicon wafer are measured. The number of obtainable parameters is discussed with respect to the shape of the dispersion curve. Different measurement strategies can be deduced from these finding and extend the possibilities of the laser-induced surface acoustic wave method.

4:10pm **B4-4-9 Anti-Corrosion Performance and Wear Behaviour of Laser Deposited Ni-Ti-Zn Coatings on UNS G10150 Steel.**, ***Ayanda Xulu,*** Tshwane University of Technology, South Africa; *O Fatoba,* University of Johannesburg, South Africa; *A Popoola,* Tshwane University of Technology, South Africa; *S Pityana,* Council for Scientific and Industrial Research (CSIR), South Africa

The untimely failure of engineering steels when exposed or used in harsh working environment is attributed to low hardness, poor tribological behaviour and corrosion resistance and this invariably restricting its applications. Since the durability of steel is determined by its deterioration over time which is affected by the environment, tailoring of the surface composition and microstructure through laser deposition becomes very vital. The investigation of Ti-Zn-Ni coatings by laser deposition technique is aimed at enhancing the properties of Ti-Zn-Ni coatings on UNS G10150 steel. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the deposition process was utilized for the fabrication of the coatings. The fabricated coatings were investigated for its hardness, corrosion and wear resistance performance at different laser processing parameters. The corrosion behaviour was investigated in 1M H_2SO_4 and 3.65wt.% NaCl solutions at 28^oC via Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization techniques. The optical microscope (OM), field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The improved hardness and wear resistance performance were attributed to hard Ti_2Ni intermetallic compound, martensitic TiNi and TiZ_{16} phases. The coatings were found to have uniform and fine microstructures free of cracks and pores. The enhanced corrosion resistance was also attributed to NiTi and TiO_2 phases formed.

4:30pm **B4-4-10 Effect of V Addition on the Thermal Stability, Oxidation Resistance and Tribological Performance of Self-lubricant TiSi(V)N Coatings Deposited by HiPIMS in DOMS Mode**, ***Filipe Fernandes,*** *R Serra, A Cavaleiro,* SEG-CEMUC, University of Coimbra, Portugal

Effective lubrication and wear protection at high temperature and in cyclic environments are continuing challenges that are crucial for energy efficiency in turbomachinery, machining tools and aerospace applications. In recent years, various self-lubricating coatings have been developed by combining hard and wear resistant binary or ternary coatings (such as TiN, TiAlN, CrN, CrAlN, YSZ) with specific elements (e.g. Ag, V) that reduce friction by diffusing to the surface and/or forming a low friction tribolayer on the wear surface. Despite the improvement in friction and wear resistance, the quick depletion of the lubricious specie from the coating system by rapid out diffusion and consequently loss of improved tribological behavior delayed their upscaling to the industry. A promising approach for controlling diffusion of the lubricant element is the use of a diffusion barrier layer. This is the case of the TiSiN coating system, which deposited as nanocomposite structure the amorphous Si-N phase can work as an antidiffusion barrier. Thus the aim of this work is to evaluate the effect of V additions on the structure, thermal stability, oxidation resistance and tribological performance of TiSiN films deposited with dissimilar Si contents, with emphasis on the development of selflubricant coatings with control release of the lubricious phase. TiSi(V)N coatings with different vanadium and Si contents were deposited by DOMS. Temperature effect on the structure of the V rich coating was characterized in open air in-situ by hot-XRD device in the range of 500 °C to 750 °C. Thermal stability was studied in a protective atmosphere in the range of 500 °C to 1000 °C. The oxidation behavior of coatings was studied by thermogravimetry (TGA). Bright field scan transmission electronmicroscopy STEM/EDX maps and elemental profiles along the cross section of the oxidized coatings were acquired to understand the kinetics of ions diffusion and oxide scale growth. Tribological behaviour of coatings was characterized in a high temperature tribometer. After wear tests, the wear tracks and wear debris were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopy. Oxidation resistance of coatings decreased with V additions. Tribological tests showed that friction and wear rate of coatings decreased progressively with increasing vanadium content.

4:50pm **B4-4-11 Wear Study of PVD AlTiN Coatings with High Al Content**, ***Joern Kohlscheen,*** *C Bareiss,* Kennametal GmbH, Germany; *C Charlton, D Banerjee,* Kennametal Inc., USA

AlTiN coatings are widely used as protective coatings in the cutting tool industry. It is generally accepted that increasing the aluminum content from 50 to about 65 at. % (metallic fraction of the compound) improves the tool performance in many applications. However, for high hardness the coating structure needs to remain essentially cubic (fcc). If deposition parameters are not optimized or the Al content is increased further, considerable amounts of the soft hexagonal phase will be deposited and wear resistance of the film is reduced. We present a study of AlTiN coatings with compositions near an elemental ratio of 2:1 (Al:Ti). Carbides samples were coated by arc PVD using a commercial system. Phase change in the films was promoted with selected variants by annealing up to 1000 degree C under vacuum. Structural analysis was done by SEM and XRD (BB and GI mode). Basic mechanical properties were determined by universal hardness testing. The wear behavior of the coatings was studied by cyclic indentation on the macro and micro scale and the resultung wear is described in detail. As expected, aluminum contents above 65 at. % lead to rapid decrease in wear resistance. Formation of the undesired hexagonal phase could be delayed by suitable deposition parameters (magnetic field at the arc source). Annealing for extended periods of time reduce coating performance again as more hexagonal phase is formed. The wear behavior in the laboratory test generally reflects the results obtained under more complex loading situation (dry milling of ductile cast iron).

5:10pm **B4-4-12 Tribological Behavior of MoBCN-MoSx Coating under Elevated Temperature***, **Xiaodong Zhu**, Q Li, L Qiu, K Xu,* Xi'an Jiaotong University, China

To extend the utilization of tribological coatings, people have designed adaptive or "chameleon" coatings which reduce friction and wear by changing surface chemistry and microstructure in response to the change of environment and loading. In these coatings, a wear-resistant phase was chosen as the main phase and some lubricating phase as assistants. The wear-resistant phase usually has a high friction and large amount of lubricant is necessary to reduce the coefficient of friction, and thus leads to low hardness and reduced oxidation resistance . MoBCN coating was found to have low friction coefficient from room temperature to 600 ℃ . By adding lubricating phases of MoS_2, the $MoBCN/MoS_2$ composite coating may possess better tribological propertiesfor wide temperature range.

In this study, $MoBCN/MoS_x$ coatings were prepared by ion beam enhanced magnetron sputtering from a Mo/B_4C /MoS_x composite target. The content of boron and sulfur was controlled by the number of the corresponding mosaic targets. The friction and wear behaviors of these composite coatings were evaluated by ball-on-disc wear test at different temperatures. The introduction of sulfer reduces the coefficient of friction and wear rate at room temperature. However, it is oxidized into MoO_3 and loses its character of lubrication at elevated temperature, accordingly its oxidation tendency increases. It is shown that more content of boron may reduce the negative effect of sulfur on the oxidation resistance, and thus its tribological behavior at elevated temperature is improved. Therefore, boron is proved to be the key element in enhancing tribological performance of $MoBCN/MoS_x$ coating at elevated temperature.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-2

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa Ltd., USA, Klaus Böbel, Bosch GmbH

8:00am **B3-2-1 Tribological Behavior of Unlubricated Sliding between Steel Ball and Si-DLC Deposited by Ultra-high-speed Coating Employing MVP Method**, *T Nakano, K Yamaguchi, **Ippei Tanaka**, H Kousaka,* Gifu University, Japan*; H Hashitomi,* Cnk Co., Ltd., Japan

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction, the application of DLC (Diamond-Like Carbon) is spreading gradually and steadily. In this field, higher-speed coating method with applicability to 3-dimensional shapes is strongly desired. Plasma CVD is a promising candidate for such demands due to its excellent capability for coating 3-dimensional shapes; however, typical coating speed of DLC with conventional plasma CVDs is not so high, ~1 µm/h; in addition, further drastic increase of the coating speed is not expected due to the use of low-density ($n_e \sim 10^8$–10^{10} cm^{-3}) DC or RF plasma in such conventional methods. The use of higher-density plasma is considered to be essential for increasing the coating speed. Thus, we have proposed a high-speed coating method of DLC with a novel plasma CVD employing much higher-density plasma ($n_e \sim 10^{11}$–10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface on metal surface. In our previous work, a considerably high deposition rate of 156 µm/h and hardness of 20.8 GPa was obtained. In this work, we investigated the effect of film composition on friction property of Si-containing a-C:H films in such ultra-high-speed DLC coating.

Si-containing a-C:H films (one type of DLC) were deposited on steel substrates by different 2 methods: DC plasma and microwave-excited high-density near plasma, or our newly proposed method, where the gas composition of Ar, CH_4, C_2H_2, and TMS in source gas flow was changed. Friction tests were conducted in a ball-on-disk apparatus under dry condition, where a SUJ2 ball 8 mm in diameter contacted to a DLC-coated disk at a normal load of 1 N. Sliding test was conducted for 60 minutes at a rotation speed of 250 rpm. The atomic composition of the films was evaluated by XPS for C, O, and Si, and RBS-ERDA for H/C.

The hydrogen and silicon contents were from 25 to 35 at% and from 7.76 to 28.43 at%, respectively. Friction coefficient of Si-containing a-C:H films was decreased from 0.12 to 0.025 with decreasing oxygen content from 0.75% to 4.15%. This result indicates the possibility of decreasing friction coefficient by oxygen content in Si-containing a-C:H films .

8:20am **B3-2-2 Tribological Behavior of DLC Coatings on AISI 4340 Steel Deposited in PECVD DC-Pulsed Technique with Additional Cathode for Automotive Applications**, ***MarcoA. Ramirez R.**, D Lugo,* National Institute for Spacial Research INPE, Brazil*; N Fukumasu, I Machado,* Surface Phenomena Laboratory - Polytechnic School - University of Sao Paulo - Brazil, Brazil*; E Mitma P., V Trava-Airoldi,* National Institute for Spacial Research INPE, Brazil

Diamond-Like Carbon (DLC) coatings have attracted significant attention due to its low friction, high hardness, high wear resistance, among others. These films meet conditions that can be used in some mechanical applications in aerospace and automotive industries. The major disadvantage of these coatings is the low adhesion on metallic substrates, caused by elevated compressive residual stresses after deposition. Some plasma conventional methods require a high consumption of energy that are used to grow DLC films, resulting in a high level of temperature and pressure during the deposition, which affects the adhesion of the film to the substrate. The use of PECVD-DC Pulsed with additional cathode, allows to grow DLC films in extremely low pressure and temperature. In this work, DLC coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD with additional cathode at temperature as low as 90 C and pressure as low as 0.1 Pa, which allowed a collisionless regime and a higher plasma density. Acetylene gas was used as a precursor. In order to overcome low adhesion of DLC films on steel substrate, a thin amorphous silicon interlayer was deposited as an interface. Resulting coatings were analised with SEM-FEG and Raman scattering spectroscopy in terms of morphology and atomic arrangement,respectively. The total residual stress was evaluated by the curvature method. The tribological behavior (friction and wear) was analyzed by reciprocating wear tests at room temperature. Adhesion was evaluated in accordance with the VDI3198 norm, based on a Rockwell C indentation test. XPS analyses, will also be used in order to get a relationship among the adhesion and the silicon interface on set nucleation parameters. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and acetylene as a precursor gas to grow DLC films on engineering steels may represent a new alternative to improve the mechanical behavior in automotive applications.

8:40am **B3-2-3 Structural Evolution and Temperature-sensitivity of W-containing Diamond-like Carbon Films Deposited by a Hybrid Linear Ion Beam Systems**, ***Peng Guo**, L Sun, P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In present study, W-containing diamond-like carbon (W-DLC) films (0.3~70.4 at.%) were fabricated by a hybrid beams system consisting of a DC magnetron sputtering and a linear ion source. The influence of composition and microstructure on the room temperature (300 K) resistivity and temperature coefficient of resistance (TCR, 300~400 K) of the W-DLC films were also investigated. As evidenced by XPS, XRD, TEM and Raman measurements, the microstructure of W-DLC films evolved from amorphous carbon matrix with dissolved W atoms into composite materials made of WC_{1-x}/W_2C nanocrystallites embedded in amorphous carbon matrix with increasing W concentration. The electrical resistivity of the temperature of all the films exhibited a negative TCR. The mechanism of the temperature sensitivity in the W-DLC films was also discussed.

9:00am **B3-2-4 Effects of Carbon Content and Argon Flow Rate on the Triboperformance of Self-lubricating WS_2/a-C Sputtered Coating**, ***Huatang Cao**, J Th.M De Hosson, Y Pei,* University of Groningen, Netherlands

Layered transition metal dichalcogenides (TMD) such as WS_2 are materials well-known for their solid lubrication properties [1]. However, the lubricating property degrades through oxidation or moisture and it is also limited by its low hardness and low load-bearing capacity. In contrast amorphous diamond-like carbon (DLC) films are reported to have many features that contribute to excellent tribological characteristics, such as high hardness, anti-wear property with both low friction coefficient and low wear rate[2.] The present research aims at depositing WS_2/a-C nanocomposite coatings by magnetron co-sputtering method. The effects of carbon content and argon flow rate on the microstructure and mechanical performance were investigated. The WS_2/a-C nanocomposite tribocoating was scrutinized by electron microscopy and mechanical testing. Transmission electron microscopy reveals feathery WS_2 platelets, randomly distributed in the amorphous carbon matrix. The nanocomposite coating turns out to be more amorphous-like with increasing carbon content. Nanoindentations tests show that the hardness and elastic modulus of the coating increase with increasing carbon addition while decreasing with a higher argon flow from 10 sccm to 25 sccm.

Ball-on-disk tribotests (100Cr6 steel ball as a counterpart) show that the coefficient of friction can be as low as 0.017 in a dry environment (<5% relative humidity). It reaches 0.15 in a high humidity surrounding and remains stable within 20000 sliding cycles.

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9:20am **B3-2-5 Industrial Development of Carbon-based Coatings**, ***Ruud Jacobs**, G Fransen, R Tietema, D Doerwald, J Landsbergen,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

In this presentation an overview will be presented on the developments of carbon-based coatings for applications in automotive technology.

Initially the introduction of high pressure diesel injection technology required the introduction of wear resistant coatings to protect the steel parts against wear to prevent leakage of pressure and damage to components. In the earliest phase of development, metal doped DLC's produced by sputtering were applied, soon however because of a demand for higher wear protection followed by the introduction of hydrogenated DLC's produced in hybrid sputter/PECVD processes. Due to the improved fuel efficiency, power densities increased causing strain on other components in the engine, as well as in the valve and power train, consequentially leading to a demand for wear protection coatings on those parts as well.

In the last decade the requirement for reduced emissions of CO_2 gave a strong boost to the market for components. Reduced friction, reduced weight and increased efficiency in fuel combustion were necessary to meet the new demands.

Developments in lubricants tend to go in the direction of lower viscosity. Hybrid technology and start-stop engines increase the operating time of the engine in mixed-mode lubrication. Both trends in automotive development direct to increasing wear resistance requirements. This has been leading to large scale introduction of ta-C (tetrahedral carbon) coatings produced by arc technology after 2010. These ta-C coatings are offering for many cases an optimum of highest hardness in combination with lowest friction, but a post-treatment is required to optimize the surface quality of the coated components. Newest developments in tribological contacts tend to go in the direction of higher operating temperatures combined with high wear resistance and minimum friction, whereas also the cost of the system plays an important role.

10:00am **B3-2-7 Glow Discharge and Deposition of Thick DLC Film in Cage-shaped Hollow Cathode System with Adjustable Bias***, **Xiubo Tian**, M Wu, C Gong,* Harbin Institute of Technology, China*; R Wei,* Southwest Research Institute, USA

Diamond-like-carbon (DLC) has been widely utilized in related industries to tribological, optical, electrical applications, etc. A cage-shaped hollow cathode discharge (C-HCD) has been utilized to produce high-density plasma for deposition of DLC films. To further optimize the microstructure and surface properties of the DLC films, a new approach is proposed, in which the energy of ions incident to the sample surface can be independently controlled by an additional bias between the samples and the metal cage (mesh). The samples are biased with a voltage from 0V to -500V with respect to the cage biased with 1000-4000V (pulse). The internal sample bias has a critical effect on the cage hollow cathode discharge. Generally the glow discharge of C-HCD system is enhanced by the sample bias. However with a higher C-HCD current, there exists a certain sample bias which weakens the glow discharge. It is attributed to the competing effect of both self-discharge and ion consumption induced by negatively-biased sample. Compared to conventional method, additional bias effectively removes thecarbon contamination and some macro-burring on the sample surface. And the bias also leads to the formation of the surface protuberances with nanoscale size. The clean surface and mechanical lock structure have effectively improved the adhesion between the film and substrate. Si-DLC films have been synthesized with a mixture of Ar, C_2H_2 and tetramethylsilane (TMS). The results demonstrate that the DLC films have been deposited with a higher rate (4~6um/h) due to higher plasma density produced by high-current pulse in the mesh cage. The intense ion bombardment significantly densified the microstructure and reduced the H contents, and consequently increased the nanohardness (*H*) of DLC films. As an example, a DLC film was deposited on HSS with thickness of 40um and critical load of ~100N. Our results have proven that this novel set up may be a very effective tool to fabricate DLC films with high deposition rate and excellent surface properties with denser microstrcture.

10:20am **B3-2-8 Enhanced Adhesion Of Hard Dlc Coatings On Metallic And Insulating Substrates***, **Ivan Fernandez**,* Nano4energy Sl, 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 properties, DLC has good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear.

As the industrial success of DLC films in tribological contacts is strongly dependent on their adhesion properties, two different approaches were used to enhance DLC coating adhesion onto both metallic and insulating substrates.

- HiPIMS metal ion etching and implantation with both Ti and Cr plasmas was used to pre-treat the M2-HSS metallic substrates, obtaining Rockwell HF1 values and critical loads in the macro-scratch tests above 100N .

- Positive ion-assisted pre-treatment [1] was used to etch glass substrates and promote strong adhesion of thin DLC layers. Taber abrasion tests were performed to evaluate the pre-treatment process effect on the coating adhesion. A significant DLC coating adhesion improvement was observed.

10:40am **B3-2-9 Low Friction of Graphene Nanocrystalline Embedded Carbon Nitride Coatings Prepared with MCECR Plasma Sputtering***, **Pengfei Wang**,* Institute of Nanosurface Science and Engineering, Shenzhen University, China*; W Zhang,* Xi'an Jiaotong University, China*; D Diao,* Shenzhen University, China

The excellent mechanical and tribological behaviors of amorphous carbon nitride coatings, especially the super-low friction performance (friction coefficient of less than 0.01 in dry nitrogen gas environment) made them good candidates as solid lubrication coatings in advanced engineering applications. However, the low friction mechanism of carbon nitride coatings in nitrogen gas environment is still not yet clearly understood. The objective of this research is to clarify the key factors of atomic composition and structure of the carbon nitride coating itself in achieving the low friction in nitrogen gas environment.

In this work, graphene nanocrystalline embedded carbon nitride (GNECN) coatings were fabricated with the mirror confinement electron cyclotron resonance (MCECR) plasma sputtering method under low energy electron irradiation. It is clearly observed that the deposition rate, internal stress, surface roughness and hardness of the prepared GNECN coatings change with the variation of the flow ratio of argon and nitrogen gas in the operating gas under a pressure of 0.04 Pa. Moreover, graphene nanocrystalline structure was identified in the amorphous carbon nitride matrix from the analyses of TEM, XPS and Raman spectroscopy. Furthermore, stable and low friction coefficient of less than 0.05 of GNECN coating was achieved after a short run-in period when slid against Si_3N_4 ball in nitrogen gas environment. A uniform transfer film was formed on the worn surface of counterpart ball material according to the optical image. It is believed that the introduction of graphene nanocrystalline structure plays a key role in achieving low and stable friction coefficient of GNECN coatings, which could help us better understanding the low friction mechanism of CNx coatings in nitrogen gas environment from the viewpoint of the composition and structure of the coating. Moreover, the clarification of the relationship between the low friction behavior and electric output property of the contact surfaces is beneficial for understanding the tribo-electrification principle as well as exploring the application of GNECN coatings in tribo-energy field.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B6

Coating Design and Architectures

Moderators: Nina Schalk, Montanuniversität Leoben, Shou-Yi Chang, National Tsing Hua University

1:30pm **B6-1 Radial Symmetry of the Compound Layer Growth in Plasma Nitriding of Pure Iron***, F Castillo,* ***Joaquin Oseguera****, E Hernánez, J Otero, D Melo-Maximo, A Jimenez,* Instituto Tecnologico y de Estudios Superiores de Monterey, Mexico

Radial symmetry plays a fundamental role in tribological systems, where spinning on axes takes place. This is the case for crankshafts, camshafts and driveshafts among others.Thermochemical treatments, which involve diffusion of one element such as nitrogen, oxygen or boron, produce a concomitant layer growth. Usually, layer growth kinetics has been studied by modeling from a Cartesian coordinate perspective, using plane fronts. The use of thermochemical treatments on radial symmetry surfaces makes relevant to employ different approaches in order to improve the obtained results so far.

The present work proposes a mathematical model which describes the compact layer growth kinetics during plasma nitriding of a pure iron solid cylinder. The erosion effect at the plasma-solid interface due to sputtering is taken into account. The model constitutes a moving boundary value problems, for which radial symmetry solutions are found. The numerical simulation of the model is performed using both finite differences and the Heat Balance Integral Method (HBIM).

1:50pm **B6-2 Self-assembled Nano-lamellar $Ti_{1-x}Al_xN$ LP-CVD Coatings: Development and Analysis***,* ***Jakub Zalesak****, J Todt,* Montanuniversität Leoben, Austria*; I Matko,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; M Petrenec,* Tescan Brno s.r.o, Brno, Czech Republic*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; R Pitonak,* Böhlerit GmbH & Co KG, Austria*; R Daniel, J Keckes,* Montanuniversität Leoben, Austria

Recent progress in low-pressure chemical vapour deposition introduced self-organized nano-lamellar $Ti_{1-x}Al_xN$ coating system with outstanding mechanical and thermal properties [1]. This system exhibits a complex three-dimensional ordering of nano-lamellar microstructure, whose composition and period depend on the overall composition. A combinatorial search for optimal process gas flow ratios, to reach dedicated phase composition, microstructure and mechanical properties, was performed using a „graded coating“ concept [2]. The analyses of the phasecomposition, microstructure and mechanical properties were performed by using X-ray nanodiffraction, TEM imaging and micromechanical testing of microcantilever beam specimens. Based on the iterative multi-parameter-analysis, refinedprocess gas flow ratios were identified. The optimized cubic self-organized nano-lamellar coating with overall composition of $Al_{0.8}Ti_{0.2}N$ was subsequently heteroepitaxially grown onto a single crystalline 0001 sapphire substrate and subjected to further detailed analyses with the aim to understand the self-organisation mechanisms. For semi-quantitative compositional characterization, EFTEM, EELS and EDX methods were employed. The combination of elemental composition analyses and imaging revealed multi-dimensional periodical compositional oscillations of Ti, Al and N. This singularity, in combination with oriented nano-lamellar microstructure, pointed out that the self-organization effect has its origin in oscillating reactions.

[1] Todt et al. / Surface & Coatings Technology 291 (2016) 89-93

[2] J. Zalesak et al. / Acta Materialia 102 (2016) 212-219

2:10pm **B6-3 Fundamental Properties of TM Nitrides: Materials Design Strategies for Extreme Properties***,* ***Joe Greene,*** University of Illinois at Urbana-Champaign, USA **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties; they offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields which can be exploited. We show results for vacancy hardening (not associated with film strain) in 3d Group-IV $TiN_x(001)$ and Group-V $VN_x(001)$; the hardness H of epitaxial layers increases dramatically, while the elastic modulus E and the relaxed lattice constant decrease linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. Over the same x range, the resistivity ρ(x) increases linearly due to electron scattering from N vacancies. In contrast, H(x), E(x), and ρ(x) for 5d Group-V $TaN_x(001)$ remain constant due primarily to the presence of isoelectronic antisites.

All Group IV TM nitrides TiN, ZrN, and HfN are very good metallic conductors with room temperature resistivities of 12-14 µΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV and a direct X-point gap of 2.4 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN(001)$ layers show TiN is strongly reflecting up to the reflectance edge at $\hbar w_e$ = 2.3 eV, while ScN is transparent and w_e µ $x^{0.5}$. ZrN is intermediate with $\hbar w_e$ = 3.04 eV. Thus, hard decorative coating can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes. Self-organization strategies include controlled phase separation, surface-induced spinodal decomposition, surface segregation-induced renucleation, strain-induced roughening, surface anisotropy, and dynamic resputter yield amplification.

An issue with superhard ceramic films, however, is that they are typically brittle leading to failure by crack propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). Groups IV-V alloys such as $V_{1-x}W_xN$, exhibit metal-atom ordering on adjacent 111 planes in the cation sublattice leading to, in addition to increased hardness, enhanced ductility. Vacancy-induced toughening is also observed in understoichiometric VN_x and $(V,Mo)N_x$ alloys. A final example represents an entirely different approach: designing TM nitride multilayers which are defined not by composition differences, but by bonding differences in alternating layers of essentially the same composition.

2:50pm **B6-5 Stabilisation of Cubic MoN and TaN Systems: the Role Point Defects***,* ***David Holec,*** Montanuniversität Leoben, Austria*; N Koutná, F Klimashin, P Mayrhofer,* TU Wien, Austria

Point defects are unavoidably present in materials, either due to thermodynamic reasons (equilibrium) or due to the growth process (non-equilibrium). The latter is the case of physical vapour deposition (PVD), a technique often employed for synthesising nitride-based protective coatings. Both MoN and TaN have recently received attention due their unique mechanical, electrical and chemical properties. The stable variants of both of them are hexagonal structures. However, under specific deposition conditions, they may be prepared in a cubic rock-salt structure. In this contribution we will present our recent *ab initio* based insights into the role of point defects on the stabilisation of these cubic phases. In particular we will show that both materials prefer a presence of vacancies. While in the case of MoN, both Mo and N vacancies possess the same stabilisation effect, in the case of TaN a strong preference for Ta vacancies is demonstrated. Furthermore, we can show that the vacancies are preferably distributed in a disordered fashion in MoN, while both ordered and disordered configurations yield comparable changes of the energy of formation in TaN. Phase diagrams for various deposition conditions will be presented and a relevance to our recent experimental data on N-deficient MoN will be also discussed.

References:

[1] N. Koutná, D. Holec, O. Svoboda, F.F. Klimashin, and P.H. Mayrhofer, J. Phys. D Appl. Phys. **49**, 375303 (2016).

[2] F. F. Klimashin, N. Koutná, H. Euchner, D. Holec, and P.H. Mayrhofer, submitted.

3:10pm **B6-6 Vacancy Induced Mechanical Stabilization of Cubic Tungsten Nitride***,* ***Karthik Balasubramanian,*** Rensselaer Polytechnic Institute, USA

First principle calculations are employed to determine the mechanical stability and the formation energies E_f of point defects in rock-salt phase group III B – VI B transition metal nitrides and carbonitrides. Interstitials and antisite defects have relatively high E_f values, in average 3.9 and 9.7 eV higher than those for anion and cation vacancies, such that the latter are the energetically preferred point defects to account for deviations from stoichiometry. The vacancy formation energy decreases when moving towards the right in the periodic table, from E_f = 5.1 to -7.1 eV for anion vacancies in ScN and WN, respectively, and from E_f = 3.2 to -12.0 eV for the corresponding cation vacancies. This decrease is accompanied by a decrease in the single crystal shear modulus, from c_{44} = 161 for ScN to 164, 126, and -120 GPa, for TiN, VN, and CrN, indicating a transition to mechanical instability of rock-salt nitrides and carbonitrides with increasing valence electron concentration above 5.3. The negative E_f values for both cation and anion vacancies in group VI B nitrides indicate that the rocksalt structure is thermodynamically unstable, despite experimental observations of cubic rock-salt type WN and MoN. We investigate this discrepancy by comparing the energetic and mechanical properties of WN in the experimentally reported rocksalt and theoretically predicted NbO phases. The rocksalt WN is both mechanically and thermodynamically unstable with a formation enthalpy H_f= 0.637 eV per formula unit and a negative c_{44} = -86 GPa while the NbO phase is stable with H_f= –0.825 eV and c_{44}= 175 GPa. Charge distribution and electronic density of states analyses reveal that the mechanical instability of rocksalt WN is due an increased overlap of t_{2g} orbitals upon the application of shear strain along [100], resulting in electron migration from the expanded [110] to the shortened [1-10] direction and a negative shear modulus. The mechanical transition from the unstable NaCl to the stable NbO phase is further explored using supercell calculations of the NaCl structure containing C_v= 0 to 25 % of both cation and anion vacancies. The structure is mechanically unstable for C_v <5 %. At this critical vacancy concentration, the isotropic elastic modulus is zero but increases steeply to 445 GPa for C_v= 10 % and to 561 GPa for the NbO structure with C_v= 25 % which is in good agreement with experimentally measured elastic moduli ranging from 110 – 360 GPa. These results show that the experimental reports of a cubic WN phase can be explained by the mechanical stabilization of the rocksalt phase by a minimum of 5% anion and cation vacancies.

3:30pm **B6-7 Nitrides and the Impact of Entropy on their Phase Stability**, ***Paul H. Mayrhofer***, TU Wien, Austria; *D Holec*, Montanuniversität Leoben, Austria; *F Klimashin, N Koutná*, TU Wien, Austria

Transition metal based nitrides are fascinating materials, owing to their excellent performance against mechanical attack. Since Jien-Wei Yeh's work in 2004 on "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes", research activities on the impact of configuration entropy on the stability of solid solution phases increased. Corresponding to amorphous metals, also high entropy alloys have the potential for increased strength with a combined high fracture, corrosion, and oxidation resistance. Here we discuss in more detail the impact of configurational entropy on the phase stability, mechanical properties and thermal stability of hard ceramic coatings (like Ti-Al-N, Cr-Al-N, Mo-Al-N, Ta-Al-N and combinations thereof). Additionally, we will also treat vacancies (present especially in Mo, W, and Ta containing nitrides) as an important partner for the configurational entropy and discuss their impact on mechanical properties and phase stabilities.

3:50pm **B6-8 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, *D Edström, D Sangiovanni, L Hultman*, Linköping University, IFM, Sweden; *I Petrov, J Greene*, University of Illinois at Urbana-Champaign, USA; ***Valeriu Chirita***, Linköping University, IFM, Sweden

The Modified Embedded Atom Method (MEAM) interatomic potential is used within the classical Molecular Dynamics (MD) framework to perform simulations of important model materials such as TiN, in order to understand the processes which control TiN growth modes on a fundamental level. We report the results of large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in good qualitative and quantitative agreement with Ab Initio MD based on Density Functional Theory [3], [4]. We deposit 85% of a monolayer of TiN on 100x100 atom TiN(001) substrates maintained at 1200 K, at a rate of 1 Ti atom per 50 ps, for total simulation times of 212.5 ns. We use N/Ti flux ratios of 1, 2, and 4, and incident N energies of 2 and 10 eV, to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For N/Ti flux ratios of 1 at 2 eV incidence energy, films exhibit Ti-rich surface regions which serve as traps to nucleate higher layers, leading to multilayer growth. Increasing the N/Ti flux ratio shifts the growth mode to layer-by-layer and modifies the overall film composition from under- to over-stoichiometric. As the N content of films is increased, N-terminated <110>-oriented island edges become increasingly dominant and the substrate vacancy concentration changes from being N- to Ti-dominated. We discuss the implications of these results on thin film growth and process tailoring.

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4:10pm **B6-9 Development of Reliable Interaction Potential for and Results of Molecular Dynamics Simulations of ZrO_2 Film Growth**, ***Jiří Houška***, University of West Bohemia, Czech Republic

Thin films of ZrO_2 are of high interest due to a wide range of useful technological properties. In this contribution the growth of ZrO_2 is studied by atom-by-atom molecular dynamics simulations, focused on intrinsic process parameters such as the energy (E) and energy distribution function (EDF) of arriving atoms or the surface temperature (T).

The first part deals with the development of an interaction potential for a realistic description of atom-by-atom ZrO_2 growth. Owing to the fact that for many metal oxides including ZrO_2 only full-charge (Zr^{+4} and O^{-2}) interaction potentials are available in the literature, special attention is paid to the effect of the Zr and O elemental charges. Parameters of the short-range part of the Buckingham interaction potential leading to experimental lattice parameters and formation energies have been identified in a wide range of elemental charges. Simulations reveal that the structures grown using the presently available full-charge interaction potentials are in contradiction with the experiment (the atoms have too low coordination numbers). Correct partial charges and potential parameters leading to experimentally relevant structures (with correct coordination numbers) have been identified [1].

The second part shows how do the film densification, crystal nucleation and uninterrupted crystal growth depend not only on E delivered into the growing films (i) per fast atom (ion) or (ii) per any atom, but especially (iii) on the EDF (namely the fraction of fast atoms in the particle flux) and (iv) on the mass of fast atoms (Zr or O). On the one hand, the nucleation of c–ZrO_2 (the most desired phase) is T-dependent and requires (in order to take place on a short time scale) high E. On the other hand, the growth of previously nucleated (or epitaxial growth of) c-ZrO_2 is much easier, T-independent, and highly dependent on the EDF. Optimum EDFs which allow uninterrupted crystal growth at as low E delivered into the growing films as possible are characterized by (i) narrow EDF and (ii) high momentum delivered into the growing films (i.e. the combination of fast Zr and slow O leads to a better densification and crystallinity than the opposite) [2].

The results (in addition to the methodological importance of the interaction potential development) facilitate defining new synthesis pathways for ZrO_2, and constitute phenomena which may be relevant for other coating materials (isostructural HfO_2 at the first place) as well.

Acknowledgment

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[1] J. Houska, Comp. Mater. Sci. 111, 209 (2016)

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4:30pm **B6-10 Experimental Validation of Metal-on-insulator Thin Film Growth Theory**, *B Lü, L Souqui, V Elofsson*, ***Kostas Sarakinos***, Linköping University, Sweden

The current understanding of thin film growth dynamics relies to a large extent on the widely accepted theory of morphology evolution in metal-on-metal homoepitaxial systems which exhibit a strong thermodynamic tendency towards 2D growth. This understanding is, however, challenged when considering the deposition of metal vapor on insulating surfaces; which is governed by a complex interplay between formation, growth, and coalescence of 3D atomic islands. This interplay is described quantitatively by the less established theory for metal-on-insulator (MOI) growth, which originates from the literature of water vapor condensation and the formation of breath figures, most notably reviewed by Family and Meakin. In contrast to water clusters, 3D atomic islands formed upon vapor condensation, exhibit a size-dependent coalescence rate leading to a so-called elongation transition, which occurs upon sufficient deposition such that coalescing islands become kinetically frozen into elongated shapes. This transition is a key component in the MOI growth theory as it entails information about film growth dynamics encoded in scaling relations between the nominal film thickness (i.e., coverage θ) at elongation, θ_{Elong}, and the rates of vapor deposition, adatom diffusion and 3D island coalescence. While this scaling behavior has been confirmed quantitatively by computer simulations, the lack of a suitable method to measure θ_{Elong} has left experimental proof of the theory ambiguous. In this study, we combine experiments and kinetic Monte-Carlo simulations to develop and implement a method for measuring θ_{Elong} for Ag grown on amorphous SiO_2. Our data confirm the theoretically predicted θ_{Elong} power laws which are then used to calculate the adatom diffusion and coalescence rates for Ag/SiO_2 in good agreement with the literature. The data presented herein constitute a first step towards an experimental validation of the prevailing MOI growth theory and thereby lay the foundation for establishing a universal understanding of thin film growth dynamics. In practical terms, knowledge of the adatom diffusivity and coalescence rates, could facilitate more informed decisions regarding growth manipulation by, e.g., doping, surfactant action or tuning of the deposition rate and growth temperature. This may be of importance for a number of applications where MOI is relevant, such as architectural glazing, microelectronics, catalysis, and the metallization of graphene.

Hard Coatings and Vapor Deposition Technologies
Room Grand Exhibit Hall - Session BP

Symposium B Poster Session

BP-8 Large Lattice Strain-caused Change in Nanoscale Plastic Deformation Behavior of Multi-component (AlCrTaTiZr)$N_xC_ySi_z$ Nanocomposite Coatings*, Y Lai, Y Hsiao,* National Tsing Hua University, Taiwan*; **Shao-Yi Lin**,* National Chung Hsing University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

The relationship between the nanostructure and nanoscale deformation behavior of nanocomposite coatings is of importance to their mechanical performance and thus of interest for investigation. In this study, multi-component face-centered cubic (fcc) (AlCrTaTiZr)N_x, (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z coatings were prepared by sputtering, and their nanostructures and nanoscale plastic deformation behavior were characterized using nanoindentation and transmission electron microscopy. The multi-component (AlCrTaTiZr)N_x coating had a simple fcc solid-solution structure and exhibited a typical full dislocation-mediated plastic deformation. With the addition of C or Si (the incorporation of covalent –C or –Si bonds), an fcc nanocomposite structure (with small-angle domain boundaries) formed in the (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z coatings. Large lattice strains (severe lattice distortions) in the multi-component nanocomposite coatings caused the change of plastic deformation behavior. Under a large indentation stress, low-energy small-angle dislocation structures (with extended partial dislocations or stacking faults) were formed at the small-angle domain boundaries. When the applied stress (the stored high strain energy) was released, many of the stacking faults were removed, and a near-perfect ordered crystal structure was observed. The activities of stacking fault decahedra consisting of highly reversible 1/6 <112> and 1/9 <222> partial dislocations were expected to dominate the plastic deformation and recovery (W_e ~ 76%) of the multi-component (AlCrTaTiZr)NC_y and (AlCrTaTiZr)NSi_z nanocomposite coatings.

BP-9 Advanced Deposition of Hard a-C:Me Coatings by HPPMS using Ne as Process Gas*, K Bobzin, T Brögelmann, N Kruppe, **Martin Engels**,* Surface Engineering Institute - RWTH Aachen University, Germany

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example on highly-loaded components of the automotive powertrain. The hardness and roughness of these coatings contribute to the reduction of the component wear. The hardness correlates with the sp^3/sp^2 bond ratio between the carbon atoms, where sp^3 bonds are similar to the diamond structure. The roughness is strongly influenced by the physical vapor deposition (PVD) technology such as the pulsed laser deposition (PLD) or the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS). In a previous work it was shown that hard a-C coatings with a low roughness can be deposited by means of HPPMS in a high volume coating unit using Ne as process gas. Furthermore, the doping of hydrogenated a-C:H coatings by means of plasma-assisted chemical vapor deposition (PACVD) with metals is the subject of current research. Significant changes of the coating properties have been found. The formation of nanocomposite a-C:H:Me coatings was reported, which exhibit an increased hardness or reduced plastic deformation, compared to a-C:H coatings. However, a-C:H coatings generally exhibit lower hardness values, compared to a-C coatings. Therefore, the deposition of metal doped a-C:Me coatings by means of HPPMS might contribute to a performance increase in tribological applications. Hence, in the present work a-C:Me coatings were successfully deposited in a high volume coating unit by means of two HPPMS cathodes with Zr and C targets. Furthermore, a correlation with a hybrid process using one direct current magnetron sputtering (dcMS) cathode and one HPPMS cathode was performed. Based on previous works, Ne was used as process gas to increase the ionization in the carbon plasma. Therefore, a high content of sp^3 bonds in the a-C matrix was expected. The average power of the cathode with the Zr target was varied between P = 600 W and P = 1,200 W in order to obtain coatings with different chemical compositions. The resulting coating properties were analyzed by means of nanoindentation, Raman spectroscopy, scanning electron microscopy, X-ray diffractometry and confocal laserscanning microscopy. In summary, the deposition of a-C:Zr coatings by means of HPPMS was successful, since hard coatings with HU > 25 GPa with a low roughness Ra < 0.05 µm are deposited. Finally, the plasma was analyzed by means of energy resolved mass spectroscopy to correlate the coating properties with the composition of the plasma.

BP-10 Plastic Deformation Behavior of Nanostructured CrN/AlN Multilayer Coatings Deposited by Hybrid dcMS/HPPMS*, K Bobzin, T Brögelmann, **NathanChristopher Kruppe**, M Arghavani,* Surface Engineering Institute - RWTH Aachen University, Germany

The physical vapor deposition (PVD) is a commonly applied technology for deposition of hard coating systems such as chromium (Cr)-based nitride coatings on tools and components in tribological applications. In such applications the tools and components are subjected to complex loads, which can lead to elastic-plastic deformation of coating/substrate compounds or crack formation. One approach to increase the life time of compounds under significant loadings is the deposition of nanostructured coatings such as CrN/AlN-nanolaminates with promising hardness and crack resistance. The understanding of the deformation behavior of such multilayers is, however, a key factor for further coating developments. Implementation of nanoscratch analyses in conjunction with high resolution microscopy techniques is an approach to study the tribological behavior of nanostructured coatings and gain information about their plastic deformation under normal and lateral loads. Nanoscratch analyses on the coating system CrN/AlN-nanolaminate deposited on quenched and tempered AISI 420 steel substrate and investigations on the resulted plastic deformation are the subjects of current research. In the present work, a hybrid technology, consisting of direct current and high power pulse magnetron sputtering dcMS/HPPMS, was used for deposition of the coating. The CrN/AlN-nanolaminate was deposited with a bilayer period (thickness CrN + AlN) of Λ = 10 nm. In order to study the plastic deformation of the coating, nanoscratch analyses were performed applying a Berkovich tip. The deformation of coating system under nanoscratch loads was quantitatively analyzed by means of depth profiling using confocal laser scanning microscopy (CLSM). A comprehensive study of the plastic deformation and crack resistance was furthermore performed using scanning electron microscopy (SEM). The SEM analyses were carried out on surface and cross section fractures of the nanoscratch tracks. Scanning transmission electron microscopy (STEM) was applied to explore the micro-scale cracking underneath the nanoscratch tracks. High resolution transmission electron microscopy (HRTEM) was furthermore applied to explore the mechanism of plastic deformation of the investigated coatings. Based on the results, the CrN/AlN-nanolaminate exhibited a significant resistance against plastic deformation and crack formation. Furthermore, the plastic deformation of the investigated coating was explained by reorientation and sliding of grains imbedded in individual layers CrN and AlN.

BP-13 Control and Characterization of Texture in CVD α-Al_2O_3 Coatings*, **Chen Chen**, P Leicht, R Cooper, Z Liu, D Banerjee,* Kennametal Inc., USA

CVD Alumina coating has been one of the most important components of coated cutting tools for many years. Recently, texture control in α-Al_2O_3 has attracted increasing attention due to the possibility to further improve the anisotropic properties such as thermal conductivity and mechanical properties. The influence of process parameters on textures is complex. In this study, we have investigated the influence of nucleation surface condition and catalyst (H_2S) on the texture in CVD α-Al_2O_3 coatings. The α-Al_2O_3 coatings were deposited by CVD in a hot wall vacuum deposition reactor on WC substrates, and were characterized by advanced analytical techniques including SEM, XRD and EBSD. It has been shown that without the addition of catalyst, the crystal orientation in the Al_2O_3 coatings is primarily dominated by the surface condition, while the effect of reactant composition on texture is minimal. On the other hand, in the presence of catalyst during growth, reactant composition also plays an important role in affecting the crystal orientation. This effect is likely due to the strong interaction between the surface the catalyst.

BP-14 New Tools and Models for Industrial Surface and Coating Optimization of Composite Structures*, **Nick Bierwisch**, N Schwarzer,* SIO, Germany

Nowadays the used materials or material combinations in all application fields (e.g. optical, avionic, fun sports or automotive industry) are getting more and more complex. These complex structures are needed in order to increase the performance and lifetime of the components. Such improvements of each part of your complex device, tool or structural element are necessary to reach the performance goals demanded by the desired application. This increased complexity demands extended analyzis and optimization methods. Engineering knowledge and rules of thumb aren't enough anymore.

Proper characterization and optimization of such structures requires invertible mathematical tools of sufficient holistic character. Unfortunately, as such tools are still not available one often finds trial and error or half empirical sensitivity analysis methods in combination with FEM or BEM. Faster tools could help here a lot to save development time and costs [1].

All models (FEM or analytical based) will need exact and generic material parameters for each part of our material system.

A few years ago, SIO developed a model and a dedicated software package called Oliver & Pharr for Coatings (OPfC® [2]) which allows the determination of true generic material parameters (like Young's modulus and Yield strength) for a coating by knowing the parameters of the substrate and all underlying layers.

The software package FilmDoctor® [3] contains analytical models which dramatically speed up the simulation of complex contact situations compared to FEM systems.

The poster will focus on the results of a joint project with Naish international [5] about standup paddling boards and paddles. It will present how the models and software packages are used to improve the performance in critical application conditions dramatically.

References:

[1] N. SCHWARZER, Scale Invariant Mechanical Surface Optimization - Applying Analytical Time Dependent Contact Mechanics for Layered Structures, Proceedings of the 28th International Conference on Surface Modification Technologies, 287-327, SMT 28, June 16th – 18th, 2014, Tampere University of Technology, Tampere, Finland, Publisher: Valardocs, ISBN Number:978-81-926196-1-3

[2] www. [http://siomec.de/OPfC]

[3] www [http://siomec.de/FilmDoctor]

[4] www.naish.com

BP-15 Selection of a Reactive Magnetron Sputtering Method to Produce Films for Biosensors*, Brenda García*, *L Melo-Máximo, O Salas, D Melo-Maximo, A Murillo,* Tecnológico de Monterrey-CEM, Mexico*; J Lin,* Southwest Research Institute, USA*; J Oseguera,* Tecnológico de Monterrey-CEM, Mexico

Three different reactive sputtering methods were evaluated for the production of Al/AlN/Al thin film architectures for biosensing applications. The methods included were direct current, radiofrequency, and modulated pulse power reactive magnetron sputtering. The films were deposited on Si substrates at equivalent power densities and characterized by optical microscopy, glancing angle x-ray diffraction, and scanning electron microscopy + microanalysis. The comparative analysis of the films was based on the most relevant film features for biosensing, namely control of the type of crystalline phases formed, control of preferred orientations, easiness to produce inclined structures, and adhesion to the substrate. Other features such as surface morphology, and density of the films were also considered, as no systematic studies regarding their effect on biosensing have been published.

BP-20 Preparation of Carbon based Multilayered Coatings by means of Pulsed Laser Deposition: Outstanding Mechanical Properties and Enhanced Film Toughness*, René Bertram,* University of Applied Sciences Mittweida, Germany*; M Hess,* Fritz Stepper GmbH & Co.KG, Germany*; H Gruettner, D Haldan, S Weißmantel,* University of Applied Sciences Mittweida, Germany

It will be presented how amorphous carbon coatings can be deposited at low temperatures with mechanical characteristics varying in a wide range depending on deposition parameters and that these properties such as hardness and elasticity can easily be assessed by Raman spectroscopy. For this the indentation hardness and indentation modulus of carbon films deposited at various laser pulse fluences were determined by means of nano indentation and brought into correlation with the peak ratio of the disordered (D-) and graphite (G-) peaks. This offers a fast and simple method to assess H_{IT} and E_{IT} for carbon single layers, for the presented coatings in the range of roughly 20 GPa to 60 GPa and 290 GPa to 620 GPa, respectively.

It will also be shown that the architecture of films designed as multilayered stacks of such different carbon compounds strongly affects the toughness of protective coatings when exposed to high mechanical stresses induced in scratch test or indentation at high loads. Nano indentation measurements showed that this multilayered design does not result in a loss in hardness and elasticity if suitable layer structures are built up. The preliminary computation of stress evolution in the film-substrate system and the actual layer behavior for several layer stack designs will be part of the presentation as well. These coating systems combine a very good adhesion on several metal and hard metal substrates, very high hardness and low abrasive wear, very high elasticity up to 80 % elastic recovery in nano indentation and high crack resistivity in scratch tests and indentation experiments. These superior properties indicate the high potential of laser deposited carbon multilayer as wear protective coatings for cutting tools, bearings and engine components to name but a few.

BP-22 Elastic Constants of Epitaxial Cubic Tantalum Nitride: Thin Film Growth and *ab initio* Calculations*, Gregory Abadias,* Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; P Djemia, C Li,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM), France*; Q Hu,* Shenyang National Laboratory for Materials Science, China*; L Belliard,* Université Pierre et Marie Curie-INSP, France*; F Tasnadi,* Linköping University, (IFM), Sweden

Information is still scarce concerning the properties of single-crystal cubic metastable TaN thin films. This work aims at providing some new insights on the elastic and structural properties of TaN epitaxial nitride thin films, especially regarding the influence of defects and nitrogen stoichiometry. 150 nm-thick TaN films were deposited by magnetron sputtering under reactive $Ar+N_2$ plasma discharges on MgO(001), (110) and (111)- oriented substrates, at a temperature of 650°C. In parallel, *ab initio* calculations were performed in the framework of the density functional theory (DFT) using the VASP software. It has been evaluated how vacancies influence the lattice parameter, the mass density and elastic constants of c-TaN.

The thickness and mass density were determined by x-ray reflectivity measurements, while x-ray diffraction pole figure and reciprocal space maps were employed to study epitaxial orientation and determine the lattice parameters. Elastic constants of thin films can be accurately studied by photoacoustic measurements. The Brillouin light scattering (BLS) technique allows measuring sound velocity of a few kinds of surface acoustic waves (V_{SAW}) in thin films and thus estimating single-crystal elastic constants (ρV^2), in the case of epitaxial films, if the mass density ρ of the film is known. The Rayleigh surface wave is much more dependent on the shear elastic constant C_{44}, thus BLS can provide at least this constant. It is well adapted for thin films and can be conveniently combined with the picosecond ultrasonics technique that measures the sound velocity of longitudinal waves (V_L) that are travelling forth and back within the film along the direction perpendicular to the film plane, i.e. [001], [110] and [111] crystallographic directions.

We used this combination of techniques to measure the elastic constants C_{11}, C_{12} and C_{44} of our epitaxial nitride films. Our results show good agreement between experiments and DFT calculations if defects are taken into account

BP-24 Mechanical and Structural Properties of CrN/AlN Superlattices*, David Holec,* Montanuniversität Leoben, Austria*; M Friak,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic*; Z Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; M Bartosik, P Mayrhofer,* TU Wien, Austria

Density Functional Theory is a well established tool for predicting structural and mechanical properties of bulk materials. Recent progress facilitated by modern efficient codes and increased computational power has opened doors to studying also extended systems. Examples of such are superlattices, an important design approach of materials with controlled architecture.

In this contribution, we will report on first principles calculations of structural and mechanical properties of CrN/AlN superlattices. The *ab initio* predicted oscillating interplanar distances are corroborated by high-resolution transmission electron microscopy analysis. Further on, we will present fully quantum mechanical calculations of directionally-resolved Young's modulus [1]. We will demonstrate that these yield comparable results with a simple continuum model of Grimsditch and Nizzoli [2]. Also these predictions are in excellent agreement with experimental measurements [1]. Finally, we will discuss the ideal tensile strength of these superlattices.

References:

[1] M. Friak, D. Tytko, D. Holec, P.-P. Choi, P. Eisenlohr, D. Raabe, and J. Neugebauer, New J. Phys. 17, 093004 (2015).

[2] M. Grimsditch and F. Nizzoli, Phys. Rev. B Condens. Matter 33, 5891 (1986).

BP-25 Characterization of the Hard Coating on Gray Cast Iron Under Hydrogen Charging*, Noe Lopez Perrusquia,* *M Doñu Ruiz, M Reyes Cortes,* Universidad Politecnica Del Valle De Mexico, Mexico*; C Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico*; V Cortes Suarez,* Universidad Autónoma Metropolitana, Mexico

This work enhance the mechanical properties on pearlitic gray cats iron with hard coating under hydrogen charging. The formation of hard coating was carry out by boron paste dehydrated at temperature of 1173 and 1193 K, with 8 hour exposure time. The characterization of hard coating were using: optical microscopy (OM), X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and the mechanical properties: elastic modulus and hardness were obtained nanoindentation and the adhesion by Rockwell C indentation test. All sample boride were subjected to hydrogen charging and evaluate the behavior of hydrogen on gray cast iron with FeB/Fe_2Bcoating using three point bending results. The mechanical properties enhance the surface on gray cast iron due to hard coatings and increase the bending stress value.

BP-27 Characterization and Growth of B-doped Diamond Grown on HPHT Diamond Substrates using Mode Conversion Type Microwave Plasma CVD*, Tomoya Sakuma,* Chiba Institute of Technology, Ogura Jewell Industry Co., Ltd., Japan*; A Suzuki, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω・cm. However, it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} is used as a dopant to synthesize B-doped diamond. Though these dopants are toxic to humans. Trimethyl-borate {$B(OCH_3)_3$} is harmless. Furthermore, accuracy of the machined surface with single crystalline diamond is better than polycrystalline diamond and it is essential for ultra-precision machining and ultra-precision measurement.

In this report, growth and characterization of B-doped diamond on HPHT diamond substrates using mode conversion type microwave plasma CVD were studied.

B-doped diamond was synthesized on single crystalline diamond substrates using mode conversion type microwave plasma CVD apparatus. HPHT diamond substrates were synthesized using high pressure high temperature method and their (1 0 0) facets were crystal orientation. Reaction gases were used CH_4 (15 SCCM) and H_2 (100 SCCM). Trimethyl-borate was used as a boron source. Vapor of trimethyl-borate was carried by H_2 carrier gas into the vacuum chamber with its flow rate of 3 SCCM. Pressure was 20.0 kPa and microwave power was 1.0 kW, respectively. The surface and cross sectional morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy and Laue pattern. Electrical resistivities were measured by the four-point probe method.

In the cross sectional SEM image after laser cutting, epitaxial layer of 0.1 mm thickness was observed.

Raman spectra of B-doped diamond growth layer, the broad peak at around 500, 1230 $cm^{-1}$and the weak peak at 1333 cm^{-1} were observed in each spectra. These peaks were due to high concentration boron inclusions.

As a result of Laue pattern from deposits, clear Laue pattern and weak halo pattern were confirmed.

As a result of the electrical resistivity measurements by the four-point probe method, the minimum electrical resistivitiy was 4.2×10^{-3} Ω・cm.

As a conclusion, single crystalline B-doped diamond was fabricated on HPHT diamond substrate. In the Raman spectra of the film, the peaks caused high boron inclusion were observed.

BP-28 Effects of the Reaction Gas Flow Rates on the Plasma State during Boron-doped Diamond Synthesis*, Asuka Suzuki,* *Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity order of 10^{16} Ω・cm. However it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. However, the liquid B source in the bubbling tank was evaporated at room temperature, it is difficult to control flow rates because it is introduced using H_2 carrier gas, and control range is so narrow. Towards further industrial applications, it is desirable to extend electrical resistivities range by using a relatively less toxic liquid B source. Application to a variety of electronic components to be able to safely control the volume resistivities of the B-doped diamond can be expected to spread.

The investigation was carried on the effects of the reaction gas flow rates on the plasma state during boron-doped diamond synthesis.

Boron-doped diamond films were synthesized using mode-conversion type microwave plasma CVD apparatus. Si substrate was scratched by diamond powder and then cleaned ultrasonically in acetone solution. Reaction gases were used CH_4 and H_2. Vapor of $B(OCH_3)_3$, the boron source, was introduced by H_2 carrier gas into the vacuum chamber. Their flow rate was $H_2/CH_4/H_2$ carrier=100/15/3, 200/30/6, 300/45/9 sccm , respectively pressure was 20.0 kPa and microwave power was 1.0 kW. Reaction time was fixed to 3h. During synthesis, plasma states were estimated using optical emission spectroscopy (OES) . The surface was observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Volume resistivities were measured by the four-point probe method.

As a result of OES, the peaks of B(249nm), BH(433nm), BO(436nm), CH(387nm,431nm), H_α(656nm), H_β(486nm) and C_2(404nm, 406nm, 473nm, 516nm, 563nm, 619nm) were observed for each conditions. In the SEM observation, the grain sizes of deposits were 1 to 3 mm. In the Raman spectra of the deposits, the broad peak at about 500, 1230 cm^{-1} and the weak peak at 1333 cm^{-1} were obtained for each samples . These peaks due to inclusion of high concentration boron in the films. As a result of the electrical resistivity measurements by the four-point probe method, the minimum Volume resistivities of 0.2Ω・cm was obtained. With the reducing of B/Hα, BH/Hα and BO/Hα emission intensity ratio in emission spect ra, volume resistivity is reduced.

As a conclusion, relationship between volume resistivit ies of boron doped diamond and intensity ratio of B-system emissions in OES spectra was suggested.

BP-29 Effects of Pluse Frequency and Duty Cycle on Synthesis of Carbon Nitride using Pluse Microwave Plasma CVD*, Koudai Yarita,* Chiba Institute of Technology, Japan*; I Tanaka,* Gifu University, Japan*; Y Sakamoto,* Chiba Institute of Technology, Japan

Carbon nitride has fascinated properties such as high hardness and high current density of field emission. In addition, if a β-C_3N_4 or c-C_3N_4 structure can be synthesized, it is possible to obtain a hardness higher than that of diamond. Our laboratory had investigated to obtain crystalline carbon nitride, and α-C_3N_4 was obtained from a CH_4– N_2 reaction gas system by microwave plasma CVD. In addition, pulse plasma is possible to control the state of plasma such as electron temperature. Also, pulse microwave CVD is possible to vary particle size and density.

Investigation was carried out on the effects of pulse frequency and duty cycle on synthesis of carbon nitride using pulse microwave plasma CVD。

Carbon nitride was synthesized using an improved microwave plasma CVD apparatus equipped with a water cooled substrate holder and can be selected microwave radiation mode cw or pulse. Si was used as the substrate. A mixture of CH_4 and N_2 was used as a reaction gas system. CH_4 and N_2 flow rates were 2 and 200 SCCM, pressure was 4.0 kPa. The reaction time was 5h. The reaction time was at 5h and the peak microwave power was 1000W. Pulse frequency was varied from 30, 300 and 3000Hz, duty cycle was varied 30, 50 and 70%. The deposits were estimated by Scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The plasma state was estimated by Optical emission spectroscopy (OES).

As a result of SEM observation, crystalline particles were obtained at pulse frequency of 30Hz, duty cycle of 50 and 70%, at frequency of 300 and 3000Hz, duty cycle of 30, 50 and 70%. However, Ball-like particles were obtained at pulse frequency of 30Hz and duty cycle of 30%. Particle densities were from 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle. As a result of Raman spectroscopy, the peak corresponding to Si was observed at pulse frequency of 30 to 3000Hz and duty cycle of 30 to 70%. On the other hand, the peak corresponding to amorphous carbon was observed at pulse frequency of 30Hz and duty cycle of 30%. As a result of XPS, the Si_3N_4 and C-N bond peaks were observed in at all sample. In OES spectra, the peak of CN radical emission was observed for all condition.

Examination result of effect of pulse frequency and duty cycle of microwave plasma on carbon nitride synthesis, crystalline carbon nitride was obtained proper synthesis condition. Also, Particle densities were about 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle.

BP-30 Duplex Coating of DLC on High Speed Tool Steel Substrates*, Y Kikuchi,* ***Ryohei Fujita****, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond-like carbon (DLC) is applied to a wide variety of fields in the industry because of its tribological properties and hardness. However, one of the major issues is the adhesion strength between DLC films and the metal substrate. Many efforts have been made to obtain a higher adhesion strength, such as the formation of an interlayer and the modification of the surface layer. In contrast, radical nitriding is one of the most suitable methods for the pretreatment of duplex coatings, because it possible to increase the surface hardness while maintaining the roughness of the original surface. According to this process, a diffusion layer is formed in the surface region using plasma state control.

High-speed tool steel was used as the substrate. A radical nitridation apparatus was used for the radical nitriding and PNC processes. The conditions for the radical nitriding process were a pressure of 133 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, an external heater temperature of 843 K, and a processing of 60 min. The conditions for the PNC process after radical nitriding were a pressure of 532 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, a CH_4 flow rate of 50 SCCM, an N_2 flow rate of 1 SCCM, an external heater temperature of 843 K, and processing times that were varied from 5 to 10 to 15 min.

After the plasma treatment process, the DLC film was coated onto the substrate using RF magnetron sputtering equipment. The target was graphite, the sputtering gas was Ar, the RF power was 50 W, the pressure was 0.4 Pa, and the processing time was 60 min, respectively. The DLC films were prepared after pre-sputtering under the same conditions for 10 min. The DLC film thickness was 300 nm.

DLC coated on an untreated substrate exhibited extensive delamination and micro-cracks that extended from the vicinity of the crater. High adhesion strength of DLC coatings on high-speed tool steel was accomplished via PNC treatments. In particular, PNC showed the best adhesion strength in this study at 5 min after radical nitriding.

Radical nitriding formed a nitrogen-diffusion layer, followed by the formation of a carbon layer by nitrocarburizing without the formation of a brittle compound layer. It maintained surface roughness compared with the untreated substrate. The resulting DLC films exhibited better adhesion to the treated-steel substrates than to the untreated ones.

BP-33 The Stability of Diamond-Like Coatings under Thermo-Mechanical Conditions*, Q Liu,* ***Xiaoying Li****, H Dong,* The University of Birmingham, UK

Diamond-like carbon (DLC) is an attractive carbon-based coating material for many applications due to their unique combination of low-friction, self-lubrication and high wear resistance in conjunction with good biocompatibility. However, the metastable nature of the amorphous structure restricts the wide application of DLC coatings under harsh conditions. Although there have been many reports on the thermal stability of DLC, limited or no work has been conducted to investigate the stability of DLC coatings under both thermal and pressure conditions.

This work presents a study on the stability of DLC coatings: a-C, a-C:H, a-C:Si and a-C:H:Si thermo-mechanical conditions using a hot isostatic pressure (HIP) furnace to apply both high-temperature and high-pressure. In order to investigate the influence of the applied pressure, thermal stability was also conducted by heating the DLC samples up to 600ºC in air and in argon without pressure. The microstructure of the as-deposited, heat treated and HIPped DLC samples were fully studied using XRD, Raman, FIB/SEM and XTEM; the change of their mechanical and tribological properties were investigated using nano-indentation and tribo-meters.

The experimental results reveal that the high isostatic pressure introduced during HIPping accelerated the graphitization process and hence reduced the stability of these DLC coatings at elevated temperature; the introduced isostatic pressure also reduced the adhesion between the top DLC coatings and the substrates. The mechanisms involved are discussed based on XTEM, XPS and Raman analysis.

BP-38 Growth of DLC Films on the Internal Surface of a Long Metallic Tube Using the PECVD Technique*, E Mitma Pillaca, M Ramirez Ramos, D Lugo González,* ***VladimirJesus Trava-Airoldi,*** National Institute for Spacial Research INPE, Brazil

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a well established method for growing DLC films on substrate with complex shapes, in a fast and efficient way. By this technique, surfaces of mechanical components, for example, are protected from wear and corrosion due to excellent properties that feature this film. However, coating inside tube owns some disadvantages. For example, homogeneous deposition is usually difficult to be achieved in tubes with low aspect ratio. On the other hand, coating in long tubes (some meters) using plasma are not economically feasible due to need for vacuum chambers with greater dimensions than the own tube. In this work, a tube with 0.1 m diameter and 2 m length was prepared to be used as the own vacuum chamber for the growth of DLC film on its internal surface by PECVD technique. Electric tests were performed to study the response of discharge current, as a function of the gas pressure and of the applied voltage in Ar plasma. These results have shown that the plasma inside of the tube is sustained at pressure as low as 5 mTorr and at negative applied voltage as low as -400 V. Different conditions were figuring out for silicon deposition as an interface and also for DLC deposition. Thus, SiH_4 and C_2H_2 has been used as a precursor gas for the silicon and DLC films, respectively. Matching of some parameters in terms of inside pressure, applied bias voltage and gas flow were established in order to get the DLC films with good adhesion, high hardness and good structural quality. A 1500N indentation, nano indentation and Raman spectroscopy analysis has been confirmed the DLC properties deposited on Stainless Steel substrates placed along of the tube. The uniformity along of the tube of DLC films in terms of friction coefficient and growth rate is an important part of this study.

BP-39 Characterization and Tribologic Study in High Vacuum of Hydrogenated DLC Films Deposited using Pulsed DC PECVD System for Space Applications*, D Lugo González,* ***Marco Antonio Ramirez Ramos,*** *V Trava-Airoldi, P Santana da Silva, E Mitma P., E Corat,* National Institute for Space Research - INPE, Brazil*; C Rodriguez, N Fukumasu,* University of São Paulo, Brazil

DLC is a metastable form of amorphous carbon that has excellent properties such as high hardness, high elastic modulus, chemical inertness, high wear resistance, and low friction coefficient. DLC has been studied as a promising solid lubricant since liquid lubricants are ineffective and undesirable for many space applications. Solid lubricants require performing properly under space environment conditions, such as high vacuum. This paper reports the structure, morphology, adhesion, and high-vacuum tribologcal performance of DLC films with different hydrogen content. The films were deposited by pulsed DC PECVD technique with an additional cathode and using acetylene as a precursor gas. An amorphous silicon interlayer was deposited in order to guarantee the adhesion between coating and substrate. For the films characterization, Raman spectroscopy, Scanning Electron Microscopy (SEM), Rockwell C indentation test, and scratch test were performed. In addition, hydrogen content in the DLC films was determined by Elastic Recoil Detection Analysis (ERDA). Friction coefficient value and wear rate of DLC films in high vacuum conditions were obtained applying loads of 2N and 5N at different sliding speeds. Results showed that DLC films deposited by pulsed DC PECVD can act as a space solid lubricant due to its low friction coefficient value, high adhesion and keeping its structural quality in high vacuum environment.

BP-40 Numerical Analysis on Gas-Pressure and Input-Power Dependence of Substrate-Incident Hydrocarbon Species in Tetramethylsilane Plasmas for Silicon-Containing Diamond-Like Carbon Thin-Films Coatings*,* ***Akinori Oda****, K Ohki,* Chiba Institute of Technology, Japan*; S Kawaguchi, K Satoh,* Muroran Institute of Technology, Japan*; H Kousaka,* Gifu University, Japan*; T Ohta,* Meijo University, Japan

Diamond-like carbon (DLC) films are the hydrogenated amorphous carbon films, which is composed of a mixture of sp^2- and sp^3-bonded carbon. Since this films have excellent material properties in high wear resistance, high hardness, low friction, and chemical stability, the films have been widely used for many technological applications such as automotive, semiconductors, medical devices, and so on. Recently, silicon-containing DLC (Si-DLC) films have been investigated, since the Si-DLC films with lower friction coefficient, compared with conventional DLC films, can be obtained. However, the effect of silicon in Si-DLC films on friction properties has not been clarified. Therefore, the understanding of fundamental properties in tetramethylsilane (TMS, $Si(CH_3)_4$) plasma, which are ion and radical source of Si-DLC films deposition, has been strongly required. Previously, our research group have developed a self-consistent one-dimensional fluid model of capacitively-coupled radio-frequency TMS plasmas, composed of the continuity equations for electron and sixteen TMS-derived ion species, the Poisson equation, and the electron energy balance equation, coupled with the Boltzmann equation solver. And then, the influence of process parameters (e.g. gas pressure, input power) on the plasma properties has been discussed. In this paper, in order to simulate the TMS plasma in realistic geometry (i.e. plasma chamber with realistic size), we developed the axially-symmetric three-dimensional fluid model of TMS plasma, and then examined the process parameter dependence of carbon-containing ion and radical fluxes onto substrate. As a result, it was clarified that three hydrocarbon ion species such as $Si(CH_3)_3^+$, $Si(CH_3)_4^+$ and $HSi(CH_3)_3^+$ are important and dominant ion species with higher density magnitude of 10^9 cm^{-3} in TMS plasma. Other simulation results will be presented in this conference. Acknowledgement: This work was partly supported by KAKENHI (No. 26420247).), and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities 2013-2017 (s131104).

BP-41 The Effect of Substrate Bias on the Structure and Mechanical Properties of the a-C:N Films by a 90^o-Bend Filtered Cathodic Arc Plasma (FCAP) System*, **Chih-Chiang Wang**,* National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

The carbon-related materials have been attracting lots of attention for decades in flat panel display, optoelectronic devices, etc. due to their unique chemical, electronical, mechanical, and thermal properties. In this study, amorphous nitrogenated carbon (a-C:N) films have been prepared on silicon wafer at 800°C with varying substrate bias upto -650V in a 90^o-bend filtered cathodic arc plasma (FCAP) system. The magnetic coil removes neutral carbon atoms and macroparticles from the plasma stream and in this case only the carbon arc discharge is available to form nitrogen ions. XRD showed the peak of (111) plane actually from the nanodiamond nucleated in the a-C:N films and agreed well with the result of HRTEM of d-spacing of 1.76 Å. The hardness of the resulting film was found to be 12.2GPa under an optimal bias of -350V.

The ratio of I_D/I_G of the Raman analysis increased to ~3.5 under the bias of -350V, indicating enriched sp^3-bonded carbon of the graphite domain. The FTIR spectra showed that the higher intensity at 1330cm^{-1} of D-band and 709 cm^{-1} of plane bending mode resulting from the graphite-like domains with N ions incorporated; more sp^3 bonds facilitated the completion of the nanodiamond structure. Binding energies of C1s, e.g., 287.6 (sp^3), 285.5 (sp^2), and 284.6 eV (free carbon), and N1s, e.g., 402.0 (N-O), 400.0 (sp^2), and 399.0 (sp^3) eV, have been resolved in the XPS spectra. The ratios of N/C were able to reach as high as 50% at -350V, indicating that higher substrate temperatures together with higher contents of nitrogen promotes the sp^3 clusters in the a-C:N films. These properties and the structure of the a-C:N film are sensitive to the energy of depositing C^+ and strongly dependent on the substrate bias.

BP-42 Stress Optimized Hard Nitride Coatings for High-performance Gear Hobbing*, **Martin Beutner**,* Otto von Guericke University, Germany*; A Lümkemann, M Morstein,* PLATIT AG – Advanced Coating Systems, Switzerland*; B Karpuschewski,* Otto von Guericke University, Germany*; M Jilek, Jr.,* PLATIT AG., Czech Republic*; T Cselle,* PLATIT AG – Advanced Coating Systems, Switzerland

In 2015 the automobile production and therefore also the transmission production exceeds the 90 million. Containing of several gears the manufacturing is of major importance. As the dominating green manufacturing process gear hobbing is applied the most. Here cutting conditions regarding chip thickness and cutting length change continuously within every generating position. Hence, the load at the cutting edge varies critically too and affects abrasive and crater wear on the tool. Nowadays gear hobbing is performed more and more without coolant which intensifies the thermal load and thus the wear phenomena.

To examine the performance of different coatings, cutting trials were carried out using the well-established fly-cutter analogy test. Subsequently the worn out single hob teeth are examined by REM and fringe projection to evaluate the wear phenomena.

To reduce crater wear and to extend the lifetime of gear cutting tools a range of AlCrN-based coatings was deposited in an industrial π411 rotating arc cathodes PVD unit. Significant performance differences between the chemically and structurally modified coatings were found. In this contribution the authors are focusing on the influence of the internal stress of AlCrN-based Hard Nitride Coatings on the wear behavior and tool life for both, high speed steel and solid carbide fly-cutters.

BP-43 Growth of B-Doped Diamond using Hot Filament CVD*, **Mai Imamiya**, Y Sakamoto,* Chiba Institute of Technology, Japan*; Y Takahashi, K Sugiura,* Material Processing Studio Co.,Ltd., Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω･cm. However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus.

However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} are used as dopant to synthesize boron-doped diamond. In this report, growth of B-doped diamond using Hot Filament CVD.

Hot Filament CVD was used for preparation of diamond. Reaction gases were used CH_4 and H_2. Boron sourse was trimethyl-boron. The synthesis pressure was 4.0 kPa, reaction time was 5 h and distance between the filament and the substrate was kept 8 mm. The surface morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Electrical resistivities were measured by the four-point probe method.

As a result of SEM observation, particle was about 1 μm in diameter. Crystal orientation of the deposits was (1 1 1) facet. In Raman spectra, of all the samples, the broad peaks at around 500cm^{-1}, 1230cm^{-1} and the weak peak at 1333 cm^{-1} were observed. These peaks due to the films includes of boron. As a result of the electrical resistivity measurements by the four-point probe method, the lowest electrical resistivitie was 1.6×10^{-4} Ω･cm.

As a result of investigation, boron-doped diamond films were fabricated using Hot Filament CVD and films were orientated to (1 1 1) facets. In the Raman spectra of the films, the peaks caused high boron concentrations were observed.

BP-44 Formation Of Anti-Reflection Double Layers For Si Lens By Atomic Layer Deposition*, **Jaeyeong Heo**, K Kim,* Chonnam National University, Republic of Korea

Increasing demand for mobile services like SNS and movies requires high-speed optical connectivity. In this regard, silicon (Si) photonics takes the center stage in which data is transferred among computer chips by optical rays. Optical transceiver is an integrated circuit that transmits and receives data using optical fiber. For optical transceiver, silicon has recently been highlighted as a material for optical coupling lens due to its low transmission loss and high refractive index. It is expected to increase the coupling efficiency further by fabricating a proper anti-reflection (AR) coating. First, we used Essential Macleod program to simulate the reflectance of single and double-layer anti-reflection coating. Then, we used atomic layer deposition for fabricating anti-reflection coating on Si substrates such as TiO_2 and Al_2O_3. Single layer and double-layer schemes were compared. Detailed structural and optical properties of these AR coatings will be presented.

BP-45 Texture, Mechanical and Electrochemical Properties of Magnetron Sputtered $Cr_{1-x}W_xN/Si_3N_4$ Super Hard Nanocomposite Thin Films for Protective Coatings*, **Ravi Prakash**, D Kaur,* Indian Institute Of Technology Roorkee, India

The effect of tungsten content in $Cr_{1-x}W_xN/Si_3N_4$super hard nanocomposite coatings deposited using reactive DC magnetron sputtering on the silicon substrate (100) has been investigated. The texture, surface morphology, hardness, young modulus and corrosion resistance were studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), nanoindentation and electrochemical potentiostat respectively. The XRD results show that the $Cr_{1-x}W_xN/Si_3N_4$solid solution formed with preferred orientations of dominant (111) and (200). The crystallite size initially decreased and the increased with the W content. The XRD peaks shifts towards higher angle with the increased as W content increases. Hardness and young modulus of films initially increase and then decrease with increasing tungsten concentration. The maximum values of hardness 42~45 Gpa and young modulus ~500 Gpa were found for tungsten content in the range 4-32 at %. Electrochemical studies of the films indicate that the best corrosion rate (38 nmy) was found at 43% of tungsten content which is excellent compared to other reported value. This study proposed that $Cr_{1-x}W_xN/Si_3N_4$nanocomposite thin films could have future potential as protective coatings.

BP-46 Internal Stress on Adhesion of Hard Coatings Synthesized by Multi-arc Ion Plating*, L Qiu, **Xiaodong Zhu**, K Xu,* Xi'an Jiaotong University, China

Hard coatings have been widely employed in tools, dies and wear-resistant parts. Most commercial coatings are limit in a few microns due to the adhesion problem induced by the stress developed at the film/substrate interface during film deposition and subsequent cooling processes. The residual stress state is considered to be key factor governing the adhesion of thick hard coatings. It is significant to understand the relationship between the residual stress and the bonding strength of hard coatings.

In this work, one group of TiN coatings was prepared by multi-arc ion plating (MAIP). In order to investigate the influence of the residual stress on coating's adhesion, all coatings were synthesized with the same pretreatment and interlayer to obtain an identical interfacial state. During the coating deposition, the working pressure and bias voltage were varied respectively to obtain different residual stress. The average residual stress of the coatings was calculated from the bending deformation of the sliced steel substrate. The bias voltage is shown to have a strong impact on the residual stress of coatings. As the bias voltage increases from -10 V to -200 V, the residual stress increases from -1.8GPa to -3.2 GPa for the coatings with thickness of 10 µm, and the corresponding critical load by scratch test decreases from 60N to 40N. The working pressure is another important parameter that affects the residual stress. The stress level of the coating deposited under 6 Pa is -1.8 GPa in comparison to -2.2 GPa which deposited under 1 Pa, and the critical load by scratch is higher. Higher bias or lower working pressure may cause higher ion energy transferred to deposition ions, and produce fine grain structure.

Another group of TiN coatings with five thicknesses (3.7µm, 5.8µm, 9.7µm, 15.5µm and 25µm) was coated under same parameters and different deposition time. Low critical loads by scratch and indentation tests are obtained for the thick coating indicating the high interfacial stress, yet its average residual stress is lower. Finite element analysis was employed to reveal the stress at the interface. It is found that high residual stress results in a lager shear stress at the interface. This implies that the accumulated residual stress is more appropriate than the average one in characterizing the residual stress effect on coating adhesion for those with different thicknesses.

BP-47 Diamond-like Coatings using High Power Impulse Magnetron Sputtering*, **Tomas Kubart**, A Aijaz,* Uppsala University, Sweden

Diamond-like carbon (DLC) coatings exhibit excellent mechanical, electrical and optical properties such as high hardness, low friction coefficient, high refractive index which make them attractive for a wide range of applications from cutting tools to engine components. The main limitations of existing DLC solutions stem from its high internal stresses and limited thermal stability. High internal stresses in excess of ~10 GPa limit the maximum achievable thickness due to poor adhesion and limited thermal stability makes DLCs unsuitable for high temperature applications. In order to address these issues, strategies for developing a new generation of DLC coatings exhibiting low-stresses, high hardness, good adhesion and good thermal stability are desired.

This work deals with the development of a deposition process for DLC coatings based on High Power Impulse Magnetron Sputtering (HiPIMS). We synthesize DLC coatings using Ne-based HiPIMS process to enhance the ionization of C. For comparison, plasma and film properties using standard Ar-HiPIMS process are also studied.

The plasma properties investigated by time-resolved Langmuir probe measurement reveal that Ne-based HiPIMS discharge provides high density plasma with higher electron temperature that entails a higher C^+ ion fraction as compared to Ar-HiPIMS discharge. A direct consequence of higher C^+ ion fraction is the higher mass densities (up to 2.7 g/cm^3) obtained using Ne-HiPIMS process. Surprisingly, even the Ar-HiPIMS process led to a pronounced increase in the density (2.5 g/cm^3) albeit lower than in in Ne-HiPIMS. Results from time-resolved behavior of electron temperature and plasma density are discussed with respect to the properties or resulting films for both process gases.

Acknowledgement: The work has been carried out in frame of M-Era.Net project TANDEM supported by VINNOVA.

BP-48 Synergistic Effect of Cu/Cr Co-doping on the Wettability and Mechanical Properties of Diamond-like Carbon Films*, **Lili Sun**, P Guo, X Li, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

By choosing carbide-forming element Cr and non-carbide-forming element Cu as co-doped metal elements, we firstly fabricated Cu and Cr co-doped diamond-like carbon (Cu/Cr-DLC) films using a facile hybrid ion beam deposition system. The effect of Cu/Cr co-doping on wettability and mechanical properties of DLC films were focused. The resultant Cu/Cr-DLC films were shown to afford good hydrophobicity and superior mechanical performance. In particular, the film with Cu11.88%Cr6.57% (at.%) exhibited a relatively high water contact angle of 103.6°, lower residual stress of 0.89 GPa and high hardness of 13.44 GPa. The combined structural analysis demonstrated that the synergistic Cu/Cr co-doping resulted in the critical and significant relaxation of distorted C-C bond length, which ultimately caused the reduction in residual stress. Due to the formation of hard Cr carbide nano-particles in amorphous carbon matrix, the films maintained the high value of hardness. Noted that the interesting wetting variety from hydrophilic to hydrophobic state was attributed to the enhanced surface graphitization and emergence of copper oxidation phases. The film topographical structure could also promote the hydrophobicity when the maximum height of roughness was in a certain range. These results provide an expected robust method to make DLC film a promising protective coating for long lasting hydrophobic application and related harsh fields.

BP-49 Novel Technology for ta-C Coatings Deposition*, **Jan Kluson**, M Jilek, Jr.,* PLATIT a.s., Czech Republic

Platit presents a novel patented technology enabling to prepare ta-C coatings with their unique properties in industrial scale. The technology is based on the cathodic vacuum arc burning on the cylindrical rotary cathode. The achieved coatings are designated as DLC^3 and represent the 3rd generation in the Platit DLC family. These coatings are characterized by very high mechanical hardness around 80GPa. Measurements of microhardness were complemented with Raman spectrometry which revealed sp^3 to sp^2 ratio up to 85%. DLC^3 coatings are further characterized by very low friction coefficient and low roughness. The given parameters can be achieved with a new focusing magnetic field source PisCoat (Pi smooth Coating) for particle filtering. Various applications of the technology will be shown.

BP-53 Evaluation of Plant-Extract-Based Metallic Nanoparticles for Corrosion Inhibition of Metallic Component*, **Omotayo Sanni**, A Popoola, O Fatoba,* Tshwane University of Technology, South Africa

Corrosion of metal is costly material science problems which originate from the day of metal discovery. Corrosion inhibitor usage is an effective way of addressing metallic corrosion in aggressive environments but continued usage of synthetic chemicals for inhibiting corrosion is indefensible as a result of toxicity of the chemicals to the environmental ecosystem. Eco-friendly corrosion inhibiting alternatives, including plant-extract usage, are therefore needed. Characterization of this nanoparticles material will be studied using. Ultra violet analysis, morphology by SEM-EDS and TEM analyses, phase composition by XRD analyses, inorganic element constitute analyses by RAMAN spectroscopy and organic element constituents' analyses by FTIR spectroscopy. Effect of the nanoparticles on metallic samples in different aggressive environment will be studied in the laboratory using weight loss method. The samples exposed to the inhibitors showed a lower corrosion rate values and excellent polarization resistance as compared with the corrosion rate samples without inhibitor. Grey relational used in this research correspond with the experimental results.

BP-55 Deposition of Crystalline Cr_2O_3 Coatings by Reactive Radio-frequency Magnetron Sputtering*, M Mohammad Taheri, Q Yang, **Jesus Corona Gomez**,* University of Saskatchewan, Canada

Reactive radio-frequency magnetron sputtering technique was employed to study the deposition conditions for crystalline chromium oxide films with Cr_2O_3 stoichiometry. Chromium oxide coatings with a thickness of 1-2 micrometers were deposited on Silicon wafers under various oxygen partial pressures and substrate temperatures. The effect of deposition parameters on the chemical composition, crystal structure, microstructure, phase composition, and hardness of coatings were investigated by electron dispersive spectroscopy, X-ray diffraction (XRD), scanning electron microscope, Raman spectroscopy, and nanoindentation, respectively. Crystalline coatings obtained by increasing the oxygen flow rate or the substrate temperature, however vitrification of coatings was triggered again by flowing more oxygen. No coatings could be deposited at temperatures higher than 300 ° C due to volatilization behavior of chromium oxides at high temperatures. The results illustrated that pure crystalline Cr_2O_3 coatings with highest hardness could be obtained at a substrate temperature of 300 °C and an oxygen content of 6 vol. %.

BP-56 Cerium Doping of Ti-Al-N Coatings for Excellent Thermal Stability and Oxidation Resistance*, H Asanuma,* Mitsubishi Materials Corporation, Japan*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; F Klimashin, H Riedl, **Paul H. Mayrhofer**,* Institute of Materials Science and Technology, TU Wien, Austria

Ti–Al–N thin films are well established due to their outstanding thermo-mechanical properties. Nevertheless, this system is still a subject of many research activities to further enhance their oxidation resistance and thermal stability. The addition of reactive elements, such as Cerium, can significantly improve especially the oxidation resistance of various materials. Therefore, we study in detail the impact of Ce (2 at% alloyed to powder metallurgically prepared $Ti_{0.50}Al_{0.50}$ targets) on growth processes, structure, mechanical properties, thermal stability, and oxidation resistance of magnetron sputtered $Ti_{1-x-y}Al_xCe_yN$ coatings prepared with DC bias potentials of U_{bias} = -25, -50, -75, and -100 V. The deposition rate is significantly increased by a factor of ~1.75 (U_{bias} = -25 V) to 1.45 (U_{bias} = -100 V) when using $Ti_{0.49}Al_{0.49}Ce_{0.02}$ instead of $Ti_{0.50}Al_{0.50}$ targets. Furthermore, also the hardness of the resulting single phase face centered cubic $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ is with ~35.2 GPa above that of $Ti_{0.42}Al_{0.58}N$ with ~33.7 GPa, for coatings on polycrystalline Al_2O_3 and U_{bias} = -50 V. Coatings on steel substrates typically show ~5 GPa higher values.

All temperature dependent characteristics of $Ti_{0.42}Al_{0.58}N$ are improved significantly by the addition of Cerium. Wurtzite-structured AlN formation within $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ can only be detected at T_a = 1100 °C, about 200 °C higher as for $Ti_{0.42}Al_{0.58}N$. Their peak-hardness, due to spinodal decomposition of the supersaturated cubic phase is ~37.0 GPa with T_a = 900 °C, as compared to 34.6 GPa with T_a =800 °C for $Ti_{0.42}Al_{0.58}N$. Additionally, even after exposure to ambient air at 950 °C for 3 h, still > 50 % of the $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ coating is intact (below the ~1.2 µm thin oxide scale), whereas $Ti_{0.42}Al_{0.58}N$ is already fully oxidized.

Based on our results we can conclude, that Ce-doping improves the deposition characteristics and mechanical properties as well as thermal stabilities (incl. oxidation resistance) of Ti–Al–N, to be used as protective coatings for a wide range of high-demanding applications.

BP-57 Arc Evaporated W-alloyed Ti-Al-N Coatings for Improved Thermal Stability, Mechanical, and Tribological Properties*, S Glatz,* Institute of Materials Science and Technology, TU Wien, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* ***Helmut Riedl,*** Institute of Materials Science and Technology, TU Wien, Austria*; P Mayrhofer,* Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, TU Wien, Austria

The protection of various tools and components through wear resistant coatings is imperative in highly efficient and precise industrial manufacturing processes. Especially, physical vapour deposited $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ coatings have been commonly used as hard protective coatings due to their outstanding thermal stability and mechanical strength. However, to increase the applicable working temperatures by simultaneously enhancing the wear performance (e.g., to allow for higher cutting speeds) further improvements are required.

Therefore, we studied in detail the impact of tungsten (W)—in combination with the substrate bias potential (U_{bias})—on the thermo-mechanical properties and wear performance of arc evaporated

$Ti_{1-x-y}Al_xW_yN$ thin films. With increasing W content the quality of our coatings significantly increases due to pronounced reduction of growth defects (quantity of macro particles). All coatings studied crystallise in a supersaturated, single-phased face-centred cubic $Ti_{1-x-y}Al_xW_yN$ structure and their hardness (H) increases whereas the indentation modulus (E) decreases with increasing W content. This results in increased H^3/E^2 values, with a maximum of 0.19 GPa for $Ti_{0.50}Al_{0.41}W_{0.09}N$ prepared with U_{bias} = -120 V (H ≈ 35 GPa, E ≈ 483 GPa). All W-alloyed coatings exhibit wear rates below $2 \cdot 10^{-5}$ mm³/Nm during our dry sliding pin-on-disk tests against alumina balls at room temperature, with a tendency for reduced values if more droplets are present. The highest thermal stability, with respect to the decomposition of the supersaturated $Ti_{1-x-y}Al_xW_yN$ phase towards the stable constituents (at high temperature) TiN, AlN, and W, is obtained for $Ti_{0.53}Al_{0.42}W_{0.05}N$ prepared with U_{bias} = -80 V. Here, the formation of the wurtzite-structured AlN can be delayed to 1000 °C after 60 min lasting isothermal annealings in vacuum.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B7

Plasma Diagnostics and Growth Processes

Moderators: Ante Hecimovic, Ruhr-Universität Bochum, Peter Bruggeman, University of Minnesota, USA

8:00am **B7-1 Plasma Surface Interaction Model for Titanium Nitride Thin Film Growth***, **Tobias Gergs**, J Trieschmann,* Ruhr University Bochum, Germany*; M Hans, D Music, J Schneider,* RWTH Aachen University, Germany*; T Mussenbrock,* Ruhr University Bochum, Germany

Reliable correlations between a set of plasma parameters and corresponding surface phenomena on the atomistic scale are scarce. The main reason being the complex physics of the two different states of matter, where at least one of which - the plasma - is far from an equilibrium state. In this contribution, we provide an initial step towards a consistent plasma surface interaction model, which covers the combination of generic materials as well as plasma discharges. As a proof of concept, we present a model which couples a direct current magnetron sputtering discharge with the resulting deposition of a titanium nitride thin film. In particular, the nucleation of cubic titanium nitride is studied at various substrate temperatures and fluxes starting from the amorphous state. Initially, the desired plasma parameter range is found by the extrapolation of classical molecular dynamics findings, validated by density functional theory calculations. This *a priori* knowledge is employed as a starting point for test particle simulations taking consistently into account the plasma and its global parameters. The resulting heavy particle fluxes and corresponding distribution functions are then again input to molecular dynamics simulations. Finally, the outcome of these simulations are compared to experimental results for the respective plasma discharge. In conclusion, it is argued that the proposed plasma surface interaction model is applicable to various plasma and material systems as well as surface modification phenomena.

Financial support provided be the German Research Foundation (DFG) in the frame of the collaborative research centre SFB-TR 87 is gratefully acknowledged.

8:20am **B7-2 Correlation of the Debye Sheath Thickness and (Cr,Al)N Coating Properties for HPPMS, dcMS and PCAE Processes***, K Bobzin, T Brögelmann, N Kruppe, M Arghavani, **Martin Engels**,* Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposited (PVD) coatings are widely-used in tool applications such as the plastics processing. Predominant aims of the PVD coating application on the tools are the enhancement of the tool lifetime and an improvement of economic efficiency. The achievement of these aims amongst others strongly depends on a homogeneous distribution of the coating properties with respect to the entire functional surface, in particular on complex shaped tools. In many cases, due to the line-of-sight characteristics in PVD processes this homogeneity is hard to achieve. Besides the commonly used rotation of the tools or extensive mounting concepts, another possibility to overcome this issue is the choice of a suitable PVD technology such as the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS), or the pulsed cathodic arc evaporation (PCAE). In order to characterize the influence of the different technologies on the coating homogeneity, the corresponding plasma properties, especially the Debye sheath thickness, can be used. Due to the positive charge in this area, the transport of positive charged ions of the coating material to the tool surface is strongly influenced. Therefore, it can be expected that a decreasing thickness increases the homogeneity of the coating, especially on complex surfaces with sharp edges, since the shielding of the surface is reduced. In the present work measurements on plasma properties as well as on coating properties using the high performance plasma processes HPPMS and PCEA with varying process parameters average power P, pulse length t_{on} and frequency f were carried out. In addition, the investigations were carried out as reference with a direct current magnetron sputtering (dcMS) process. In order to determine the Debye sheath thickness and the correlating homogeneity of coatings, the coating system (Cr,Al)N was chosen, as it is widely used as protective coating for plastics processing tools. In a first step, the plasma was analyzed using a Langmuir probe system. From the results of the U-I curves the plasma properties, especially the Debye sheath thickness, were determined. In a second step, (Cr,Al)N coatings were deposited with selected promising process parameters on structured substrates to determine the coating homogeneity. The coatings were analyzed regarding the morphology by scanning electron microscopy, the chemical composition by means of glow discharge optical emission spectroscopy as well as the universal hardness and the indentation modulus by nanoindentation. In summary, significant correlations between the processes and parameters, the Debye sheath thickness and the coating homogeneity were identified.

8:40am **B7-3 The Study of Spoke Merging and Splitting in HiPIMS Plasma***, **Jaroslav Hnilica**, P Klein,* Masaryk University, Czech Republic*; F Lockwood-Estrin,* University of Liverpool, UK*; P Vašina,* Masaryk University, Czech Republic*; J Bradley,* University of Liverpool, UK

High power impulse magnetron sputtering (HiPIMS) discharges demonstrate plasma self-organization, in which distinct ionization zones (often called spokes) can be seen to rotate in the ExB direction. Recently, a phenomena of spoke splitting and merging was observed in HiPIMS plasma using an array of phase correlated azimuthally arranged Langmuir probes around the discharge perimeter.

In our experiments, to gain more information on the temporal and spatial behaviour of self-organized spoke structures in HiPIMS plasmas, a correlation between the broadband 2-D optical image of an individual spoke and the current it delivers to the target has been made for a wide range of magnetron operating conditions. As a spoke passes over a set of embedded and isolated strip probes in the niobium cathode target, a distinct modulation in the local current density is observed, typically up to twice the average value associated with the spoke, as it delivers more current that the background plasma between spokes. It matching very well the radially integrated optical emission intensities obtained using 200 nanosecond time-resolved remote ICCD camera imaging. This allows us to relate the shape of spokes seen optically to their "electrical" footprint on the target.

The dual diagnostic system allows us to study the merging and splitting of a set of rotating spokes. It is found that during the merging process the trailing spoke retains its velocity. However, it is unclear whether during the merging process the leading spoke has decreased its velocity or the merging spokes have increased their azimuthal lengths. In the merged spoke both the plasma emission intensity and current collected by the embedded probes is redistributed to have their maximum at a trailing edge. In the spoke splitting process, the total charge collected by an embedded probe is conserved. Merged or split spokes are not always stable in time. Often the spoke system reverses to its former state a short time later.

A simple phenomenological model is developed to describe a stable spoke configuration. Assuming that argon presence is essential for spoke sustainment and based on spoke dimensions, spoke velocity and background gas atom velocity a stable amount of spokes can be predicted. The model provides realistic estimates for particular spoke and plasma conditions.

9:00am **B7-4 Al_2O_3- ZrO_2 Composite Coatings on Aluminum through a Hybrid Plasma Electrolytic- Electrophoretic Process***, **Nastaran Barati**, E Meletis,* University of Texas at Arlington, USA

Alumina-zirconia nanostructured layers were coated on 7075 Al alloy through a Plasma Electrolytic based technique in DC potentiostatic mode in the range of 540- 600 V. The layers were coated in an electrolyte containing nano ZrO_2 powder as the zirconia source. The microstructure and phase composition of the coatings were studied along with their tribological properties as a function of processing voltage.

The results showed formation of alumina- zirconia composites with different properties for the layers treated at different voltages. It was found that at higher processing voltage, the composite layers consist of high temperature phases (tetragonal zirconia and a-alumina) in addition to monoclinic zirconia. Also higher voltages introduced larger amounts of zirconia to the coated layers due to higher applied energies to the nanoparticles in electrolyte. The layers coated at 540 V and 580 V showed the lowest friction coefficient (0.14) compared to untreated Al alloy (0.69) in addition to better wear resistance (about 100 times higher in comparison to bare Al alloy). These improvements can be attributed to the formation of hard phases at high processing voltage. Furthermore, formation of tetragonal zirconia with better toughness and mechanical properties can result in improved wear resistance. The results revealed a hybrid of plasma electrolytic oxidation (PEO) and electrophoretic process as an effective coating method. In this regard, PEO was responsible for the formation of transformed tetragonal zirconia, while deposition of unchanged monoclinic zirconia from the electrolyte resulted from the electrophoretic process.

9:20am **B7-5 Low-temperature Atmospheric Pressure Plasma Processing and its Diagnostics for a Healthcare Device***, **Masaru Hori,*** Institute of Innovation for Future Society, Nagoya University, Japan **INVITED**

The healthcare has attracted much attentions from viewpoints of the innovation of industries and medicine. Technologies for the healthcare which is available everywhere and anytime has made a rapid progress by integrating various kinds of cutting edge multidisciplinary technologies in semiconductor manufacturing, plasma processing and bio fields. In recent years, microfluidic devices have received significant attention for a healthcare devices involving single cell trapping and analysis. We have been developing the non-equilibrium atmospheric pressure plasma for the fabrication of healthcare devices. The plasma is excited by a high-voltage alternating current (AC) power supply that provides a half peak voltage of 7 kV_{0-P} for a sinusoidal waveform with a frequency of 60 Hz. Argon (Ar) gas was supplied. The electron density and gas temperature were measured by the laser Thomson scattering method and optical emission spectroscopy.

The spatial distribution of absolute densities of O and N atoms were measured by the vacuum ultraviolet absorption spectroscopy (VUVAS). NO and OH were measured by laser induced fluorescence (LIF). Based these diagnostics results, the spatial distribution of radicals was systematically discussed.

The atmospheric pressure plasma was applied to the surface modification and the deposition of SiCHx films on the glass substrate. The surface wettability of micro-sized holes in glass substrates that are similar to those used as flow channels in glass microfiltration devices was drastically changed by the plasma treatment. As a result, the liquid transport flows were driven by internal Laplace pressure differences based on the surface tensions of droplets placed on the front and back sides of the tested substrates and thus cells were successfully trapped in the holes. The non-equilibrium atmospheric pressure plasma was also applied for the direct and indirect treatment of cells.

Using the multiplex coherent anti-Stokes Raman scattering (CARS) microscope, the dynamics of living cells during plasma treatments was observed. The multiplex CARS microscope enabled to obtain label-free information of the plasma-induced effects on the nature of chemical vibrations by probing signals of lipids and mitochondria from living cells

On the basis of these results of plasma diagnostics and plasma processing, plasma processes for the future healthcare are introduced.

10:00am **B7-7 Effects of Incident Particle Fluxes on the Growth and Properties of Ga-doped ZnO Films Deposited by Ion-plating with dc Arc Discharge***, **Hisashi Kitami,*** Sumitomo Heavy Industries, Ltd., Japan*; J Nomoto,* Kochi University of Technology, Japan*; T Sakemi,* Sumitomo Heavy Industries, Ltd., Japan*; H Makino,* Kochi University of Technology, Japan*; Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan*; T Yamamoto,* Kochi University of Technology, Japan

We have investigated the influences of incident particle fluxes during film growth on the growth and properties of gallium-doped zinc oxide (GZO) films on glass substrates (@200 °C) deposited by ion-plating with dc arc discharge. The Ga_2O_3 contents in the pellets was 4.0 wt.%. Deposition conditions were as follows: the oxygen (O_2) gas flow rates (OFRs) and discharge current (I_D) were varied from 0 to 20 sccm and from 100 to 140 A, respectively.

We measured the incident particle flux of the neutral atoms and ions for each species quantitatively at the substrate level using a mass-energy analyzer (Hiden, EQP300), a Langumuir probe and a diaphragm gauge during the deposition. To clarify the factors limiting the growth rate, carrier density (N), hall mobility (μ_H) and optical mobility (μ_{opt}) of GZO films, we investigated the relationship between the growth rates, N, μ_H, μ_{opt} and incident flux (IF) properties of Zn species such as neutral Zn atoms and Zn^+ ions and O species such as neutral O atoms, O^+ and O_2^+ ions.

We found that an increase in the sum of IFs of O, O^+ and O_2^+ during the film growth increased the growth rates of GZO films. For lower OFR values of 0 to 10 sccm, we found that N slowly decreased and μ_H rapidly increased with increasing the neutral O ratio (= $O/(O+O^+ +2O_2^+)$), regardless of I_D. With further increasing OFR up to 20 sccm, N decreases rapidly and μ_H increases slowly, regardless of I_D. On the other hand, we found that μ_{opt} increased linearly with increasing the neutral O ratio. The above findings imply the strong relationships among growth rates, a microstructure with point defects associated with O species and electrical properties of GZO films. We will discuss it in more detail.

10:20am **B7-8 Mapping Potential of an Ionization Zone in Magnetron Plasma***, **Matjaz Panjan,*** Jozef Stefan Institute, Slovenia*; A Anders,* Lawrence Berkeley National Laboratory, USA

Investigations over the last few years have shown that plasma in continuous and pulsed magnetron discharges is not azimuthally uniform rather it is organized in dense structures called ionization zones or spokes [1-2]. In this work we present measurements of the plasma potential of moving ionization zone in a direct current magnetron sputtering [3]. Measurements were recorded in a space and time resolved manner using movable emissive and floating probes. This allowed us to make a three-dimensional representations of the plasma potential and derive the related electric field, space charge and electron heating distributions. The data reveal the existence of strong electric fields parallel and perpendicular to the target surface. The largest **E**-fields result from a double layer structure at the leading edge of the ionization zone. Measurements imply that the double layer plays a crucial role in the energization of electrons since electrons can gain several tens of electronvolts from azimuthal **E**-field. As electrons drift over the magnetron there is a sustained coupling between the potential structure, electron heating, and ionization processes. The ionization zone moves in the $-\mathbf{E}_z\times\mathbf{B}$ direction from which the to-be-heated electrons arrive and into which the heating region expands. The motion of the zone is dictated by the force of the local electric field on the ions at the leading edge of the ionization zone. We postulate that electron heating caused by the potential jump and physical processes associated with the double layer also apply to high power impulse magnetron sputtering.

[1] A. Anders *et al.*, *J. Appl. Phys.***111** (2012) 053304

[2] M. Panjan *et al.*, *Plasma Sources Sci. Technol.***24** (2015) 065010

[3] M. Panjan and A. Anders, *J. Appl. Phys.***121**, 063302 (2017)

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