Monday Afternoon, May 20, 2019

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

PVD Coatings and Technologies II

Moderators: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), **Jyh-Ming Ting**, National Cheng Kung University, **Qi Yang**, National Research Council of Canada

1:40pm **B1-2-MoA-1 Harlan™: High Rate-High Density Pulsed Magnetron Sputtering Source for Depositing Metal & Ceramic Coatings for Industrial Applications.**, *B Abraham, **Roman Chistyakov**,* Ionex Corp, USA

A patented & proprietary high density/high rate magnetron deposition source developed in-house from the ground up. The development includes a newly designed high-density plasma generator and an improved magnetron deposition source far more superior to any conventional magnetron technology in the market today. The data presented will include deposition rates and X-SEM images of different thin films such as DLC , High Rate Metal Nitrides (MeN) and High Rate Metal Oxide (MeO), Highly Ionized Metal (Me).

2:00pm **B1-2-MoA-2 Arc Sources for Low Defect Coatings and High Target Utilization**, ***Victor Bellido-Gonzalez**, D Monaghan, B Daniel, R Brown, J Price, A Azzopardi,* Gencoa Ltd, UK

Cathodic arc deposition, also known as arc ion plating or arc evaporation, is a PVD technique utilizing arc sources to deposit non-reactive and reactive coatings, such as carbide, nitride, carbonitrides, diamond like carbon, etc. Compared to traditional magnetron sputtering, denser coatings can be obtained by arc sources due to a higher degree of ionization and thus higher potential energy of the vapour flux towards the substrate. Also the ability of generating metal ions enables adhesion enhancement in some particular processes, like hard coating on cutting tools. Usually, target evaporation by arcs rather than momentum transfer in sputtering leads to a higher deposition rate in arc deposition, and provides a higher degree of heat on the substrate, which is beneficial for some processes. Unlike in Reactive Magnetron Sputtering, reactive arc has a very wide window of process conditions for a successful reactive process. However the deposition conditions all affect the arc parameters and the levels of macroparticle defect on the coating. Different solutions for filtering of the macroparticles have been devised, such as venetian blinds and Magnetic Guidance Filters. It is desired however that the basic level of macroparticles is reduced at its origin.

This work aims to obtain low defect coatings without using macroparticle filters and to obtain high target utilization by controlling the arc travelling. A 125mm circular arc source with optimized design will be employed for nitride deposition. Reliable arc triggering has been realized without mechanical trigger. The arc source will be powered by an arc generator with the capability to vary the arc current during deposition. A small but effective and easily adjustable controller will be used for varying the magnetic field. The effects of varying the arc current and the magnetic field on the defect generation and the target erosion will be investigated. SEM/EDX will be used to characterize the coating defects.

2:20pm **B1-2-MoA-3 Cutting Tools in the Era of Industrial Internet of Things and Additive Manufacturing**, ***Aharon Inspektor**, A Rollett, P Salvador,* Carnegie Mellon University, USA

The Industrial Internet of Things (IIoT), which involves multi-level internet-connectivity of machines and systems, and additive manufacturing (AM) of complex 3D printed items hold great promise to revolutionize the manufacturing industry. In this paper we will discuss the impact of IIOT and AM on the machining sector and anticipated challenges and opportunities for cutting tools and hard coatings. We will examine how sensors that provide real-time internet-connected feedback on the conditions of the cutting edge will allow confident increase in cutting speeds and other machining parameters. This will lead to expansion of the safe zone in wear maps and call for improvements in tool materials and coatings. We will then review the structure and surface properties of AM 3D printed metal parts. Economic, large scale finish machining of rough 3D printed metals will challenge current finish cutting routines and accelerate suitable changes in design and structure of cutting tools. The IIOT sensors will affect, primarily, machining of bulk materials. AM and 3D printed metals will speed up progress in finish cutting. We will discuss both cases with appropriate examples of tools and coatings for machining high temperature alloys, gray cast iron, and carbon composites.

2:40pm **B1-2-MoA-4 Overstoichiometric Transition Metal Nitride Films**, ***Zuzana Čiperová**, J Musil, Š Kos, M Jaroš,* European Centre of Excellence, University of West Bohemia, Czech Republic

Transition metal nitride films TMN_x with a high stoichiometry $x = N/TM > 1$ are advanced films with new unique properties; here TM are the transition metals such as Ti, Zr, Mo, Ta, Nb, W, etc. We report on their properties and formation by the reactive magnetron sputtering using dual hybrid magnetron. The principle of formation of overstoichiometric $TMN_{x>1}$ films is explained. Three $TMN_{x>1}$ coatings were investigated in detail: $ZrN_{x>1}$, $Ti(Al,V)N_{x>1}$ and TiN_2 dinitride films [1]. It was found that (1) the overstoichiometric $ZrN_{x>1}$ films are two-phase films with c-ZrN and o-Zr_3N_4 structure, (2) the overstoichiometric $Ti(Al,V)N_{x>1}$ and $TiN_{x>1}$ films are one-phase films with c-TiN structure, (3) the one-phase overstoichiometric $TMN_{x>1}$ nitride films can form the TMN_2 dinitride films such as TiN_2 dinitride, (4) the film stoichiometry x is a strong parameter which enables to control its mechanical properties and electric conductivity; for example, the electrical resistivity of the ZrN_x film varies with increasing x from well electrically conducting films with $x \le 1$ through the semi-conducting films with x ranging from 1 to ≤ 1.26 to non-conductive with $x \ge 1.3$, and (5) the high base pressure $p_0 \ge 0.001$ Pa in the deposition chamber after its evacuation strongly influences the structure and phase composition of sputtered nitride films.

Reference

[1] J.Musil, M.Jaroš, Š.Kos, R.Čerstvý, S.Haviar: Hard TiN_2 dinitride films prepared by magnetron sputtering, J. Vac. Sci. Technol. A 36(4) 2018, 040602-1 to -3.

3:00pm **B1-2-MoA-5 Introducing of New Hybrid LACS® Technology (Lateral ARC and Central Sputtering by Rotating Cathodes)**, ***Radek Zemlicka**, M Jílek (Sr.), M Jílek (Jr.), A Lümkemann, T Cselle, D Bloesch, V Krsek,* Platit AG, Switzerland

The flexible coating units which are able to work with ARC, sputtering and PACVD technologies are very suitable for the small and medium size enterprise. While the ARC brings the highest performance for cutting tools in cca 85% of the applications, the sputtering achieves very smooth surfaces for better chip evacuation and DLC coatings, made by PACVD, avoids build up edges at cutting sticky materials. The combination of these 3 technologies in one coating unit enables the use the advantages of all of them.

We would like to introduce the new LACS® technology (Lateral ARC and Central Sputtering by rotating cathodes) . The new feature of this hybrid technology is the combination of arc evaporated non-alloyed metallic (Ti,Al,Cr,W, etc) and magnetron sputtered ceramic (TiB2, B4C) targets, resp. cathodes.

It allows to deposit different high-performance coatings, like AlCrN/BN, AlTiN/BN, TiWN, TiCNWCC or TiB2. On the other hand, the supplementary electron injection provided by ARC discharge can improve the microstructure and performance of the plasma-enhanced magnetron sputtered coatings.

On the example of BN-containing coatings we would like to illustrate how is it possible to optimize mechanical parameters of the coating by tuning of the process parameters. We will also present industrial applications of the optimized coating.

3:20pm **B1-2-MoA-6 Edge-related Effects During Arc-PVD Deposition Processes**, ***Tim Krülle**, F Kaulfuss, O Zimmer, A Leson, C Leyens,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

The deposition of different coatings on shaped surfaces, such as on cutting tools (drills) faces problems especially on edges [1-2]. Normally the radii of such cutting edges are dramatically increased, if the coating thickness is increased. Also defects, damaging or resputtering of material on edges may occur. A multilayered coating based on AlCrSiN instead showed an interesting effect of edge sharpening during the deposition process. With this approach it would be possible to overcome the problem of edge rounding in PVD coating technology. The pictures below show different edge radii varying with the negative bias voltage and leading to a smaller edge radius as compared to the uncoated tools or tools without additional bias voltage [3].

Therefore the deposition process and important deposition parameters were investigated and the geometry of such edges was measured. Accompanying nano indentation hardness measurements give an overview of mechanical properties around the surface also in dependence of position and chemical composition of the coating.

REFERENCES:

[1] H. A. Jehn, “PVD coating of 3D parts studied with model samples”, Surface and Coating Technologies, Vol. 94-95, pp 232-236, 1997.

[2] J. Bohlmark, “Evaluation of arc-evaporated coatings on rounded surfaces and sharp edges”, Materials Science Forum, Vol. 681, pp 145-150, 2011.

[3]T. Krülle, FhI-IWS Dresden, Annual Report 2016, “Sharp edges thanks to coatings”, pp 106-107.

3:40pm **B1-2-MoA-7 Reactive Sputtering for Highly Oriented HfN Film Growth on Si(100) Substrate***, **Yu-Siang Fang**, K Chiu, H Do, L Chang,* National Chiao Tung University, Taiwan

Hafnium nitride have excellent properties such as high melting point, high hardness, low resistivity, which makes them potential in many technological fields. HfN have been investigated for diffusion barriers in semiconductor devices. $HfSi_2$ has been used for high temperature oxidation resistant coatings. However, there are no detailed studies for growth of epitaxial HfN/$HfSi_2$ films on Si substrate.

HfN films were grown on Si(100) substrates by reactive DC magnetron sputtering with Ar/N_2 gas mixture using a Hf target. The deposition was carried out by varying N_2 flow ratio and the power at 5 mTorr and 850℃.

XRD results with cross-sectional TEM/STEM show that low N_2 flow ratio favors the formation of the HfSi- interlayer between HfN and Si, while no HfSi-$_2$ diffraction peaks can be seen for high N_2 flow ratio of 12.5% . Also, increasing the applied power for sputtering results in the increase of the HfN peak intensity ratio of (200)/(111). Furthermore, it is shown that the orthorhombic $HfSi_2$ interlayer is in epitaxy with Si (100) and those (100) oriented HfN grains are found in epitaxy with both $HfSi_2$ and Si as well. The epitaxial relationship is HfN (100) [011] // $HfSi_2$ (020) [100] // Si (100) [011].

4:00pm **B1-2-MoA-8 Study of Orthorhombic $ZnSnN_2$ Fabricated using Zn–Sn_3N_4 Composition Spreads through Combinatorial Reactive Sputtering***, **Kao-Shuo Chang**,* National Cheng Kung University, Taiwan **INVITED**

The piezo-related properties of $ZnSnN_2$ (ZTN) will be presented. Natural Sn_3N_4 and Zn thickness gradients were fabricated using combinatorial magnetron sputtering to form Zn–Sn_3N_4 composition spreads to enhance the relative variation of the cation ratios and to promote the formation of orthorhombic ZTN. Sn_3N_4 and the single crystallinity of orthorhombic ($Pna2_1$) ZTN nanocolumn arrays growing along the [001] direction were confirmed by locked-coupled XRD and TEM. The diffusion and variation of the atomic binding state of constituent elements were studied using SIMS depth profiling and XPS. The band gap of ZTN was estimated to be approximately 2.0 eV from a UV–vis measurement. The piezotronic and piezophototronic effects of ZTN were ascertained and illustrated by the Schottky barrier height variations. Excellent piezophotocatalysis was also observed, which was attributed to the reduced recombination of the photogenerated e^-–h^+ pairs. In addition, $^{\bullet}O_2^-$ radicals were predominate in the photodecomposition process.

4:40pm **B1-2-MoA-10 Angular Resolved Mass-energy Analyses of Species Emitted from a d.c. Magnetron Sputtered NiW-target***, **Martin Rausch**,* Montanuniversität Leoben, Austria*; S Mraz, J Schneider,* RWTH Aachen University, Germany*; J Winkler,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Advanced thin film applications e.g. in thin film transistors, electrochromic glasses or hard coatings frequently require sputtering targets consisting of multiple chemical elements with large differences in atomic weight. An understanding of sputtering, gas-phase transport and deposition characteristics of thin film systems deposited from such multi-element targets becomes increasingly important. For the previously investigated system $Mo_{0.70}Al_{0.20}Ti_{0.10}$ (m_{Mo}=95.95 u, m_{Al}=26.98 u, m_{Ti}=47.87 u) it was shown that not only (*i*) element-specific differences in sputter yield and initial emission angle, but also the (*ii*) transport of sputtered particles through the gas, accompanying (*iii*) collisions with background gas atoms with concomitant energy loss of sputtered particles, and (*iv*) the interaction of transmitted energetic particles with the surface of the growing thin film, such as preferential re-sputtering, will have an impact on the film morphology as well as the chemical composition of the films [1]. For the system NiW, which is used for the deposition of electrochromic thin films, the difference in atomic weight of the target constituents is significant (m_{Ni}= 58.69 u, m_W=183.84 u), making it an ideal model system to study the mechanisms mentioned above. Since it was concluded in [1] that the initial emission angle and the corresponding energy of sputtered atoms have a substantial impact on differences in morphology and chemical composition of the films, a 180 ° turnable magnetron with a mass-energy analyzer mounted opposite the target at a distance of 80 mm was used to d.c. sputter a $Ni_{0.80}W_{0.20}$ target at Ar pressures ranging from 0.01 to 1 Pa. This setup allowed measuring both, flux and energy of sputtered Ni and W, but also of Ar reflected from the target and ionized in the plasma, at any given angle between 0 and 90° with respect to the target normal. Subsequent thin film deposition with a spherical-shell substrate holder covering the examined angles at deposition positions from 0 to 80 ° in 10 ° steps allowed correlating the mass-energy measurements with thin film growth experiments. Film thickness measurements, structure and composition analysis yielded insights into the relation between emission angle and energy of transmitted particles and angular dependent structure and composition evolution of the deposited films.

[1] M. Rausch, M. Pavlovič, P. Kreiml, M.J. Cordill, J. Winkler, C. Mitterer, Applied Surface Science 455 (2018) 1029–1036.

5:00pm **B1-2-MoA-11 Effect Produced by Architecture of Nanolayer Composite Coatings Deposited with Filtered Cathodic Vacuum Arc Deposition (FCVAD) Technology on their Mechanical and Performance Properties***, **Alexey Vereschaka**, S Grigoriev,* Mstu Stankin, Russian Federation*; N Sitnikov,* National Research Nuclear University MEPhI, Russian Federation*; N Andreev,* National University of Science and Technology “MISiS”, Russian Federation

The paper deals with the technique of forming coatings with nanolayer structure, including nanolayers (formed due to rotation of a turntable in a chamber) and subnanolayers (formed due to planetary rotation of rigging elements). The SEM and TEM methods were used to study the coating structure. In particular, the Ti-TiN-(Ti,Al,Si)N, Zr-ZrN-(Zr,Cr,Al,Si)N and ZrNb-ZrNbN-(Zr,Nb,Cr,Al,Si)N coatings were considered. The thickness of binary nanolayers in the coatings under study was 20-70 nm, while the thickness of subnanolayers was 2-20 nm. The study also considered the mechanism of coating failure in scratch testing, depending on thickness of nanolayers and subnanolayers. The investigation found significant differences in the value of the critical failure force L_{C2} and the pattern of failure, depending on the thickness of coating nanolayers. The change in the value of adhesion component of the friction coefficient for samples with the coatings under study within the temperature range of 20-1000°C was studied. Cutting tests were conducted for carbide tools with the coatings under study in turning steel C45 at f = 0.25 mm/rev, a_p = 1.0 mm, v_c = 200-350 m/min. The patterns of wear and failure for coated tools were studied, as well as oxidation and diffusion processes. As a result of the conducted studies, a range of values for optimal thickness of nanolayers was determined to make it possible to increase the cutting speed by 25-30% while maintaining the tool life period and the high quality of the machined surface.

5:20pm **B1-2-MoA-12 Effects of Nitrogen Flow Rate and Substrate Bias on Structure and Properties of Molybdenum Nitride Thin Film***, **Cho-Cheng Chou**, J Huang,* National Tsing Hua University, Taiwan

Molybdenum nitride is well known as a wear resistant material with high hardness, which has three different thermodynamic stable crystal structures, tetragonal β-Mo_2N, cubic γ-Mo_2N, and hexagonal δ-MoN, among which γ-Mo_2N possesses the best mechanical performance. However, there is little research on the relationship of β- and γ-Mo_2N transformation. The purposes of this study are to investigate the order-disorder phase transformation of $Mo_{2-x}N$ thin film by controlling the deposition parameters, including nitrogen flow rate and substrate bias, and to explore the relationship between mechanical properties of different phases. The $Mo_{2-x}N$ thin films were prepared on Si substrate using unbalanced magnetron sputtering with different nitrogen flow rate and substrate bias. After deposition, the film hardness and crystal orientation were characterized by nanoindentation and X-ray diffraction, respectively. The residual stress of the thin film was measured using laser curvature and XRD $\cos^2\alpha\sin^2\psi$ methods, which may affect hardness and adhesion of the thin film. The microstructure was observed by scanning electron microscopy and atomic force microscopy. The electrical resistivity and chemical compositions were measured by a 4-point probe and X-ray photoelectron spectroscopy. Based on the experimental results, the mechanical properties were correlated to structure of the thin films.

Author Index

Bold page numbers indicate presenter