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

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Qi Yang, National Research Council of Canada, Jyh-Ming Ting, National Cheng Kung University

8:00am **B1-1-1 Boon and Bane of Internal Interfaces and Microstructure Defects***, **David Rafaja**,* TU Bergakademie Freiberg, Germany **INVITED**

The highest priority in materials technology is avoiding the material defects during the materials production. On the other hand, a targeted integration of microstructure defects into the materials structure can be as a very efficient tool for improving the materials properties. Still, when considering the defect engineering as a possible instrument of materials design, one should always distinguish between 'good' and 'bad' microstructure defects. In this contribution, several examples of microstructure defects and their impact on the properties of the thin films of nitrides and oxides of transition metals will be given with the emphasis on the production of metastable phases and on their stabilization at elevated temperatures by utilizing particular microstructure defects.

For titanium nitride coatings alloyed with aluminum it will be shown, how the partially coherent interfaces between adjacent crystallites can be formed in a deposition process and how the presence of such interfaces influences the hardness of the cathodic arc evaporated (Ti,Al)N coatings and the stability of metastable (Ti,Al)N having the rock-salt crystal structure. In this context, the role of the lattice misfit and the role of the microstructure defects like dislocations and stacking faults will be discussed. On the example of the (Ti,Al)N/(Al,Ti)N multilayers with partially coherent interfaces, the competition between the Gibbs energy and the strain energy will be illustrated.

As examples of metastable transition metal oxides, the $(Cr,Zr)_2O_{3+x}$ coatings deposited using reactive ion beam sputtering and the thin films of $(Zr,Ta)O_{2+x}$ deposited using radiofrequency magnetron sputtering will be addressed. For the first system, the solubility of zirconia in chromia driven by the microstructure defects and in particular the mechanisms of the incorporation of zirconium into the crystal structure of Cr_2O_3 will be discussed. For the second system, the deposition of oversaturated $(Zr,Ta)O_{2+x}$ having an orthorhombic crystal structure will be reported. For both oxide systems, it will also be shown, how the formation of nanocomposites and the presence of internal interfaces influence the thin films properties.

8:40am **B1-1-3 The Material (in) Dependency of Impurity Affected Thin Film Growth***, F Cougnon, D Altangerel, R Dedoncker, **Diederik Depla**,* Ghent University, Belgium

It is a well-known fact that the growth of metal thin films by physical vapour deposition is affected by the presence of contaminants or impurities. This is understandable due to the high chemical reactivity of metal thin films. First results have already been reported in the earlier seventies of previous century. A surprising point when analysing this older work is the presence of a power law between the domain size and the impurity-to-metal impingement flux ratio. In this paper the correlation between the domain size on the one hand, and the impurity-to-metal impingement flux ratio was studied in more detail for different materials for metals (Cu, Cr, Al), binary alloys (NiCr, CuNi) and complex alloys (CoCrCuFeNi). The thin films were deposited by DC magnetron sputtering, and the impurity flux was controlled by leaking air in the vacuum chamber. The domain size was determined by XRD which permits also to study the thin film texture and the behaviour of the lattice parameter. The analysis revealed that a power law behaviour between domain size and the impurity-to-metal impingement flux ratio was valid for all studied materials. Further, the materials could be separated in two groups depending on the power law exponent, and some interesting textural changes could be observed. Moreover, a linear correlation between the lattice parameter and the impurity-to-metal impingement flux ratio was observed for most materials. This material (in)dependency is intriguing which asks for a rather general valid explanation. Some of the possible reasons for this behaviour will be discussed in this paper.

9:00am **B1-1-4 Stress in Sputtered Metal Thin Films: Dependence on Growth Rate and Pressure***, T Kaub,* University of Alabama, USA*; Z Rao,* Brown University, USA*; G Thompson,* University of Alabama, USA*; **Eric Chason**,* Brown University, USA

Stress in sputtered films is a critical issue that affects the performance and lifetime of coatings. Many parameters play a role in stress evolution such as the growth rate, temperature, grain size and gas pressure. Therefore, a deeper understanding requires systematic studies combined with control and characterization of the microstructure. To address this, we have performed measurements of stress evolution in sputtered metal films at different growth rates and gas pressure. Metals with relatively high atomic mobility (Cu and Ni) were studied so that the effects of thin film growth and energetic particle bombardment could both be seen. This leads to a change in the dependence on growth rate at high and low gas pressures. The results are analyzed in terms of a model for stress evolution that includes both non-energetic and energetic processes.

9:20am **B1-1-5 Improved Ionization Fraction and Film Quality Using a Serpentine Linear Magnetron and a Modified HiPIMS Waveform***, **Ian Haehnlein**, B Wu, I Schelkanov,* University of Illinois at Urbana-Champaign, USA*; J McLain,* Starfire Industries LLC, USA*; D Patel,* University of Illinois at Urbana-Champaign, USA*; B Jurczyk,* Starfire Industries LLC, USA*; D Ruzic,* University of Illinois at Urbana-Champaign, USA

High Power Impulse Magnetron Sputtering (HiPIMS) produces film qualities superior to that of Direct Current Magnetron Sputtering (DCMS) at the cost of deposition rate attributed to returned ions to the target surface. By altering the magnetic field strength over multiple magnetic confinement regions, or multiple effective regions, the magnetic field strength can be made to drop off by 90% within 5cm of the target surface. This allows for controlled electron loss producing escape paths for ionized target material by ambipolar diffusion. Introducing a timed lower potential positive polarity pulse following the main negative polarity high power pulse while operating in HiPIMS utilizes the escaped ions by further accelerating the ionized target material away from the target surface that would otherwise be trapped within the magnetic field.

Through modification of the magnetic field in a 12.7cm by 25.4cm linear magnetron, a decrease in the confinement parameter of the magnetron allows for an increase in deposition rate for Cu yielding average deposition rates for HiPIMS of approximately 5.6nm/s +/- 0.1nm/s. For the same power DCMS using a standard magnetic field configuration, deposition rate was 5.5nm/s +/- 0.1nm/s. An increase in ion to total particle flux fraction from 13% +/- 2% to 35% +/- 3% at the substrate surface was measured using deposition rate in a gridded energy analyzer (GEA) with the same discharge conditions in HiPIMS. Introducing a positive polarity kick pulse following the high power pulse showed an even further increase in deposition rate (~15%) attributed to the increased repulsion of ions following the pulse. The positive kick induces a potential that increases the flux and energy of ions. This resulted in a decrease in residual tensile stress to from 1000 MPa +/- ~150 MPa with standard HiPIMS to 350 MPa +/- ~50 MPa using modified HiPIMS. This work presents the effects of various magnetic field configurations along with the plasma density and deposition rate effects of a positive polarity pulse modified HiPIMS.

9:40am **B1-1-6 Microstructural, Mechanical and Erosion Properties of Cylindrical Magnetrons Sputter Deposited TiSiCN, TiAlVN and TiAlVSiCN Coatings on Inner Surface of Cylinder***, **Ronghua Wei**, E Langa, J Lin,* Southwest Research Institute, USA*; W Zhao, L Li,* Beijing Sanju Enviro. Protect. & New Matls., China

In order to improve the erosion resistance of plunger valve expander, cylindrical magnetron sputtering (CMS) was used to deposit nanocomposite coatings. Three coatings of TiSiCN, TiAlVN and TiAlVSiCN were deposited via sputtering a tubular target made of either pure Ti or Ti-6Al-4V in a gas mixture of Ar+N2 with or without TMS (trimethylsilane, (CH3)3SiH). The TiSiCN coating was selected because it has been studied extensively in planar magnetron systems and it shows excellent erosion resistance, while TiAlVN and TiAlVSiCN, though less studied, also show good wear resistance. The coatings were initially deposited on stainless steel coupon samples that were mounted on the inner surface of carbon steel tubes that simulated the expander made of tungsten carbide (WC). After the depositions, the coating on the coupon samples were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), nano-indentation, micro-indentation, RC indentation for the coating thickness, morphology, microstructure, hardness and adhesion. Then the coupons were erosion tested using 50 µm alumina at two incident angles of 30° and 90°. The microstructural analyses indicate that the coatings have a nanocomposite structure consisting of nanocrystalline TiCN or Ti(AlV)CN with the grain size of 4-10 nm in a matrix of amorphous Si-C-N. These coatings are fairly hard in the range 20-30GPa. They also showed excellent erosion resistance. Based on the test results, two actual WC valve expanders were deposited with TiSiCN and TiAlVSiCN that will be tested in actual service. In this paper, we will discuss the design and characteristics of the cylindrical magnetron, the deposition process of the TiSiCN, TiAlVN and TiAlVSiCN coatings, and the microstructure and the erosion resistance of the coatings.

10:00am **B1-1-7 Template Effect on Texture Evolution of VN Thin Films Deposited by Unbalanced Magnetron Sputtering***, **Po-Chi Su**, J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the texture evolution of VN films deposited under the influence of Ti or V templates. Texture is a crucial factor in film mechanical properties, such as hardness and residual stress. Previous studies indicated that the texture of VN thin films can be controlled by nitrogen flow rate, substrate temperature, and substrate bias. At low temperature and high nitrogen flow rate (or low energy conditions), VN films showed loose-packed zone 1 columnar structure with (111) preferred orientation, while at high temperature and low nitrogen flow rate, the structure of VN films changed to zone T with dense columnar structure, and the texture became (200) prevailed. Since the atomic configuration of Ti (0002) is similar to VN(111), a Ti template layer with (0002) orientation was used to enhance the growth of VN(111). The goal is to change the microstructure of VN films with (111) texture from zone 1 to zone T, and further improving the mechanical properties of the VN thin films. On the other hand, the atomic configuration of V(110) is similar to VN(200), which may facilitate the formation of VN(200) texture. Thus, V template with strong (110) texture was applied to examine the texture evolution for the VN films deposited at conditions favoring the growth of (111) texture. By this way, the effect of template on the texture evolution of VN thin films can be evaluated. After deposition, the crystal structure and texture of the VN thin films were characterized using X-ray diffraction. The residual stress of the films was determined using laser curvature method. Film hardness and roughness were measured by nanoindentation and atomic force microscopy, respectively. The results showed that the Ti(0002) template may enhance the VN(111) texture, while V(110) template can facilitate the VN(200) preferred orientation. Based on the experimental results, the correlations between texture and different templates were explored.

10:20am **B1-1-8 *IN SITU* High Resolution Stress Measurement Coupled with Interrupted Deposition in Case of Völmer-Weber Thin Film Growth***, **Quentin Herault**, S Grachev, J Wang, I Gozhyk,* Saint-Gobain Recherche, France*; R Lazzari,* Université Pierre et Marie Curie, France

Low melting point materials (Au, Ag, Cu) exhibit Compressive-Tensile-Compressive (CTC) stress behavior during deposition. A new high resolution *in situ* stress measurement approach allowed us to observe such a behavior during sputter-deposition of Ag in greater detail . With a help of periodic interruptions, we observed stress relaxation at different stages of growth and interpreted it by thermal effects and adatom diffusion. Thermal heating during deposition was estimated by direct measurements and appeared to be an important part of relaxation curve at most of the conditions. Due to interruptions, the tensile and compressive peaks shifted considerably indicating an impact on the percolation threshold. Interruption frequency and deposition parameters such as substrate bias, working pressure and magnetron power were varied in order to modify particles kinetic energy and surface phenomena in general. This novel approach in combination with high resolution of the curvature measurement provided a more detailed view on the nucleation of film and on the stress generation phenomena.

10:40am **B1-1-9 High-Frequency Properties of Soft Ferromagnetic Films on Cemented Carbide Substrates an Approach for Sensor Applications***, **Stefan Beirle**, K Seemann, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

The thermal and mechanical induced high frequency property changes of soft ferromagnetic Fe-Co-Hf-N films with an in-plane uniaxial anisotropy are promising for the application for sensor systems. For example, one can use the sensor signal to measure the cutting tool temperature during metal processing. Consequently, it is necessary to investigate how the soft ferromagnetic Fe-Co-Hf-N film interacts with a cemented carbide substrate, which is typically used for cutting tools, but consists itself of an approximate 10 wt% hard ferromagnetic Co phase.

In order to overcome the exchange interactions between the substrate and the ferromagnetic film, it is possible to predeposit a non-ferromagnetic buffer layer by varying the thickness from 0.5 µm up to 5 µm on the WC-Co substrate. For this purpose different hard coatings like Ti-N and Ti-Al-N and an electrically insulating Si-O buffer layer were investigated. The buffer layers were deposited by D.C. and r.f. magnetron sputtering. On top of the layers a 200 nm thick Fe-Co-Hf-N film was deposited. After film deposition the samples were annealed in a static magnetic field to induce a uniaxial anisotropy in the ferromagnetic film plane. In order to determine the static and dynamic magnetic properties of the film, MOKE measurements were carried out as well as the complex permeability was determined by a strip-line permeameter setup. The buffer materials show a different decoupling behaviour regarding the high frequency permeability due to different electrical and microstructural properties. The decoupled ferromagnetic films exhibited an in-plane uniaxial anisotropy of about 4.5 mT and a saturation polarization of 1.4 T which results into a measurable ferromagnetic resonance absorbance at a frequency of 2.2 GHz. The FWHM of the resonance line can be tuned by increasing the buffer layer thickness, but only in the case of the electrically insulating Si-O buffer layer material. This can be explained by the formation of eddy-currents in the electrically conductive substrate or Ti-N / Ti-Al-N buffer material. So, the high-frequency properties of the decoupled film system can be exploited for a mechanical stress and/or thermal sensor system.

Author Index

Bold page numbers indicate presenter

— A —
Altangerel, D: B1-1-3, 1
— B —
Beirle, S: B1-1-9, **2**
— C —
Chason, E: B1-1-4, **1**
Cougnon, F: B1-1-3, 1
— D —
Dedoncker, R: B1-1-3, 1
Depla, D: B1-1-3, **1**
— G —
Gozhyk, I: B1-1-8, 2
Grachev, S: B1-1-8, 2
— H —
Haehnlein, I: B1-1-5, **1**
Herault, Q: B1-1-8, **2**
Huang, J: B1-1-7, 2
— J —
Jurczyk, B: B1-1-5, 1
— K —
Kaub, T: B1-1-4, 1
— L —
Langa, E: B1-1-6, 1
Lazzari, R: B1-1-8, 2
Leiste, H: B1-1-9, 2
Li, L: B1-1-6, 1
Lin, J: B1-1-6, 1
— M —
McLain, J: B1-1-5, 1
— P —
Patel, D: B1-1-5, 1
— R —
Rafaja, D: B1-1-1, **1**
Rao, Z: B1-1-4, 1
Ruzic, D: B1-1-5, 1
— S —
Schelkanov, I: B1-1-5, 1
Seemann, K: B1-1-9, 2
Su, P: B1-1-7, **2**
— T —
Thompson, G: B1-1-4, 1
— U —
Ulrich, S: B1-1-9, 2
— W —
Wang, J: B1-1-8, 2
Wei, R: B1-1-6, **1**
Wu, B: B1-1-5, 1
— Y —
Yu, G: B1-1-7, 2
— Z —
Zhao, W: B1-1-6, 1