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 $x \leq 0.6$. 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.

Author Index

Bold page numbers indicate presenter