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

CVD Coatings and Technologies I

Moderators: Kazunori Koga, Kyushu University, Japan, **Francis Maury**, CNRS-CIRIMAT

1:20pm **B2-1-ThA-1 Impact of HfO_2 as a Buffer Layer on the Electrical and Ferroelectric Memory Characteristics of Metal/Ferroelectric/High-K/Semiconductor Gate Stack for Nonvolatile Memory Applications***, R Jha, P Singh,* ***Manish Goswami,*** Indian Institute of Information Technology Allahabad, India*; B Singh,* Park Systems, India

For the proposed work, the electrical properties of metal-ferroelectric-insulator-silicon (MFeIS) capacitors with $Sr_{0.8}Bi_{2.2}Ta_2O_9$ (SBT) ferroelectric film deposited on HfO_2/Si substrate has been investigated. The SBT film was deposited by RF sputtering and HfO_2 film by plasma enhanced atomic layer deposition (PEALD). The structural characteristic of the deposited ferroelectric and dielectric films was obtained using X-ray diffraction and multiple angle ellipsometric analysis. Metal/Ferroelectric/Silicon (MFeS), Metal/Ferroelectric/Metal (MFeM), Metal/Insulator/Silicon (MIS) and Metal/Ferroelectric/Insulator/Silicon (MFeIS) structures were fabricated to obtain the electrical and ferroelectric properties. MFeIS structure with 10 nm buffer layer shows the improved memory window of 5 V as compared to the 3.07 V in the MFeS structures. $MFeI_{(10\ nm)}S$ structure even show endurance higher than 10^{12} read/write cycles and data retention for more than 8 hours. The effect of thickness and annealing temperature of buffer layer has also been investigated. The improvement in remnant polarization and coercive field due to the introduction of high-K layer has also been studied and compared with previous results .

1:40pm **B2-1-ThA-2 Studies on Properties and Cutting Performance of Al-rich AlTiN Coating with Controlled Orientation via LP-CVD***, **Yasuki Kido**, A Paseuth, S Okuno, S Imamura,* Sumitomo Electric Hardmetal Corp., Japan

Al-rich AlTiN is one of the important hard coatings for cutting tool. Among them, cubic phase AlTiN (c-AlTiN) comprising c-Al(Ti)N/c-Ti(Al)N nano-lamellae structure with high Al content and controlled orientation via LP-CVD has been modern coating due to high hardness and strength, compared to conventional CVD coating also AlTiN by PVD. The aim of this study is to investigate the effect of c-AlTiN coated carbide tools, as a function of component (Al/Ti ratio) and orientation, on mechanical and thermal properties also cutting performance. Deposition of c-AlTiN with controlled component and orientation was conducted by LP-CVD using AlCl3-TiCl4-NH3 precursor system. High-resolution transmission electron microscopy revealed formation of c-AlN and c-TiN-rich domains in nanometer scale. The c-AlTiN coating showed high hardness and compressive stress with adhesion by indentation technic, X-ray diffraction and scratch test. Also thermal property was measured. Furthermore, a cutting test for cast iron milling was performed with different kinds of component and orientation c-AlTiN coating on carbide tools.

2:00pm **B2-1-ThA-3 Effects of Al Content and Growth Orientation on Mechanical Properties of AlTiN Coatings Prepared by CVD Method***, **Kosuke Yanagisawa**, T Ishigaki, H Nakamura, H Homma,* Mitsubishi Materials Corporation, Japan

AlTiN coatings with high aluminum content have attracted attention due to its beneficial properties such as high oxidation resistance and age hardening effect on metal cutting. It is well-known that conventional AlTiN coatings are deposited by PVD method and the maximum aluminum content Al/(Al+Ti) is limited to lower than 0.67 to maintain a single phase cubic. Otherwise, in the range of aluminum content Al/(Al+Ti) higher than 0.67, they contain hexagonal phase which has lower hardness.

In this work, (111)- and (100)- oriented cubic AlTiN coatings with aluminum content higher than 0.67 were prepared on cemented carbide substrates by CVD method. Microstructure of the deposited coatings was observed by scanning electron microscopy, and the crystallographic orientation of these coatings was examined by X-ray diffraction analysis. Additionally, the hardness of these coatings was measured using nanoindentation and crack resistance property was evaluated by crack length induced by Vickers indentation, respectively.

From SEM observation, all of these coatings had columnar microstructures which contained self organised nano-lamellae structures in grains. Nano-lamellae structure in (100)-oriented coatings had a tendency to be smaller periods of the compositional fluctuation compared with those of (111)-oriented coatings, despite the almost same composition. As for the mechanical properties, the coatings with higher aluminum content or preferred (111) orientation showed higher hardness and higher crack resistance property. Thus, it was suggested that the hardness or crack resistance property of coatings was correlated to not only aluminum content but also the morphology of nano-lamellae structure.

One of possible explanation for the higher hardness, the deforming energy caused by indentation was dissipated by nano-lamellae structure. This effect is similar to a pinning effect for the propagation of the dislocations at interfaces of a multilayered coating. Regarding the superior crack resistance, it was attributed to crack deflection at the nano-lamellae structure.

Besides, these coatings were tested for the dry milling operation of 42CrMo4 steel blocks. It was indicated that CVD – AlTiN coatings with higher aluminum content showed superior wear and thermal crack resistance. On the other hand, the difference of coating orientation did not affect to the cutting results in this work.

2:20pm **B2-1-ThA-4 Thermal Crack Network Formation in CVD TiCN/α-Al_2O_3 Coatings***, **Nina Schalk**, R Stylianou, M Gassner,* Montanuniversität Leoben, Austria*; D Velic, W Daves, W Ecker,* Materials Center Leoben Forschung GmbH, Austria*; M Tkadletz,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

TiCN/α-Al_2O_3 coatings grown by thermally activated chemical vapor deposition on cemented carbide substrates typically exhibit a crack network as a result of the different thermal expansion coefficients (TEC) of coating and substrate material. Thus, the present work focuses on the investigation of these thermal cracks and on strategies to avoid them. The thermal cracks in industrially applied TiCN/α-Al_2O_3 coatings were studied in different conditions, i.e. in as-deposited state, after post-treatment by wet-blasting and annealing as well as after face turning, by scanning electron microscopy techniques. While wet-blasting results in closure of the thermal cracks near the coating surface due to the introduction of compressive stresses, annealing and turning lead to a relaxation of these stresses and thus in the reappearance of the cracks. In an attempt to avoid the formation or to reduce the density of cracks, TiCN/α-Al_2O_3 coatings were deposited on a series of cemented carbide substrates with cobalt contents of 6, 7.5, 10, 12.5 and 15 wt.%. The determination of the TEC of both, substrates and coating yielded a decreasing mismatch of the TECs with increasing cobalt content. At the highest cobalt content, no cracks and only low tensile stresses are observed in the coating. Decreasing the cobalt content yields first a tensile stresses maximum, followed by decreasing tensile stresses at even lower cobalt contents as a result of stress relaxation due to promoted crack formation. Finally, finite element simulations of the residual stresses in the coating after deposition, considering different crack distances, corroborate the experimental results.

3:00pm **B2-1-ThA-6 Structural and Piezoelectric Properties of Chemical Vapor Deposited AlN Films on Metallic Substrates***, **Juan Su**, M Pons, F Mercier, D Chen, R Boichot,* Université Grenoble Alpes, CNRS, France

To monitor the state of stress and damage in cutting tools or critical equipment working under extreme conditions such as high temperature, high pressure or aggressive chemical environment, the strongly textured AlN as a piezoelectric layer was successfully deposited on metals by Chemical Vapor Deposition (CVD) method. Low temperature textured TiN by CVD from $TiCl_3$-H_2-NH_3 system or AlN by Atomic Layer Deposition (ALD) is applied as a buffer layer to avoid the instability of metal substrates in CVD reactor during growth and decrease the huge mismatch between substrates and AlN layer. A design of experiment (DOE) is used to analyze the influence of 7 main process parameters and find a suitable experimental condition for depositing dense, covering and textured AlN. The morphology, XRD results and piezoelectric coefficient d_{33} are compared and analyzed. Unexpectedly, the results show that (200) textured TiN is a good buffer layer to obtain (002) textured AlN on WC-Co. On the contrary, the AlN with the thickness of 90 nm deposited by ALD is the best buffer layer for TZM. At last, the relationship between texture coefficient and d_{33} is studied considering 10 different orientations of AlN. It proves that when (002) texture coefficient is less than 2, d_{33} almost keeps constant at 0.14 pC/N, then it increases linearly to more than 2 pC/N while the theoretical bulk piezoelectric coefficient for AlN is around 6 pC/N.

3:20pm **B2-1-ThA-7 Aluminum Nitride Based Coatings for High Temperature Solar Receiver Systems***, **DanYing Chen,*** Université Grenoble Alpes, CNRS, France*; J Colas,* PROMES-CNRS, France*; J Su,* Université Grenoble Alpes, CNRS, France*; L Charpentier, M Balat-Pichelin,* PROMES-CNRS, France*; F Mercier, M Pons,* Université Grenoble Alpes, CNRS, France

There is a growing interest in concentrating solar power plants as electricity generation systems, whereby the sunlight is redirected and focused onto a receiver heated to high temperature. One of the challenges is to build the solar receiver which can work at temperatures near or higher than 1000 °C for optimizing the yield. Current candidate materials are metallic alloys such as Inconel, or bulk ceramics like silicon carbide, but their operating temperatures may be limited due to oxidation or mechanical problems. Aluminum nitride (AlN) coating, deposited by chemical vapor deposition at 1100 °C, was selected for its high thermal conductivity, low thermal expansion coefficient, high temperature stability and its oxidation resistance. It forms stable and protective alumina scales at temperatures higher than 1000°C. Oxide dispersion strengthened (ODS) FeCrAl alloy (Kanthal APMT), also alumina-forming, was chosen as a model substrate to study the potential of AlN coatings. Accelerated cyclic oxidation and high temperature emissivity measurements were performed in Odeillo solar furnace facilities (France), confirming the potential of aluminum nitride coatings as materials for high temperature central receivers. The AlN based multilayered system exhibits low degradation after 1500 h of oxidation at 1100 °C in air. The modelling and simulation of stresses during thermal cycles taking into account the creep and growth of the oxide layer are used to show the limits of use of these materials.

3:40pm **B2-1-ThA-8 Residual Stress and Quantitative Texture of CVD Al_2O_3 Coatings***, **Zhenyu Liu,*** Kennametal Inc., USA*; S Tan,* University of Pittsburgh, USA*; D Banerjee,* Kennametal Inc., USA

Conventional CVD coatings on cemented carbide are characterized by tensile stress, due to high temperature of deposition and thermal expansion mismatch between substrate and coating materials. The stress results in a mesh like cracking pattern in the coating, and may reduce toughness of coating leading to premature failure. It has been demonstrated that the tensile stress can be reduced, or reversed into compression by different postcoat blasting treatment. It is clear that postcoat blasting can reduce the extent of tensile stress in functional layer or even modified the stress state into compressive. At the same time, the residual stress of deposited coating and stress relieve during the high temperature caused by *in situ* heating during the metal-cutting practice, in another word, the stress situation in the coating, will affect the ultimate metal-cutting performance as well.

Anisotropic properties of crystal material make the texture of coated thin films a very important factor to affect the metal-cutting performance. Most of investigations on coating texture are determined by texture coefficient. There is still lack of the quantitative textural analysis of the tool coatings. With the aid of XRD/EBSD, the quantitative analysis of texture components can be determined then provide better evaluation on the highly textured coatings, such as Al_2O_3.

4:00pm **B2-1-ThA-9 Gas Source Chemical Vapor Deposition of Wafer-scale Mono- and few-layer MX_2 (M=W or Mo and X=S or Se) and Their Alloys***, **Mikhail Chubarov,** T Choudhury, D Reifsnyder Hickey, S Bachu, N Alem, J Redwing,* The Pennsylvania State University, USA **INVITED**

Transition metal dichalcogenides (TMD) like WS_2, WSe_2, MoS_2 and $MoSe_2$, when thinned to a monolayer (ML) thickness show direct bandgap, valley spin polarization, reasonable charge carrier mobilities and relatively high optical absorption; properties relevant to many applications. In addition to binary materials, alloys of TMD materials are also promising. It was reported that electronic transport properties are not dramatically deteriorated for the TMD alloys, and alloying allows for bandgap engineering over a wide range between 1.56 eV (794.8 nm) for $MoSe_2$ and 2.01 eV (590.4 nm) for WS_2. To push these materials towards practical applications, wafer-scale epitaxial growth of ML and few-layer (FL) films is necessary which can be achieved using CVD. In this study, to achieve ML and FL epitaxial layers of TMD materials and their alloys, we use gas source CVD and sapphire ((0001) α-Al_2O_3) as substrates.

For the growth we employ metal hexacarbonyls ($W(CO)_6$ and $Mo(CO)_6$) and hydrides (H_2S, H_2Se) as precursors diluted in hydrogen (H_2) carrier gas. Deposition temperature for this class of materials is in the range between 800 and 1000 °C at a pressure of 50 Torr for sulfides and 200 Torr for selenides. For the growth of binary compounds, a previously developed multistep growth process was employed while for the alloys, a single step was implemented to minimize routes for the formation of compositional gradients in the resulting layers.

As a result, we obtained ML and FL films of TMD materials. Acquired samples showed epitaxial relation with the substrate, high intensity photoluminescence and, for the alloys, composition control was achieved over a wide range as determined using X-ray photoelectron spectroscopy. Growth of WS_2 films resulted in growth of epitaxial ML films ((10-10)WS_2//(10-10)α-Al_2O_3) with in plane twist of 0.1°, room temperature photoluminescence (PL) showed emission maximum at 2 eV and width of 0.04 eV with pronounced exciton and trion components as well as defect-bound exciton emission. Domain size and distribution of antiphases were studied using transmission electron microscopy (TEM). This showed a relatively low fraction of isolated antiphase regions.

$WMoS_2$ alloys showed variation in the PL peak position as well as a change in the Raman scattering spectra which can be correlated with the composition of the film. Microstructure of the films was studied using TEM that showed no distinct segregation of the metal atoms when continuous flows of metal precursors were used.

Further details on the growth and characterization of MoS_2, WSe_2 and $MoSe_2$ will be presented along with the results obtained from ternary alloy growth and characterization.

4:40pm **B2-1-ThA-11 The Effect of Dopants and Bilayer Period on Microstructure and Mechanical Properties of CVD Ti(B,C)N Hard Coatings***, **Christina Kainz,** N Schalk, M Tkadletz, C Mitterer,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria

The cutting performance of CVD TiN hard coatings can be improved by both, the alloying with additional elements, or through the application of a multilayered coating design. However, limited literature is available on the mutual influence of chemical composition and architecture on the properties of CVD Ti(B,C)N coatings. Thus within this work, a comparison of mono- and multilayered CVD hard coatings within the system Ti(B,C)N with a particular focus on their microstructure, mechanical properties and microscopic fracture behavior is presented. The coatings were grown onto cemented carbide substrates in an industrial-scale thermal CVD plant using BCl_3, CH_4, $TiCl_4$, N_2 and H_2 precursors. Transmission electron microscopy investigations showed a higher defect density and grain refinement in the ternary and quaternary coatings compared to binary TiN. X-ray diffraction confirmed the presence of the hexagonal TiB_2 phase embedded in the B-containing coatings within the face-centered cubic TiN or TiCN matrix. Nanoindentation revealed an increase of hardness with decreasing bilayer period for the multilayer coatings and the highest hardness (32.2±1.0 GPa) and Young's modulus (587±29 GPa) for the TiBCN monolayer coating. Finally, bending tests, performed with free-standing coating micro-cantilevers prepared by focused ion beam milling, provided insights into the effect of alloying and bilayer period on coating strength and toughness. This juxtaposition of different chemical compositions and architectures enables to identify the most promising coating for application in metal cutting.

Keywords: CVD, Ti(B,C)N, hard coatings, TEM, micromechanical testing

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