New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F4-2-WeA
Functional Oxide and Oxynitride Coatings II

Moderators: Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, **Marcus Hans**, RWTH Aachen University, **Jörg Patscheider**, Evatec AG

3:00pm **F4-2-WeA-4 Structural, Optical and Electrochromic Properties of Nanocrystalline WO_3 Thin Films***, **Madhuri Venkat Kalapala,*** VFSTR University, India

In the present work, WO_3 thin films were coated onto well cleaned corning 7059 glass, Silicon and ITO coated glass substrates by electron beam evaporation (EBE) technique under an oxygen partial pressure of $2x10^{-4}$ mbar by maintaining the substrate temperature at 6-8 °C and room temperature (RT). The deposited films were subsequently annealed at 400 °C in air at about 2 hours and the films were systematically characterised to analyse the electrochromic properties which are useful in emerging chromogenic technology. The structural, morphological, vibrational, optical and electrochromic properties of WO_3 films were studied by XRD, AFM, Raman, UV-VIS spectroscopy and Cyclic voltammetry respectively. XRD studies reveal that the prepared WO_3 films are completely monoclinic structure with different orientations. The AFM images and the grain sizes are comparable with the XRD data. The optical transmission and energy bandgap of the films increases with the lowering of temperatures to 6-8 °C. Finally it is found that, the coloration efficiency at the wavelength of 550 nm for the annealed films deposited at 6-8 °C is maximum 72.60 cm^2C^{-1}.

3:20pm **F4-2-WeA-5 Structure, Mechanical Characteristics and Thermal Stability of HS-PVD $(Al,Cr)_2O_3$ Coatings***, K Bobzin, T Brögelmann, C Kalscheuer, **Martin Welters,*** Surface Engineering Institute - RWTH Aachen University, Germany

Alumina coatings with corundum structure, α-Al_2O_3, bear great potential concerning the application under harsh conditions even at temperatures above T ≥ 900 °C and in corrosive or oxidative environments. Typically, α-Al_2O_3 is used on cutting and molding tools. However, the industrial deposition of α-alumina coatings is typically performed by chemical vapor deposition (CVD) at temperatures between 800 °C ≤ T ≤ 1,100 °C, which limits the choice of base materials. In the last decades $(Al,Cr)_2O_3$ coatings deposited by physical vapor deposition (PVD) attract great interest as an alternative to CVD α-Al_2O_3, due to their potential to form corundum-type structure at lower process temperatures. $(Al,Cr)_2O_3$ coatings with high Al content promise similar characteristics to α-alumina. However, the deposition of crystalline α-$(Al,Cr)_2O_3$ by PVD technology with high alumina content, $x_{Al} > 70$ at.%, is still one of the greatest challenges. So far, various PVD technologies, such as cathodic arc deposition and magnetron sputtering, were investigated concerning the deposition of α-$(Al,Cr)_2O_3$. The investigations showed that low deposition temperatures, T ≤ 650 °C, and high aluminum contents, $x_{Al} > 70$ at.%, frequently led to the formation of metastable amorphous or crystalline alumina phases. Further drawbacks are low coating thicknesses and deposition rates for the deposition of oxide coatings as well as challenges regarding the coating of complex geometries. A promising technology to overcome these challenges is the high speed (HS)- PVD technology, basing on a hollow cathode discharge. Owing to the promising technology characteristics, the potential of HS-PVD concerning the deposition of α-$(Al,Cr)_2O_3$ was fundamentally investigated. After successful process adjustment, the deposition of crystalline tetragonal $(Al,Cr)_2O_3$ coatings and semi-crystalline α-$(Al,Cr)_2O_3$ coatings with high Al content, $x_{Al} \geq 70$ at.%, was possible by HS-PVD at a substrate temperature of $T_s = 570$ °C. The analyses regarding structural characteristics confirm that the deposition of thick, s ≥ 20 µm, oxide coatings with high deposition rates above 35 µm/h is possible by HS-PVD. Furthermore, nanoindentation shows that an indentation hardness of $H_{IT} = 24$ GPa can be achieved for the crystalline $(Al,Cr)_2O_3$ coatings. Moreover, the oxidation and diffusion behavior of the thick $(Al,Cr)_2O_3$ coatings was investigated by thermal annealing up to T = 1,300 °C in ambient air. Thereby, the annealing tests were evaluated by scanning electron microscopy, X-ray diffraction and nanoindentation. Analog annealing tests in vacuum confirmed the stability of the α-$(Al,Cr)_2O_3$ phase up to T = 1,300 °C.

3:40pm **F4-2-WeA-6 Reactive HiPIMS Deposition of γ -Al_2O_3 Thin Films using Transition Metal Doped Al Targets***, **Stefan Kagerer**, L Zauner,* TU Wien, Institute of Materials Science, Austria*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; J Čapek, T Kozák, P Zeman,* University of West Bohemia, Czech Republic*; H Riedl,* TU Wien, Institute of Materials Science, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

The outstanding oxidation resistance, thermo-mechanical stability, and chemical inertness of alumina attracts particular attention in academia and industry. Especially, in the field of hard protective coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. To overcome the thermodynamic barrier stabilizing these structure types, extremely high deposition temperatures are crucial during film growth (either in CVD or PVD). Apart from this fact, the formation of isolating Al_2O_3 layers on the target surface may lead to massive arc events, and hence destabilizes PVD based deposition process.

Therefore, alternative concepts involving PVD based synthesis at low temperatures are extremely interesting. Within this study, we investigated in detail the influence of small amounts of transition metals such as M = Cr or W on the process stability and phase formation of DC as well as high power impulse magnetron sputtered $(Al_{1-x}M_x)_2O_3$ thin films in reactive gas atmospheres (Ar/O_2 mixtures). Through the introduction of high amplitude impulses at relatively low duty cycles, the amount of ionized species, either for the target-near gas or sputtered target-atoms, can be increased drastically. To gain an in-depth understanding on the influence of small amounts of tungsten compared to pure Al targets but also on different HiPIMS parameters (e.g. frequency, pulse length, power density, or synchronized bias signals), the ionization of e.g. Al^+, Al^{++} or O_2^+ was investigated by ion mass spectroscopy methodically. In addition, the obtained coating structures were analyzed with respect to phase formation and morphology applying X-ray diffraction combined with electron imaging techniques (SEM and HR-TEM).

4:00pm **F4-2-WeA-7 Influence of V Content on Phase Evolution and Thermal Stability of Reactive Pulsed DC Magnetron Sputtered $(Al,V)_2O_3$***, **Ludvig Landälv,*** Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden*; C Carlström,* Sandvik Coromant R&D, Sweden*; J Lu,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; M Johansson-Jõesaar,* SECO tools AB, Sweden*; M Ahlgren, E Göthelid,* Sandvik Coromant R&D, Sweden*; B Alling, L Hultman, P Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited corundum structured α-Al_2O_3 coatings have been a long sought goal for the cutting tool industry. Various PVD synthesis routes have been evaluated comprising, e.g., Cr alloying in $(Al,Cr)_2O_3$ to stabilize the corundum phase [1, 2]. Correspondingly, based on V_2O_3 crystallization in the corundum structure, similar possibilities are indicated for phase stabilization in $(Al,V)_2O_3$ alloys, although this material system has not yet been studied as much.

This work aims to investigate the influence of V concentration in reactive co-sputtered $(Al,V)_2O_3$ coatings on phase stabilization and phase evolution, correlated to its mechanical properties by nanoindentation. XRD and SEM characterization of the as-deposited coatings reveal three different phase-regions as a function of V content in the coating with a solid solution γ-$(Al,V)_2O_3$ for low V content, a defect spinel at around 50 at % metal fraction V and a corundum phase at large V content.

The phase stability and mechanical properties of $(Al,V)_2O_3$ coatings were studied after annealing in air at different temperatures up to a maximum of 1100 °C. SEM, XRD and nanoindentation was performed after each temperature step. The annealing resulted in formation of vanadiumoxide phases, predominantly V_2O_5, at the coating surface with an onset temperature correlated to the amount of V in the coating. A higher V-content resulting in a lower onset temperature. The effect of the oxidation behavior of the coatings with respect to mechanical properties will be discussed.

[1] Ramm, J., et al., Surf. Coat. Technol., 2007, **202**(4–7): p. 876-883.

[2] Khatibi, A., et al., Acta Mater., 2013, **61**(13): p. 4811-4822.

4:20pm **F4-2-WeA-8 Al Vacancies in Wurtzite Al-(Si-)(O-)N: Theory and Experimental Assessment***, **Maria Fischer**, M Trant, K Thorwarth, D Scopece, C Pignedoli, D Passerone, H Hug,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Transparent hard films can be fabricated from Al, Si, O and N by reactive direct current magnetron sputter (R-DCMS) deposition. Al-Si-N and Al-O-N are two possible ternary combinations. Up to 6% Si / 8% O, the coatings can maintain the crystalline structure of wurtzite AlN and incorporate Si / O in the form of a solid solution. As Si is an electron donor like Al, it will substitute the latter on a cationic lattice site. O, in contrast, is an electron acceptor like N, and thus replaces the latter on an anionic lattice site.

These two contrary substitutions induce the same microstructural evolution in wurtzite. The reason for this was found in the formation of cationic Al vacancies (V(Al)) in both cases, because both Si and O impose an electron excess onto the crystal system. The presence of V(Al) in Al-Si-N and Al-O-N has previously been supported by X-ray diffraction measurements, *ab initio* calculations and entropic considerations. With the present study, further experimental evidence for V(Al)s has been provided through Positron Annihilation Spectroscopy (PAS) and Lifetime (PALS) measurements of the latter. To corroborate the hypothesis on vacancy formation, PA(L)S has also been performed on a complementary material system containing anionic vacancies.

4:40pm **F4-2-WeA-9 Thermal Atomic Layer Etching of Oxide and Nitride Thin Films***,* ***Steven M. George,*** University of Colorado at Boulder, USA **INVITED**

Nanofabrication requires atomic layer control over both material deposition and removal. Thermal atomic layer etching (ALE) is based on sequential, self-limiting surface reactions. Thermal ALE is the reverse of atomic layer deposition (ALD). Thermal ALE yields isotropic etching. Thermal Si ALE complements plasma ALE processes that utilize directional ions and produce anisotropic etching. This talk will focus on the thermal ALE of oxide and nitride thin films.

Thermal Al_2O_3 will be described using sequential fluorination and ligand-exchange reactions [1]. During these reactions, HF is utilized to fluorinate the Al_2O_3 surface and produce an AlF_3 surface layer. Trimethylaluminum (TMA) is then used to remove the AlF_3 surface layer through a ligand-exchange reaction. During this ligand-exchange, fluorine transfers from AlF_3 to TMA and, concurrently, methyl groups transfer from TMA to AlF_3. This ligand-exchange process yields volatile $AlF(CH_3)_2$ products. Al_2O_3 etch rates of 0.51 Å/cycle are observed at 300°C [1].

Thermal SiO_2 ALE will also be demonstrated using a "conversion-etch" mechanism with TMA and HF as the reactants [2]. During SiO_2 ALE, the TMA is able to convert the SiO_2 surface to an Al_2O_3 surface layer. The Al_2O_3 surface layer is then removed by thermal Al_2O_3 ALE as described above. The conversion of SiO_2 to Al_2O_3 requires higher TMA pressures. Larger SiO_2 etch rates are observed at higher TMA pressures [2]. In addition, thermal TiN ALE will be presented using oxidation of TiN to TiO_2 and then the removal of the TiO_2 surface layer by fluorination to a volatile fluoride [3]. TiN ALE at 250°C using O_3 and HF as the reactants yields a TiN etch rate of 0.2 Å/cycle.

[1] Y. Lee, J.W. DuMont and S.M. George, *Chem. Mater.***28**, 2994 (2016).

[2] J.W. DuMont et al., *ACS Appl. Mater. & Interfaces***9**, 10296 (2017).

[3] Y. Lee and S.M. George, *Chem. Mater.***29**, 8202 (2017).

5:20pm **F4-2-WeA-11 Growth and Characterization ALD Films with a new Continuous Flow Process***,* ***Birol Kuyel****, A Alphonse, K Hong,* Nano-Master, Inc., USA

Growth and film deposition characteristic in a downstream ICP PEALD reactor are studied using a unique new process called Continuous Flow Process* that cuts the cycle time in half. This process is implemented in an PEALD reactor where uniform variable density O_2 and N_2 or H_2 plasmas is produced but any contact of the plasma with the substrate is prevented. Precursors are not allowed to enter the plasma production region making it possible to obtain repeatable operation free of deposits or instabilities. Design features will be discussed and application of this Continuous Flow Process in depositing PEALD GaN, Al_2O_3, AlN, SiO_2 and Si_3N_4 films on Si substrates will be shown. Examples of Continuous Flow process is presented showing ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. Future applications will also be discussed.

*US Patent # 9,972,501 B1 May 15, 2018

Author Index

Bold page numbers indicate presenter