

## Advanced Surface Engineering Division Room 202C - Session SE+NS+TF-MoM

### Nanostructured Thin Films and Coatings

**Moderators:** Jianliang Lin, Southwest Research Institute, Matjaz Panjan, Jozef Stefan Institute, Slovenia

**8:20am SE+NS+TF-MoM-1 The Role of Mechanical and Chemical Bonding Mechanisms in Adhesion of Nanoporous Anodic Aluminium Oxides (AAO),** *Shoshan Abrahami*, Vrije Universiteit Brussel (VUB), Belgium; *V Gudla*, Technical University of Denmark; *K Marcoen*, Vrije Universiteit Brussel, Belgium; *J de Kok*, Fokker Aerostructures; *T Hauffman*, Vrije Universiteit Brussel, Belgium; *R Ambat*, Technical University of Denmark; *A Mol*, Technical University Delft, Netherlands; *H Terryn*, Vrije Universiteit Brussel, Belgium

Anodic aluminum oxides (AAOs) are important nanostructures in many engineering applications. But despite their popular use, the important parameters that control their (dis-)bonding to an organic coating are not fully understood. This study uses an original approach that employs porous- and barrier AAO specimens for both chemical characterization and mechanical tests, thereby enabling the distinction between chemical and morphological contributions to the surface affinity for interfacial bonding. A validation for the cooperative effect of mechanical and chemical bonding mechanisms is given in this study. This was achieved by post-anodizing immersion of AAO's in sodium fluoride solution after anodizing in sulfuric acid (SAA) or a mixture of phosphoric- and sulfuric acid (PSA). Transmission electron microscopy (TEM) cross-section images show that fluoride-assisted dissolution smoothed the oxide surface, removing the fibril-like top nanostructure of the porous oxides, which are important for dry adhesion. However, chemical surface modifications were dependent on the initial oxide composition, as measured by X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Chemical analysis reveals that the surface hydroxyls of AAO are partially replaced by fluorides that do not form interfacial bonding with the epoxy resin. As a result, the peel strength of SAA under wet conditions is severely reduced due to these chemical changes. Conversely, fluoride-assisted dissolution of surface phosphates in PSA compensates for the adsorbed fluorides and the wet peel strength of PSA panels is not further deteriorated.

[1] S.T. Abrahami et al., *J. Phys. Chem. C*, 119, 19967-19975 (2015).

[2] S.T. Abrahami et al., *npj Materials Degradation*, 1, 8 (2017).

[3] S.T. Abrahami et al., *J. Phys. Chem. C*, 120, 19670-19677 (2016).

**8:40am SE+NS+TF-MoM-2 Tuning Surface States of Nanocrystalline ZnO Films by Atomic Layer Deposited TiO<sub>x</sub>,** *C Yi, Ich Tran, M Law*, University of California, Irvine

We developed a facile route to tune the surface states of sol-gel prepared nanocrystalline zinc oxide (ZnO) thin films using ultrathin coatings of titanium oxide (TiO<sub>x</sub>) grown by atomic layer deposition (ALD). The electronic structure, surface states, and optical properties of the resulting ZnO/TiO<sub>x</sub> films are characterized by X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), reflection electron energy loss spectroscopy (REELS), UV-vis absorption spectroscopy, and photoluminescence (PL) spectroscopy. The surface bandgap of TiO<sub>x</sub>/ZnO is slightly increased comparing with that of ZnO. More importantly, we found that the surface gap states and interband transitions of ZnO were significantly suppressed by the TiO<sub>x</sub> layer, which may be useful for enhancing the performance of optoelectronic devices that utilize ZnO interlayers

**9:00am SE+NS+TF-MoM-3 Two-dimensional Hexagonal Boron Nitride (hBN) Layer Promoted Growth of Highly-oriented, Trigonal-structured Ta<sub>2</sub>C(0001) Thin Films via Ultra-high Vacuum Sputter-deposition on Al<sub>2</sub>O<sub>3</sub>(0001),** *Koichi Tanaka, P Arias, M Liao, Y Wang, H Zaid, A Aleman, M Goorsky, S Kodambaka*, University of California, Los Angeles

It is generally believed that single-crystalline substrates with either the bulk or surface structure and lattice constant identical or similar to that of the film being deposited are required for the growth of high-quality crystalline thin films. Recent studies have shown that deposition on van der Waals (vdW) layers can lead to highly-oriented thin films of a variety of crystal structures and lattice parameters. Here, we show that two-dimensional (2D) hexagonal boron nitride (hBN) layers ( $a = 0.250$  nm and  $c = 0.667$  nm) improve the crystallinity of trigonal-structured Ta<sub>2</sub>C ( $a = 0.310$  nm and  $c = 0.494$  nm) thin films sputter-deposited on Al<sub>2</sub>O<sub>3</sub>(0001) substrates. Ta<sub>2</sub>C

layers of desired thickness ( $t = 17 \sim 75$  nm) are grown on bare and hBN-covered Al<sub>2</sub>O<sub>3</sub>(0001) substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1327 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto Al<sub>2</sub>O<sub>3</sub>(0001) substrates at 1327 K. The as-deposited Ta<sub>2</sub>C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques.  $\omega$ -2 $\theta$  XRD scans acquired from both Ta<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub>(0001) and Ta<sub>2</sub>C/hBN/Al<sub>2</sub>O<sub>3</sub>(0001) films with  $t = 17$  nm exhibit only Ta<sub>2</sub>C 0002 $n$  reflections (corresponding to  $c = 0.494$  nm) while thicker layers ( $t = 75$  nm) reveal the presence of additional 10 1 reflections. However, the 0002 reflection peak intensities are 5.4-fold stronger for the Ta<sub>2</sub>C layers on hBN/Al<sub>2</sub>O<sub>3</sub>(0001) than bare Al<sub>2</sub>O<sub>3</sub>(0001). High-resolution TEM images and associated Fourier transforms indicate that the layers are single-crystalline. XRD  $\phi$  scans show six 60°-rotated 1 0 - 1 2 peaks of Ta<sub>2</sub>C at the same  $\phi$  angles for 1 1 - 2 6 of Al<sub>2</sub>O<sub>3</sub> based on which we determine the epitaxial crystallographic relationships between the film and the substrate as Ta<sub>2</sub>C(0002) || Al<sub>2</sub>O<sub>3</sub>(0006) with in-plane orientation of Ta<sub>2</sub>C[1 0 -1 0] || Al<sub>2</sub>O<sub>3</sub>[1 1 -2 0]. We further show that 0002-oriented Ta<sub>2</sub>C thicker films can be obtained by inserting hBN layers at regular intervals during the deposition of thicker Ta<sub>2</sub>C films.

**9:20am SE+NS+TF-MoM-4 Nitride High Entropy Alloy Thin Films Deposited by Magnetron Sputtering and Cathodic Arc on Polymer Substrates: Structure and Electro-Mechanical Properties,** *Ao Xia*, Montanuniversität Leoben, Austria; *R Dedoncker*, Ghent University, Belgium; *M Cordill*, Erich Schmid Institute of Materials Science, Austria; *D Depla*, Ghent University, Belgium; *R Franz*, Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as strength, ductility, corrosion resistance, wear resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the synthesis of MoNbTaVW HEA thin films by two different physical vapor deposition techniques, magnetron sputtering and cathodic arc deposition. The films were synthesized in Ar/N<sub>2</sub> atmosphere with varying gas flows in order to study the influence of N addition on structure and properties of the HEA thin films. Analysis by X-ray diffraction revealed a phase change from body-centered cubic (bcc) in case of the metallic HEA films to face-centered cubic (fcc) for the nitrides. A slightly lower N<sub>2</sub> gas flow is necessary in the case of magnetron sputter deposition to trigger the phase change than in the case of cathodic arc deposition. However, in both cases an increase in hardness was observed. For example, in the case of the films deposited by cathodic arc, the hardness increased from 18 to 30 GPa with the change from bcc to fcc phase. To further characterize the mechanical and electrical properties, the films were deposited on polymer substrates. The adhesion energy as determined from the geometry of buckles formed on the surface due to compressive stresses was a few J/m<sup>2</sup>. In-situ uniaxial tensile tests revealed a brittle behavior of all films with crack onset strains of up to 3 %. The formation of elongated through thickness cracks caused a rather abrupt increase of the resistivity upon the crack appearance.

**9:40am SE+NS+TF-MoM-5 Isomeric Phase Composition and Mechanical Properties of NbN Nanocomposite Coatings Deposited by Modulated Pulsed Power Magnetron Sputtering,** *Y.G. Li, H Yuan, Z Jiang, N Pan, M Lei*, Dalian University of Technology, China

Isomeric NbN nanocomposite coatings on stainless steel substrate with face-centered cubic phase  $\delta$ -NbN and hexagonal phase  $\delta'$ -NbN were deposited by modulated pulsed power magnetron sputtering under nitrogen flow rate  $f_{N_2}$  from 15% to 30%. It was found that the nitrogen flow rate  $f_{N_2}$  had a significant influence on the energy delivered in each macropulse, which led to a marked change in the phase composition and mechanical properties. The peak power decreases from 54 kW to 16 kW as  $f_{N_2}$  increases from 15% to 30% with the energy delivered in each macropulse from 23.2 J to 9.8 J. When  $f_{N_2}$  is at 15%, NbN coatings are mainly composed of  $\delta'$ -NbN phase which usually exists at high  $f_{N_2}$  or under high compressive residual stress showing (100) and (102) preferred orientation, while  $\delta$ -NbN gradually appears with the preferred orientation from (111) to (200) as  $f_{N_2}$  increases accompanied with the decrease of  $\delta'$ -NbN phase composition. The hardness and modulus of isomeric NbN nanocomposite coatings go up to 36 GPa from 30 GPa and 460 GPa from

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366 GPa as  $f_{\text{NbN}}$  increases to 20% with residual compressive stress from 0.47 GPa to 1.93 GPa, then decrease to 29 GPa and 389 GPa with residual compressive stress of 1.01 GPa showing a nonlinear response with peak power. The NbN nanocomposite coatings with more  $\delta'$ -NbN phase show higher hardness and better toughness due to the composition variation of  $\delta'$ -NbN and  $\delta$ -NbN phases. The phase composition from  $\delta'$ -NbN to  $\delta$ -NbN phase should attribute to the delivered energy difference by peak power, and the anomalous increase in hardness should be originated from strengthening of the nanocomposite structure.

10:00am **SE+NS+TF-MoM-6 Ab initio Guided Development of Ternary Borides: A Case Study of Ti-B-N, Ti-Zr-B, Ti-W-B, Ta-W-B, and V-W-B Systems**, V Moraes, R Hahn, M Bartosik, H Riedl, TU Wien, Austria; H Euchner, Ulm University, Austria; D Holec, Montanuniversität Leoben, Austria; **Paul Heinz Mayrhofer**, TU Wien, Austria

Transition-metal borides are a special class of ultra-high temperature ceramics. Among these, refractory borides such as TiB<sub>2</sub>, ZrB<sub>2</sub>, VB<sub>2</sub>, TaB<sub>2</sub>, and WB<sub>2</sub> are attractive candidates for many applications – ranging from high temperature electrodes, cutting tools, and molten metal containment to microelectronic buffer layers – because of their thermomechanical and chemical properties, their high melting temperatures up to ~3500 °C, and excellent high temperature strengths. However, these diborides have a comparably low fracture toughness of  $K_{\text{IC}} \sim 1$  MPa $\sqrt{\text{m}}$  (here, basically obtained by in-situ micromechanical cantilever bending tests).

How diboride materials can be designed – implementing quantum chemistry guided materials design concepts – to allow for a combination of high strength, ductility, and thermal stability, is the focus of this talk. We will use recent developments of diborides – where we applied alloying and architecture concepts (e.g., composition and/or phase modulated layers) – to explore such materials-science-based guidelines for improved properties. Especially the phase stability (with respect to chemistry and temperature) of diborides is an extremely interesting task. For example, only WB<sub>2</sub> (among all binary diborides, except for TcB<sub>2</sub>) provides a G/B ratio below 0.5 (~0.34) and a positive Cauchy pressure  $C_{13}-C_{44}$  (~73 GPa), which are typical indications for dominating non-directional bonds and thus a more ductile behavior. But WB<sub>2</sub> provides these properties only in its metastable  $\alpha$ -structure (AlB<sub>2</sub>-prototype) and not for its thermodynamically stable  $\omega$ -structure (WB<sub>2</sub>-prototype). With the help of ternary diborides, such as (Ti,W)B<sub>2</sub> or even (Ta,W)B<sub>2</sub>, the  $\alpha$ -structure can be stabilized (even up to ~1200 °C). Even more important is a selective sensitivity of the  $\alpha$ - and the  $\omega$ -structure for the formation of vacancies. Especially, when using physical vapor deposition (PVD) techniques at moderate temperatures (here ~400 °C) the content of vacancies (and point defects in general) is rather high. Such defects are less penalized in the  $\alpha$ - than in the  $\omega$ -structure, allowing for growing even single-phased  $\alpha$ -WB<sub>2</sub> by PVD, exhibiting hardnesses  $H$  of ~40 GPa combined with high fracture toughness of  $K_{\text{IC}} \sim 3$  MPa $\sqrt{\text{m}}$ .

With the help of superlattices, nanocolumnar and nanocomposite structures, we show that also with architectural concepts, strength ( $H \sim 45$  GPa) and ductility ( $K_{\text{IC}} \sim 3.5$  MPa $\sqrt{\text{m}}$ ) can be improved simultaneously.

The individual concepts will allow designing materials to meet the ever-growing demand for further improved coatings, tailor made for specific applications.

10:40am **SE+NS+TF-MoM-8 Toughness Enhancement in Hard Ceramic Films by Alloy Design**, **Hanna Kindlund**, Department of Mechanical and Aerospace Engineering, University of California Los Angeles (UCLA) **INVITED** Transition-metal nitrides are refractory ceramics with high hardness, excellent wear resistance, high temperature stability, and good chemical inertness. Therefore, they are attractive in many applications, especially, as protective coatings against scratches, erosion, corrosion, and wear.

Tremendous efforts have been dedicated in enhancing hardness of ceramic films. However, in addition to high hardness, most applications also require high ductility, to avoid brittle failure due to cracking when coatings are subjected to high thermo-mechanical stresses. However, transition-metal nitrides, as most ceramics, are usually brittle, exhibiting low ductility and hence poor toughness.

Enhancing toughness in ceramic films is a challenging task that requires a fundamental understanding of the mechanical behavior of materials, which depends on their microstructure, electronic structure, and bonding nature. Theoretical studies using *ab initio* calculations predicted that alloys of VN with WN or MoN exhibit enhanced toughness as a result of their high valence electron concentrations, leading to an orbital overlap which favors ductility during shearing.

Here, I present experimental results on the growth of  $V_{1-x}W_xN_y$  and  $V_{1-x}Mo_xN_y$  alloy thin films, their microstructure, mechanical properties and electronic structure, and relate these properties with their enhanced ductility, demonstrating that it is possible to develop hard-yet-ductile ceramic coatings.

11:20am **SE+NS+TF-MoM-10 From Ab-Initio Design to Synthesis of Multifunctional Coatings with Enhanced Hardness and Toughness**, **D Edström**, **D Sangiovanni**, **L Hultman**, Linköping University, Sweden; **I Petrov**, **J Greene**, University of Illinois at Urbana Champaign; **Valeriu Chirita**, Linköping University, Sweden

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack. New DFT calculations, suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC, as inferred from the electronic structure analysis and stress/strain curves obtained for the newly formed ternary TMC alloys.

KEYWORDS: nitrides, carbides, toughness, hardness, ductility.

11:40am **SE+NS+TF-MoM-11 Mechanical Properties of  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  Thin Films**, **Daniel Edström**, **D Sangiovanni**, Linköping University, Sweden; **L Landälv**, Linköping University, Sandvik Coromant AB, Sweden; **L Hultman**, Linköping University, Sweden; **I Petrov**, **J Greene**, University of Illinois at Urbana Champaign, Linköping University, Sweden; **P Eklund**, **V Chirita**, Linköping University, Sweden

Improved toughness is one of the central goals in the development of wear-resistant coatings. Extensive theoretical and experimental work has revealed that single-crystal NaCl-structure VMoN ceramics possess inherently enhanced ductility, as well as high hardness (~20 GPa) [Kindlund et al. APL Mat 2013]. These surprising findings demonstrate that VMoN-based materials are very promising candidates for replacing other ceramics in hard, refractory protective-coating applications. However, during applications, hard coatings inevitably oxidize which can compromise material properties. Herein, we use density functional theory to evaluate the mechanical properties, as well as the thermodynamical stability, of  $V_{0.5}Mo_{0.5}N_{1-x}O_x$ , with  $x$  approximately equal to 0.05, 0.1, and 0.5. We study cubic  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  solid solutions characterized by both high and low short-range cation/anion ordering.  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  is predicted to be thermodynamically stable for  $x < 0.1$ , although higher oxygen ratios can possibly be achieved with non-equilibrium growth techniques such as physical vapor deposition. Our results show that oxygen concentrations  $x = 5\%$  and  $10\%$  have little effect on the mechanical properties of random  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  alloys, which retain both hardness and ductility. At  $x = 50\%$ , bulk, elastic, and shear moduli, as well as Cauchy pressure, are reduced by ~25%, but the material is still predicted to remain ductile. For ordered  $V_{0.5}Mo_{0.5}N_{1-x}O_x$ ,  $x = 6\%$  already results in a drastic change in mechanical properties, likely due to disruption of the cubic symmetry. A further increase in the oxygen content yields significant reductions in Cauchy pressures, indicating reduced ductility. However, the Cauchy pressure remains positive for all oxygen concentrations, suggesting that none of the investigated alloys are brittle according to the Pugh and Pettifor criteria.

KEYWORDS: oxides, nitrides, toughness, hardness, ductility.

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