

## Hard Coatings and Vapor Deposition Technologies Room California - Session B6

### Coating Design and Architectures

**Moderators:** Nina Schalk, Montanuniversität Leoben, Shou-Yi Chang, National Tsing Hua University

8:00am **B6-1 Ab Initio Inspired Design of Ternary Boride Thin Films, Vincent Moraes, D Holec, CDL-AOS at TU Wien, Austria; H Bolvardi, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; P Polcik, Plansee Composite Materials GmbH, Germany; H Riedl, P Mayrhofer, CDL-AOS at TU Wien, Austria**

The demand for discovering new materials is, scientifically as well as industrially, a continuously present topic covering all fields of application. The recent scientific work on thin film materials (especially nitride based protective coatings) has shown, that computationally-driven understanding and modelling serves as a reliable trend-giver and can be used for target-oriented experiments.

Boride-, or diboride thin films in particular, show promising results when considering their use as hard protective coatings. Their drawback in ductility for binary systems calls for improvement via further alloying elements. Instead of trial and error, when designing novel ternary coating systems, we use a semi-automated High Throughput Search (HTS) calculating the basic properties (e.g., lattice parameters, bulk moduli, elastic constants, etc.) of all different  $TMB_2s'$  in two stable/metastable hexagonal structures (space group 191 with prototype  $AlB_2$  vs space group 194 with prototype  $W_2B_5$ ) via density functional theory (DFT).

After analyzing the data on behalf of different criteria such as matching lattice constants, high bulk moduli, brittle/ductile transition and experimental feasibility, promising ternary boride thin films were synthesized via physical vapor deposition (DC magnetron sputtering). Analyzing their structure and mechanical properties reveal the potential of this material combination, by reaching superhardness-level and allowing for phase transformation induced toughening effects.

8:20am **B6-2 Enthalpy/Entropy-driven Segregation of Solute Elements of Cu Alloy Films to Self-form < 2 nm Unitary V to Quinary V-Nb-Mo-Ta-W Diffusion Barrier Layers, Yu-Ting Hsiao, S Chang, National Tsing Hua University, Taiwan**

For next-generation integrated circuits, an ultrathin (< 2 nm) robust diffusion barrier layer between Cu wires and dielectric layers is demanded to inhibit the rapid diffusion of Cu atoms into Si devices. Due to the limitation of current thin-film deposition techniques, a "self-forming" or "barrierless" technique has alternatively been developed to generate an ultrathin barrier layer at Cu/dielectric interfaces, by annealing Cu alloy films at relatively low temperatures (~ 400°C) and segregating the solute elements of the Cu alloy films to the Cu/Si interfaces. In addition, multicomponent high-entropy alloys with severe lattice distortions and high resistance to Cu/Si interdiffusion have been suggested to be very promising diffusion barrier materials. Therefore in this study, Cu(V) to Cu(V,Nb,Mo,Ta,W) alloy films were prepared, and the self-forming technique was applied to fabricate ultrathin (< 2 nm) unitary V to Quinary V-Nb-Mo-Ta-W barrier layers. The segregation behaviors of the solute elements (V to V-Nb-Mo-Ta-W), thermodynamically driven by enthalpy and entropy-dominated free energy, were also investigated. High-resolution TEM observations and elemental mappings indicated that, owing to positive mixing enthalpies, the solute elements were separated from Cu during annealing (250-400°C). For the Cu(V) alloy film, the solute atoms segregated to the Cu/Si interface and formed a < 2 nm V layer. For the Cu(V,Nb), Cu(V,Nb,Mo) and Cu(V,Nb,Mo,Ta) alloy films, the solutes segregated to the grain boundaries of the Cu alloy films and formed intermetallic compound precipitates. For the Cu(V,Nb,Mo,Ta,W) alloy film, attributable to the high mixing entropy of the five solute elements, the solute atoms segregated to the interface and formed a < 2 nm V-Nb-Mo-Ta-W solid-solution alloy layer.

8:40am **B6-3 Mechanical Properties of  $V_{0.5}Mo_{0.5}N_{1-x}O_x$  Thin Films, Daniel Edström, D Sangiovanni, L Landälv, L Hultman, Linköpings Universitet, Sweden; I Petrov, J Greene, University of Illinois, USA; P Eklund, V Chirita, Linköpings Universitet, 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 ( $\approx 20$  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  $\sim 25\%$ , 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.

9:00am **B6-4 Hard Transparent Coatings in the Al-Si-O-N System, Maria Fischer, M Trant, K Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; J Patscheider, Ruebsteinstrasse 25, 8706 Meilen, Switzerland; D Scopecce, C Pignedoli, D Passerone, H Hug, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland**

The Al-Si-O-N material system allows for the creation of various hard, transparent thin films by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). Combinations of the possible binary materials AlN,  $Al_2O_3$ ,  $Si_3N_4$  and  $SiO_2$  lead on to ternary materials such as Al-O-N and Al-Si-N, and combining the latter two yields quaternary Al-Si-O-N. As long as the films are fully nitrated and / or oxidized, they are transparent and thus interesting for optical applications.

In the work reported here, polycrystalline AlN was chosen as starting point. By gradually adding O and / or Si, the material system first transformed into a solid solution with the dopant dispersed in the crystallites. Upon transgressing a distinct solubility limit at 6-8 at% for the foreign atoms, a nanocomposite evolved with an amorphous matrix surrounding shranked crystallites. Yet higher O and / or Si amounts lead to an entirely amorphous network.

Along with these microstructural changes, physical parameters such as hardness, elastic modulus and refractive index vary. This renders it possible to tune thin films to desired properties by simply choosing according deposition conditions. Applying R-UCFDCMS as a deposition technique far off thermodynamic equilibrium for this purpose allows for the generation of metastable, yet highly inert phases.

9:20am **B6-5 Exploitation of Surface Modification and Architecture Control for Multi-Functional Coatings via Nano-Composite, Multilayer, Hybrid Organic/Inorganic and Bio-Inspired Approach, J Lee, H Chen, J Lee, P Chen, Jenq-Gong Duh, National Tsing Hua University, Taiwan INVITED**

The exploitation of surface modification technique in materials related fields opens the pathway of continuous development to render the coating to exhibit added-values on satisfactory mechanical strength, thermal stability and corrosion resistance. The design concepts of coating can be regarded as integration of architecture, composition, morphology and process control, leading to significant enhancement in properties and functionalities. The primary tasks focus on a series of nitride coating via nanocomposite and multilayer architecture to improve the hardness, corrosion and oxidation resistance. Incorporation of hybrid approach of organic/inorganic and bio-inspired conceptual framework is then conducted, paving ways for a new frontier in protective coatings. Recently anti-wear CrAlSiN nanocomposite coating under extreme environment is derived. Self-lubricating CrAlN/VN multilayer coating is fabricated via microstructure control for improved mechanical property and high-temperature tribological characteristics. A parallel study is conducted in CrMoSiN nanocomposite to enhance the mechanical reliability, especially the elevated temperature tribological property. In addition, a newly-designed Zr-Cu based thin film metallic glass with various nitrogen contents are developed for application in multiple functionalities, including

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mechanical property, thermal stability, corrosion resistance, antimicrobial and diffusion barrier characteristics.

10:00am **B6-7 The Effect of Hybrid PVD Process on the Mechanical and Antistatic Properties of TiO<sub>2</sub> Based Nanocomposite Thin Film**, *Ding-Shiang Wang, M Leu, T Chen, H Lai, J Chang, J Shih*, Industrial Technology Research Institute, Taiwan

In this paper, mechanical and antistatic properties of magnetron sputtered, filtered arc ion plating (FAIP) and a hybrid PVD process (magnetron sputtered+FAIP) prepared TiO<sub>2</sub> based nanocomposite thin film were investigated. Both of the antistatic properties of different thin films were analysis by measuring resistance values and decay times. The results showed that for magnetron sputtered and hybrid process prepared TiO<sub>2</sub> based nanocomposite thin film showed resistance around  $10^{6-10^8}$  W/sq and a short decay time. But for the FAIP process, the resistance uniformity is at about 80 %. In terms of mechanical properties, the FAIP and hybrid process nanocomposite thin film showed adhesion and hardness at around 15 N , 14 N and 15 GPa, 12GPa. For the nanocomposite thin film prepared by magnetron sputtered the adhesion and hardness are only about 9 N and 10 GPa. Thus for a high quality of antistatic tin film the hybrid PVD process was recommend due to the excellent mechanical and antistatic properties.

10:20am **B6-8 Optical, Electrical and Structural Characteristics of Mg-doped CuCrO<sub>2</sub> Transparent Conductive Thin Films**, *Ruei-Sung Yu, C Chu*, Asia University, Taiwan

CuCrO<sub>2</sub> is a transparent conductive oxide with a wide bandgap greater than 3.0 eV. The oxide is a p-type semiconductor that the main carrier is hole. CuCrO<sub>2</sub> can be used in various transparent optoelectronic p-n diodes. This study is focused on the features of magnesium (Mg) doping on the improvements of optical and electrical properties for the CuCrO<sub>2</sub> films. It is anticipated that the p-type CuCrO<sub>2</sub> with high conductivity, which is conducive to the developments of transparent p-n devices. We prepared CuCrO<sub>2</sub> films by using sol-gel method and the annealing under controlled argon atmosphere, with the attempt to identify the chemical composition, crystal structure, cross-section microstructure, surface morphology, and optoelectronic properties. The modulation of sol-gel process, the precursor solutions used were copper acetate, chromium acetate, magnesium acetate, triethanolamine, and anhydrous ethanol. The annealing temperature was 600°C for 120 minutes. XPS, XRD, FESEM, AFM, UV-Vis, and Hall effect measurements were employed to analyze the material properties. This study has established to decrease resistivity of p-type CuCrO<sub>2</sub> film by doping magnesium. The CuCrO<sub>2</sub> films with Mg were increased gradually from 0.20 at.% to 2.17 at.%. These compositions deviated from the stoichiometric proportion of 25, 25, and 50 at.% of Cu, Cr, and O, respectively. In the films, Cu and Cr were insufficient quantity. The oxygen was higher than the set proportion. The Mg were introduced in the delafossite CuCrO<sub>2</sub> films without any impurity phase. With the increase of the Mg doping, the surface root mean square roughness values of the CuCrO<sub>2</sub> decreased from 23.4 nm to 16.6 nm, and the direct bandgaps of the thin films increased from 3.09 eV to 3.13 eV. The proper contents of Mg doping in the CuCrO<sub>2</sub> can improve transmittance, and the films possess a higher absorption ability for ultraviolet light. The magnesium (Mg<sup>2+</sup>) replaced chromium (Cr<sup>3+</sup>) in the lattice sites of CuCrO<sub>2</sub>, which can form carrier and increase the concentration. The resistivities of the undoped and optimal Mg-doped CuCrO<sub>2</sub> films were respectively 41.09 Ωcm and 0.64 Ωcm.

10:40am **B6-9 Brittle Film-induced Cracking of Ductile Substrates**, *Xiaolu Pang*, University of Science and Technology Beijing, China

Film and substrate mechanical integrity is essential for the whole system's performance. In the present study, cracking of brass ductile substrate induced by brittle TiN film fracture was observed. Counter-intuitively, instead of protecting the ductile substrate, a brittle film can cause its premature fracture, as demonstrated here experimentally. Brittle film fracture could induce cracking of ductile substrate at considerably low strain level. Analytical calculation based on energy conservation during crack propagation is presented to explain this phenomenon of film-induced cracking. It is shown that crack depth penetrated into the substrate is a function of both crack velocity and the number of dislocations emitted from the crack tip. Relatively thick brittle films and fast propagating cracks favor fracture of the ductile substrates. The critical crack velocity, which can induce the cracking of brass substrate, is 61 m/s. The presence of brittle film could not only prevent dislocations escaping from the surface of the crystal and inhibit dislocations emitting from surface dislocation sources, but also initiate a channel crack with high velocity due to brittle fracture. Both of them contribute to crack propagation in soft brass

substrate. This study provides an alternative view to the notion that a brittle film can protect the ductile substrate from damage.

11:00am **B6-10 Ultra-high Vacuum dc Magnetron Sputter-deposition and Microstructural Characterization of Zr and ZrC<sub>x</sub> Thin Films**, *Hicham Zaid, K Tanaka, J Fankhauser, A Aleman, UCLA, USA; M Mato, Nagoya University, Japan; D Yu, A Ebnonnasir, C Li, UCLA, USA; M Kobashi, Nagoya University, Japan; M Goorsky, S Kodambaka, UCLA, USA*

B1-structured, Group IVB and VB transition-metal carbides are some of the hardest (>20 GPa), high moduli (>270 GPa), and highest melting point solids with high-temperature mechanical strength, and good wear-, ablation-, and corrosion- resistance. In this talk, we present results from our recent efforts focused on the ultra-high vacuum dc magnetron sputter-deposition of thin epitaxial films of ZrC<sub>x</sub> of desired composition and crystallinity.

Zr and ZrC<sub>x</sub> thin films are deposited on single-crystalline Al<sub>2</sub>O<sub>3</sub>(0001) and MgO(001) substrates at temperatures T<sub>s</sub> between 723 K and 1323 K using pure Ar and Ar/C<sub>2</sub>H<sub>4</sub> gas mixtures, respectively. The as-deposited film surface structure and composition are characterized *in situ* using low-energy electron diffraction and Auger electron spectroscopy. The bulk crystallinity, microstructure, and composition of the films are determined using a combination of x-ray diffraction, transmission electron microscopy, energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy measurements. Using pure Ar discharges, we obtain single-crystalline hexagonal close-packed (hcp) Zr(0001)/Al<sub>2</sub>O<sub>3</sub>(0001) layers at 873 K ≤ T<sub>s</sub> ≤ 973 K and {0001}-textured Zr layers at higher T<sub>s</sub>. We attribute these results to the formation of Zr-Al intermetallic compounds at the Zr-Al<sub>2</sub>O<sub>3</sub>(0001) interfaces at higher T<sub>s</sub>. With the introduction of C<sub>2</sub>H<sub>4</sub>, at low partial pressures of 2 × 10<sup>-7</sup> Torr (with Ar pressure ~ 10 mTorr), we obtain smooth, hcp-Zr(0001):C layers. With increasing fraction of C<sub>2</sub>H<sub>4</sub>, we obtain increasingly C-rich ZrC<sub>x</sub> layers whose crystallinity and composition vary sensitively with T<sub>s</sub>. We expect that our results provide previously unknown information concerning the growth-related aspects of reactively sputter-deposited ZrC<sub>x</sub> thin films.

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