New Horizons in Coatings and Thin Films
Room Golden State Ballroom - Session FP-ThP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-ThP-1 Analysis of (Al,Cr,Nb,Ta,Ti)-Nitride and Oxynitride Diffusion Barriers in Cu-Si Interconnects by 3D-Secondary Ion Mass Spectrometry, *Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at),* TU Wien, Institute of Materials Science and Technology, Austria*; F. Bohrn, H. Hutter,* TU Wien, Institute of Chemical Technologies and Analytics, Austria*; E. Pitthan, D. Primetzhofer,* Uppsala University, Department of Physics and Astronomy, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

A number of different high-entropy sublattice nitrides have been investigated in the past as diffusion barriers between Cu and Si. These investigations were performed by depositing several nanometer thin barriers on single crystalline Si substrates, followed by a thick Cu layer on top, and subsequent vacuum annealing. In this work we report on the barrier performance of a nitride, and also three oxynitrides of the high-entropy alloy Al-Cr-Nb-Ta-Ti by depositing a reversed stacking sequence. 10 nm of (Al,Cr,Nb,Ta,Ti)-O-N (between 0.5 and 63.7 at% O, obtained by Elastic Recoil Detection Analysis) were deposited on polished polycrystalline Cu substrates by magnetron sputtering at room temperature with -100 V bias, followed by deposition of 200 nm Si. The samples were then vacuum annealed at 600, 700, 800 and 900 °C for 30 min. All four investigated coatings perform similar. While Secondary Ion Mass Spectrometry depth profiling in high-current-bunched (HCBU) mode with a high mass resolution (of >12.000 amu, lateral resolution ≈1 μm) shows breakthrough of Si even at 600 °C, 3D constructed images with Burst Alignment (BA, lateral resolution of ≈2 nm) depth profiles reveal that this failure is a highly localized phenomenon. The failure is likely related to recrystallization effects at the Cu grain boundaries, leading to punctuation of the diffusion barrier, as the diffusing Si stays confined in columnar regions within the Cu. Aside from this penetration, the majority of the area of each barrier coating retains its function. This in-depth analysis shows that the barrier function of the nitride and oxynitride coatings essentially stays intact up to 800 °C and fails completely at 900 °C.

FP-ThP-2 Maximum Achievable N Content in Amorphous Nitrides, *Jiri Houska (jhouska@kfy.zcu.cz),* University of West Bohemia, Czechia

The contribution reports the latest results concerning the maximum achievable N content in amorphous nitrides prepared by atom-by-atom growth. Structures of amorphous CN_x, Si-C-N, B-C-N and Si-B-C-N are predicted by extensive ab-initio molecular-dynamics simulations (over 15 000 trajectories) in a wide range of compositions and densities [1-3]. When and only when the structures are allowed to include unbonded N_2 molecules, the predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the N_2 formation, with the aim to predict and explain the relationships between [Si]/[B]/[C] ratios and the maximum achievable content of N bonded in stable amorphous networks ($[N]_{network}$). The results reveal that N_2-free networks are characterized by maximum $[N]_{network}$ between 34% (CN_x) and 57% (SiN_x). Networks formed in parallel to the formation of unbonded N_2 molecules (which subsequently either diffuse out or stay trapped in the material) are characterized by maximum $[N]_{network}$ between 42% (CN_x) and 57% (SiN_x). The measured N contents in (Si)-(B)-C-N films prepared in our laboratory by reactive magnetron sputtering are in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation takes place at a packing factor below the critical value of 0.28 which is valid in a wide range of compositions, the lowest-energy packing factor (sometimes below 0.28, sometimes above 0.28) depends on the composition. The presented methodology constitutes a new way how to support the experiment by ab-initio simulations. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

[1] J. Houska, Acta Mater. 174, 189 (2019), 10.1016/j.actamat.2019.05.048

[2] J. Houska, ACS Appl. Mater. Inter. 12, 41666 (2020), 10.1021/acsami.0c08300

[3] J. Houska, Materials 14, 5744 (2021), 10.3390/ma14195744

FP-ThP-3 Bulk Diffusion of Impurities in TiN: An Ab Initio Study, *Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at),* Montanuniversität Leoben, Austria*; M. Popov,* Material Center Leoben, Austria*; D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V).

In this contribution, we will report on our recent work in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline materials and subsequently their relative rates. The density functional theory (DFT) is used to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. Since TiN is a harmonic crystal it gives us access to temperature-based properties derived from the lattice vibration with harmonic and quasi-harmonic approximation. We will present the DFT-based "5-frequency model" allowing us to calculate the diffusion coefficient in the crystalline material. Moreover, the influence of TiN stoichiometry on its diffusion properties is taken into account through the change in the concentrations of the intrinsic point defects as a function of composition. These concentrations are obtained via a thermodynamic formalism based on the dilute solution model. We find that in stoichiometric TiN the vanadium impurity diffusion proceeds via the vacancy mechanism on the Ti sublattice. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN.

FP-ThP-5 Data-Driven Design Guidelines for Ceramic Superlattices With Enhanced Fracture Resistance, *Nikola Koutná (nikola.koutna@tuwien.ac.at),* A. Brenner, TU Wien, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; P. Mayrhofer,* TU Wien, Austria

Superlattices—alternating coherently grown materials of nm thicknesses— showed a great potential for enhancing typically antagonistic properties of ceramics: strength and toughness. Selection of layer components, however, is far from trivial, as nanolaminated films do not combine mechanical properties of the layer materials in a simple manner. In this work, we employ high-throughput density functional theory calculations to develop design guidelines for superlattices based on cubic transition metal nitride and/or carbide ceramics. Out of 153 MX/M*X* superlattices (M, M* = Al, Ti, Zr, Hf, Nb, V, Ta, Mo, W, and X, X* = C, N) 145 are chemically and mechanically stable and most often contain vacancies on the non-metallic sublattice. Superior ductility together with moderate-to-high fracture toughness and interface strength (above that of the cubic TiN) narrow the set of the most perspective candidates. Key ingredients promoting the interface-induced enhancement of hardness and/or fracture toughness are lattices parameter and shear modulus mismatch of the layer constituents. Adding the requirement of phonon stability yields MoN/M*N, M*=Nb, Ta,Ti; TiN/WN (nitrides); HfC/M*N, M*=Mo, W; NbC/M*N, M* = Mo, W; TaC/M*N, M* = Mo,W; VC/M*N, M* = Hf, Ta, Zr (carbonitrides); as the top candidates for novel superlattice films.

FP-ThP-6 Preparation of Single and Multilayer Films of Boron Carbide, Titanium Diboride and Hexagonal Boron Nitride Using Pulsed Laser Deposition, *Falko Jahn (jahn@hs-mittweida.de),* S. Weißmantel, Laserinstitut Hochschule Mittweida, Germany

Boron containing film materials provide outstanding mechanical, thermal and chemical properties which leads to growing interest in applying these materials in wear resistance coatings. Boron carbide, the third hardest known material after diamond and cubic boron nitride, shows indentation hardness values up to 49 GPa and a very high chemical and thermal stability. Titanium diboride's thermal properties exceed even those of boron carbide with a melting point over 3200°C and exceptional hardness at high temperatures (> 2000°C). Both materials are very well suited as wear resistance coatings, especially in very corrosive or hot environments. However, the brittleness of both materials may restrict their use regarding applicable loads

The presented approach to overcome these restrictions is to combine the material properties of boron carbide and titanium diboride with the properties of a less brittle but also very hard material by forming multilayer structures. Since this material should provide a similar thermal and chemical stability, we chose hexagonal boron nitride whose hardness can

be varied between 10 GPa and 25 GPa depending on the process parameters.

The presented results contain both the produced single and multilayers using the pulsed laser deposition technology. The mechanical properties of the produced films of boron carbide, titanium diboride and hexagonal boron nitride are investigated in dependence of the process parameters such as ablation fluence and substrate temperature.

The obtained mechanical material properties are applied to simulations of various multilayer designs under certain load conditions in order to find suited multilayer parameter combinations such as thickness or mechanical property of the sublayers. Promising multilayer designs are produced and characterized. The mechanical properties of the presented thin films are measured using nanoindentation. The surface quality is characterized by scanning electron microscopy and the sublayer adhesion is estimated using instrumented scratch testing and a calotte-grinding method.

FP-ThP-7 Anisotropic Super-hardness of Hexagonal WB$_{2-z}$ Thin Films, *Christoph Fuger (christoph.fuger@tuwien.ac.at), R. Hahn, L. Zauner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; M. Weiss, A. Limbeck,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations suggest an attractive combination of Poisson's ratio, bulk-, and shear modulus for α-structured WB$_{2-z}$ (space group 191, AlB$_2$-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W$_2$B$_5$-prototype, P6$_3$/mmc) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) throughout the PVD deposition. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Here, we focus on the binary WB$_2$ material system in terms of its phase formation using DFT and further illustrate the impact of prevalent lattice orientations on the mechanical properties. We show, that the α-WB$_{2-z}$ structure is preferentially stabilized by B vacancies, exhibiting its energetic minima at sub-stoichiometric compositions of about WB$_{1.5}$ – being also experimentally underlined.The mechanical properties show that α-WB$_{2-z}$ coatings in 0001 orientation reveal super-hardness (H > 40 GPa) compared to their 10-11 oriented α-WB$_{2-z}$ counterparts (H ~ 30 GPa). This is attributed to differences in the generalized stacking fault energies (GSFE) of basal and pyramidal slip systems in hexagonal diboride crystals. Our results show that the mechanical properties, in particular H, of PVD α -WB$_{2-z}$ coatings can change significantly due to the crystallographic orientation, highlighting the feasibility of tuning mechanical properties by crystallographic orientation relations.

Keywords: WB$_2$; Physical Vapour Deposition; DFT; Structural defects; Anisotropy;

FP-ThP-10 Characterization of a Novel Ionic Liquid-Based Chromium Plating Formulation, *Cameron Longo (cameron.m.longo.civ@army.mil), D. Sconyers,* US Army - DEVCOM AC - Benet Laboratories, USA*; M. Quiroz-Guzman, D. Morrison, T. Bush, M. Arsenault,* Trion Coatings, LLC, USA*; J. Maurer,* US Army - DEVCOM AC - Benet Laboratories, USA

Hexavalent chromium electroplating has come under severe scrutiny, with increasingly strict regulations and plans for complete removal from operations within the US within the next 10 years. Hexavalent chromium poses large risks, as it is a known carcinogen and presents severe occupational and environmental hazards in its use. However, chromium coatings offer many benefits, including excellent wear and corrosion resistance, and has good hardness and adhesion properties. As such, an effective chromium plating alternative for hexavalent-based processes is sorely needed.

Several systems which utilize trivalent chromium have been proposed, which offer highly reduced health and environmental risks, and could serve as appropriate replacements. An ionic liquid-based trivalent chromium process, dubbed SAFE Chrome, has been developed as an alternative to aqueous chemistries, and utilizes a charged organic species to bind to chromium ions to facilitate deposition. The analysis of weakly-bound organometallic complexes holds many unique challenges, the most salient of which is the desire to characterize the complex as it exists in solution. Mass spectrometry techniques are some of the most attractive options, as they afford highly robust and sensitive means of characterization. Traditional techniques, such as electrospray ionization (ESI) or matrix-assisted laser desorption/ionization (MALDI), have great potential to perform structural characterization of the components of these complexes using varying ionization approaches and tandem MS analyses, while more novel technique such as liquid injection field desorption/ionization (LIFDI) may offer unique insights into the bound form of the complex. Techniques such as infrared (IR) and ultraviolet-visible (UV-VIS) spectroscopy, as well as X-ray techniques like small-angle X-ray scattering (SAXS) can also offer insights into the structure or binding of the complex, while electrochemical analyses can inform on the electron transfer processes and valence of the metals. These data together help to form a deeper understanding of the chemistry occurring in solution during plating, and enable more intelligent design and better control of these emerging plating technologies.

Author Index

Bold page numbers indicate presenter