Protective and High-temperature Coatings
Room Town & Country D - Session MA3-1-MoM

Hard and Nanostructured Coatings I

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, **Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Stanislav Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

10:00am **MA3-1-MoM-1 Nitride and Carbide Layers: Point Defects, Interfaces, Mechanical Properties**, ***Daniel Gall (galld@rpi.edu)***, Rensselaer Polytechnic Institute, USA **INVITED**

We explore transition metal nitride and carbide compounds and multilayers using a combination of epitaxial layer growth, first-principles calculations, and measurements of lattice parameters and mechanical properties. Rock-salt structure nitrides are both mechanically and thermodynamically stable for group 3 transition metals. However, increasing the valence electron concentration by moving towards the right in the periodic table increases the strength of metal-metal bonds leading to a brittle-to-ductile transition and enhanced toughness, but also decreases the vacancy formation energy on both cation and anion sublattices, resulting in vacancy-stabilized compounds like cubic WN with a dramatically reduced elastic modulus, and new thermodynamically stable phases like a 5-fold coordinated base-centered monoclinic stoichiometric MoN. Epitaxial WC_x layers exhibit a cubic phase that is stabilized by carbon vacancies but phase competition involving hexagonal and orthorhombic W_2C and amorphous carbon lead to an epitaxial breakdown. Epitaxial MoC_x shows a similar phase competition between cubic δ-MoC_x(111) and hexagonal β-Mo_2C(0001) as a function of CH_4 content in the processing gas. In contrast, epitaxial TiC_x is phase pure over a large composition range as the cubic phase is stabilized by the entropy of random C-vacancies for $x < 1$. However, carbon interstitials and small clusters are energetically unfavorable leading to amorphous C segregation for $x > 1$, as detected by photoelectron and Raman spectroscopies. This causes a decrease in the elastic modulus and hardness from 462 and 31 GPa for stoichiometric TiC to 201 and 13.5 GPa for $x = 1.8$. Epitaxial $TiC_{1-x}N_x$ (001) layers show a nearly composition independent elastic modulus but a hardness that decreases approximately linearly from 31 to 21 GPa with increasing $x = 0.0\text{-}1.0$. TiN-TiC multilayers exhibit a 5-30% superlattice hardening effect, reaching 34 GPa for an epitaxial layer with a 6 nm lattice period.

10:40am **MA3-1-MoM-3 The Influence of the Carbon Source on the Mechanical and Electrical Properties of Magnetron-Sputtered Titanium Carbonitride Coatings**, ***Juliana Kessler (juliana.kessler@kemi.uu.se)***, Uppsala University, Angstrom Laboratory, Sweden

Titanium carbonitride coatings were investigated for use in electrochemical cells. Here, contact resistance should be minimal while maintaining mechanical strength and a fairly good corrosion resistance. Similar to titanium carbides, an increased carbon content leads to the formation of an amorphous carbon (a-C) phase resulting in nanocrystalline grains of titanium carbonitride surrounded by an a-C matrix. Fine-tuning the microstructure of titanium carbonitride films contact resistance can minimise contact resistance as it is largely determined by surface properties such as hardness and formability, which in turn vary with the amount and structure of the a-C phase. Depending on the carbon source used during the sputter process, the microstructure of the deposited films changes. The aim of this work is to compare the formation of a-C during sputter deposition using two different carbon sources: graphite and methane. Films were either deposited by co-sputtering from a Ti- and a graphite target under N_2 flow or by sputtering solely from a Ti-target under N_2 and CH_4 gas flow. For each process films of different carbon content were deposited and analysed using XRD, XPS, SEM, and Raman spectroscopy. Additionally, properties such as hardness, resistivity, and contact resistance were also investigated. Results show that the carbon concentration of the films varies from 10-24 at.%. Using XPS and XRD, it was found that the films contain NaCl-type Ti(C,N) and an amorphous carbon (a-C) phase. For different carbon concentrations Ti(C,N) shows a varying lattice parameter between 4.26 to 4.32 Å. Furthermore, an increasing overall carbon content causes an increased amount of a-C phase, which has a significant effect on the properties of the films. Comparing the a-C content of films with a similar overall carbon content suggests that carbon is more effectively incorporated in Ti(C,N) grains when using methane as a carbon source. The hardness of the films varied between 12 and 35 GPa and it was found to be dependent on the carbon content, where a lower carbon content corresponded to a reduced hardness. The peak hardness of 35 GPa was found for the film with the highest carbon content deposited using methane as a carbon source. In terms of contact resistance, the lowest values (below 10mΩ) were found for titanium carbonitride coatings with small amounts of a-C, which outperformed both titanium carbide and nitride reference coatings.

11:00am **MA3-1-MoM-4 A Strategic Design Approach Controlling the B-Solubility in Transition Metal Nitride-Based Thin Films**, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)****, K. Weiss, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; E. Ntemou,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Limited B-solubility in fcc-TiN poses significant challenges to the applicability of Ti-B-N-based hard coatings. In particular, excess B tends to segregate at the grain boundaries instead of being fully incorporated in the fcc lattice. Although increasing the B content enhances mechanical properties such as hardness, forming excess amorphous grain boundary phases can significantly reduce fracture toughness. Compared to TiN, we observed an increase of 10 GPa in hardness (up to 36.9±1.8 GPa) but a decrease in fracture toughness of roughly 25 % (down to 2.1±0.1 $MPa*m^{0.5}$). Assisted by ab-initio DFT calculations, we previously demonstrated that additional Ti (to deviate from the TiN–TiB tie-line) is required to fully incorporate more B (up to 8.7 at%) in the TiN lattice while minimizing B-rich amorphous phases. Here, we expand this research by adjusting the metal sub-lattice through Ti-, Cr-, Al- or Zr-addition to a Ti-B-N compound target (50 at.% Ti, 40 at.% N, and 10 at.% B). Our study highlights the key-role of kinetics in non-reactive deposition processes to overcome the thermodynamic limits of B-solubility in TiN. Through changing the stoichiometry by knowledge-based metal addition, we propose a general strategy to enhance the B solubility in transition metal nitride-based thin films.

11:20am **MA3-1-MoM-5 The Influence of Bilayer Periods and Ratios on Mechanical and Tribological Properties of TiN/MoN Superlattice Thin Films***, Z. Gao, J. Buchinger, R. Hahn,* TU Wien, Institute of Materials Science and Technology, Austria*; Z. Chen, Z. Zhang,* Austrian Academy of Sciences, Austria*;* ***Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)****,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal nitrides are commonly used in hard and protective coating industry, but still limited by low intrinsic fracture toughness. Encouraged by the previous study that superlattices (SLs) could remarkably improve strength and ductility, in this study, some TiN/MoN SL thin films are sputtered on (100) MgO substrates. These SLs are with bilayer periods (Λ) of 2–23 nm and a bilayer ratio ($\ell_{TiN}:\ell_{MoN}$) of 1:1, 1:0.5, 1:1, 1:2, and 1:2.7. This work is aim to explore the influence of bilayer periods and ratios, and the vacancies on TiN/MoN superlattice. All SLs – independent of bilayer period, bilayer ratio, and nitrogen content – present a rocksalt structure, with high-order satellite peaks during X-ray diffraction. But a weak tetragonal β-Mo_2N signal is also detected for the SLs with $\Lambda = 7.3$ nm ($\ell_{TiN}:\ell_{MoN} = 1:2$). The SLs with bilayer ratios of 1:0.5 and 1:2 do not show superlattice effect and bilayer-period-dependent. The SLs with $\ell_{TiN}:\ell_{MoN} = 1:2.7$ provide highest hardness due to a higher nitrogen supply during deposition. Contrary, the SLs with $\ell_{TiN}:\ell_{MoN} = 1:2$ have the worst mechanical properties due to the tetragonal β-Mo_2N phase exist. Among all SLs investigated, those with $\ell_{TiN}:\ell_{MoN} = 1:1$ provide the best blend of mechanical properties, such as $H = 34.8 \pm 1.6$ GPa, $K_{IC} = 4.1 \pm 0.2$ $MPa\sqrt{m}$, and $\mu = 0.27$, when $\Lambda = 9.9$ nm. This study extends our understanding of superlattice effect in general, especially on the influence of bilayer periods and bilayer ratios, as well as nitrogen supply and heterogeneous microstructures, which is benefit to next SL design.

11:40am **MA3-1-MoM-6 TiN/CrN and TiSiN/CrN Multilayer Coatings Deposited in an Industrial–scale HiPIMS System**, ***Neus Sala (neus.sala@iqs.url.edu)****,* IQS School of Engineering - Universitat Ramon Llull, Spain*; M. Abad,* IQS School of Engineering - Universitat Ramon LLull, Spain*; C. Colominas,* FLUBETECH, S.L., Spain*; R. Franz, C. Kainz, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; C. Rojas, J. Sánchez-López,* CSIC-Universidad de Sevilla, Spain

TiN/CrN and TiSiN/CrN multilayer coatings of varying bilayer period (Λ) were deposited in an industrial-scale deposition system by means of reactive High Power Impulse Magnetron Sputtering (R–HIPIMS). For each composition, three different coatings were deposited with bilayer periods of approximately 85 nm, 15 nm and 5 nm by alternating the sputtering of the different metallic targets in a nitrogen-containing atmosphere.

The influence of the Λ is investigated in regard of the chemical composition, microstructure, and mechanical properties of the coatings.

All coatings present a very smooth and compact structure in SEM images. XRD showed separate crystalline phases for the samples with high bilayer periods. However, as the bilayer period decreases, the crystalline peaks overlap, which would suggest epitaxial growth of the two crystalline phases.

A superlattice structure is confirmed by satellite peaks in the X-ray diffractograms for the TiN/CrN coatings with $\Lambda \leq 15$ nm. TEM and EELS of the TiSiN/CrN coatings show that Si is substitutionally incorporated into the TiN crystalline lattice without segregation of amorphous SiN_X phases. However, epitaxial growth is interrupted by amorphous zones, particularly in samples with smaller bilayer periods.

For the TiN/CrN system, the highest nanoindentation hardness value obtained is 32 GPa while for TiSiN/CrN coatings, it is 28 GPa. In both cases, the maximum hardness value is found for the samples with Λ 15 nm regardless of the composition.

12:00pm **MA3-1-MoM-7 Residual Stress Measurement and Effective Deformation Thickness of Metal Interlayer in Multilayer Hard Coatings - Using TiN/Ti/TiN/Ti as a Model Architecture***, **I-Sheng Ting (gary820902@yahoo.com.tw)**, J. Huang,* National Tsing Hua University, Taiwan

High residual stress is one of the critical problems encountered in hard coatings deposited by physical vapor deposition. In industrial applications, introducing a metal interlayer, such as Ti and Cr, is a common practice to relieve the residual stress, thereby enhancing the adhesion and life span of the hard coatings. Our previous studies [1,2] proposed an energy-balance physical model to evaluate the stress and energy relief efficiency of metal interlayers in hard coatings. The assumption of the model was that the relief of stored elastic energy (G_S) in the hard coating and the bending energy of the Si substrate are balanced by the plastic work done by the metal interlayer. The results showed that the energy relief efficiency of the metal interlayer depends on the plastic behavior of the metal, where Zr interlayer has a lower extent of stress relief in ZrN/Zr coating than Ti interlayer in ZrN/Ti coating [1], because the strength coefficient (k) of Zr is higher than that of Ti. In addition, the results indicated that the plastic deformation capability of the metal interlayers is not fully consumed, and the plastic deformation of the metal interlayer is localized within a narrow layer nearby the coating/interlayer interface, which was named as effective deformation thickness (EDT). The EDT was used to depict the energy relief extent in the bilayer coatings [2]. However, whether the energy-balance model and the concept of EDT could be applied in a multilayer structure is still unclear. In this study, the alternated four layered TiN/Ti/TiN/Ti coating was selected as a model architecture to investigate the stress relief and stress distribution of multilayer hard coatings. TiN coating with Ti interlayer was deposited on Si substrate using dc unbalanced magnetron sputtering, where the TiN film and Ti interlayer were alternately stacked to produce structure, TiN, TiN/Ti, TiN/Ti/TiN and TiN/Ti/TiN/Ti. The overall stress and the layered stress of the coatings were measured using the laser curvature method and the average X-ray strain (AXS) combined with nanoindentation methods [3-5], respectively. By using the energy-balance model and the concept of EDT [1,2], the stress and energy relief efficiency of the multilayer architecture could be estimated.

[1] J.-H. Huang et al., Surf. Coat. Technol., 434 (2022) 128224.
[2] J.-H. Huang et al., J. Vac. Sci. Technol. A, 41 (2023) 023104.
[3] C.-H. Ma et al., Thin Solid Films, 418 (2002) 73.
[4] A.-N. Wang et al., Surf. Coat. Technol., 262 (2015) 40.
[5] A.-N. Wang et al., Surf. Coat. Technol., 280 (2015) 43.

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